1	**Module Name**	**Project Work on** Advanced Materials Modelling and Characterization** Interdisciplinary tutorial at the joint EMRS-EUROMAT materials weekend **Sunday 20.09.2015 in Warsaw, Poland at 9:00** Tutorial Modelling Description, **Introduction,** Prof. Peter Wellmann, Materials Department, University of Erlangen-Nürnberg, DE	**5 ECTS**
2	**Courses**	**A** EMMC Initiative, Pietro Asinari, Politecnico do Torino, IT, 45 min **B** EUMAT Initiative and activities in modelling and characterization from IK4-TEKNIKER, Amaya Igartua, ES, 45 min **C** Modelling friction and wear behavior, Anssi Laukkanen, FI, 45min **D** "Thermodynamic and kinetic simulations: The phase-field method", Ingo Steinbach, DE, 45 min **E** Hands on session phase-field simulation by OpenPhase", Oleg Shchyglo 120min (*students needs their own computer).*	3 ECTS
		G EMRS Fall meeting 2015 or EUROMAT 2015 conference	2 ECTS
3	**Teaching Staff**	**A** Pietro Asinari, POLITO, IT pietro.asinari@polito.it **B** Amaya Igartua, IK4-TEKNIKER, ES, amaya.igartua@tekniker.es **C** Anssi Laukkanen, VTT, FI Anssi.Laukkanen@vtt.fi **D** Ingo Steinbach, Ruhr-Univ. Bochum, DE ingo.steinbach@ruhr-uni-bochum.de **E** Oleg Shchyglo, Ruhr-Univ. Bochum, DE Oleg.Shchyglo@rub.de	
4	**Module Coordinators**	Prof. Peter Wellmann, Materials Department, University of Erlangen-Nürnberg, DE, peter.wellmann@fau.de Prof. Dr. A. Lindsay Greer, Department of Materials Science & Metallurgy, University of Cambridge, UK, alg13@hermes.cam.ac.uk Prof. Rodrigo Martins, Uninova, PT, rm@uninova.pt	

4	**Syllabus Outline**	Modelling activities – its past, present and future
		• Electronic, Atomistic, Mesoscopic, Continuous Modelling
		• Coupling and linking, Translators
		• Validators and End Users.
		Why?
		• Experimental **validation and modelling** of components in actual systems
		  o Materials behaviour prediction;
		  o Materials life-cycle prediction;
		  o Design multiobjectives optimization.
		• **Manufacturing process modelling**	

		○ Macro-scale process simulation to optimise the production; ○ Micro-modelling for microstructure prediction and its correlation with local mechanical properties; ○ Residual stress and strain status at the end of the process. **Opportunities for young researchers**
6	**Educational goals and Learning outcome**	- Specific skills: Gain of broad and interdisciplinary knowledge in a modern topic of advanced materials, processes and applications - Soft skills: Ability to present own literature survey and to carry out a scientific discussion. - For all skills: Can explain, apply and reflect upon the theories, technologies, specialties, terminology, boundaries and different schools of their discipline (field of gained knowledge) critically and in depth.
7	**Prerequisites**	Bachelor degree in Chemistry, Molecular Science, Physics, Nanotechnology, Materials Science or a related course
8	**Intended stage in the degree course**	Elective module during Master or Graduate Studies (interdisciplinary studies, soft skill training)
9	**Courses of study for which the module is acceptable**	M.Sc. and PhD-studies in Chemistry, Molecular Science, Physics , Nanotechnology, Materials Science or a related course
10	**Assessment and examinations**	Notes from attended conference (8 pages)
11	**Calculation of the grade for the module**	Message by e-mail passed/failed.
12	**Frequency of offer**	September 20th, 2015, only 1 day
13	**Workload**	- Tutorial day (lectures + hand on session): 5 h - Conference attendance (EMRS fall meeting or EUROMAT 2015 conference, September 2015 in Warsaw, Poland): 56 h
14	**Duration**	1 semester / term
15	**Language**	English
16	**Preparatory reading / reading list**	Selected publication list of the tutorial speakers

Additional Information
"Review of Materials Modelling. 4th version", Edited by Anne F. de Baas and Lula Rosso, EU Commission, 2015

Advanced Materials Modelling and Characterization

P. Asinari[1], A. Igartua[2], A.Laukkanen[3], I. Steinbach[4], O. Shchyglo[4]

1) Politécnico Torino, 2) IK4-TEKNIKER, 3) VTT, 4) Ruhr-Univ. Bochum

ABSTRACT

Objective

The modeling and Characterization workshop has the aim to facilitate the knowledge and available tools at different scales (nano to macroscale) **in order to make easier to predict the behavior of the products and process at design phase.**

Attendance: The workshop will be open to any interested **researchers and students** that would like to upgrade their skills for learning new tools for modeling and characterization.

When: Sunday, 20th September 2015

Duration: 3 hours presentations + 2 hours hands on session (there is not poster session planned for this tutorial)

Introduction

The tutorial will start with the **presentation of the European Materials Modelling Council (EMMC)** by **Prof. Pietro Asinari from Politécnico do Torino.** He will present the structure and activities of the European Materials Council, and also some basic classifications towards a common **vocabulary in modelling.**

The tutorial will continue by **Dr. Amaya Igartua,** Head of Tribology Unit from **IK4-TEKNIKER research Center in Spain.** She will introduce the **European Materials Platform Initiative EUMAT**, making emphasis in **modeling and characterization activities.** Their presentation will be illustrated by some **case studies performed by IK4-TEKNIKER** in modeling activities and **advanced characterization techniques.**

The third intervention will be performed by **Dr. Anssi Laukkanen,** responsible of modeling activities at the Research Institution, **VTT in Finland**. He will explain the modeling activities at VTT specially related to **friction and wear modeling tools** already developed, illustrating **with some examples.**

The fourth Intervention will be performed **by Prof. Ingo Steinbach from Ruhr-Univ. Bochum.** He will explain **Thermodynamic and kinetic simulations using the phase field method,** and their presentation will be supported by a **hands on Session** in phase-field simulation using OpenPhase by **Oleg Shchyglo.** To follow the practical session it is important that **the attendants** to the tutorial will **bring their computer.**

The participants will receive the book "Review of Materials Modelling. 4th version",

Edited by Anne F. de Baas and Lula Rosso, EU Commission, 2015.

What makes a material function?

Let me compute the ways...

Modelling in FP7 NMP Programme Materials projects

What makes a material function? Let me compute the ways…

Modelling in FP7 NMP Programme Materials projects

Fourth version, 2015

Edited by

Anne F de Baas and Lula Rosso

CONTENT

Introduction

This is the fourth and more complete Review of Materials Models (RoMM) illustrated by modelling projects funded under FP7. The publication of the first, second and third version has received extensive appreciation and the European Commission has received numerous statements and inputs that have been taken into account to prepare this fourth version.

Modelling is a powerful tool that supports materials research in the development of novel or improved applications. It provides the key information for identifying new materials, tailoring materials and design materials for structures and systems.

To foster dialogue and mutual understanding between industrial end-users, software developers and theoreticians, this publication presents the scope and achievements of the modeling in about 100 projects funded in the 7th Framework Programme (2007-2013) by the NMP Programme, unit Advanced Materials and Nanotechnologies.

> *In order to facilitate the communication a* **harmonised vocabulary and classification** *is proposed, based on the physics and Chemistry of the model.*
> *This vocabulary will later on be the basis of* **meta data** *to describe models and databases with.*

Importance of the projects to the European Industry

The use of materials modeling in industries is very versatile. Application addresses fields like Energy, Environment, Transport, Health, ICT and Manufacturing. It is supporting the creation of products like solar cells, sensors, car parts, tissues, computers, tools, coatings. Industrial application is the target of the FP7 NMP program and the projects show the continuous effort to move from model development to model application and finally upscaling for industrial application. It is important to note that, in general, models become most useful to industry when they have reached an advanced maturity. This requires strong interaction between the code developers and industry, and, because of the complexity and long timescale of the code development and validation process, the support of programmes such as NMP makes an important contribution to competitiveness.

The most crucial issue related to modeling in industrial applications is in the formulation of models that produce realistic results. In general, modeling and simulations can be the eyes of the experimentalists, helping them to access information that would not be available otherwise and interpret the experimental results. Modeling provides also invaluable predictions on the evolution of a system in a quicker or cheaper way than with trial and error methods. Industry uses modelling for:

- Saving costs by establishing a strategy for testing and by screening new material candidates, when a "try and fail" approach cannot be carried out in the industry or it would be too complicated, dangerous or expensive.
- Understanding results of measurements. This is particularly important at the nanoscale and at femtoscale where access to materials properties and processing methods is often difficult. The simulation can provide this information for every point in the sample at every time.
- Reducing the time to market, by accelerating the time scales of understanding and developing new materials and of existing materals in new applications.

- Suggesting new materials and experimental procedures to create them. Materials design by modeling is about investigation of relations between chemical and physical composition, microstructure and effective properties at a macroscale, so that a material can be designed with desired macro-properties. Modeling can be used to examine the properties of materials and devices that have not or cannot yet be created.

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Questions that can be answered by modelling

To show the value of modeling, the achievements of the models beyond experiments have been listed. The models can answer questions like:

>•*What is the influence of the automotive catalytic converter's shape on its performance?*
>•*Which hydrogen-microstructure interactions play a critical role in the degradation of materials and components?*
>•*Which are the dissipation mechanisms that contribute to the macroscopic adhesion between a metal and a polymer?*
>•*What is the role of thermodynamics and what are the reversal processes involved in ultrafast magnetisation processes?*
>• *Is it possible to control the parameters of the excitation process and of the metal oxides to create long-lived metastable phases with tailored physical properties?*
>• *Which is the role of the size of the systems in realistic nanometric devices? How is the dynamics influenced when the length scale is reduced to the nanometer size of devices (<20 nm)?*
>•*Which are the parameters that control the final state in a solar cell reached after the photo-excitation?*
>• *Which is the influence of biomedical devices on the surrounding tissues?*
>• *Which is the increase of electrical conductivity in composites upon addition of carbon nanotubes?*

What are models? What are simulations?

Fig 1 Simulation gives the numerical solution to the model applied to a specific situation (Hans Fangohr, University of Southampton, UK)

Materials are complex systems and the equations that describe the physical and chemical behaviour of real systems are often too complicated to be solved easily. In order to save computer time, which is a precious and limited resource, the description of phenomena has to be simplified. Fortunately, often not all details need be taken into account in order to reproduce and predict experimental results. Key assumptions about reality can be made ignoring the complexity that is not necessary to describe the given situation. In this Review of Materials Models, an approximated ***physics/chemistry equation*** describing generic physics and its ***closure***

relations describing a specific material and its behaviour are called "***model***"[1].

The physics equation is by its nature generic and widely applicable and this is the strength of modelling! But a physics equation alone can not be solved. The equation has to be applied to a specific case "documented" by the closure relation. (Note that the closure equation can not be "run" in isolation.) As we work in the materials domain the word "***materials relation***" will be used for the closure relation, and we note that "***constitutive equation***" is often used in the continuum modelling world.

> *Together the **physics or chemistry equations** and **materials relations** are called governing equations and they form one **model**.*

Fig 2 Model with Governing Equations

Model application and model development

> "***Model development***" is the act of finding the approximations in the physics and chemistry equations and in the closure relations. *Materials Modelling* is the establishing of governing equations (physics/chemistry equations and/or closure relations) between physical or chemical quantities. These governing equations contain the key assumptions of the model. Modelling does not include fitting parameters in existing governing equations to (simulated or experimental) data.

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[1] *Note: the word "model" is used for different concepts in many other situations (e.g. the application that will be simulated, the geometrical model of the sample, or even for the solvers). But in this RoMM different words will be used for different concepts.*

In this Review we talk about "***model application***" when we apply an existing physics equation and closure relation to a specific situation. The tuning of parameters in these equations (e.g. tuning constants in parameterisations in existing force fields expressions or in existing constitutive equations) is <u>not</u> considered to be model development.

Application of models

A model is strong if it is transferable from one materials system to another within the limits of the model. Many NMP projects are applying existing physics and chemistry models to new materials and manufacturing processes. This has generated a wealth of new information[2]. When applying an existing model to a new situation, unexpected results or new phenomena may be discovered, but these results are obtained with existing equations. An overview of the extensive fields of model application in FP7 NMP projects will be described in Chapter 8 in more detail.

Development of new models

At times, models cannot be transferred from one physical situation to another (say from energy conversion to spin-dynamics). In such cases, research projects may want to increase the complexity of the model, by incorporating new physics and chemistry in the equations. This happens when new physics and chemistry is to be described. Modellers start from the strongly approximated physics equations, and gradually add complexity to it (e.g. more transition metal orbitals, ligand orbitals, Coulomb exchange, spin-orbit, phonons, friction) until a satisfactory agreement with experiments is reached. For example, it has been necessary to develop new models in femtosecond dynamics: at the femto-scale new dynamics, physics or chemistry takes place and new opto-electronics/magnetics/ models have been developed.
Development of models may also reduce the complexity of an existing model if the accuracy is still satisfactory. This is done to save computer time.
Modelers have also establish new constitutive equations either from measurements or by applying models of a finer type and transfering the results into a coarser type of model in the form of constitutive equations with new terms expressing the added physics phenomena now taken into account. This allows them to identify what are the critical relevant processes that lead to experimental results. Also deriving a new force field by adding new terms to include physical or chemical properties previously disregarded and ignored in the approximations will be considered as a new "materials relation" and thus as a new model. New constitutive equations linking physical or chemical parameters in a new empirical equation, found as results of modeling or as results of experiments, are also included as new modeling. The basic phenomenon might not be completely understood but this new relation can at least be called a 'hypothesis'.

Chapter 7 will briefly describe the situations in which new physics and/or chemistry equations have been developed. In this chapter, adhering to the above definition of the word "model", only new physics or chemistry equations or new closure relations are discussed.

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[2] *Please note that the physical/chemical knowledge about the system or process needed to perform the model application goes beyond purely computational skills.*

Intermezzo: Some philosophy

The Schroedinger equation, Newton Dynamics and conservation equations are the foundations of materials physics and chemistry. But these equations can often not be solved and an approximated equation is taken instead. Modeling starts with an approximation which at first is seen as a good balance between complexity and computability.Development of models may either make the crude model more complex (and in principle the full physics equations will be retrieved again) or reduce the complexity of the model. Below (Fig. 3), is an illustration of model development, across time- and length-scales.

Simpler interaction model in this direction

Longer time phenomena

Constitutive equations, non-equilibrium plasma behaviour

Simplified force-fields, coarse graining, regional dynamics

Addition of heat bath to spin dynamics, surface doping irradiation effects

Complicated force-fields

Photon-electron interaction, recombination rules, physisorption, effect of thermal instabilities

High-level QM

More advanced interaction model in this direction (more physics and chemistry)

Larger systems

Fig 3 Model development works by moving along the arrow upwards or downward.
(based on Kersti Hermansson, Uppsala University, SE)

Choosing the right model

When several (validated) models exist, the scientist/industry has to choose which one to use. This "testing of models" is also a valuable part of modelling. This consists in trying to answer questions like "which model gives properties that are closest to measurements for this material?" Here the researcher is investigating which physics is needed to describe the given situation. So a model that "approximate reality by considering the neighbours as point charges and ignore temperature effects" states what is the necessary physics to describe the measurements with. Sometimes the choice of a model depends on the balance between accuracy and simplicity. The outcomes of such testing might also be important because if none of the models are adequate the result of testing is that more physics/chemistry needs to be added to existing models.

MONAMI has been testing two models to calculate the electronic structure of V_2O_3: a so called N-th order Muffin-Tin Orbital (NMTO) model, with features like massive down folding and generation of Wannier combined, and full-potential software using dynamical mean field theory for strongly correlated systems.

In *MORDRED*, large-scale atomistic simulations of oxide interfaces using dynamic charge transfer models were benchmarked against first principles simulations. Calculations of structure and charge for a large set of cluster, bulk and interface cases with both models were compared to undertands the limits of the faster and more approximated method.

OXIDES has been doing comparative tests of two first-principles methodologies, PSIC and B1-WC, by applying them to structural, electronic, and magnetic properties of a known 2-dimensional electron gas system: LaAlO3/SrTiO3. They evaluated the reliability of PSIC and B1-WC, comparing them with theoretical results presented in literature or obtained with other methods. This way, they explored the limits and capabilities of the two approaches. This testing is essential in selecting the most adequate band energy description to be exploited for transport properties, but it is not stricto sensu a new model development.

Solvers, numerical power needed and up-scaling for the industry

"Solvers" are numerical methods used to solve the physics/chemistry equation. In the Review there is a strict separation between the two concepts "solver" and "model". FE is a technique that can be used in the numerical solution, smoothed particle hydrodynamics (SPH) is a solver (used to discretise the fluid dynamics model equations) and not a model. Kinetic Monte Carlo is a way to solve mechanics equations.

Solvers sometimes use concepts like "fictitious particles" (like in phonon models), but these are not to be confused with the entities whose behaviour is to be described.

"Simulation software" is a computational code, which solves the governing equations by numerical methods and requires information about the application (boundary and initial conditions) (Note that more than one model can be integrated into a single code (toolkit/framework/workbench).)

"Models" are the governing equations for the physical and chemical entities,
          not the codes or simulation software.

Simulation of models applied to new materials involves finding a solution to the equations of the model. Solvers can become very complicated and the computational power needed may become an issue.
Design environments are developed that balance accuracy and speed. To this end, many models are solved with parallel algorithms, which allow the load to be distributed among computer processors.
Software owners have written up guidance on software engineering, which is available at www.emmc.info.
Upscaling to industry should build on the progress made in High Performance Computing (HPC), theoretical models and faster numerical processes.
Part of the effort should be directed towards the key and transverse issues of software code modularity and reusability. An integrated and user-friendly design environment must be created.
This might require vertically integrated communities with theoretical modelers, experimental data generation and validation experts, software and hardware integrators and industry end-users.

Introduction of model types

A new classification of existing models into four types is presented. Until now materials models were presented by the length and time scales of their applications, but as computers grow stronger the application areas started to overlap and the application area is no longer a good identifier of the model. In the new classification models are defined by the entity whose behaviour is described in the physics/chemistry equation. This entity can be an electron, an atom, a particle/grain or a unit cell. The entity itself is considerd to be "frozen" and processes inside are not resolved. The physics content presents the potential of the modelling!

Models are strictly classified according to the entity described by the physics and not according to the size of the application or system!

The four natural categories of materials models consist of three discrete types and one continuum type of model:

Model	Entity whose behaviour is described	Number of entities	Indicative length scale (depending on current computers)	Indicative time scale (depending on current computers)
Electronic models	electron	10-100	0.1 - 1 nm	-
Atomistic models	atom	10^2 - 10^9	0.1 - 100 nm	fs - µs
Mesoscopic models	nanoparticle, grain, molecule	10^6-unlimited	100 nm - mm	ms - s
Mesoscopic magnetism models			1 nm - 100 mm	1 ps - 1000 ns
Continuum approaches	continuum volume	unlimited	nm-m	s - ks

Fig 4 An illustration of entities in the different model types. (Pierre Severin, Coexpair and Olaf van der Sluis, Philips) The length and time scales to which the models can be applied are indicated by ellipses but as computers grow they are overlapping more and more. Hence the new classification!

Electronic models: These models are based on physics/chemistry equations, the Schrödinger equations, describing the behaviour of electrons. Quantum mechanical methods describe the behavior of the electrons which determine the properties and structures of the material. Ab initio models calculate electronic structures "from first principles" (i.e. based on fundamental quantum mechanical principles of physics) expressed in the Schrödinger's equation within a set of approximations that do not include fitting the model to experimental data. Here, the material is explicitly represented by nuclei and electrons. From the model electronic transitions and chemical reactions can be derived at the shortest atomic time/length scales.

Examples of electronic model results:
electronic band structure giving conductive/dielectric and optical properties,
force fields parameters, (magnetic) anisotropy, diffusion coefficient, activation energies,
thermodynamic stability and kinetic elementary processes for atomic defects and dopants

Atomistic models: These models are physics/chemistry equations describing the behaviour of atoms. When the electronic degrees of freedom are ignored, molecular mechanical models and classical mechanics are applied to describe the behavior of atoms and molecules. Newton Dynamics can be used to describe effective interactions between atoms, called force fields or interatomic potentials. Interatomic potentials do not treat the quantum nature of electrons explicitly, which allows models using these potentials to be enormously faster than models using quantum methods. Such interatomic potential based modeling may

not be as accurate as full quantum mechanical approaches, but can be used to simulate complex materials processes as radiation damage in nanocrystalline materials and friction between surfaces.

The most common technique here is Molecular Dynamics simulations, now routinely applied to systems including up to tens of thousands of molecules (consisting of many atoms) describing the evolution over tens of nano seconds. With these applications to longer time scales e.g. lattice motion is described. Other examples are atomistic phonon models and atomistic spin models.

> *Examples of atomic model results:*
> *trajectories, packing, stiffness, dynamical properties, surface and interface energies, constitutive equations parameters, spectral properties, heat transfer, magnetism*

Mesoscopic models: These models are physics/chemistry equations describing the behavior of nanoparticles, (parts of) molecules or grains. What happens inside these entities is not resolved. The entity is considered to be "frozen". At the supra-atomic scale where uninteresting or fast details of the atomic motions are averaged out or replaced by stochastic terms, mesoscopic models concentrate on essential motions and large-scale structures. Examples are the so-called coarse-grained models and here the fundamental unit is a "bead" consisting of parts of a molecule that interacts with other "beads" via effective soft potentials. The category of mesoscopic models also includes the magnetism models based on macro-spin approaches that combine atomic spins into a macro-spin, or discrete phase field models describing how a entire grain behaves as an entity, or mesoscopic phonon models for how particles vibrate.

> *A* **"mesoscale model"** indicates the application domain is of nanometer size, but ….it does not tell whether the modeller looks at the behaviour of electrons, atoms, molecules or considers the material to be homogenous in larger volumes.
> The word "**scale"** only relates to the size of an application domain and can **not** be used as an adjective to "**models**".

> *Examples of mesoscopic model results:*
> *morphology, domain formation and growth kinetics, thermal stability, magnetic behaviour*

Continuum models: These models are physics/chemistry equations describing the behavior of a continuum volume. In this description, the material is assumed to be continuously distributed throughout this volume and the models disregard the discrete particle-based structures and smaller detail. Continuum models can be applied to situations with a wide range of length and time scales and the lower limit is growing smaller and smaller (nm). The models applied to at "micro-scale" phenomena can predict material decomposition, defect formation, crack propagation, solidification of liquids and applied to "macro-cale" continuum models can describe behaviour of thin films and realistic nano-devices with metallic contacts and other important variables for industrial manufacturing.

> *Examples for continuum model results:*
> *macroscopic structural behaviour, heat and mass transport, permeation times, chemical reaction kinetics, electromagnetic behaviour*

Fig.5 Number of projects in the FP7 NMP Programme performing modelling of the four different types.

Methods or Workflow

The word "method" is reserved to indicate the way in which models are used. This is the workflow used to use the models either subsequently or concurrent and the workflow describes when and how to link in databases.

Interoperability of models (multi-scaling) and databases

In order to increase their predictive capability and applicability, continuum models need to be supplemented with descriptions of processes, which originate at the electronic, atomistic and nanoparticle-scale. This lays in the very nature of the continuum models, where such effects are neglected. For example, continuum models that approximate interfaces by a set of effective band offset parameters have no predictive power over interface related effects as the detailed electronic and atomistic structure near the interfaces is not taken into account.The great challenge in creating accurate and predictive models is that materials form a true multi-scale problem. A consistent hierarchy of simulations at different levels of representation is needed. With a chain of models the description of macro behaviour of materials in operation can be built up including the smallest detail.

For example, diffusivity may be simulated by first modelling electron diffusion; then ion transport is modelled at atomistic level; particle transport through membranes and finally continuum models for the electrical current. Another example is modelling of chemical reactivity using simulations of molecules at the atomistic scale and continuum reaction kinetics thereafter. The large majority of the in FP7 NMP materials projects combined models of different types.

For sequential modelling we use the term "**Linking models**" and this means running different models consecutively.

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For concurrent modelling we use the term "**Coupling models**" and this means running different models concurrently.

A major issue in linking models is transfer of data from one model to another.

The operation of reduction and extraction of model **output into input** for the next model is called "***post-processing or homogenisation***". Homogenisation can be purely mathematical fitting data when the value of a parameter in a known materials relation is calculated. But homogenisation involves physics, when the modellers are looking for a new materials relation. Then they have to have an idea (assumption, postulation) for what physics relation they are looking. And when this relation is supported by the data it is adopted.   In continuum modelling, often the results of continuum models applied at meso-scale (nm) are fed into the continuum model applied at macro-scale model (µm) in the form of constitutive equations – which in the language of this Review are called "material relations" - or as boundary conditions. The establishment of such constitutive equations represents a big challenge in contemporary modelling. Another example of homogenisation is finding a new template relation for a force field including extra physics/chemistry processes.

Fig 6 Workflow: physics equations and closure relations

Multi-scaling is linking models, where each model is dealing with part of the physics/chemistry.
In material engineering (micromechanics) it is quite common to applying the same physics model
(conservation equations of mass and energy) to different length and times scales; e.g. the same continuum
model applied to the nm structure and at mm-scale (fine and coarse grids). The results of the model
applied to finer scale(nm) is processed into a (new) constitutive equation or boundary conditions providing
the specific material characteristics simulated with the model applied to course grids at macro-scale (μm).
Here the difficulty is homogenization and this can involve physics considerations and this represents a big
challenge in contemporary modeling.
In a second type of multi-scaling models of a different type are linked and the major issue is the reduction,
extraction and transfer of data from one model to another and this is a very active subject of research. For
example, semi-empirical pseudo-potentials, which can be used to calculate the accurate electronic
structure, are based on first principles calculations at a smaller scale (Hartree-Fock, density functional
theory, and higher level QM methods.
Note that also the notion "**Multi-physics/chemistry modeling**" is often used. This usually means connecting
different (continuum) models describing different physics/chemistry apllied to the same length and time
scale. An example is describing micromechanics and fluid mechanics, both with continuum models.

The linking of the models represents a considerable challenge and 80% of the projects linked different types
of models.

Finally, last but not least, in a multi-scale multi-physics approach not only models should be connected but
such an approach should also integrate **experimental data** in a clever way.

Modelling for interpretation of experimental results/characterisation

The interpretation of experimental data as material properties relies on models as well. In Fig 1
"experimental results" contains BOTH the "getting the signal" phase and "making the interpretation" phase.
This includes deciding which formula (model) to use to convert the signal into a property. It can also involve
the post-processing of measured quantities into other physical/chemistry properties.

> *METACHEM is processing transmission, reflection and ellipsometry spectra of metamaterials measured
> at different angles of incidence (ellipsometric data) to extract values of optical constants of
> metamaterial. This is done with the help of electromagnetic wave propagation models, but the
> interpretation model used is at the moment a debated research topic discussing the existence of
> concepts like "refractive index".*

In the following, the models of each type will be introduced and it will be presented how they are used. This
Review of Materials Models shows that an efficient materials modelling approach shortens the
development process of materials-enabled products in all industrial sectors.

Vocabulary

This chapter is concluded with a last remark on vocabulary. It is not always clear whether expressions deal with the entity, the physics equation, the closure relation, the input, the output….and short sentences are not always precise enough:

> *Examples of unclear expressions:*
> *A model for atoms: Is the atom the entity or is it the output that describes an atom?*
> *The model accounts for friction: Is friction the adaptation of the physics in the equation or is it the output describing these phenomena in the application?*

It is the hope that this Review will make it easier for modellers to talk across fields!

Chapter 1
Electronic models

Electronic models are physics/chemistry equations describing the behaviour of electrons. The theoretical framework of electronic models is the Schrödinger equation, with which the evolution at the quantum level of any atomic or molecular system with time can be calculated. The Schrödinger equation is defined by two elements: the so called wavefunction of the quantum system, and H, the Hamiltonian operator. The wavefunction is a function which represents, at each moment in time, the positions, momenta and spins of all particles in the system. However, the spin part of the wavefunction is often not explicitly carried in calculations that do not focus on magnetic properties. The most crucial element is H, the Hamiltonian operator, which represents the total energy of any given wavefunction and takes different forms depending on the external forces acting on the material. In magnetics, the Hamiltonian includes terms expressing energy due to exchange interaction, spin-orbit interaction, and Zeeman interaction.

In practice, quantum mechanical models are finding suitable approximations of the full Hamiltonian and/or of the molecular orbitals, in order to simplify the numerical calculations of the electronic degrees of freedom without compromising the quality of the simulated results. Further approximations and semi classical approaches may also be used.

Fig.1.1 Number of projects that used one of the four main types of electronic models treated here.

1.1. Ab initio quantum mechanical (or first principle) models

The Schrödinger equation can be solved exactly only for a few problems of limited interest. To solve the equation for systems of practical use, approximations are in general required. *Ab initio* models may be based on a series of approximations that do not include fitting the model to experiments. This is also called a first principle approach because the model is using the Schrödinger equation and is still based purely on fundamental principles of physics.

Quantum mechanical chemistry models are routinely used to calculate the ground state of atomic and molecular systems and the energy and configurations (electronic structure) of the excited states. This can be applied to several problems of practical use.

> *Ab initio models are applied, to calculate the mechanism of new catalysts and proton conductance in proton exchange membranes (HYPOMAP), surface energies and activation energies of catalytic nanoparticles (NEXT-GEN-CAT) and to calculate the formation energy of inclusion complexes in layered magnesium oxides, HTLC, which is relevant for the synthesis of quasi-solid electrolytes (MINOTOR).*
>
> *Interface processes can be studies at the quantum level, for example adhesion of metal-ceramic interfaces and internal grain boundaries in realistic conditions (ROLICER); interfacial hydrogen bonding and adsorption of water and carbohydrates on cellulose surfaces (SURFUNCELL); the energy barriers and binding energies of hydrogen in normal interstitial sites and around point defects (MULTIHY).*
>
> *In solar cell material development, ab initio models are used to calculate changes in the work functions of metal electrodes upon deposition of self-assembled monolayers (MINOTOR) and the energy, electronic distribution and properties of nanostructures in PV excitonic solar cells (INNOVASOL).*
>
> *These models can also cover superconducting systems and are then used to predict electronic and superconducting properties at interfaces of layers with different axis orientation (SUPER-IRON).*

Given the challenges of solving the Schrödinger equation, quantum mechanical calculations can only be performed for isolated systems (in vacuo) and at zero temperature. However, often the output of ab initio quantum mechanical models is used as input to develop parameters for models at higher scales, in the development of interatomic potentials or to calculate partial atomic charge distribution. This ensures the incorporation of crucial quantum effects and properties for larger, more realistic, systems simulations at a reduced computational costs and time.

The Schrödinger equation can be solved for small molecular systems if one considers that the mass of the nuclei is much larger than the mass of the electrons, the Born-Oppenheimer approximation. This assumption is valid if the electrons move much faster than the nuclei and the electrons feel the electric field of the nuclei *as if* the nuclei are in a fixed position. The electronic wavefunction of the electrons depends then only on the position of the nuclei and not on their momenta.

Basis sets

To solve the Schrödinger equation numerically the concept of basis sets of wavefunctions is introduced. The orbitals are expanded as a linear combination of such functions with the weights or coefficients to be determined.

Often a simple and effective basis set is made of linear combinations of atomic orbitals (LCAO) centered on the nuclei. Basis sets composed of Gaussian functions centered on the nuclei are also popular because of their flexibility in implementation and, only if needed, functions centered on bonds or lone pairs are added.

In solids and other systems with periodic boundary conditions, it is common, and sometimes more appropriate to use basis sets composed of plane waves up to a cutoff wavelength. These functions are naturally periodic and independent of the atom positions and are therefore appropriate to describe the delocalized electrons in solid crystal (electron gas).

In all cases, the choice of the most appropriate basis functions depends on the system under consideration and the level of accuracy that is needed in the final result. A large number of ready-made basis sets are available and implemented in commercial codes, but new basis set are sometimes generated to study systems that present new challenges.

1.1.1 Hartree-Fock (HF) model

In so-called wave-function based approaches, the Hartree–Fock (HF) model is the conceptual starting point of molecular poly-electron structure calculations. The orbitals of the system are expressed in a set basis functions (discussed in the previous section) and the coefficients of this expansion are obtained numerically using a variational procedure that iteratively refines the individual electronic solutions to obtain the configuration that yields the lowest total energy (also known as the SCF, self-consistent field method).

Several approximations are applied in a Hartree-Fock calculation. First, the Born-Oppenheimer approximation is assumed and relativistic effects are neglected. Moreover, each particle is thought to be subjected to the mean field created by all other particles. This means that the method is neglecting the electron-electron correlation terms in the Hamiltonian. This method thus fails to represent strongly correlated systems, and systems close to the dissociation limit, as well as the weak dispersion interactions between molecules.

> *Ab initio Hartree-Fock electronic calculations have been used to calculate structures, electronic density distribution and mobilities, partial atomic charges and electric dipoles ([INNOVASOL](), [MUST](), [ONE-P]() and [ORAMA]()).*

1.1.2 Higher level ab initio models

The Hartree-Fock method has fundamental limitations. It provides a localised representation of molecular orbitals which is not appropriate in highly dispersive systems and electron correlation is neglected. Higher level quantum chemical methods have been developed to overcome these simplifications and provide the most accurate calculation results of electronic structure.
These methods include: Configuration Interaction (CI), which includes the excited states in the description of the electronic state. Coupled Cluster (CC) takes the basic Hartree–Fock molecular orbital method and constructs multi-electron wavefunctions using the exponential cluster operator to account for electron correlation. Møller–Plesset perturbation theory (MP2, MP3, MP4, etc.) improves on the Hartree–Fock method by adding electron correlation effects as a second order perturbation of the Hartree-Fock Hamiltonian. These methods devise schemes which can, at least in principle, be infinitely refined by the addition of higher level terms. For example, a CCSD(T) calculation simply means a calculation done using a coupled-cluster method, which includes singles and doubles fully and triples are calculated non-iteratively.Note that due to their higher computational cost, these methods can only be applied to systems very limited in size.

> *Traditional post-Hartree-Fock methods (e.g. MP2 or CCSD(T) methods) on cluster models has been used to study the catalytic activity of MOFs by modelling reactions catalysed by Lewis acid sites ([MACADEMIA]()); and to study the proton conductance in the proton exchange membranes ([HYPOMAP]()).*

1.1.3 (Electron) Quantum Density Functional Theory

A popular and versatile model that includes (some of) the effect of electron correlation (albeit approximately) is quantum Density Functional Theory (DFT).

Quantum DFT is based on the Hohnberg-Kohn theorem that states that ground-state energy is uniquely defined by the electron density. The properties of a many-electron system are then determined by using functionals, i.e. functions of the spatially dependent electron density. Quantum DFT calculations usually consist in solving the Kohn–Sham equation which is the Schrödinger equation of a fictitious system (the "Kohn–Sham system") of non-interacting particles (typically electrons) that generate the same density that the real system of interacting particles would generate. This simplifies the formulation greatly because instead of explicitly including the real potential of many interacting electrons, the Kohn–Sham equation contains a local effective (fictitious) external potential of non-interacting particles.

Although continuous notions like electron density are used, these models describe the behaviour of electrons and are thus called "electronic".

Typically, the biggest additional modelling necessary in quantum DFT is the formulation of the exchange-correlation functionals, which need to model not only the electron exchange and correlation energy terms but also the difference between the kinetic energy of the fictitious non-interacting system and the real one. The equations are then solved using an iterative self-consistent approach based on the variational principle.

The simplest way to implement quantum DFT is using the local density approximation (LDA) where the functional depends only on the density at the place where the functional is evaluated. A further refinement is obtained considering the generalized gradient approximation (GGA) which is still local but also takes into account the gradient of the density at the same place.

However, for many solid-state systems, and in calculations of electron behaviour in molecules (chemistry), more sophisticated functionals are often needed, and a huge variety of exchange-correlation functionals have been developed. For calculation of electron behaviour in molecules, the so-called B3LYP functional is widely used, and is mentioned as an example of a hybrid functional in which the exchange energy, in this case from Becke's exchange functional, is combined with the exact energy from Hartree–Fock theory. The adjustable parameters in hybrid functionals are generally fitted to a 'training set' of molecules. Although the results obtained with these functionals are sufficiently accurate for many applications, there is no obvious systematic way of improving them (in contrast to some of the higher level ab initio methods like configuration interaction or coupled cluster theory). In the current quantum DFT approach, error is estimated comparing the results to other methods or experiments.

Computational costs are relatively low when compared to higher level ab initio methods based on the complex many-electron wavefunction. However, there are still difficulties in using quantum Density Functional Theory to properly describe charge transfer excitations; transition states, global potential energy surfaces and strongly correlated systems; and there are inaccuracies in quantum DFT calculations of the band gap in semiconductors, to mention a few examples.
 Improving quantum DFT calculations by modifying the functional or by the addition of terms to overcome these problems is an active research topic.

Spin polarized quantum DFT is an extension of quantum DFT which includes both the electron density and the up and down spin densities explicitly in the Kohn-Sham equations.

In chapter 2 and in chapter 3 it is presented how the theory can be extended to atoms and particles.

Density functional theory (DFT) has been used to perform quantum mechanical electronic calculations in a large number of projects (GOFAST, GRENADA, HIPERSOL, HYPOMAP, INNOVASOL, LEMSUPER, MONAMI, MORDRED, NAMASTE, NEXT-GEN-CAT, ONE-P, ORAMA, SURFUNCELL).

DFT has been applied to model non-collinear magnetism, electric fields applied to surfaces, electric polarization and the mapping of the electronic structure to tight-binding Hamiltonians (IFOX).

The catalytic activity of MOFs is explored modelling reactions catalysed by Lewis acid sites, using periodic DFT calculations and toi characterise the chemisorption processes occurring at the surface of open metal centres of metal organic frameworks (MOFs) (MACADEMIA). DFT has been used to calculate electronic properties (critical temperatures and magnetic anisotropy) of thin polycrystalline magnetic films and to study the influence of the electronic correlations at the interface in hybrid metal/oxide-based magnetic bilayers in a nanocomposite system (NANOPYME). DFT has also been used to calculate the adhesion of metal-ceramic interfaces and internal grain boundaries in realistic conditions (ROLICER). Spin polarized DFT is used to calculate to calculate the magneto-crystalline anisotropy and the exchange interaction between atomic spins (ULTRAMAGNETRON, REFREEPERMAG, MAGNONICS, DYNAMAG, ATHENA, CRONOS). In ROMEO the role of the specific structural distortion near grain boundaries on the magneto-crystalline anisotropy and magnetization will be determined by means of first principles DFT calculations.

1.2. Many body models and effective Hamiltonians

The many-body problem is a general name for a vast category of physical problems where a large number of equations for a large amount of particles need to be solved in order to provide an accurate description of the system. This is e.g.the case in a large many-electron system or when it is necessary to include the effect of the surroundings on the system of interest (for example, in solvation models the weak interactions of the (small) quantum system with the (many) solvent molecules are treated approximately to keep the computational costs limited).

A large number of many-electrons systems can be studied theoretically by the models that have been discussed in the previous paragraph. However, when the system size increases the calculations required by full ab initio methods and DFT methods become very quickly unfeasible.

In addition, ab initio methods are commonly solved through approximations which limit their accuracy. For example, in highly correlated systems and in solids where electrons may be considered as nearly localised, solving the Schrödinger equation within an independent electron scheme fails to reproduce experimental results.

There are several ways to approach a many-body quantum problem, depending on the characteristics of particular system at hand, however it most often relies on more drastic approximations on the Hamiltonian or wavefunctions representation.

Effective Hamiltonians

Except in few simple cases, models that treat many-body electron interactions require the definition of an "effective" Hamiltonian. This is a simplified representation of the true Hamiltonian where some parameters are derived from empirical data. These methods are very popular because they allow to treat large systems (up to millions of non-equivalent atoms), where a full ab-initio method without the approximations would often be computationally too expensive.

<u>Dynamic Mean Field Theory</u>

The many body Dynamical Mean Field Theory (DMFT) is a method to approximate many body Hamiltonians and it is designed to deal with strongly correlated materials. In such materials, the approximation of independent electrons, which is used in Density Functional Theory band structure calculations, breaks down. DMFT adds the contribution of the local interactions between electrons and bridges the gap between the nearly-free electron gas model and dense condensed-matter models. DMFT can be used to model the phase transition between a metal and a Mott insulator, a process where the strength of electronic correlations increases.

> *DMFT has been successfully applied to real materials to calculate material properties of strongly correlated systems like high temperature superconductors (MONAMI, GOFAST and LEMSUPER)*

1.2.1 Nearly-free electron model

The electronic band structure of metals can be described by the simplest effective Hamiltonian, which treats electrons in a solid as moving almost freely through the crystal lattice.

1.2.2 Pseudopotentials

Pseudopotentials provide an approximation of the full Hamiltonian. They can be developed to approximate the core (i.e. non-valence) electrons of an atom and its nucleus with an effective potential, or pseudopotential. This approach considers the nuclear charge as effectively screened by tightly bound core electrons. As a consequence, only the chemically active valence electrons are treated quantum mechanically, thereby reducing the number of electrons in the Schrödinger equation and the size of basis sets.

> *Semi-empirical pseudopotentials have been used to calculate electronic energies and lifetime of charge carriers in large structures (10-100nm) with up to millions of non-equivalent atoms (HIPERSOL).*

1.2.3 Semi-empirical tight binding potential (TB) model

The opposite extreme to the nearly-free electrons is the case where the electrons in the crystal are tightly bound and behave much like the atoms, as in the tight binding model (TB). The method is closely related to the LCAO method used in ab initio models. Electrons are viewed as occupying the standard orbitals of their atoms, and then 'hopping' between atoms during conduction.
Tight binding models are applied to a wide variety of solids. The approximation often works well in materials with limited overlap between atomic orbitals and limited overlap between potentials on neighbouring atoms. Band structures of materials like Si, GaAs, GaN, SiO_2 and diamond for instance are well described by TB-Hamiltonians.

> *This model can be used to perform finite-temperature simulations, and calculate thermoelectric properties and electronic transport calculations (OXIDES), to evaluate hydrogen trapping at extended crystal defects such as grain boundaries and dislocations (MULTIHY) to explore effects connected to finite temperature and disorder (ATHENA) and to describe electronic and optical properties of GaN based nanowires (SMASH). Effective tight-binding Hamiltonians will be constructed starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (Jc, Hc, Tc) by*

means of Bogoliubov-De Gennes equations. This will give information on the superconducting properties: order parameters in real space across the boundary, superconducting current flow at the boundary and critical currents (Jc° and how the superconducting properties of FeSCs are affected by the mis-orientation angle will be predicted. First-principles models of effective interactions between electrons, including spin fluctuations, will be elaborated to provide fundamental information on the superconducting transition, and its dependance on the critical temperature. The calculation of superconducting properties will be done extending the ab-initio SuperConducting Density Functional Theory with electronic pairing interactions (SUPER-IRON).

1.2.4 Hubbard model

The Hubbard model is the simplest model of interacting particles in a lattice, with only two terms in the Hamiltonian: a kinetic term allowing for tunneling ('hopping') of particles between sites of the lattice and a potential term consisting of an on-site interaction, which stems from the Coulomb repulsion between electrons occupying the same atomic orbital. For electrons in a solid, the Hubbard model can be considered as an improvement on the tight-binding model, which includes only the hopping term. The Hubbard model is actually the simplest model able to describe the interaction-driven transition from a metal to an insulator, commonly known as the Mott transition. Mott insulators are commonly found within transition metal oxides and organics, where the Coulomb repulsion overwhelms the very narrow bandwidth. More recently, the Bose- and Fermi-Hubbard models has been used also invoked to describe the behavior of ultra-cold atoms trapped in optical lattices. The Hubbard model is a good approximation insofar the effect of all other bands but the conduction ones can be neglected, which corresponds to low enough temperature and energy so that all interband transition are uninfluential. If interactions between particles on different sites of the lattice are included, the model is often referred to as the 'extended Hubbard model'.

The fact that the Hubbard model cannot be solved analytically in arbitrary dimensions has led to intense research into numerical methods for strongly correlated electron systems.

The Hubbard model can also be studied within the Monte Carlo statistical method for example to study the electronic exchange interaction in non-equilibrium situations (FEMTOSPIN). Molecular Hubbard models for ground state and low temperature properties of strongly correlated materials have been used to calculate long ranged electron-electron interaction and insulator-superconductivity transitions in lattices under pressure (LEMSUPER) and to model the Hamiltonian of inorganic metal nanoparticles embedded in matrices of conjugated organic materials (HYMEC).

1.2.5 k·p effective Hamiltonian

This is a technique that allows a band structure to be approximately described in terms of just a few parameters. The technique is commonly used for semiconductors, and the parameters in the model are often determined by experiment.

This model can be used to calculate conduction and valence band valence band structure around a point of symmetry and effective masses of the charge carriers. Thereafter these values can e.g. be used as input to a drift diffusion model calculating the electron and hole transport (SMASH) or to micromagnetic models for magnetisation (NAMASTE).

1.2.6 Polarisable continuum model

The polarisable continuum model (PCM) is commonly used to model a solvent-mediated chemical reaction. For a system with very many solvent molecules, the computational cost of modeling would grow prohibitively high, if it were necessary to consider each solvent molecule as a separate molecule. Instead the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecules. The solvated molecules electronic field is modelled with one of the available electronic models.

> *This model has been used to simulate the effect of surrounding solid electrolyte weakly interacting with the conductive molecules in excitonic solar cells (INNOVASOL).*

1.2.7 Envelope function approximation

This is a model that proposes an approximation of the wavefunction, based on the fact that the wavefunction varies very quickly close to the cores of the atoms of the lattice. In the he *envelope approximation* only the slowly varying "envelope" modulating the rapidly varying part of the wavefunction is considered. The boundary conditions are applied to the envelope function directly, rather than to the complete wavefunction.

> *This method is used to calculate the quantum states of confined particles in nanostructures (SMASH).*

1.3. Quantum mechanical in response to time dependent fields

To study electronic and spin dynamics under the effect of external time dependent potentials, such as electric or magnetic fields, time dependent models are needed.

1.3.1 TD-DFT and TD(Spin)DFT

Time-dependent density functional theory (TDDFT) is a quantum mechanical model used to investigate the properties and dynamics of many-body systems in the presence of time-dependent potentials, such as electric or magnetic fields. The effect of such fields on molecules and solids can be studied with TDDFT to extract features like excitation energies, frequency-dependent response properties, and photo-absorption spectra.

As TDDFT is an extension of DFT, the conceptual and computational foundations are analogous and use the effective potential of a fictitious non-interacting system which returns the same density as any given interacting system. Numerically, this TDDFT model is much more complex then DFT, most notably because the time-dependent effective potential at any given instant depends on value of the density at all previous times. Note however that at present most of the implementation assume a local time-dependence of the potential (adiabatic approximation).

> *TDDFT is able to account correctly for magnetic fluctuations in the paramagnetic state of iron and other itinerant ferromagnets, the effects of vibrations (electron-ion dynamics) on photo-energy conversion (CRONOS, INNOVASOL) and it is used to calculate transport properties in systems with a strong correlation term between particles (HYMEC).*

> *If needed, the equation of motion for the spin degrees of freedom can be derived with time-dependent spin-density-functional theory TD-SDFT, which includes the spin density interacting with the external magnetic field. This can then be used to calculate non-linear interactions between spin, conducting electrons and laser light ([FEMTOSPIN](#) and [CRONOS](#)).*

1.3.2 The time-dependent k·p-model

This quantum kinetic model describes the time evolution of the multi-band electronic state and is a linear coupled system of Schrödinger equations. The evolution is governed by the k·p Schrödinger operator which as an extension to the single-band models describes a system of bands of the band structure, usually the four topmost valence bands.

1.3.3 Other time-dependent models

The time-dependent approach based on the Gutzwiller wave function and approximation is a very simple tool that allows simulating for quite long times the non-equilibrium evolution of correlated electron models. It is in essence an improvement of the time-dependent Hartree-Fock approximation, endowing a Hartree-Fock Slater determinant with local many-body correlations that better capture the collective nature of the Mott localization phenomenon. It is a rigorous variational approach in the limit of large lattice-coordination, but seems to provide qualitatively correct results also beyond that limit.

> *The time-dependent Gutzwiller approach is able to model the temporal evolution of correlated materials brought out-of-equilibrium by ultra-fast laser pulses ([GOFAST](#)).*

The Blonder-Tinkham-Klapwijk model is used to describe the normal-superconducting microconstriction contacts at the crossover from metallic to tunnel junction behavior. The Blonder-Tinkham Klapwijk (BTK) model in its simplest form does not require any input from other models. In its 3D extension, the BTK model requires in input the shape of the Fermi surface. In any case, this model allows fitting the gap features of the point-contact Andreev-reflection (PCAR) spectra and thus obtaining the amplitude and the symmetry of the superconducting gap(s).

The multiband Eliashberg theory includes interband spin-fluctuation interactions and describes superconductivity-induced infrared optical anomalies. The multiband Eliashberg model requires some input from band structure calculations (normal DOSs at the Fermi levels) and contains 2 free parameters (namely the coupling strengths) that can be adjusted to reproduce the gaps provided by the BTK fit of the spectra and the experimental critical temperature.

In particularly good contacts, the point-contact spectra also contain electron-boson structures that cannot be fitted by the simple BTK model; in these cases, since one of the outputs of the Eliashberg model is the whole energy-dependent gap function, this may be put in the extended BTK model to calculate theoretical point-contact spectra that feature electron-boson structures that can be compared to the experimental ones.

> *These models have been used to calculate the intrinsic physical parameters (superconducting transition temperature, penetration depth, upper critical field) and superconductance energy gaps ([IRON-SEA](#))**,** which are very important intrinsic physical parameters in superconductors.*

1.4. Statistical charge transport model

To describe the transport of charge carriers in solids or liquids, statistical methods can be used, like statistical approaches to drift-diffusion (also called convection-diffusion) and the statistical percolation model described below. It should be noted that the underlying methodology can be applied to other entities like atoms and molecules, see Chapter and and

1.4.1 Statistical semi-classical transport model for drift-diffusion

In simple homogeneous materials transport (convection-advection-diffusion-drift) can be described by continuum description of a diffusion-advection equation (also called drift diffusion) with a well-defined diffusivity coefficient. However in disordered material this does not work and therefor a statistical semi-classical model to describe the transport of charge carriers in solids has been developed.
The Boltzmann Transport Equation model has been used in the analysis of transport in semiconductors. This is an equation for the probability of particle occupation of energy at position and time. The solution to the BTE is cumbersome but can be solved numerically by a stochastic Monte Carlo method. This describes hopping of the entity (here electrons but in Ch 2 and 3 resp. the equation is used to describe the motion of atoms and particles) on a lattice of sites (hopping rate equation). To arrive at the behaviour at longer time and length scales a process of averaging is applied. This becomes equivalent to a continuum drift-diffusion equation with a diffusivity specific for the material. The carrier density distribution can be modelled using quantum mechanical Fermi-Dirac statistics or Boltzmann statistics. The necessary input parameters like band gap, carrier mobility and electron diffusion coefficient are obtained empirically or with separate theoretical calculations, using the Einstein relation. Disorder has to be taken into consideration if the sites of lattice are randomly distributed and hopping rates might depend on energy states on the sites. Monte Carlo simulations have been performed in order to approximate the diffusivity for certain disordered systems. External forces might be added to the equation.

> *The statistical transport model has been used to simulate electronic transport in large diameter hetero-junction nanowires with tunnel junctions (AMON-RA), to calculate electron transport across oxides interfaces (MORDRED), electron and holes transport in Gallium Nitride based nano-rod structures (SMASH) and to calculate steady state conductivity (high and low state) in organic semiconductor device (HYMEC).*

1.4.5 Percolation models

Statistical approaches for electrical conductivity are also applied in percolation models.Transport due to percolation is represented as movement through a three-dimensional network of vertices in which the edge or "bonds" between two neighbors may be open (allowing the particles through) or closed with a certain defined probability. Electron tunnelling is described with quantum mechanical percolation models which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunneling between carbon nanotubes with a given probability.

> *Electron tunneling percolation models are used to predict electron percolation thresholds for polymer/CNT composites and electrical conductivity of polymers reinforced with CNT (IMS & CPS).*

Chapter 2
Atomistic models

Atomistic models are physics/chemistry equations that describe the behavior of atoms and are simulating the behaviour of larger e.g. molecular systems (typically between 10^2 and 10^9 atoms) maintaining individual atomistic detail, but removing an explicit representation of the electrons. Although the application systems are not always large enough to be considered macroscopic, they are often sufficiently large to reproduce experimental results within the desired accuracy and at the same time detailed enough to detect their microscopic origin.

Fig.2.1 Number of projects that used one of the four main types of atomistic models treated here.

Input to atomistic models: Interatomic potentials

Atomistic models need as physics input a description of the forces on the entities (atoms).

In order to describe atom behaviour in molecules/lattices, the interaction forces between the atoms can be expressed by interatomic potentials. Interatomic forces are forces of attraction and repulsion which act on atoms. Interatomic forces may be represented by the Lennard-Jones potential, which contain an attractive term and a repulsive term. The attractive term approximates dipole-dipole forces, ion-dipole forces, van der Waals forces (Keesom force, Debye force, and London dispersion force). The repulsive term approximates the Pauli repulsion.

This input to the atomistic models (interatomic potential functions and parameter sets) can be derived from experiments or calculated by smaller scale electronic models (see Chapter 1) for a small number of appropriate test atoms. Validation of parameter sets is done against experimental results on larger and more diverse systems. Often an iterative procedure for the refinement of the parameters is needed. The most important aspect in the development of the interatomic potentials is to ensure transferability of parameters across a diverse range of systems and test the accuracy limits of the parametrisation.

The next step is to model the interactions expressing the potential energy functions between the atom considered and surrounding atoms.

 Molecular Mechanics Force Fields

Interatomic potentials can be described using so-called "molecular mechanics force fields". This approach can be used in molecular mechanics, Molecular Dynamics or Monte Carlo simulations. To describe the potentials in molecules, typically, first each atom is modelled by assigning a radius (usually the van der Waals radius), a polarisability and a constant net charge (generally derived from quantum calculations and/or experiment). Force fields usually consist of a sum of additive terms. The terms represent both bonded interactions (between atoms that are actually covalently bonded) and non-bonded interactions. Terms between bonded atoms include: bond terms between 2 atoms, bend terms between 3 atoms, and torsional (dihedral) terms between 4 atoms. Bond and bend terms are often treated as springs with an equilibrium distance equal to the experimental or calculated value. The dihedral or torsional terms have multiple minima and cannot be modeled as springs, and their specific functional form varies in different force fields. Additionally, "improper torsional" terms may be added to enforce the planarity of aromatic rings and other conjugated systems, and "cross-terms" may be added that describe coupling of different internal variables, such as angles and bond lengths. Some force fields also include explicit terms for hydrogen bonds.

The non-bonded terms are much more computationally costly to calculate in full, since a typical atom is bonded to only a few of its neighbors, but interacts with every other atom in the system. The electrostatic force between charged particles is a typical non-bonded interaction and is given by Coulomb's law. Long-range electrostatic interactions are often important features of the system under study (especially for proteins) but the electrostatic terms are notoriously difficult to precisely calculate well because they do not fall off rapidly with distance. A variety of methods are used to address this problem; the simplest approximation consists in using a cut-off range for these interactions and atom pairs whose distances are greater than the cutoff have a van der Waals interaction energy of zero.

 Other more sophisticated but computationally intensive methods are known as Particle Mesh Ewald (PME) and the multipole algorithm. To account for electronic polarisability and in order to produce better agreement with experimental observations, parameters can be buffered or scaled by a constant factor.

Other non-bonded forces are London dispersive interatomic forces (attractive) and electron-electron short range forces (repulsive). These are typically modelled together using the so-called Lennard-Jones potential.

Notwithstanding their simplicity, force fields can reproduce quite well a wide variety of chemical and biological problems, including drugs binding, protein folding kinetics and protonation equilibria.

Bond Order Potentials (BOP)

Bond order potentials belong to a class of analytical potentials which is used in molecular simulations. Examples include the Tersoff potential, the Brenner potential, the Finnis-Sinclair potentials, ReaxFF, and the second-moment tight-binding potentials. They have the advantage over conventional molecular mechanics force fields in that they can, with the same parameters, describe several different bonding states of an atom, and they may thus, to some extent, be able to describe chemical reactions correctly. The potentials were developed partly independently of each other, but share the common idea that the strength of a chemical bond depends on the bonding environment, including the number of bonds and possibly also angles and bond length.

Flory-Huggins interaction potential

In classic polymer solution theory, this potential gives an expression for the Gibbs free energy change ΔG_m for mixing a polymer with a solvent and approximates three molecular interactions: solvent-solvent, monomer-monomer (not the covalent bonding, but between different chain sections), and monomer-solvent.

In chapter 3 this theory is extrapolated to interactions between particles.

Statistical Mechanics

Most of the model described in this chapter, are based on statistical mechanics, statistical thermodynamics and other probabilistic theory. They consist in treating the many-atoms system as a large statistical population, whose behaviour is determined by the forces applied to each single atom. Simulations are performed keeping the number of particles, temperature and total energy constant (the so-called microcanonical ensemble); the number of particles, temperature and volume constant (the so-called canonical ensemble) or the chemical potential, temperature and pressure (the so-called grand canonical ensemble). Statistical mechanics provides the mathematical framework for relating the microscopic properties of individual atoms and molecules to the macroscopic bulk properties of materials that can be observed in everyday life. These models explain macroscopic structural, thermodynamical and dynamical observables (e.g. temperature, pressure, work, heat, free energy, entropy and spectra of these variables) based on classical and quantum-mechanical descriptions of statistics and mechanics at the microscopic level. For example, a macroscopic observable like temperature is due at microscopic level to the collisions between particles and can therefore be mathematically derived sampling the velocities of the atoms.

For the statistical mechanics formulation to be valid, the averaging has to be done over all possible configurations of the system, i.e. all possible positions and momenta of all particles (ergodic condition). This is true if the simulation is infinitely long, and approximately true if the system is allowed to evolve for a sufficient amount of time. The ergodic condition may be more difficult to achieve in systems with many degrees of freedom, or with large energy barriers between possible configurations, as the systems may be trapped in one local energy minimum. Methods to overcome this problem and speed up the configurational sampling are an active field of research.

To determine whether or not to use continuum models or statistical mechanics, the Knudsen number may be evaluated for the problem. The Knudsen number is defined as the ratio of the molecular mean free path length to a certain representative physical length scale. This length scale could be, for example, the radius of a body in a fluid. More simply, the Knudsen number is how many times its own diameter a particle will travel on average before hitting another particle. Problems with Knudsen numbers at or above unity are best evaluated using fine scale (atomistic and mesoscopic) statistical mechanics for reliable solutions.

In general, atomistic models need input describing the interactions between the atoms and equations that are used to obtain the macroscopic properties that can be compared with experiments.

2.1 Classical Density Functional Theory and Dynamic Density Functional Theory

Density Functional Theory (DFT) equations (see [chapter 1.1.3](#)) can also be used to describe the behaviour of atoms using classical potentials. In classical DFT, the forces acting upon the atoms are described by an external (effective) free energy potential (similar to the ground state energy in the electronic model) which is a unique functional of the atomistic density profiles. As in the quantum equivalent, the modelling challenge is to formulate approximate density functionals for atoms in complex situations such as inhomogeneous complex fluids.

Classical DFT is used to study colloids, fluids at interfaces or in presence of an external potential, and phase transition phenomena.

The time-dependent extension of the classic DFT is Dynamic Density Functional Theory (DDFT).

The time evolution of the average density of Brownian particles (atoms) is given by the generalization of Fick's law to the diffusion of interacting particles in terms of the equilibrium Helmholtz free energy functional (or the grand canonical functional).

DDFT resolves density variations on length scales down to the particle size but only works for slow relaxing dynamics close to equilibrium.

2.2 Molecular Mechanics

Molecular mechanics uses classical mechanics to model molecular systems in order to calculate molecular geometry, energy, and various molecular properties. It does this by finding the lowest energy conformation of a molecule. The potential energy is calculated using force fields. The (local) minimum is searched for by an appropriate algorithm (e.g. steepest descent). Global energy optimization can be accomplished using simulated annealing, the Metropolis algorithm and other Monte Carlo methods, or using different deterministic methods of discrete or continuous optimization. Molecular mechanics can be used to study small molecules as well as large biological systems or material assemblies with many thousands to millions of atoms.

2.3 Statistical Mechanics models: Molecular Dynamics (MD)

The first important aspect of atomistic models concerns the descriptions of the forces between the atoms. The second important aspect of atomistic model is what physics or chemistry equations can be solved to obtain the macroscopic proprieties that are then compared with experiments.

The equations used in Molecular Dynamics to obtain macroscopic properties are the Newton equations of motion for all atoms in the system. Molecular Dynamics consists in simulating molecular trajectories by integrating the equations of motion. The time evolution of the simulation is broken down in small time steps. Using a numerical integration scheme, the dynamics of each atom in the system under the effect of the interatomic forces is calculated for each time step. The length of the time step chosen is a compromise between a value large enough to allow a reasonably long simulation time for the purpose of the study and a value small enough to capture all the required fundamental frequencies of motion in the system and conserve the energy between integrations steps. Typically this is in the range of 1-10 fs, but depends on the range of motions allowed in the system. Multiple time scale calculations, where rapidly changing forces are updated more frequently than slowly changing forces, are also possible in order to reduce the required computational time.

Large systems which are repetitive at a certain scale can be simulated using periodic boundary conditions. In these, forces are calculated only for atoms contained in a unit cell and then replicated across 1, 2 or 3 dimensions to simulate the effect of particles entering and leaving the unit cell. The size of the unit cell needs to be large enough so that each particle does not feel the influence of its mirror image in one of the replicated cells.

Temperature and pressure can be controlled using numerical methods that simulate the effect of a thermostat or barostat or using stochastic methods like Langevin dynamics that add friction and random forces to account for molecular collisions.

The main advantage of molecular dynamics with respect to some other molecular simulation methods is that not only does it allow obtaining macroscopic properties (e.g. temperature, pressure, work, heat, free energy, and entropy) that can be compared with experiment, but also the trajectory of the system during the simulation from which dynamical and structural quantities can be obtained.

Simulations with molecular dynamics can reproduce conditions in real life experiments and even experiments that are not possible, safe or wise to perform.

2.3.1 Classical Molecular Dynamics

Molecular Dynamics (MD) calculations performed using force fields and integrating the classical Newton's equations of motions for atoms are called classical MD. Several software packages are available (see Annex II) and several implement their own force field. If the force fields parameters are derived from experimental data, classical Molecular Dynamics is often called empirical Molecular Dynamics.

Classical molecular dynamics has been used for the calculation of the trajectories of guest molecules within the metal-organic frameworks and then the calculation of the guest diffusivity by means of the Einstein mean squared displacment plots (AMCOS). Molecular Dynamics (Garofalini force field) has been used to model cement hydration (CODICE). Classical molecular dynamics has been used to model morphological properties of solar cells, light emitting diodes, transistors, batteries and ultra capacitors. They are used to generate the Si/Ag and Si/Ni interfaces accounting for strain and misfit dislocations to investigate influence of N content and gradients on the trap density at the interface (HIPERSOL). Classical molecular dynamics has also been used to calculate the interface dipole at organic/organic interface (MINOTOR), to predict the bulk organization and simulate realistic interfaces between the insulating layer and the organic semiconductor at the nanometre scale (ONE-P).
Classical molecular dynamics has been used to calculate physical properties of nanostructured materials (MONAMI), to calculate dynamic charge transfer in nanoelectronics devices (MORDRED) and to calculate properties of branched polymers as host matrices for Li-ion battery solide polymer electrolytes (SUPERLION).

Classical molecular dynamics has been extensively used to study interface problems in matrices, composites, coatings, cracks and defects structures. In particular, it has been used to simulate deposition of atoms and formation of lattice structures of coatings and layer interfaces in thermodynamic process in multi-layered films as input for micromechanical models (M3-2S) to calculate the selectivity and transport properties of different materials for industrial separation processes in different mixtures and state (MACADEMIA) to determine average confirmation, chain stiffness, degree of counterion condensation of polyelectrolyte chains, formation of surfactant polyelectrolyte complexes and adsorption of single electrolyte chains, formation of polyelectrolyte layer (MUST), to study large scale defect structures in the ceramics such as dislocation and incoherent grain

boundaries ([ROLICER](#)), to calculate strength of hydrogen bonding and dispersion interactions and adsorption of water or carbohydrate in cellulose surfaces ([SURFUNCELL](#)). In surface engineering of reinforced and nanostructured composite and polymers, classical molecular dynamics has been used to simulate the effect of functionalization of the mechanical properties of the CNT and calculate the stress strain slope as well as the interfacial interactions between CNTs and polymeric matrices ([POCO](#)), to extract local traction and crack opening displacement data and calculate densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties to validate the simulation of the polymer network formation in the epoxy resin ([NANOINTERFACE](#)).
In hydrogen storage and fuel cells development, it has been used to simulate adsorption in proton exchange membranes ([HYPOMAP](#)). Large scale molecular dynamics will be used to study the crystallization dynamics and thermal properties of several phase change compounds amorphous phase in the bulk and in nanowires, by using empirical interatomic potentials ([SYNAPSE](#)).

2.3.2 Ab initio Molecular Dynamics

With the progress of computational speed and memory, it is possible to perform calculations of Molecular Dynamics which take into consideration explicitly the effect of the electrons in the calculation of the forces (ab initio MD). Although still limited to smaller systems and shorter periods of time than classical MD, a significant advantage of using ab-initio methods is the ability to study, without empirical parameters, reactions that involve breaking or formation of covalent bonds, tunneling and proton transport mechanisms.

The main challenge consists in calculating efficiently and accurately the forces acting on the nuclei due to the electrons. Since many electrons are in the system their potential energy is represented by a multidimensional surface for each nuclei configuration. Assuming that it is possible to decouple the motion of the electrons from the motion of the nuclei (Born-Oppenheimer approximation), the classical equations of motion for the nuclei are integrated using the sum of the interatomic potential and the forces derived from the electron potential energy surface. At each time step, the ground-state electronic potential surface can be calculated using standard quantum mechanical methods (Born-Oppenheimer Molecular Dynamics) or introducing fictitious dynamics for the electrons which follow adiabatically the nuclei and are subjected to small readjustments "on the fly" during the nuclei evolution to keep them close to the ground state potential surface **(**Car-Parrinello Molecular Dynamics).

Car–Parrinello and Born–Oppenheimer first principle Molecular Dynamics simulations were conducted for the calculation of the charge distribution in metal-organic frameworks ([AMCOS](#)). Ab initio MD has been used to model mechanical, magnetic and electrical properties of graphene ([GRENADA](#)), to calculate pressure induced metallisation of potential high pressure superconductors ([LEMSUPER](#)), to calculate ab initio surface and interface energies in metal alloys and electric active materials ([MINTWELD](#)), and to calculate magnetic properties, solvatochromism, non-linear optical properties, like hyper-polarisability and two-photon absorption of large solvated systems including more than 10,000 atoms ([MONAMI](#)). Defect diffusion will be studied without an external field either using classical force fields or fully ab-initio Car-Parrinello methods ([IFOX](#)).Car-Parrinello-like molecular dynamics simulations based on density functional theory will be performed to model the atomistic structure of the amorphous and crystalline phases of chalcogenide alloys ([SYNAPSE](#)).

2.3.3 Quantum Mechanics/Molecular Mechanics (QM/MM)

For systems in which full consideration of electrons is not feasible, it may still be possible to perform calculations that retain some quantum mechanical details. Quantum Mechanical/Molecular Mechanics methods (QM/MM) consist in finding a working subdivision of the system into a part that needs to be calculated at quantum mechanical level and a (larger) part that can be calculated using classical force fields. *In the strictest sence this is thus a method encompassing an electyronic and an atomistic model.* They are used to model atoms for energy optimization calculations, calculation of reaction paths and other explorations of the potential energy landscape, and molecular dynamics simulations. For example, a QM/MM scheme can be used to calculate the reactions occurring between a drug and the target protein binding site atoms, while the rest of the protein is simulated with classical molecular dynamics. The challenge is to define the forces at the interface between the region treated with QM and the region treated with MM.

> *QM/MM has been used to calculate the adhesion of proteins at the interface between a glassy SiO2 phase and a water solution, relevant to pharmaceutical applications and the cohesion between a glassy SiO2 phase and crystalline TiO2 phases, relevant to thin-layer-based conditioning of glass materials for applications in architectural glass and photovoltaic cells (ADGLASS).*
> *ONIOM-like scheme (DFT/MM) have been used to simulate the formation energy of inclusion complexes in layered magnesium oxides, relevant for the synthesis of quasi-solid electrolytes to be used in solar cells and binding energy of the different crystallographic phases to organic passivants (INNOVASOL).*
> *DFT/MM gives reaction paths and relative energies of stationary points on the reaction paths for large systems of metal organic frameworks (MACADEMIA) and in organic-based electronic devices (MINOTOR).*

2.4. Statistical Mechanics models: Monte Carlo Molecular Models

In the mathematical framework of statistical mechanics, it is not necessary to follow the dynamics of the systems to calculate macroscopic observables. These are in fact derived from an accurate sampling of all equivalent microscopic configurations of the system.

First a model of the potential energy of the system, like in Molecular Dynamics is established. The Monte Carlo technique is then used for sampling all possible configurations of the system. This technique consists in generating configurations of the system The new configuration is then accepted or rejected on the basis of the energy change that the results for the move, in general. Although Monte Carlo is a well-known technique used for sampling in a variety of different fields in the context of molecular simulations, the fact that it does not describe the dynamics of a system influences the physics and chemistry that can be included in the simulation and leads to definitions of the energy potential that would not be possible in Molecular Dynamics.

Statistical thermodynamics equations are subsequently used to derive the macroscopic observables (e.g. temperature, pressure, work, heat, free energy, and entropy) from the positions of the atoms in all configurations sampled, even if each subsequent configurations are not connected with each other in time. With MC technique the sampling efficiency can be increased, which is particularly important where the potential surface contains many local minima (as in close to state transitions, in large proteins etc). Note also that the random sampling of Monte Carlo based methods fulfills the ergodic condition intrinsically.

The success of this technique in statistical mechanics has led to various generalisations, such as the method of simulated annealing for energy optimisation of a system, in which a fictitious high temperature is introduced to obtain a fully random sample and then gradually lowered to obtain a configuration close to the ground state. Hybrid Monte Carlo methods introduce an acceptance criterion into molecular dynamics simulations, allowing the use of large time steps.

Note that the Monte Carlo technique is often used as a solver, for example in "Kinetic Monte Carlo methods". Kinetic Monte Carlo methods apply the same statistical principles to simulate the time evolution of the processes under consideration. But it is the physics/chemistry model that has to prescribe the forces, typically expressed by transition rates with which these processes evolve. Kinetic Monte Carlo methods and other solvers are described in more detail in Ch. 5.2. There should also be no confusion with kinetic reaction models, which are continuum models of chemical reactions (Ch 4.5)

Monte Carlo Molecular Models have been used to predict the CO2 sorption isotherms in the investigated materials: zeolitic imidazolate frameworks, hyperbranched aminosilicas, and functionalised polymers (AMCOS), to study the aggregation of C-S-H particles growth of microstructure using macroscale parameters (CODICE), to calculate diffusivities of charge carriers and band structure for up to 10000 atoms (HIPERSOL), to describe adsorption phenomena when specific interactions occur that can't be treated using generic force field (MACADEMIA), to calculate charge carrier propagation and density in the doped layer (MINOTOR), to calculate statistical variability of electrical impact of defects (MORDRED). Atomistic Monte Carlo simulations have also been used to determine adsorption sites of Phase Change Materials (PCMs) molecules inside the pigment at different pressures and temperatures and to calculate interactions energies between nanoparticles/pigment surfaces, in order to select the more suitable conditions for adsorption, predict the kind of molecules that can be adsorbed (type of functional groups and sizes of the molecules) and preferred adsorption sites (NANOPIGMY).

2.5. Atomistic spin models

Spin models are used to describe magnetic material properties. A spin here normally represents the magnetic moment of an atom, the energy of which is typically parameterized within a Heisenberg formalism, though even relativistic interactions, like Dzyaloshinskii-Moriyam interactions or anisotropies can be taken into account. The fact that magnetic structures are described on an atomic level allows for an investigation of ferromagnets as well as ferrimagnets and antiferromagnets or even heterostructures composed of different materials.
In the classical limit the equation of motion is the Landau-Lifshitz-Gilbert (LLG) equation.
The LLG equation describes the spin precession that follows from Heisenberg's equation of motion and its relaxation into an equilibrium direction via a damping term (either after Landau and Lifshitz or after Gilbert) with a corresponding damping parameter. Though the LLG equation is partly pheno-menological this approach turns out to be very successful.

FEMTOSPIN developed a model which currently can treat up to 10^8 spins for 2-D structures corresponding to up to 1000 nm length scale, and up to some nano seconds time scale.This model has been used to calculate dissipation channels and energy transfer in order to identify optimal materials for ultrafast optically induced magnetic switching and the relevance of the specific spin ordering in ferro-, ferri-, antiferro-magnetic and magnetic semiconductors.

2.6 Statistical Mechanics for atomistic systems

Statistical mechanics (see introduction of Chapter 2) provides a framework for relating the properties of individual atoms and molecules to the continuum properties of materials that can be observed in everyday life.

The Langevin equation describes advection, diffusion, and other phenomena in an explicitly stochastic way. One of the simplest forms of the Langevin equation is when its "noise term" is Gaussian; in this case, the Langevin equation is exactly equivalent to the convection–diffusion equation. Its use at atomistic level is discussed in Chapter 2.5.

2.6.1 Langevin Dynamic method for magnetic spin systems

The Landau-Lifshitz-Gilbert equation is an equation used to solve time-dependent micromagnetic problems. When augmented by a stochastic term describing thermal fluctuations as random fields, the LLG equation is converted into the Langevin equation of the problem. Langevin Dynamics (LD) is the principal method for dynamic models of atomistic and mesoscopic spin systems at non-zero temperature. It allows for the calculation of thermal equilibrium and non-equilibrium properties of magnetic systems where the heatbath can be described by phononic or electronic degrees of freedom. With that approach equilibrium properties like magnetic phase transitions can be described and investigated as well as ultra fast phenomena like optically induced switching events. The properties of the random field are determined via the fluctuation-dissipation theorem. Following this approach the random field values are determined by a correlator dependent on the damping constant representing the coupling of the spin system to the heat bath, and also the magnitude of the spin. LD is used on two lengthscales. It was first introduced to model temperature dependent properties in the mesoscopic formalism (micromagnetics see Ch 3.3) and later to atomistic spin models. In using LD it is necessary to ensure that the time integration follows Stratonovich calculus, which is generally achieved using the Heun integration scheme, although normalization of the spin after each timestep fulfills this basic requirement.

> *LD calculations at atomistic scale were used in ULTRAMAGNETRON to study ultrafast spin dynamic processes driven by femtosecond lasers, particularly foscussing on the opt-magnetic reversal phenomenon. The simulations demonstrated an entirely new (linear) reversal mode which is governed by the longitudinal relaxation time and which gives rise to the ultrafast reversal. It was also shown that heating with an ultrafast laser pulse was a sufficient stimulus for magnetisation switching. FEMTOSPIN is further developing these ideas and strengthening the link between ab-initio and atomistic simulations with calculations of the opto-magnetic field and ab-initio simulation of the intrinsic magnetic properties and studies of the energy transfer channels linking the spin system to the heat bath.*

2.6.2 Semi-classical non-equilibrium spin transport model

Irradiation of a ferromagnetic metal layer with a femtosecond laser pulse causes a sudden demagnetization within a few hundred femtoseconds. The non-equilibrium spin transport model describes the laser-induced non-equilibrium transport occurring on the nanoscale using statistical principles. It treats explicitly the

laser-created distribution of highly energetic, spin-polarized electrons, which immediately start to move randomly through the material (typical velocities of several nm/fs). These hot non-equilibrium electrons undergo random scattering with other electrons or with phonons and thereby they loose energy, i.e., the process of electron thermalization

> *[FEMTOSPIN](#) developed this non-equilibrium spin transport model to uncover the underlying physical mechanism of ultrafast laser-induced demagnetization. Computational modelling is needed to unravel the various possible contributions to the demagnetization processes.*
>
> *Solving numerically the derived transport equation, using spin-lifetimes taken from ab-initio calculations, revealed that laser-excited hot electron transport occurs neither in the diffusive nor ballistic regime, it is superdiffusive. Moreover, as spin-majority and minority electrons have distinct lifetimes, fast spin-dynamics on the femtosecond time scale is generated. [FEMTOSPIN](#) is using the non-equilibrium spin transport model to simulate the laser-induced hot electron transport on the femtosecond time-scale, treating magnetic layered heterostructures with a total layer thickness of about 100 nm.*

2.6.3 Statistical transport model at atomistic level

The same statistical methodology that can be used to simulate electronic transport (Chapter [1.4](#)) can be adapted to simulate transport of molecules (transport at atomistic level). This can again be used for diffusion or percolation phenomena.

In physics, specifically non-equilibrium statistical mechanics, the Boltzmann equation (or Boltzmann transport equation) describes the statistical behaviour of a fluid not in thermodynamic equilibrium, i.e. when there are temperature gradients in space causing heat to flow from hotter regions to colder ones, by the random (and biased) transport of particles. The equation expresses the probability that a number of particles all occupy a very small region of space centered at the tip of the position vector, and have very nearly equal small changes in momenta from a momentum vector, at an instant of time. The set of all possible positions and momenta is called the phase space of the system. In the equation there is a collision term. It is a statistical term representing the particle collisions, and requires knowledge of the statistics the particles obey, like the Maxwell-Boltzmann, Fermi-Dirac or Bose-Einstein distributions.

The probabilistic Boltzmann equation can be used to derive the fluid dynamic conservation laws for mass, charge, momentum and energy. In [Chapter 4](#) the continuum equivalent (Navier–Stokes, Nernst-Planck and there approximations diffusion, diffusion and convection (advection) equations for scalar tansport will be discussed.

> *In [CODICE](#), a statistical growth model is used to simulate aggregation of C-S-H particle.*
>
> *[HYMEC](#) used a statistical mechanics model for percolation of nanoparticles based on random walk over a network of nodes to simulate creation, transport and recombination of charges (including charging and de-charging of metal nanoparticle). Each node represents a metal nanoparticle NP and so a possible site for charges and it is connected to a certain number of other nodes. The problem is solved using a Monte Carlo method and solving a Pauli Master Equation.*

2.7 Atomistic phonon models

In order to describe heat transported by atoms the concept of phonons is used, which are lattice vibrational waves exciting many atoms in a periodic, elastic arrangement in a collective and coherent way. A phonon is often referred to as a quasiparticle, it represents an excited state in the quantum mechanical quantization of the modes of vibrations of elastic structures of interacting atoms. The Boltzmann transport equation (BTE) may be applied.This equation deals with collective vibrations of the atoms. These models describe lattice dynamics e.g. in semiconductors. The atom lattice may be visualized as a system of balls connected by (classical or quantum) springs. Due to the connections between atoms, the displacement of one or more atoms from their equilibrium positions give rise to a set of vibration waves propagating through the lattice. The forces between each pair of atoms may be characterized by a potential energy function that depends on the distance of separation of the atoms. The potential energy of the entire lattice is the sum of all pairwise potential energies.

This BTE equation describes the motion of atoms once the inter-atom forces are given the physics). Even though the concepts "density function" and "particles" are used, we still classify this as an atomistic model. The fact that the application can be mesoscale (nm), does have no influence on the classification.

Note that "lattice dynamics" is the generic name for the physics governing the motion of lattices, and particularly the quantum mechanics of phonons. This should not be confused with structural mechanics models ([Chapter 4.2](#)) or the solver lattice automata see ([Ch apter 5.1](#))

Phonons are described by the Boltzmann transport equation. This equation describes the statistical behaviour of a thermodynamic system not in thermodynamic equilibrium. It calculates the time evolution of the probability density function by an advection term, a force field term acting on the particles and a random term to describe the effect of collisions between particles. The random term is the addition to the standard convection–diffusion equation, which describes physical phenomena where particles, energy, or other physical quantities are transferred inside a physical system due to two processes: diffusion and convection (advection). Depending on context, the same equation can be called the advection–diffusion equation, drift–diffusion equation, or (generic) scalar transport equation.

The BTE equation can be solved with Monte Carlo techniques (e.g. Direct Simulation with Monte Carlo (DSMC)).The BTE is based on the classical Hamiltonian-statistical mechanics. BTE considers particle states in

terms of position and momentum vectors and this is represented as the state occupation probability. The occupation has equilibrium distributions (the known boson, fermion, and Maxwell–Boltzmann particles) and transport of energy (heat) is due to nonequilibrium (caused by a driving force or potential). The output (probability density function) calculated by the BTE can be processed into total current, thermal conductance/conductivity and local temperature as a function of macroscale parameters.

Central to the transport is the role of scattering which turn the distribution toward equilibrium. The scattering is presented by the relaxation time or the mean free path. The relaxation time (or its inverse which is the interaction rate) is found from other calculations (DFT or MD) or empirically.

> *QUANTIHEAT is modelling heat conduction in air between probe shapes and flat samples (scanning thermal microscopy) with the BTE for both atoms (atomistic) and molecules (mesoscopic).*
>
> *NEAT is modelling heat conduction in power electronics with a Boltzman Transport Equation (BTE) model.*

Chapter 3
Mesoscopic models

Mesoscopic models are approximated physics/chemistry equations describing the behaviour of **entities** like nanoparticles, grains, agglomerates, large bio-molecules or macrospins. These particles are considered to be frozen, and the detail inside is not resolved. The models are e.g. applied to beads consisting of 10^6 up to unlimited number of atoms, particles with length scales of 10nm-mm and timescales of ms-s. The length scale of the entity does not determine the type of model, if the inside of te entity is not resolved it is a mesoscopic model!

Molecular models, if they group more than one atom together in an entity, belong to this class of models describing the behaviour by a physics or chemistry equation (**the physics equation of the model**). For example, in order to speed up the calculations, in certain cases certain atoms may be combined and considered as one entity: a single particle or bead. These are called united-atom force fields and some atoms, like hydrogen and carbon atoms in methyl and methylene groups, are treated as a single unit. This approach has been extended into general mesoscopic considerations where grouping of larger atomic moieties are made to simulate larger systems for longer times and this is treated in this chapter. These mesoscopic models need as input the description of <u>forces between the particles. Potentials and force fields for mesoscopic interactions are defined in an analogous way as for atomistic potentials (see introduction to Chapter 2)</u>.Their output are the position and velocity of the entities. The macroscopic bulk observable properties of materials are given by conformational sampling relating the calculated positions and velocities with pressure, temperature, density and free energies.

Also micro-magnetics is classified in this group as it describes a group of coupled spins as one macrospin. Even if the physics of many models may be similar to the ones already discussed and doesn't need to be repeated here, some implications and unique aspects of meso-scopic models will be highlighted in this Chapter. Also DFT for modelcules (Ch 3.1), phase field modeling of microstructures (Ch 3.5); micro-magnetism models (Ch 3.6) and phonon models for molecules/particles (Chapter 3.7) are described.

Mesoscopic and mesoscale

Mesoscopic models are categorised into one class based on the type of entity they describe. This is not necessarily directly related to the size of the application domain the model can simulate.

When the application domain is of nm size, we say that the model is applied to the meso-scale. We strictly classify models according to the entity described, not according to the size of the application and thus warn the reader for the different way in which words can be used.

Note that in micromechanics and in materials engineering in general the term "mesoscale modelling" is used for a continuum model applied to an application domain of nm-mm lengthscale. We want to stress that this use of the word relates to the size of the application domain, while the model remains continuum.
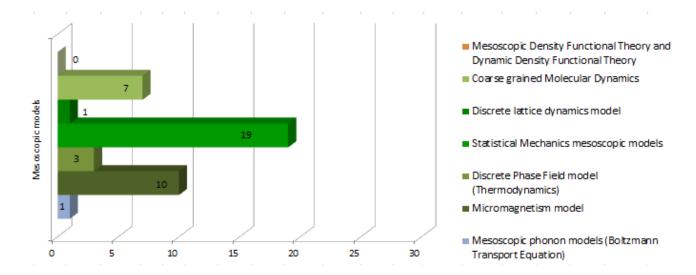

Fig.3.1 Number of projects that used one of the main types of mesoscopic models treated here.

3.1 Mesoscopic Classical Density Functional Theory and Dynamic Density Functional Theory

Classical Density Functional Theory (DFT) equations (see Chapter 2.6) can also be used to describe the behaviour of mesoscopic entities using specially defined classical potentials.

In mesoscopic classical DFT, the forces acting between **parts of molecules (e.g. segments of polymer chains), molecules, groups of molecules or grains particles (these mesoscopic entities are further on called "particles")** are described by an **external (effective) free energy potential** which is a unique functional of the particle density profiles. As in the atomistic equivalent, the modelling challenge is to formulate approximate density functionals for with complex shapes and internal degrees of freedom.

Also Dynamic DFT can be expanded to mesoscopic versions.

> *The MODENA project used classic Density Functional Theory to calculate surface tensions in polyurethane agglomerates based on the PC-SAFT (perturbed-chain statistical associating fluid theory) equation of state up to hundreds of nanometers in size and classic Dynamic DFT to estimate complex morphologies and thermodynamic properties in polyurethane foams.*

3.2. Coarse-grained Molecular Dynamics

Coarse-grained Molecular Dynamics is a particular kind of classical (deterministic) molecular dynamics where the entity whose behaviour is described is **a group of atoms forming a large single unit, also called pseudo-atom (the entity)**. The behaviour is decribed by **a particular force field (the physics equation of the model).**
The simplest form of coarse-graining is the "united atom" (sometimes called "extended atom") and was used in most early MD simulations of proteins, lipids and nucleic acids. For example, instead of treating all four atoms of a CH_3 methyl group explicitly (or all three atoms of CH_2 methylene group), one represents the whole group with a single pseudo-atom. This pseudo-atom must, of course, be properly parameterized so that its van der Waals interactions with other groups have the proper distance-dependence. Similar

considerations apply to the bonds, angles, and torsions in which the pseudo-atom participates. In this kind of united atom representation, one typically eliminates all explicit hydrogen atoms except those that have the capability to participate in hydrogen bonds ("polar hydrogens"). This approximation can provide substantial savings in computer time as coarse-grained models can provide a simpler representation of nucleotides and acids which are large molecular units for the simulation of larger systems: DNA/RNA strands, long chain polymer, membrane lipids and proteins.

The modelling challenge is in the calculation of the forces, in the determination of the pseudo-atoms charge distribution and in the parametrisation of these coarser-grained potentials.

> *Coarse grained MD models are used to describe the competition between cohesive and adhesive failure and cross-linked models of epoxy networks (NANOINTERFACE) and to study the structure and dynamics of silica-polystyrene nanocomposite systems (NANOMODEL). Coarse-grained MD models have also been used to calculate the flow of latex particles to obtain semi-quantitative predictions of linear and non-linear rheology (MODIFY) and the formation of layers of nanoparticles on cellulose surfaces (SURFUNCELL).*

3.3 Discrete lattice dynamics model

The discrete lattice dynamics model describes the (deterministic) behaviour of discrete **units like bars or trusses (the entity).** The behaviour of the bar is **described by an inter-entity potential (the physics equation of the model).**

The simulation is then done with an "atomic" finite element method, where the units like bars, or trusses, function just like the elements in a standard finite element analysis. This enables an atomic lattice to be modelled by an assemblage of units that deform according to a prescribed interatomic potential, which governs their relative separations under applied loading. A key feature of the atomic finite element method is that it results in a finite element equation with displacement degrees of freedom. An atomic finite element mesh can be directly coupled to other element types and to find element models at larger scales. Note that this resembles the Finite Element approach in micromechanics, but there the elements describe a continuum.

> *The discrete lattice dynamics model has been used to calculate breaking of atomic bonds between the discrete elements for the prediction of dislocation generation, crack nucleation and growth in coating materials (M3-2S).*

3.4 Statistical Mechanics mesoscopic models

Statistical Mechanics models based the theory discussed before (see Chapter 1.4 2.3, and 2.5) can also be used to describe **entities like nanoparticles and grains.** It describes the motions of the entities as stochastic (not deterministic) and this can be used to describe diffusion and percolation at the mesoscale and using conformational sampling also thermodynamic properties are derived.

> *In CODICE a mesoscopic statistical model is used to simulate grain based flow in cement and together with an agglomeration description this gives the growth of the cement.*

> *MONAMI used mesoscopic coarse-grained models with effective soft potentials with stochastic terms to simulate essential motions.*
>
> *A kinetic mesoscopic Monte Carlo model has been used to evaluate effective H diffusivities under different strain conditions and trap densities and temperature (MULTIHY).*
>
> *Monte Carlo models describing the behaviour of mesoscopic entities have been used to calculate thermodynamic properties such as the Curie temperature, and non-equilibrium properties such as kinetic growth in oxide heterostructures, on the mesoscale (IFOX).*
>
> *Exploiting the polymer mean field approximation, Monte Carlo based particle simulations were performed on micrometer-sized domains of the nanocomposite system, wherein the nanofillers are represented as solid spheres (interacting via Hamaker integrated potentials) and the polymer chains as freely jointed sequences of Kuhn segments (NANOMODEL).*

3.4.1 Dissipative Particle Dynamics (DPD)

Another Statistical Mechanics model is Dissipative Particle Dynamics (DPD. It is a stochastic Lagrangian technique describing a set of **beads (entity)** moving in continuous space and discrete time. In the DPD model, a bead may represent many atoms, whole molecules or even fluid regions**. The forces between the beads consists of simplified pairwise dissipative and random forces, so as to conserve momentum locally and ensure correct hydrodynamic behaviour (model).** The model is used to simulate the dynamic and rheological properties of fluids at the mesoscale.

> *DPD was used (in addition to the lattice gas model) to simulate the propagation of inhibitor/healing agent upon the mechanical impact during formation of mechanical defects (MUST);*
>
> *DPD was used to generate cross-linked epoxy structure by simulating the dynamics of beads representing the repeating unit of the epoxy (NANOINTERFACE) and to study the structure and dynamics of silica-polystyrene nanocomposite systems where each "superatom" or bead represented a monomeric unit or a meso or racemo diad of styrene monomers (NANOMODEL).*

3.5 Discrete Phase Field models

Phase Field models are a recent approach to address discrete phenomena at small scales, like the description of **individual particles** moving in a continuum (gas/liquid) and microstructure formation. Phase field models are constructed to predict the microstructure formation in time and space. Note that thermodynamics does NOT comprise any information about structures as thermodynamics do not comprise time/length scales and this should be alleviated by these Phase Field models

The properties of materials follow from their crystal structures on an atomic (or Å) length scale and from their microstructure (i.e. "the arrangement of phases and defects") on the nm-cm length scale. In a microstructure interfaces appear between phases. Phenomena related to the microstructure can be modeled by mesoscopic models describing the behaviour of e.g. **grains.** The equilibrium nature of microstructures can be interpreted by considering the phase diagram, which itself can be predicted by computational thermodynamics.

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Phase Field models describe the state of the entire microstructure by representing **structural and/or chemical spatial homogenous assemblies (mesoassemblies), such as domains or grains**, with constant phase field(s) or order parameter(s) while allowing diffuse interface across thin boundary layer between the mesoassemblies by continuously interpolating its bulk values of order parameter(s).

Mesoscopic Phase field models derive the potential "driving force" usually from the difference in Gibbs energy across the interface. The dynamics of one or more order parameter (s), that is the evolution of the microstructure with time, are governed **by set of non-linear partial differential equations** (i.e. Cahn-Hilliard, time-dependent Ginzburg-Landau, and other Newtonian based dynamics) through a minimization of phenomenological free energy functional (or potential or driving force). This functional (potential) is expressingthe influence of the Gibbs free energy (where thermodynamics plays its role), interfacial energy, elastic energy and other contributions executed by external fields including electrical, magnetic and applied stress fields, etc). In order to do so, the free energy functional is written in terms of the order parameters including composition and other fields (temperature, pressure, strain, electrical, magnetic, etc).

Microstructure formation in time and space during phase transitions can be calculated with these models if complemented by a diffusion equation.

Mesoscopic Phase Field models were originally developed to predict fundamental properties of extended defects, such as interface and critical nucleus, and the associated energy and nucleation and migration, whose chemical and structural inhomogeneity occurs at length scale usually between 1 and 100 nm. The coarse-grained phase field, subsequently developed to describe collective behaviors of "large" mesoscale assemblies, covers length scales up to mm for the heterogeneity during dendritic solidification, grain growth, domain coarsening and coalescence, and various phase transformations events.

Note that Mesoscale refers to a scale "in between" the nanoscale and the microscale, typically distances of 10–100 nanometres, however these models can be applied up to mm in coarse-grained models, where the quantum physics meets the classical physics, or where systems are on the boundary between interacting and isolated systems

> *[HIPERSOL](#) does mesoscopic phase field modelling of Ag, combined with diffusion and firing described with COMSOL to calculate the dissolution and transport of Ag.*
>
> *[MINTWELD](#) is using mesoscopic phase field models (nm and µm scale) to describe grain boundary and interface chemistry and structure.*

3.6 Micromagnetic models

The underlying assumption in micromagnetics is that the spins at electronic and atomic level are coupled to one **"macro-spin" (entity). The interactions between the macrospins are described by several competing energy terms (model)**. Exchange interaction (responsible for the very existence of ferro- and antiferromagnetic materials) 'attempts' to align adjacent magnetic moments (in ferromagnetic materials) or antiparallel (in antiferromagnetic materials). Magnetodipolar contribution accounts for the energy of a magnetic moment in the (dipolar) field created by all other moments of a magnetic body. Anisotropy energy is mainly due to the spin-orbit interaction and the anisotropy of the crystal lattice: it is low when the

magnetic moments are aligned along a particular crystallographic direction. Zeeman energy describes the interaction between magnetic moments and external magnetic field and is at its lowest when the moments lie parallel to this external field. The competition of these interactions under different conditions is responsible for the overall behavior of a magnet.

Since the equilibrium arrangement of magnetic moments ("magnetisation configuration") is usually (but not always!)the one in which the total magnetic energy is lowest, the sum of these four energy terms will 'attempt' to become as small as possible (with some energy terms decreasing at the expense of the others), yielding complex physical interactions.

A form of the Landau-Lifshitz-Gilbert equation is used to solve time-dependent micromagnetic problems. An essential merit of the micromagnetic theory concerns the answer to the question, how the effective magnetic field depends on the relevant interactions, namely, (i), on the exchange interaction; (ii), on the so-called anisotropy interaction; (iii), on the magnetic dipole-dipole interaction creating the internal field; and, (iv), on the external field (the so-called "Zeeman field").

Usually the exchange interaction and the magnetic dipole-dipole interaction term play the dominating role, usually a *competing* one. In particular: due to the last term the effective field is a *nonlocal* function of the magnetisation, i.e. although the Landau-Lifshitz-Gilbert equation looks relatively harmless, one is actually dealing with a complicated nonlinear set of integro-differential equations.

The necessary material constants can either come from measurements or from electron-spin and atomistic ab-initio models (10^{-10}m). These electronic models can e.g. give the lattice distortions near interfaces and compute the anisotropy as function of lattice constant. They also give the reversal curves.

The micromagnetic models are used to describe the magnetics at the nanoscale in domains (which have an magnitude of the order of 10^{-6}m) nucleation of domains, pinning and expansion behavior of magnetic domains and wall motion.Input to the model can be grain size, shape, boundary type and boundary phases. Outcome will be the macroscopic properties coorcivity, remanence, max energy product and thermal stability (thermal dependance of coercivity).

DYNAMAG is using micromagnetics models OOMF and NMAG for spin dynamics including spin transfer and anti-ferromagnetic and ferromagnetic sub-lattices interactions.

FEMTOSPIN   is using micromagnetics model called 'Madrid/Konstanz code' to predict the behaviour of ferrimagnetic and anti-ferromagnetic materials and magnetic semiconductors for heat assisted recording.

MAGNONICS uses several micromagnetic codes (finite-difference codes MicroMagus and OOMMF and a finite-element package Nmag) to compute magnetization reversal processes and pico- and nanosecond magnetization dynamics in structured arrays of magnetic nanoelements.

MASTER is using a micromagnetics model based on the Landau-Lifshitz-Gilbert equation called SPINPM to predict magnetisation dynamics in an array of hetero-structures.

NAMASTE is using an in-house micromagnetics code to calculate magnetisation, relativistic magneto-crystalline anisotropy constants, gilbert damping coefficients and magneto-resistance coefficients of metals and magneto-transport properties of ferromagnetic semiconductor nanostructures.

NANOPYME is using a micromagnetic model to evaluate which magnetisation processes take place in thin polycrystalline magnetic films, which structural and magnetic parameters (characteristics) determine the hysteretic behaviour of such materials and to study how the exchange coupling through the interphase boundary affects magnetisation processes.

ROMEO is using micromagnetic to compute the influence of the local change of intrinsic magnetic properties near grain-boundaries in grain-boundary engineered magnets. They will compute the minimum required thickness of the layer that contains heavy-rare-earths. Using numerical optimisation techniques combined with micromagnetic simulations. They will apply the non-zero temperature micromagnetics based on the elastic band method.

REFREEPERMAG is using micromagnetics dynamic models based on Landau-Lifshitz-Glibert equation called FEMME and MAGPAR to calculate the shape anisotropy and hysteresis properties of meso-scopic magnetic structures including coercive field and switching times. Also the thermal stability depending on geometry and the size of the magnetic volumes is calculated.

SSEEC is using a micromagnetics model to provide the exchange coupling at nano-scale between "particles" in a composite (meta-) material.

ULTRAMAGNETRON has used a micromagnetics code based on the LLBloch equation at nm scale taking the exchange coupling as well as the dipolar interaction into account to calculate magnetisation at elevated temperatures and the dynamics of ferrimagnetic materials.

3.7 Mesoscopic phonon models

In order to describe heat transported by molecules (particles) the concept of phonons is used similarly to the model for heat transport by atoms (Ch 2.7). The phonons are vibrational waves exciting many in a collective and coherent way. The Boltzmann transport equation (BTE) may be applied. This equation then deals with collective vibrations of the molecules. This BTE equation still describes the motion of molecules and even though the concept "density function" is used, we still classify this as a mesoscopic model.

QUANTIHEAT is modelling heat conduction in air between probe shapes and flat samples (scanning thermal microscopy) with the BTE for both atoms (atomistic) and molecules (mesoscopic).

Chapter 4
Continuum modelling of materials
Parts of this text have been taken from Wikipedia

This chapter is concerned with the designing of materials with desired macroscale (nm-mm) properties. Modeling for materials design is about investigation of relations between chemical composition, microstructure and effective properties.

Materials, such as solids, liquids and gases, are composed of molecules separated by empty space. Physical and chemical processes at the smallest scale are modeled by electronic, atomistic or mesoscopic models as addressed in Chapter 1 & 2. However, certain physical phenomena can be modeled assuming the materials exist as a continuum, meaning the matter in the body is continuously distributed and fills the entire region of space it occupies. Many physical phenomena are multi-scale in nature and researchers must look to multi-scale methods that couple electronic, atomistic, mesoscopic and continuum simulations. This linking will be addressed in Chapter 5. In this Chapter continuum models (approximated physics/chemistry equations) describing the behaviour of continuum unit cells will be presented.

The length scale for the entity (unit cell) modelled in continuum models has two limits: the lower limit is related to the notion "continuum" and this lower limit is so big that even heterogeneous materials can be considered to vary in a continuous fashion; the upper limit is related to the requirement that the model adequately describes reality and this upper limit is thus smaller than any spatial variation in material properties. When the spatial variation length scales are not much greater than that of inter-atomic distances or when a continuum of a finer resolution is to be established statistical mechanics is used (see Chapter 3) and modellers employ statistical volume elements and random continuum fields linking continuum mechanics to statistical mechanics. Specifically for fluids, the Knudsen number is used to assess to what extent the approximation of continuity can be made.

In continuum modeling it is possible to apply a chain of modelling that uses the same physics and chemistry equations applied to different scales. Often the application of models to a smaller scale is called "micro-modeling" and the results of these models are, after being homogenised, fed into "macro-models" in the form of new macroscopic constitutive equations.

This chapter will deal with
    4.1 Solid Mechanics
    4.2 Fluid Mechanics
    4.3 Heat flow and thermo-mechanics
    4.4 Continuum Thermodynamics and continuum Phase Field models
    4.5 Chemistry reaction (kinetic) models (meso and continuum)
    4.6 Electromagnetism (including optics, magnetics, electrical)
    4.7 Process and device modelling

> The text has been rigorously organised along the concepts:
>   1. Physics and chemistry equations (often the conservation equations)
>   2. Material relation: specification of the particular material in constitutive equations and constraints

Fig.4.1 Number of projects that used one of the seven main types of continuum models treated here.

		Elasticity and visco-elasticity Describes materials that return to their rest shape after an applied stress.	
Continuum mechanics The study of the physics of continuous materials	Solid mechanics The study of the physics of continuous materials with a defined rest shape.	Plasticity Describes materials that permanently deform after a sufficient applied stress.	Rheology The study of materials with both solid and fluid characteristics.
	Fluid mechanics The study of the physics of continuous materials which take the shape of their container.	Non-Newtonian fluids	
		Newtonian fluids	
	Continuum Thermodynamics The study of energy conversion		

Chapers 4.1- 4.4 cover the above models. In Chapter 4.5 chemistry reaction (kinetic) models (meso and continuum) will be described and in Chapter 4.6 Electromagnetism (including optics, magnetics, electrical). In the last Chapter 4.7 we shortly discuss Process and Device modelling but often these rely on models already discussed.

Conservation equations (Phyics and chemistry equations)

Fundamental physical laws such as the conservation of mass, the conservation of momentum, and the conservation of energy are including the physical principles that govern the mechanical response of a continuous medium. These laws allow us to write mathematical equations of physical quantities like displacements, velocities, temperature, stresses and strains in mechanical systems. The solution to the equations, once closed with a constitutive equation, represents the material behaviour. The equations of motion and equilibrium e.g. are derived from the fundamental principle of conservation of linear momentum. Heat flow is derived from the energy conservation law.

Constitutive equations (closure relations or materails relations)

Information about the particular material studied and its response to external agents (e.g. forces fields) is added through a constitutive equation (CE), expressing that the material is homogeneous or inhomogeneous, isotropic or anisotropic, linear or nonlinear or thermo-elastic or that the material shows plasticity, visco-elasticity, or visco-plasticity. In more general terms the constitutive equations relate the primary field variables (like density, temperature, displacement and velocity) to secondary field variables (energy, heat and stress). The detail employed may be macroscopic or microscopic, depending upon the level necessary to the problem under scrutiny.

These CEs might be derived from experiments or they might be "phenomenological". The relations might also be derived from theory, models applied to a finer scale whose output is processed into a formula. The theoretical derivation of a material's constitutive equations is a common, important, and sometimes difficult task in theoretical materials science and includes physics considerations. Phenomenology goes beyond purely empirical data as it involves a certain concept. A phenomenological constitutive equation is not completely based on physical mechanisms responsible for the behaviour. Constitutive equations can take the form of simple formulas like Hooke's law, complicated formulas like REAFF force fields, a system of equations (of algebraic, differential or integral type) with a number of parameters (or functions) to be identified from experiments.

Kinematic constraints

The model equations are the conservation equations. Material information enters the system via constitutive equations and material information can also enter via constraints on the solution. Such constraints are e.g. used in simplified Molecular Dynamics and in Material Mechanics. In Material Mechanics kinematic constraints express the limits on the movement. This can be due to the properties of the material like incompressibility, but more frequently kinematic constraints reflect the requirement of internal kinematic compatibility of motion of the continuum (e.g. across boundaries between different constituents of a heterogeneous material) or compatibility with external boundary conditions of kinematic type (e.g. including periodic boundary conditions). The latter (and more frequent internal or external) constraints are independent of the physical properties of the material and constitute a part of the formulation of a micromechanical model of the material. In Mechanics of Materials kinematic

constraints are additional restrictions on the motion of a system under investigation. They are usually separate from physical properties of the material.

Geometric changes in a continuous medium (in static or dynamic equilibrium under mechanical and/or thermal forces) are expressed by the conservation laws, constitutive equations and kinematic constraints considered jointly. The solution describes how each little part of a material moves and where it will go and how large a space will be occupied in a certain place and time.

(People involved in continuum mechanics call this solution "the kinematic equations".)

Kinematic behavior as expressed in the solution is often a necessary basis for the formulation of constitutive equations for models applied to larger scales. Also the temperature gradient can be part of this description.

Governing equations

The conservation equations together with the constitutive equations and constraints are called the governing equations.

4.1 Solid Mechanics

Solid mechanics is the branch of mechanics, that is concerned with properties and behavior of solid matter under external actions like external forces, temperature changes, applied displacements. Contact mechanics is the study of deformation and behaviour of bodies that touch each other and may undergo relative motion and contact phenomena such as friction, lubrication, wear, heat transfer. Modeling of materials behavior under service conditions is about predicting materials behavior under e.g. mechanical (static or dynamic) loading, thermo-mechanical loading, chemically aggressive environment (e.g. all types of corrosion) and combinations thereof.

In continuum modeling also a chain of modeling can be applied that uses the same physics and chemistry equations applied to different scales. When continuum mechanics is applied to the smaller (nm and μm) scale it is called "continuum micro-mechanics" (note this name refers to the dimensions of the sample only) and the larger scale case is called "macro-mechanics".

Micromechanics

Heterogeneous materials, such as composites, solid foams, poly-crystals and human intervertebral discs, consist of clearly distinguishable constituents (or phases) that show different mechanical and physical material properties. Micromechanics of materials predict the response of the heterogeneous material on the basis of the geometries and properties of the individual phases. The results are then "homogenised" to describe the properties and behaviour of a heterogeneous material. Such properties and behaviour are often difficult to measure experimentally, and micromechanics models can avoid expensive tests that would involve a large number of permutations of constituent material combinations; fibre and particle volume fractions; fibre and particle arrangements and processing histories.

Micromechanics of materials can also evaluate the local (stress and strain) fields in the phases for given macroscopic load states, phase properties, and phase geometries. Such knowledge is especially important in understanding and describing material damage and failure.

> *LISSEN does 3D microstructural modeling of battery cells for an assessment of the role of electrode structure. The morphological parameters of cathode and anode, needed for single-cell reactive-transport models are e.g. volume fractions of the components, volume-specific surface areas and phase boundaries and these will be obtained by interpreting micromechanical models which calculate the changes in the porous electrodes (geometrical considerations of structural changes of individual pores, particles, or particle agglomerates)) during the chemical reactions.*
>
> *PMJOIN uses a micromechanical model to predict the most appropriate micro-structured pattern geometry in the metallic part of polymer-metal joined structures, which facilitates anchorage of the melted polymer during the joining operation.*

Macro-mechanics

The same continuum mechanics governing equations (conservation and constitutive equations of the same form) can be applied to larger (macro) scales and this is called "continuum macro-mechanics". The constitutive equations can either be calculated by micromechanics or experimental or phenomenological constitutive equations can be used.

> *Examples of micro and macro-mechanics modelling*
>
> *Heterogeneous materials, such as composites, solid foams and poly-crystals have been modelled a.o. by MATRANS, IMS & CPSand NANOINTERFACE.*
>
> *CODICE developed micro and macro models to predict the structural evolution of cement.*
>
> *DISC REGENERATION is modelling the biphasic properties of soft tissues of the intervertebral disc to calculate hydrostatic stresses and deformation of the disc using poro-hyper-elastic constitutive equations.*
>
> *IMS & CPS is modeling materials consisting of composites or fibers which move during fabrication or during in-service operations.*
>
> *MODIFY developed a model for the response of polymer acrylics to elongational deformation fields.*
>
> *NPMIMETIC developed a hybrid model, using the multi body system tool to predict the motion and deformation of intervertebral discs. The kinematics, stress distribution and its effects can be analysed simultaneously, allowing a more precise definition of the loading state of the different parts.*
>
> *PMJOIN uses micromechanical modelling to model the constitutive behaviour and the nature of breaking of the joint interface of polymer-metal joined structures.*
>
> *SIMUGLASS is modelling glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process to predict the index drop inside glass material.*

Stress-Strain constitutive equations for solid mechanics

A material has a rest shape and its shape departs away from the rest shape due to stress (force per unit area). The amount of departure from rest shape is called deformation; the proportion of deformation to original size is called strain. The strain induces stresses in the material (and vice versa) and how they exactly do this in a particular material is expressed in the constitutive equations for solid mechanics relating the strain to the stress.

> *Macromechanical models will be used to calculate the mechanical stress at the interface of thermoplastics and thermoplastic based composites joint with dissimilar materials, especially metals (YBRIDIO).*

There are four major models that describe how a solid responds to an applied stress:

1. Elastically – If the applied stress is sufficiently low (or the imposed strain is small enough), almost all solid materials behave in such a way that the strain is directly proportional to the stress; the coefficient of the proportion is called the modulus of elasticity. This region of deformation is known as the linearly elastic region. When an applied stress is removed, the material returns to its un-deformed state, i.e. no permanent strain remains after unloading. Linearly elastic materials, those that deform proportionally to the applied load, can be described by the linear elasticity constitutive equations such as Hooke's law. When the strain becomes larger the material might react non-linearly and this is called hyper-elasticity.

> *DISC REGENERATION is using poro-hyper-elastic constitutive equations in their model for biphasic properties of soft tissues of the intervertebral disc. With this they calculate hydrostatic stresses and deformation of the disc.*
>
> *MATRANS is using standard linear thermo-elasticity constitutive equations in their thermo-mechanics model applied to macro-scale. Material parameters in the constitutive equations for composites are obtained from micromechanics.*
>
> *SIMUGLASS is using elastic and viscoelastic constitutive equations in their macro-mechanics models and combined with the ideal gas equation they model glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process and to predict the index drop inside glass material.*
>
> *SMASH is using linear elasticity constitutive equations in the model for strain in hetero-structures and with this they predict structure parameters for optimised LED performance.*
>
> *ROLICER is using elastic and thermo-elastic constitutive equations in ANSYS and ABAQUS to obtain material stresses as a function of material properties and realistic working conditions.*

2. Viscoelastically – These are materials that behave elastically, but also have damping: when the stress is applied and removed, work has to be done against the damping effects and is converted in heat within the material resulting in a hysteresis loop in the stress–strain curve. This implies that the material response is time dependent or rate sensitive. This is modeled by constitutive equations resulting from the superposition of the elastic (spring) and viscous (dashpot) models, which can be joined in series (Maxwell solid) or in parallel (Kelvin solid) or as various combinations of spring-dashpot assemblies.

> *NPMIMETIC is using an in-house hyper-visco-elastic constitutive equation in their model for bulk material. With this they simulate the mechanical properties of the native nucleus pulposus within the intervertebral disc.*
>
> *ROLICER is using an elasto-hydro-dynamics constitutive equation to calculate loading limits.*
>
> *SIMUGLASS is using elastic and viscoelastic constitutive equations in their macro-mechanics models and combined with the ideal gas equation they model glass behaviour including thermal transport phenomena and large scale deformation in a thermo-moulding process and to predict the index drop inside glass material.*

3. Plastically – Materials that behave elastically generally do so when the applied stress is less than a yield value. When the stress is greater than the yield stress, the material behaves plastically and does not return to its previous state. That is, deformation that occurs after yield is permanent. This is modeled by constitutive equations in which the total strain is decomposed into elastic and plastic part. The onset of plastic flow is characterised by a yield condition and the elastic strains are related to the stresses by Hooke's law, whereas the constitutive equation for the plastic strain increment (flow rule) is obtained from the plastic potential, often assumed the same as the yield function. The plastic potential specifies the components (to within a multiplier) and the direction of the vector of plastic strain increment (exterior normal of the flow surface) through the system of partial differential equations.

> *NANOINTERFACE is using a semi-analytical plasticity constitutive equation for Cu/polymer interfaces to establish cohesive/adhesive interfacial delamination criteria under external loading and to quantify the effect of roughness on adhesive properties.*
>
> *M3-2S is using discrete dislocation plasticity modelling to link the crystal plasticity model and the atomic finite element model.*
>
> *MATRANS is using elasto-plastic constitutive equations to model residual stresses after sintering of composites and FGMs.*

4. Rheologically - Rheology is the study of the flow of ''soft solids' or solids which respond plastically rather than deforming elastically in response to an applied force (see also Chapter 4.2). It applies to substances which have a complex molecular structure, such as muds, sludges, suspensions, polymers and other glass formers (e.g. silicates), as well as many foods and additives, bodily fluids (e.g. blood) and other biological materials. This is modeled by constitutive equations of non-Newtonian fluid mechanics or linear or nonlinear viscoelasticity and plasticity.
Here speaking of a linear elastic material, plastic material, viscoelastic material, means that their behavior under external loading follows that of the corresponding constitutive equation.

> *GRENADA is modeling the morphological structure (a.o. number of layers, defects and roughness) of graphene using a rheology code.*

The above classification does not cover possible non-mechanical effects. Among them, heat conduction and temperature effects play an important role in a number of applications. [Chapter 4.3](#) treats briefly this issue.

5. Fatigue/damage

In materials science, fatigue is the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. If the loads are above a certain threshold, microscopic cracks will begin to form. In homogeneous materials, like metals, eventually a crack will reach a critical size, and the structure will suddenly fracture. In heterogeneous materials fatigue damage can be distributed and material can still bear load notwithstanding excessive micro-cracking.

The shape of the structure will significantly affect the fatigue life; square holes or sharp corners will lead to elevated local stresses where fatigue cracks can initiate. Round holes and smooth transitions or fillets are therefore important to increase the fatigue strength of the structure.

Fatigue is modeled with the solid mechanics equations closed by constitutive damage equations like Miner's, Paris's or Goodman's rule. This system describes how so-called damage variables change under applied stress-strain state and give the change of the load-carrying ability (for example, material stiffness) with the changing damage variables.

For multi-scale modeling (models applied to the micro- and macro-scales) the same physics (physical principles) for both scales can be used (multi-scale modelling type I). To model fatigue the energy equations are formulated to describe the energy balance with account for the stress transfer at a fine scale with different possible scenarios of damage localisation. The results are then fed into a mechanics model applied to macro-scale.

> *IMS & CPS has developed simple in-house solid mechanics analytical & FEM models to describe damage initiation on the macro-scale. The constitutive equation is of the static linear mechanics type. This model predicts transverse damage initiation in carbon fabric/polymer composites with and without carbon nanotubes.*
>
> *MATRANS is modelling fatigue using the elastic strain energy balance and the particle-matrix interactions. They also use damage theory to model micro-cracking due to residual stresses after sintering. The same physics is used at the micro and macro scale considering the stress transfer between the brittle particles, interphase and ductile-matrix.The constitutive equation is that of linear thermo-elasticity with damage for the ceramic reinforcement and the elasto-plastic for the metal matrix.*
>
> *RADINTERFACES is using a new hybrid kinetic Monte Carlo-Molecular Dynamics model to describe damage accumulation and with this they generate damage constitutive equations*

6. <u>Fracture mechanics is</u> the field of mechanics concerned with the study of the propagation of cracks in materials. In modern materials science, fracture mechanics is an important tool in improving the mechanical performance of materials and components.

Fracture mechanics is a typical multi-scale problem: the initial crack starts at a very small scale (having a very small process zone). It uses methods of solid mechanics to calculate the driving force on a crack and those of experimental solid mechanics to characterize the material's resistance to fracture. With the

knowledge of the crack driving force and the crack resistance Griffith's or Irwin's criterion is then used to assess the criticality of a crack.

Macroscopically speaking, the crack propagates if the driving force is larger than the fracture toughness (i.e., Griffith's energy balance). Now, the driving force and the fracture toughness are both defined by multi-scale processes:

-the driving force is dependent on the mechanics at molecular-meso-micro-macro-scale (i.e., different dissipation mechanisms at different scales such as creation of new surfaces and micro-scale plasticity)

-the fracture toughness is dependent on the physical properties of the material(s) at molecular-meso-micro-macro-scales.

On the macro-scale, the integrity of structural members, such as beams, columns and shafts is also an important issue, which is not only addressed by strength of materials or fracture mechanics methods. The models employed to predict the response of a structure under loading and its susceptibility to various failure modes may take into account various properties of the materials other than material yield strength and ultimate strength; for example, failure by buckling is dependent on material stiffness and thus Young's Modulus.

CODICE is using constitutive equations in a lattice fracture model in which the continuum is replaced by a lattice beam elements. The constitutive equations are derived from results of a atomistic and analytical micromechanical models calculating the microstructure(linear-brittle behaviour of the phases) which is mapped on the lattice beams by assigning them different properties (elastic modulus and tensile strength of porous cement), depending on where the beams lie (cement grain, inner C-S-H variety, overlapping C-S-H variety).

IMS & CPS has developed simple in-house solid mechanics analytical & FEM models to describe delamination propagation on the macro-scale. This model predicts transverse delamination propagation in carbon fabric/polymer composites with and without carbon nanotubes.

MATRANS is using finite element method to compute configurational forces. The method is capable of treating inhomogeneous (functionally graded) materials under static and dynamic loadings. The crack driving force is computed as function of the loading, the crack length and the elastic properties, which can vary in space. On micro-level a damage mechanics approach was used (i.e. in the thermo-mechnical homogenisation) while in the macro mechanical approach the focus is on fracture mechanical concepts (energy release rate). The damage mechanics approach was rather simple using a maximal principal stress criterion in the brittle ceramics, while a plastic strain criterion was used in the metallic phase. If the damage indicator reached a critical value the element was "killed" from the FEM calculation.

ROLICER is using a solid mechanics model to describe crack nucleation based on traction separation laws. Then they use a structural model applied to macro-scale to study crack formation, crack propagation, and fracture behaviour in ceramic materials. They also examine the fracture properties of silicon nitride. They are testing the assumption of anisotropic fracture of the β-grains with a micromechanical finite elements simulation.

7. Creep

In materials science, creep is the tendency of a solid material to move slowly or deform permanently under the influence of stresses. It occurs as a result of long term exposure to high levels of stress that are below the yield strength of the material. Creep is more severe in materials that are subjected to heat for long periods, and near melting point. Creep always increases with temperature. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function. But moderate creep in concrete is sometimes welcomed because it relieves tensile stresses that might otherwise lead to cracking.

The rate of this deformation is a function of the material properties, exposure time, exposure temperature and the applied structural load. Unlike brittle fracture, creep deformation does not occur suddenly upon the application of stress. Instead, strain accumulates as a result of long-term stress. Creep is a "time-dependent" deformation. The constitutive equations for creep are those of the plastic flow (cf. above) with the concept of yield condition and associated flow rule or a creep potential function different than the yield function.

> *DISC REGENERATION is modeling the effect of creep on the relaxation of soft tissues under sustained compression simulating the standing of a person during daily activities.*

8. Wear

In materials science, wear is erosion or sideways displacement of material from its "derivative" and original position on a solid surface performed by the action of another surface. Wear is related to interactions between surfaces and more specifically the removal and deformation of material on a surface as a result of mechanical action of the opposite surface (see also chemical diffusion under CFD in Chapter 4.2)

Impulse wear e.g. can be described by a constitutive equations based on a synthesized average on the energy transport between two travelling solids in opposite converging contact.

The micro-scale calculations are performed to obtain the averaged activation parameter for the oxidation process. The macro-scale calculations are done to explicitly model wear and oxidation. But the time dependent parameters needed to do that are obtained from micro-scale calculation. The temperature distribution around a single asperity can reach very high values. This might be lost in homogenisation as on the macro level, the averaged temperature in the unit cell containing the asperity, can be well below the oxidation threshold. Thus micro scale calculations are needed to obtain the exact temperature distribution around the asperity. To do that standard heat conduction models can be applied with the heat flux acting on the upper surface of the conical asperity. Having this micro-scale temperature, an averaged activation factor for oxidation can be calculated, which allows the oxidation to take place for relatively low temperatures on the macro scale.

In short: on the micro-scale only heat conduction and temperature distribution need to be calculated. But on the micro-level, a completely different geometry is used, a conical asperity, whereas on the macro scale the contact zone could e.g. be flat. On the macro scale other mechanical processes can be simulated, not part of micro-level simulations.

> *CODICE has developed models for the development of wear and fracture and predicted the degradation by ammonium nitrata of porous cement structures. It is a finite element model, which solves the Nernst-Plank equations over a voxeled cementitious structure (composed of cement grains, C-S-H varieties and pore space) in which ammonium nitrate solutions flow*

through the porous network. The phenomenological constitutive equations for the wear model import information about the micro-structural changes which take place when the ammonium nitrate ions react with the solid phases and calcium ions are released into the solution. Upon this reaction the diffusion constants are readjusted. The model can simulate the effect of accelerated calcium leaching (an intrinsic osteoporosis-like degradation process) for cementitious structures.

MATRANS is modelling progressive wear. The constitutive equation is of the Archard type, i.e. wear volume is proportional to energy dissipated at the contact interface (equivalently, the wear volume is proportional to normal force and sliding distance). For the description of material deformation, heat transfer, and temperature distribution the same constitutive relation in macro and micro scale are used but calculations are performed assuming different geometries. On the micro-scale the real surface topography is considered, and Finite Element Analysis with thermo-mechanical coupling was used for the calculation of averaged wear-oxidation parameters. On the macro scale a flat surface was assumed.

9. Corrosion (oxidation) is to be included in wear phenomena, when the damage is amplified and performed by chemical reactions rather than mechanical action. The constitutive equations can be chemical, but can also be purely phenomenological without any account of the underlying chemical process. In such models the rate of change of mass of the corrosion product (oxide) is related to temperature and time based on experimentally observed relations from thermo-gravimetric analysis (TGA). Chemical properties of the oxide layer are considered through parameters in the phenomenological function approximating results of the TGA.

10. Other chemical reactions

MATRANS is using a coupled heat conduction model for oxidation and wear to predict oxide masses. On the micro-scale a conical geometry of the asperity is used, whereas on the macro-scale the contact zone is modeled as flat.

New constitutive equations for solid mechanics

Note that the conservation equations are not often subject to new modelling and it is thus rather rare that mechanical models discover new physics. However, development of the constitutive equations does take place to model the material properties.

MODIFY developed new macroscopic constitutive equations capable of describing quite reliably the deformation equations (e.g., the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

MULTIHY has developed macroscopic models based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the

description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before.

POCO developed an electro-dynamics constitutive equation relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

4.2 Fluid Mechanics

Fluid mechanics is the study of the motion of fluids due to forces. (Fluids include liquids, gases, and plasmas if sufficiently dense to be a continuum). The foundational axioms of fluid dynamics are the conservation laws, specifically, conservation of mass, conservation of linear momentum (also known as Newton's Second Law of Motion), and conservation of energy (also known as First Law of Thermodynamics). These can be reworked to give the Navier–Stokes equations, named after Claude-Louis Navier and George Gabriel Stokes, which are a non-linear set of differential equations that describes the flow of a fluid whose stress depends linearly on velocity gradients and pressure. The solution to a fluid dynamics problem typically involves solving these equations calculating speed, pressure, density and temperature.

Flow of electrically conducting fluids (e.g. fluids including plasmas, liquid metals, and salt water) in electromagnetic fields need to be described by coupled Navier-Stokes equations and Maxwell's equations of electromagnetism, which need to be solved simultaneously. This part of fluid dynamics is called magneto-hydrodynamics.

SIMBA is doing plasma modeling for reaction chambers.

Flow models

Modelling efforts simplify the principle physical equations in a number of ways, and set of approximations will be discussed.

GRENADA is using computational fluid dynamics to model fluid dynamics inside the Chemical Vapour Deposition (CVD) reactor used to grow graphene.

Diffusion

The simplest model for diffusive mass transport is the differential equation (continuum model) describing the phenomena at macro scale by balancing diffusion and advection.

AMON_RA models diffusion in semi-conductors with diffusion equation (CFD) using a non-linear Poisson equation for the electrostatic potential.

ARTIVASC-3D used an advection-diffusion equation for transport of nutrients and O2 (microscale)

Compressible vs incompressible flow

All fluids are compressible to some extent, that is, changes in pressure or temperature will result in changes in density. However, in many situations the changes in pressure and temperature are sufficiently small that the changes in density are negligible. In this case the flow can be modeled as an incompressible flow. Otherwise the more general compressible flow equations must be used. Mathematically, incompressibility is expressed by saying that the density ρ of a fluid parcel does not change as it moves in the flow field. This additional constraint simplifies the governing equations, especially in the case when the fluid has a uniform density.

Viscous vs inviscid flow

Viscous problems are those in which fluid friction has significant effects on the fluid motion.
The Reynolds number, which is a ratio between inertial and viscous forces, can be used to evaluate whether viscous or inviscid equations are appropriate to the problem.
Stokes flow is flow at very low Reynolds numbers, $Re \ll 1$, such that inertial forces can be neglected compared to viscous forces.
On the contrary, high Reynolds numbers indicate that the inertial forces are more significant than the viscous (friction) forces. Therefore, one may assume the flow to be an inviscid flow, an approximation in which viscosity is neglected completely, compared to inertial terms.
This idea can work fairly well when the Reynolds number is high. However, certain problems such as those involving solid boundaries, may require that the viscosity be included. Viscosity often cannot be neglected near solid boundaries because the no-slip condition can generate a thin region of large strain rate (known as boundary layer) which enhances the effect of even a small amount of viscosity, and thus generating vorticity. The standard equations of inviscid flow are the Euler equations. Another often used model, especially in computational fluid dynamics, is to use the Euler equations away from the body and the boundary layer equations, which incorporates viscosity, in a region close to the body.
The Euler equations can be integrated along a streamline to get Bernoulli's equation. When the flow is everywhere irrotational and inviscid, Bernoulli's equation can be used throughout the flow field. Such flows are called potential flows.

<u>Laminar vs turbulent flow</u>
Turbulence is flow with a high Reynolds number and is characterized by recirculation, eddies, and apparent randomness. Flow in which turbulence is not exhibited is called laminar. It should be noted, however, that the presence of eddies or recirculation alone does not necessarily indicate turbulent flow—these phenomena may be present in laminar flow as well. Mathematically, turbulent flow is often represented via a Reynolds decomposition, in which the flow is broken down into the sum of an average component and a perturbation component.
Equations for the perturbation component are subject to different models (k-eps, second order models etc).

> *SIMUGLASS is using an incompressible viscous fluid dynamics model to describe the behaviour of the laminar flow of protection gasses.*

<u>Newtonian vs non-Newtonian fluids and Rheology</u>
If fluids can be characterized by a single coefficient of viscosity for a specific temperature they are called Newtonian fluids. Although this viscosity will change with temperature, it does not change with the flow rate or strain rate. Only a small group of fluids exhibit such constant viscosity.
For a large class of fluids, the viscosity change with the strain rate (or relative velocity of flow) and are called non-Newtonian fluids. The behaviour of non-Newtonian fluids is described by rheology. These materials include sticky liquids such as latex, honey, and lubricants.
For example, ketchup can have its viscosity reduced by shaking (or other forms of mechanical agitation, where the relative movement of different layers in the material actually causes the reduction in viscosity) but water cannot. Ketchup is a shear thinning material, as an increase in relative velocity caused a reduction in viscosity, while some other non-Newtonian materials show the opposite behaviour: viscosity going up with relative deformation, which is called shear thickening or dilatant materials.
Rheology is the study non Newtonian-fluids or otherwise describes as the flow of matter, primarily in the liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. It applies to substances which have a complex molecular structure, such as muds, sludges, suspensions, polymers and other glass formers (e.g. silicates), as well as many foods and additives, bodily fluids (e.g. blood) and other biological materials. Theoretical aspects of rheology are the relation of the flow/deformation behaviour of material and its internal structure (e.g., the orientation and elongation of polymer molecules), and the flow/deformation behaviour of materials that cannot be described by classical fluid mechanics or elasticity.

> *MODIFY is studying rheology with the POM-POM tube constitutive equation to study flow and deformation of acrylic polymers.*
>
> *MUST is using an in-house diffusion model and phenomenological model of formation of liquid emulsion cores by membrane emulsification (balance of hydrodynamic, capillary and buoyancy forces) to calculate the optimal composition and structure of the coating to deal with corrosion of metallic and polymeric substrates and structures.*
>
> *ORAMA is using a CFD code for droplet formation and optimization of Ink-Jet and Sol-Gel processes.*

<u>Two phase flows</u>
Without the wish to be complete it should be stated that many flows need their own models like e.g. two-phase flows where interactions between the phases have to be modeled.

Constitutive equations for flows
Besides modeling of the fundamental physics equations, there are also different constitutive equations in use and some projects have developed new ones.

<u>Constitutive equation for the diffusion of chemical species</u>
<u>Fick's first law</u> relates the diffusive flux to the concentration under the assumption of steady state. It postulates that the flux goes from regions of high concentration to regions of low concentration, with a magnitude that is proportional to the concentration gradient (spatial derivative). This constitutive equation is used to close the conservation of mass (flow) equations reduced to diffusion only.
Diffusion of interstitial atoms due to chemical potential gradients can be described by an extended Fick's diffusion equation with added terms due to chemical potential gradients (stress and temperature).The <u>Nernst–Planck equation</u> is a constitutive equation used to close the conservation of mass equations to describe the diffusion of charged chemical species in a fluid in an electric field. It relates the flux of ions under the influence of both an ionic concentration gradient and an electric field. It extends Fick's law of diffusion for the case where the diffusing particles are also moved with respect to the fluid by electrostatic forces. If the diffusing particles are themselves charged they influence the electric field on moving. Hence the Nernst–Planck equation is applied in describing the ion-exchange kinetics. Please see also the diffusion equation described at atomistic level.

> *ARTIVASC-3D used a constitutive equation of the Nernst-Planck type in the advection-diffusion-deposition model for the permeation-times of nutrients and O2.*
>
> *MULTIHY is using Fick's diffusion equation as constitutive equation extended with terms due to chemical potential gradient and trapping. This is used with codes to obtain a description of hydrogen diffusion under broader range of conditions (temperature variations, trap occupancy) at the specimen and component level.*
>
> *CODICE used the Nernst-Planck constitutive equations simulating grain-based flow and hydrogen diffusion with their continuum model.*

<u>Constitutive equation for the poro-elastic flow</u>
When fluids are streaming through a porous medium a combination of solid mechanics and fluid mechanics is to be applied. Two mechanisms play a key role in this interaction (i) an increase of pore pressure induces a dilation of the porous solid, and (ii) compression of the solid causes a rise of pore pressure, if the fluid is prevented from escaping the pore network.
The fluid transport in the interstitial space can be described by the well-known Darcy's law, which is an empirical (phenomenologically) derived constitutive equation that describes the flow of a fluid through a porous medium (see also Chapter 4.2). Darcy's law works with variables averaged over several pore-widths. It can also be derived from Navier-Stokes equations by dropping the inertial terms, so this is an example of a constitutive equation being derived from the physics equations. Darcy's law is a simple

proportional relationship between the instantaneous discharge rate through a porous medium, the viscosity of the fluid and the pressure drop over a given distance.

> *DISC REGENERATION coupled poro-hyper-elastic constitutive equations and vascular transport models to predict the movement of solutes within the intervertebral disc. They simulated the disc mechanical response to external compressive loads which affect diffusion of oxygen and lactate and thus their content within the disc. They also simulated fluid-solid interaction within high porous polymer implants as well as interaction between implants itself and surrounding intact biological structures and test different disc replacement configurations.*

Scales

Also in this part of continuum mechanics, models can be created for the behaviour at different scales and also in this discipline a chain of flow models applied to different scales might be used. State-of-the-art models for flow at the smallest scale are e.g. the so called "atomistic" finite elements which can be applied to length scales of 100 nm – mm and timescale of ms to s. (This scale is called meso by electronic modellers and micro by continuum modelers, here the first name is adopted.)

> *M3-2S is using atomistic finite element flow models (discrete lattice model) to model the breaking of atomic bonds between the discrete elements.*

The calculated properties can be used as constitutive equations in the flow models applied to larger scales.

4.3 Heat Flow and Thermo-mechanical behaviour

On the crossing point of micromechanics and fluid dynamics there is the domain of heat flow and its influence on mechanical properties. Thermomechanics studies the properties of materials as they change with temperature. The materials might show a change of dimension (expressed in the calculated macroscopic thermal expansion coefficients) or of a mechanical property. The bonding in the material determines this response. Crystallinity and fillers introduce physical constraints to motion. Cross-linking between molecules will restrict the molecular response to temperature change since the degree of freedom for segmental motions is reduced as molecules become irreversibly linked.

Principle physical equation describing heat flow
The conservation of energy equation contains the energy change due to heat flow. This term can be modeled by different assumptions and this is expressed in different constitutive equations.
Heat transfer may take place due to conduction (also called diffusion), convection (energy taken away by the surroundings solids or fluids) or radiation.

Constitutive equations
The thermo-elastic constitutive equation defines a relationship between stress, strain and temperature, and thermal conductivity equation relates the heat flux density to temperature gradient. For anisotropic solids, both have to be written in a tensor form. Coefficients of these equations depend themselves of the temperature and represent thus material functions rather than constant parameters for a specified material. Other material functions determine temperature dependence of parameters in constitutive

equations of plasticity, visco-plasticity and rheology. Such material functions are usually determined empirically.

A constitutive equation for conductive heat flow is the Fourier's law that states that the heat flow is proportional to the temperature gradient.

A constitutive equation for convective heat flow can be Newton's law of cooling.

A constitutive equation for radiative heat flow is the Stefan Boltmann's law.

MATRANS modelled the effective linear thermo-elastic properties of the functionally graded materials with micromechanical (incl. heat conduction) approaches and the optimal content of the ceramic phase was searched for meeting the required thermo-mechanical properties of the composite for the target applications.

A multi-scale model of thermal residual stresses in graded metal-ceramic composites, generated during the cooling phase of the sintering process, was developed. The constitutive equations used in the finite element computations of thermal stresses were those of linear elasticity for the ceramic and elasto-plasticity for the metal phase.

MATRANS is using parameters of thermal conductivity and thermal expansion as well as mechanical properties at elevated temperatures to characterize quality of composite materials.

MACADEMIA uses multi-scale mass transfer model (IAST, Heterogeneous Ideal Adsorbed Solution Theory (HIAST) and VST) and heat transfer model to calculate the equilibrium adsorption of mixtures from single component isotherms and thus their selectivity for a series of gas mixtures.

PMJOIN uses continuum thermal modelling to provide thermal gradients, weld seam geometry and thermal distortions of polymer-metal joined structures, based on laser parameters, material properties and clamping conditions.

SYNAPSE will use Fourier's heat law to understand, or predict, the thermal behaviour of nanoscaled devices.

YBRIDIO will use continuum modeling of heat transfer in solid to calculate induction heating of composite laminates and metal composite hybrids.

4.4 Continuum Thermodynamics and continuum Phase Field models

4.4.1 Thermodynamics

The two fundamental principles of thermodynamics are summarized in the first and second law of thermodynamics referring to conservation of energy and positive production of entropy, respectively.

Different types of energy are distinguished in thermodynamic models. The portion of the internal energy associated with the kinetic energies of the atoms/molecules (rotation and vibration of the atoms about the center of mass) is called sensible energy. The internal energy associated with the atomic bonds in a molecule is called chemical energy. Mutual potential energy of the atoms as they change their distance inside the molecules is part of the internal energy. Stresses in the material can be regarded as part of the internal energy. The energy associated with the phase –change process related to the bonds between molecules/atoms and is called latent heat. Nuclear energy is not considered in NMP projects.

The second law – requiring a positive rate of entropy production in a closed system for any process - is probably explained best and easiest as the tendency of a system to relax towards the most probable state under given conditions. An instructive example are atoms of two species A and B being in a container (volume) being divided into two parts by a wall. All A atoms are in one part and all B atoms are in the other part. The entire container is at the same temperature, which is high enough that any bond energy between the atoms A-A, B-B and A-B can be neglected. Under these given conditions this system is in equilibrium. When removing the wall, the energy of the system is not changed, but the atoms will start to mix until they reach the most probable state – a homogeneous distribution of all A and B atoms in the entire volume.

Reduction of the temperature in this example then will make the interactions between the atoms become dominant and bound states of a number of atoms will form first as clusters and eventually as solid phases. Depending on the relative strength of the A-A, B-B and A-B bonds either a demixing or the formation of superstructures will occur. In case A-A and B-B bonds are stronger than A-B bonds regions of a phase containing only A elements and regions of a phase containing only B elements will from. In contrast, in case A-B bonds are stronger – an AB compound phase will form.

These two principles thus can be used to describe the equilibrium state of a system comprising a large number of interacting atoms (which may be the same or different chemical elements) under given external conditions like e.g. temperature, pressure (or also electric/magnetic fields) and especially thermodynamics can describe the new equilibrium state being established when changing these external conditions.

Thermodynamic models consist in a description of the Gibbs energy as a function of external and internal system conditions (p, V, T, relative composition). They describe the equilibrium of the system under given conditions and are used to study materials being processed. There are several types of models available to describe the Gibbs Energy of a phase and how it changes as function of (T, p, V, relative composition). These models in general are in the form of polynomials and other functional dependencies (e.g. sublattice model, ideal mixtures, Redlich-Kister polynomials). The parameters occurring in these equations – the polynomial coefficients - have to be derived from other sources of knowledge (experimental, empirical or theoretical). The calculation by electronic or atomistic models is today possible for low temperatures and for simple systems, which only have few different chemical elements (see atomistic models). In the current state of the art, thermodynamic databases integrate the results obtained from theoretical calculations using molecular simulations and from experimental data (e.g. measurements of specific heat, heat capacity etc.). Collection and assessment of these data and subsequent decisions on exclusion or inclusion or modifications of the databases is a very difficult task requiring a fundamental understanding of the phenomena involved.

From the notion of the Gibbs energy a number of further thermodynamic entities (e.g. specific heat capacity, thermal expansion coefficient, latent heat of fusion, latent heat of vaporization, molar volume, density and many more) can be derived by applying their respective definition, which usually involves partial derivatives of the Gibbs energy.

Thermodynamic databases in general are limited to equilibrium data and can thus be used to predict equilibria and also metastable equilibria. Thermodynamics however does not provide any information

about the time requested to reach the equilibrium and also no information about the spatial distribution of the phases. The challenge for modelling the microstructure thus is describing the kinetics of the relaxation process from non-equilibrium to equilibrium in a spatially resolved way. Respective models – called phase field models and describing this relaxation processes are also derived from the basic principles of thermodynamics and will be described in the following section.

> *IMS&CPS does thermodynamics models of percolation at nm scale to predict percolation thresholds of composites.*
>
> *MONAMI does continuous thermo-dynamical and kinetic modelling of local mass density and energy density.*

4.4.2 Phase Field models (continuum)

The term "**microstructure**" is not uniquely defined. Typical perceptions are e.g. "what you see under the microscope" or "all defects in a material". At the state of current knowledge a possible and meaningful definition would read: "All internal structural features in a Representative Volume Element (RVE) affecting the properties of the material". In other words microstructure is a spatial distribution of elements/atoms and defects. Nature helps to reduce this very general description by the self-assembly of regular structures (crystals/phases/grains/molecules) allowing to treat thousands or even millions of atoms as a single object. Microstructure thus is an "arrangement of objects in a RVE". The objects may be 1D, 2D or 3D like e.g. phases, grains, precipitates, defects, dislocations, nano-precipitates, atoms and much more. This definition at least comprises following phenomena: phases and phase boundaries (phase transformations), grains and grain boundaries (recrystallization, grain growth), precipitates, point defects, vacancies (diffusion, phase transformations), dislocations (crystal plasticity, recovery), crystal structure of the phases (defect properties), crystal orientation (anisotropy, texture), elemental distribution (chemical composition, segregation) and probably much more.

It is important to note that microstructure is – besides the overall chemical composition - the state variable of material properties. There are no direct "Processing–Property relationships" but the relation goes via "Processing– Microstructure relationships" and "Microstructure–Property relationships".

The basis for the description of a microstructure is given by the RVE which defines the volume of material under consideration. The RVE maybe 2D or 3D and in many cases it has to be 3D. The microstructure can then be described at different levels of detail: the RVE scale, the object scale, and eventually the continuous scale between or within the objects.

RVE scale: If properties/structures do not vary over the RVE, the average, homogeneous property is equal to the local property at each point. Such a description holds for liquids and gases and amorphous structures or if anisotropy is neglected. As soon as crystallinity comes into play anisotropy becomes important. The homogeneous RVE then corresponds to a single crystal but now revealing full crystalline anisotropy.

As soon as multiple phases are present in the microstructure a first approach is to know the fractions of these phases in the RVE without knowing their spatial distribution. Such phase fractions can nowadays be easily determined/estimated by thermodynamic software tools for given boundary conditions of temperature and pressure and overall chemical composition of the RVE.

Knowledge about the phase fractions already allows for estimation of effective properties of the RVE e.g. by using volume averaging concepts. A next refinement of the microstructure description are distribution functions for the different objects e.g. grain size distributions or precipitate size distributions, orientation distribution functions etc. A number of current models refer to the calculation of such distribution functions and their evolution during processing.

Object scale: Sizes, aspect ratios, positions, orientations and mutual arrangement of all individual objects in the microstructure i.e. the topology is described. In a first approximation these objects each have homogeneous properties (e.g. same concentration of alloy elements anywhere in the object) which may however change from object to object. In a further refinement down to full spatial resolution (e.g. down to a single voxel in a numerical representation or down to the continuum in real world) takes local variations inside the objects into account.

The highest level of detail comprises data for each voxel, which themselves have been simulated/ calculated considering the single voxel itself again as an RVE but at a much smaller scale. Examples for the latter are e.g. size distributions of nano-precipitates within a grain.

A large number of models for microstructure evolution exist for the different levels of detail. In the following some models for 2D/3D description and prediction of microstructure topology (phase field models, phase field crystal models and crystal plasticity models) will be shortly addressed.

The evolution of the phases (solid, liquid) in a continuum model is described by a number of coupled differential equations which all can be derived from thermodynamic principles: energy conservation equations expressed as an equation for temperature, diffusion equations for all alloy elements concentration, and phase field equations for each of the phases describing the evolution of the local equilibrium state for each finite volume element in the application area, often called RVE.

> Phi is describing the existence or non-existence of a specific phase at a point in space a time (e.g. phi=1 is solid, phi is 0 is liquid) under given external conditions (e.g. temperature)).

Phase-Field models ("the model") thus comprise a set of continuum equations (for Phi, T and C and..) which can be derived from thermodynamic principles and describe the behavior (or local equilibrium state) of continuum "finite volume" elements also called "cells" (the entities).

The continuum Phase-field equation for Phi contains a diffusion, stabilising and interface moving term. These models have been extended to multi-phase field models at the end of the last century allowing the description of multicomponent, multiphase alloys as used in engineering applications. The conditions for the local stability of the phases are calculated e.g. on the basis of thermodynamic data and respective databases for all phases being present in the RVE. These coupled equations for Phi, T and C and.. describe phase changes due to the temperature being different from the phase equilibrium temperature (which itself is – amongst others - defined by the local concentration conditions of all alloy elements).

The application area is often called RVE and to give just one example: it can contain 100*100*100 cells (finite volumes) with a size ranging from 1 mm via 1 micron down to a few nanometers (1000 atoms) allowing the continuum view of for "solid" or "liquid" of the cell. The collective outcome of the simulation done for a number of interacting finite volume elements is called the "microstructure". This describes the morphology which in general is polycrystalline and polyphase. Thus the RVE/domain comprises different objects "grains" (typical diameter 20-50 micron) and precipitates (nms to microns) of different phases for mm^3 type RVEs. Together with the other results the output is called the "microstructure". Temperature,

concentration of alloy elements c_i or other fields like dislocation densities, stresses, orientations etc. may vary across the grains. There are phase-field models simulating nucleation and e.g. polymer crystallization at the nm scale.

Another type of continuum model is the <u>crystal-plasticity model</u> describing the deformation of poly- or single crystalline materials (the "output") based on the description of the slip-systems (the "equations") within the individual grains (the "entity"). Interesting output is the interfaces between grains at the nanoscale, the formation and evolution of defects like e.g. dislocations resp. dislocation densities and data about plasticity after experimental calibration. Promising developments currently show up in the combination of Crystal Plasticity FEM and phase-field models.

The phase field crystal model can both be considered as a higher order expansion of the phase-field model equations and also as a homogenized solution of a density functional theory model. It thus naturally bridges the scales between atoms/lattices and the objects in the microstructure. It opens pathways to investigate "interacting lattices" (interfacial energies etc..) at the nanoscale of grain boundaries and phase boundaries.

Crystal-plasticity FEM models describe the deformation of polycrystalline materials based of the slip-systems within the individual grains. Interesting topics again are the interfaces between grains at the nanoscale, the formation and evolution of defects like e.g. dislocations resp. dislocation densities. Promising developments currently show up in the combination of Crystal Plasticity FEM and phase-field models.

4.5 Chemistry reaction (kinetic) models (meso and continuum)

Chemical reaction (kinetics) models are mathematical models that describe the characteristics of a chemical reaction, for example to study the effect of a catalyst. Normally, all the different chemical intermediate molecular species are represented explicitly. These models are based on thermodynamics and the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances. The <u>rate equation</u> is a differential equation, and it can be integrated to obtain an integrated rate equation that links concentrations of reactants or products with time. Although some of the parameters in the kinetic reaction models may need to be determined experimentally, such models can still be re-used for a wide range of operating conditions and are more versatile than purely empirical phenomenological methods ("operational" kinetics).

Chemical reaction kinetics models are used to determine the rates of chemical processes and how different experimental conditions (e.g. the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction) can influence the speed of a chemical reaction. They yield information about the reaction's mechanism and transition rates and can be used in combination with other continuum models to take into account the changing relative concentration of the chemical species.

Electrochemistry reactions are chemical reactions which take place in a solution at the interface of an electron conductor and an ionic conductor (the electrolyte) e.g in batteries. These reactions involve electron transfer between the electrode and the electrolyte or species in solution where oxidation and reduction reactions are separated in space or time, and may be connected by an external electric circuit. To

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model such reactions the forward reaction rate coefficient for each reaction is usually calculated by a modified Arrhenius formulation incorporating also the influence of the electric potential difference. All reactions are considered surface reactions and are modelled to happen on defined interfaces between solid species and/or the liquid electrolyte.

> The chemistry kinetic model should not be confused with the solver kinetic Monte Carlo!

> *FREECATS is using a reaction kinetic model combined with hydrodynamics at nm scale to detail surface reactions and adsorption processes of the new catalysts.*
>
> *LISSEN models chemical reactions in a battery cell based on a 1D continuum approach. The multi-species redox chemistry of sulphur to lithium sulphide via polysulfides (and vice versa) will be modelled at the cathode. At the anode, lithium deposition/intercalation into an anode material will be described. Parasitic side reactions (e.g. polysulfide reduction at the anode) will be implemented as appropriate. When useful and feasible, the intercalation induced volume changes of electrodes as well as pore size changes resulting from dissolution and precipitation of solids will be modelled.*
>
> *NANOINTERFACE is using an exponential continuum cohesive-zone model to quantify metal-oxide-polymer adhesion properties at the macro-scale level.*
>
> *NEXT-GEN-CAT is using catalytic reaction kinetic models (CO oxidation, CxHy oxidation and NOx reduction) for the simulation of species concentration in gas near and far from catalytic surfaces along the flow direction.*
>
> *SUPERLION is doing electrochemical modelling to simulate current-voltage relationships for the porous electrodes.*

4.6 Electromagnetism (including optics, magnetics and electrical)

Electromagnetism is the branch of science concerned with the forces that occur between electrically charged particles. In electromagnetic theory these forces are explained using electromagnetic fields. Electromagnetic force is one of the four fundamental interactions in nature, the other three being the strong interaction, the weak interaction and gravitation.

The electromagnetic force is the one responsible for practically all the phenomena one encounters in daily life above the nuclear scale, with the exception of gravity. Roughly speaking, all the forces involved in interactions between atoms can be explained by the electromagnetic force acting on the electrically charged atomic nuclei and electrons inside and around the atoms, together with how these particles carry momentum by their movement. This includes the forces experienced in "pushing" or "pulling" ordinary material objects, which come from the intermolecular forces between the individual molecules in our bodies and those in the objects. It also includes all forms of chemical phenomena.

In classical electromagnetism, the electromagnetic field obeys a set of equations known as Maxwell's equations, and the electromagnetic force is given by the Lorentz force law.

The dynamics of free charges and currents are described by Maxwell's equations directly, but the dynamics of bound charges and currents enter Maxwell's equations through the constitutive relations. The constitutive equations link the electrical and magnetic field to the electrical flux density (displacement) and the magnetic flux density. Each type of material (magnets, conductors etc.) has their own relation.

An often used technique is the plan wave method which is a computational technique in electromagnetics to solve the Maxwell's equations by formulating an eigenvalue problem out of the equation. This method is popular among the photonic crystal community as a method of solving for the band structure (dispersion relation) of specific photonic crystal geometries.

Most projects solve the EM equations via FE techniques but also ray tracing methods with Monte Carlo algorithms for the scattering are employed.

The projects AMON-RA used the Maxwell equations and semi-classical drift-diffusion model for the calculation of electro-optical properties for nanostructured solar cells.

LIGHT.TOUCH.MATTER uses electromagnetic models to predict the effective dielectric constant (i.e. piezo-electric sensitivity) of the piezoelectric composite material in relationship to the composites, composition and the electromagnetic field applied during composite formation.

MAGNONICS makes electromagnetic and spin dynamics models using the dynamical matrix method and Ewald-FFT method to calculate the magnetic behaviour of dipole-coupled and arrays of anti-dots and the magneto-dipole interaction field, to characterise the nature and spatial structure of magnons in magnonics array.

METACHEM uses the Maxwell equations (nm scale) and generalised Mie model (mm scale) to calculate individual polarizabilities of complex scatterer (electric and magnetic), surface susceptibilites of metasurfaces (electric, magnetic and magnetoelectric), refractive index, thickness and bi-anisotropy of metamaterials and to calculate scattering by cluster of simple and core-shell spheres in order to determine optical devices performance with metamaterials.

MONAMI used a coarse grained model with effective soft potentials for calculation of spin dynamics in small magnetic clusters.

NANOMAGMA solved Maxwell's equations in presence of magneto-optical effects in magneto-plasmonic nanostructures

NIM-NIL did characterisation based on electromagnetic wave theory (Maxwell solver) to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents.

PMJOIN used ray tracing software to model the behaviour of the laser beam through the polymer. The laser beam is used to heat materials to be joined.

> *POCO* developed constitutive equations for electro-dynamics.These are used for the alignment of CarbonNanoT ubes under electric fields. They used these to describe crystallisation of thermoplastics with and without CNT and for the determination of alignment of CNT in viscous media under electric fields.
>
> *SMASH* uses electromagnetic models for the calculation of optical properties of nanorods, optical extraction efficiency, emission directionality and polarization and to calculate the radiation characteristics as input to processing technologies.
>
> *YBRIDIO* will use Maxwell equations in the Eddy current (induction-diffusion) approximation to calculate the electromagnetic behaviour.

Magnetics, Elect(ron)ics and Optics.

Electromagnetics at electronic level is discussed in Chapter 1

The continuum level is not discussed here and the reader is referred to the literature. It is only noted that electric fields and magnetic fields are different aspects of electromagnetism, and hence are intrinsically related. A changing electric field generates a magnetic field and via versa.

> *AMON-RA* calculates the electrical properties of nanowire arrays using the software CELS/QUATRA and DESSIS for electronic transport and Esaki interband tunneling diode simulation in large diameter hetero-junction nanowires with tunnel junctions.
>
> *IMS&CPS* models electrical conductivity and percolation at nm scale to predict electrical conductivity and percolation thresholds of composites
>
> *IRONSEA* models resistively and capacitively shunted junctions with electrical device modelling to calculate the characteristic of junctions based on Fe-based superconducting films.
>
> *NANOPYME* is using a continuum macromagnetic model to predict magnetic performance of of macroscopic magnetic components in operation conditions and possible performance decay.
>
> *MINOTOR* uses classical micro-electrostatic model (at nm scale) to calculate energetic profile of the charge carriers around the interface to optimize mechanism of chemical doping in organic layers providing energetic disorder
>
> *SYNAPSE* will use Poisson's equation for electrical conductivity to understand, or predict, the electrical effects occurring in nanoscaled devices.

Optics is the branch of physics which involves the behaviour and properties of light, including its interactions with matter. Because light is an electromagnetic wave, most optical phenomena can be accounted for using the classical electromagnetic description of light.

Some phenomena depend on the fact that light has both wave-like and particle-like properties. Explanation of these effects requires quantum mechanics and this is discussed in Chapter 1.

> *ORAMA* uses electromagnetic codes to calculate magnetic and optical properties of their devices.

4.7 Process and Device Modelling

Manufacturing process models

Once the material has been designed it has to be produced. The manufacturing processes too can be designed and optimised via modelling. Manufacturing processes that can be modelled are a.o.

- deposition (isotropic (sputtering) or anisotropic),
- etching (basic etching is treated as the opposite of deposition and is modeled as a pure geometric process, which is e.g. (an-)isotropic, of fourier-type, directional, crystallographic), oxidation (basic oxidation models only calculates a velocity however, the influence of mechanical stress can also be considered for oxidation and etching),
- dopant diffusion during growth,
- all sorts of thermal induced reactions during annealing steps,
- interface movements or
- epitaxy (also reactions based on gas flows).
-

The simulation tool will allow the researcher to select operational parameters to be investigated and visualize the influence of each parameter, as well as to compute the influence of mechanical stresses in devices etc. This review concentrates on the modelling of materials and their behaviour, but ofcousre projects also often do process and device modelling.

> *MACADEMIA have used macroscopic models like the Simulated Moving Bed and Pressure Swing Adsorption for different separation processes (propane/propene, acid gas....) to evaluate the materials on the process scale and to predict material behaviour and ageing in real applications.*
>
> *NEXT-GEN-CAT is doing process modelling with mass, energy and momentum balances to predict the performance of catalytic converters and to predict the concentration distribution of the chemical species.*
>
> *ORAMA is doing PVD and process control for deposition in a PVD chamber.*
>
> *SIMBA is using CFD models for plasma behaviour in of a lab-scale reactor. The models include electro-magnetism, thermodynamics and chemistry processes. With these they can calculate non-equilibrium plasma and nanopowder nucleation out of the gas phase.*
>
> *SOLARDESIGN is using process simulation TCAD SENTAURUS PROCESS will deal with modelling (2D-or 3D-) of the fabrication steps of solar cells/modules, like e.g. different types of depositions, etching, oxidation, diffusion, and implementation of models for custom solar cell processes in different process conditions like the ambient chemical composition, pressure, temperature etc.*

Device modelling

And, last but not least, the material will be used in applications and integrated in devices, and also this can be optimised via modelling.

> MORDRED uses RANDOMSPICE to predict reliability of electronic devices. RANDOM SPICE is a Monte Carlo circuit simulation engine for ICT devices, which enables simulations of statistical and process variability, data harvesting and statistical analysis of the simulation results. RandomSpice provides the facilities necessary for accurate statistical circuit and standard cell characterisation, and supports power–performance–yield (PPY) analysis. Input includes bias, temperature, materials etc., but also a lot of non-physical fitting parameters and output is current/voltage behaviour.
> SOLARDESIGN will use an advanced multidimensional device (TCAD) simulator capable of simulating electrical, thermal, and optical characteristics of CIGS solar cells/modules, for development and optimization of their performance.
> SUPERLION is doing nano-scale battery architecture models to calculate the efficiency of the battery.

Chapter 5
Linking of models and Numerics

5.1 Linking different models (multi-scaling) and meta data

Depending on the length and timescale of the phenomena and the accuracy needed, models describing different entities can be applied, or models can be solved on different size grids and the results need to be transferred from one model to another.

It might also happen that different physics and chemistry need to be coupled to describe pheniomena at the same scale like solid and fluid mechanics with thermodynamics or reaction kinetics.

The data generated by the first model need to be post-processed into input data for the next model.

This could be the determination of values for parameters in the next model (physics equations or the materials relation (constitutive equation, closure relations)). In that case the operation is of the mathematical type.

This type of workflows are called <u>multi-scale modelling</u> (see Fig 6 in the Introduction)

> *A few linking examples, out of the 80 projects who linked models:*
>
> *Developing composites for aircraft is a multiscale problem, where first the fiber-matrix system is modelled at electronic and atomistic level, then the composite ply at mesoscopic level, and finally the laminate and structural part for the airplane at macroscale level. (IMS & CPS)*
>
> *MINTWELD will use the multiscale framework shown in Fig. 1. Ab-initio molecular dynamics simulations were used to calculate multi-component force fields and to provide an extensive configurational database for the energetics and dynamics of alloys in complex environments. These data will be used as input in molecular dynamics modelling. Molecular dynamics modelling was then performed to explore the process of grain boundary formation under various conditions using results from micro-scale phase-field modelling as input data. The atomic-scale grain boundary structure and chemistry will be determined and this information will then be used in ab-initio simulations and mesoscale phase-field modelling. Phase Field modelling is used obtain a complete picture of microstructure and defect (e.g. cracking) formation in the welding process. The input (structure of the interface and its thermodynamics properties) is provided by atomistic molecular dynamics simulations. The predicted results on transformation kinetics and interface morphology are fed to grain-scale models; the calculated chemistry and crystal orientation and stress can be feed back as input for molecular dynamics modelling. At the continuum level, CFD modelling is taking into account a wide range of predicted thermal and grain structure information of welded interfaces to relate the process variables to the properties of the weld pool. The dynamics of welding interface evolution is solved to give the local chemistry and the flow of molten liquid in the weld pool, through linking the continuum models with the mesoscopic solidification model. Grain scale (at the mesoscale, from cm to tens of µm) models are being used to model grain structure evolution, such as grain size and distribution, and local solidification profile (e.g. mushy zone) for continuum computational fluid dynamics (CFD) modelling of weld flow; predicted thermal and grain structure information is used as input for micro-scale continuum modelling, as shown in Figure 1.*
>
> *The multi-scale framework developed in NANOINTERFACE starts with Molecular Dynamics simulations to describe the thermo-mechanical and failure behaviour of epoxies, copper, copper oxides and the respective interfaces. At the mesoscopic level, coarse grained models are used to transfer structural and force information from molecular simulations to continuum and vice versa.*

At the continuum scale, metal-oxide-polymer adhesion properties are determined by describing the relevant dissipative mechanisms that affect adhesion, including the underlying microstructural mechanisms obtained through a sequential coupling.

The project NEXT-GEN-CAT calculated reaction kinetics of catalysts reactivity with ab initio modelling. This will be used in fluid flow simulations for the prediction automotive catalytic converter performance.

In ORAMA (see Fig.2) first principle modelling is used to calculate the electronic structure and doping mechanisms of oxide materials foreseen for electronic application as n- or p-type oxide semiconductor. Self-interaction correction is performed to calculate realistic band structures. Grain boundary effects are also taken into account. ORAMA used parametrised electron density distribution obtained through ab initio quantum mechanical models to develop semi-empirical potentials. These were used in molecular dynamics simulation at the atomistic scale. In ORAMA the multifunctional oxides structures resulting from molecular dynamics simulations at the atomistic scale have been fed into mesoscopic models that solve the Boltzmann transport equation for the description of gas flow phenomena by means of Direct Simulation Monte-Carlo (DSMC) techniques. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena. ORAMA used the Statistical Mechanics (Boltzmann) transport equation for the description of gas flow phenomena as atomistic level and used the diffusivities extracted in the continuum fluid flow models.
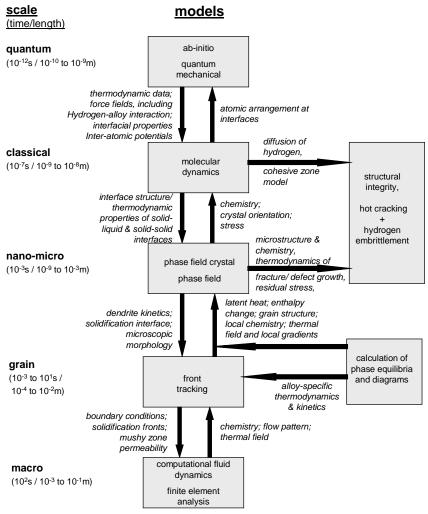

Fig 5.1. Data flow in multiscale modelling in *MINTWELD* (Hongbiao Dong, Leicester University, UK)
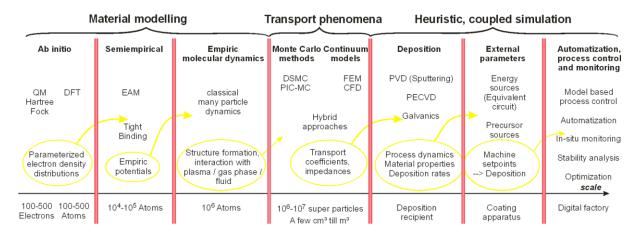
Material modelling   **Transport phenomena**   **Heuristic, coupled simulation**

Ab initio	Semiempirical	Empiric molecular dynamics	Monte Carlo methods	Continuum models	Deposition	External parameters	Automatization, process control and monitoring
QM Hartree Fock DFT	EAM	classical many particle dynamics	DSMC PIC-MC	FEM CFD	PVD (Sputtering)	Energy sources (Equivalent circuit)	Model based process control
	Tight Binding		Hybrid approaches		PECVD	Precursor sources	Automatization
					Galvanics		In-situ monitoring
Parameterized electron density distributions	Empiric potentials	Structure formation, interaction with plasma / gas phase / fluid	Transport coefficients, impedances		Process dynamics Material properties Deposition rates	Machine setpoints --> Deposition	Stability analysis
							Optimization
100-500 Electrons 100-500 Atoms	10^4-10^5 Atoms	10^6 Atoms	10^6-10^7 super particles A few cm³ till m³		Deposition recipient	Coating apparatus	Digital factory

scale

Fig. 5.2 Data flow in multi-modelling linking in *ORAMA* (Bernd Szyszka, FhG, DE)

Meta data

Another aspect of linking is how to categorise and how to make the data available. Simulation data should be published in a semantic (knowledge base) fashion so that others can use it too. Simulation data is encoded in documents containing text, table, images, etc. This data is not really recognized by other models. If computers cannot recognize the data, the data cannot properly be shared or even found. Data should be put in a form that allows models to properly recognize it long with its meaning. This can be done based on meta-data.

> Metadata are data that describe and give information about other data.
> Meta data can be used to describe models, databases and platforms.

In conjunction with the data, a vocabulary should be included for describing the data. This is where semantics comes to the fore. This vocabulary for a specific materials modelling field will contain a formal language. (E.g. the Web Ontology Language (OWL) is such a language and the "vocabulary" is really an ontology describing the formal language of a specific domain such as computational chemistry.) Metadata allow modellers to publish their data in a structured way such that it can be found and used by anyone. This makes it possible to do science in a new collaborative way that will change science forever.

Such metadata will enable exchange of information between materials modelling codes. It will ofcourse also allow "publishing data" in a way that is requested by journals or open access databases. Meta data can deal with the complexity of (correctly, safely and maintainable) sharing data between multiple tools (in-house and commercial; proprietary and open).

The meta-data can also be used for validating type correctness (avoid confusion about types, units, dimensions etc.), and automatic configuration of generic file import/export filters. Furthermore, it can be used for code generation (meta-programming of classes and structures), and even generation of source code that can be used to extend existing software.

The establishement thereof is a topic under research at the moment.

> *SIMPHONY, MMP, MODENA, NANOSIM and DEEPEN have formed a cluster establishing meta data and data file exchange formats. Later platforms will be addressed. ICMEg is a Coordination action supporting this field and aiming at wide-spread agreement.*

5.1.1 Linking between different electronic models

DEEPEN did electronic structure calculations which were used in tight-binding models to calculate vertical transport in electronic devices.

GOFAST uses LDA-DFT to calculate realistic Hamiltonian parameters from ab-initio LDA-DFT to be used in DMFT models.

HYMEC uses the time-dependent mean-field theory to calculate transport properties and the electronic drift-diffusion model for the jump rate and the coordination numbers (substantially related to the density of nanoparticles).The output is used in a statistical mechanics model for percolation.

INNOVASOL used DFT to calculate the formation energy of some inclusion complexes in layered magnesium oxides (HTLC) which is relevant for the synthesis of quasi-solid electrolytes to be used in solar cells. When necessary, the solvent effects were included in the calculations through the Polarizable Continuum Model, where the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecule(s).

In IRON-SEA modelling is used to calculate transport properties in superconductors (mainly Josephson Junctions). The multiband Eliashberg model requires input from band structure calculations (normal DOSs at the Fermi levels) provided by the Blonder-Tinkham-Klapwijk model.The connection between the models is schematized below:

1. the Fermi surface is an input to the 3D-BTK model, with which we can fit the experimental PCAR spectrum and obtain the number, amplitude and symmetry of the gaps Δi. Note that, in this step: i) the gap amplitudes Δi are constant (do not depend on energy), ii) it is NOT possible to fit the electron-boson spectral features often present in the spectra, but only the gaps.

2. Eliashberg calculations require as an input the partial DOSs from DFT calculations (see above) and the typical boson energy. The latter can be obtained from neutron scattering experiments (in literature) or, if these lack, can be inferred from the PCAR spectra themselves, by analyzing the second derivative of the current with respect to the voltage (this is a standard procedure for tunnel and point-contact spectroscopy to determine the electron-boson features). Within the Eliashberg theory we can determine the coupling strengths that allow reproducing the gap amplitudes Δi provided by the BTK fit of the experimental PCAR spectra and the critical temperature. The model however has also various other outputs: it allows calculating many physical observables that can be compared to experiments. It finally provides also the full $\Delta i(E)$ functions (in Eliashberg theory, unlike in BCS theory, the order parameter is not a constant but a function of energy). These functions contain all the information about the electron-boson coupling.

3. The $\Delta i(E)$ functions can be in turn used to calculate, within an extended BTK model, the PCAR spectrum that however now shows not only the gap features but also the structures connected to the electron-boson coupling. The resulting spectrum can be finally compared to the experimental one.

In ORAMA first principles modelling is used to calculate the electronic structure and doping mechanisms of oxide materials foreseen for electronic application as n- or p-type oxide semiconductor. Self-interaction correction is performed to calculate realistic band structures. Grain boundary effects are also taken into account.
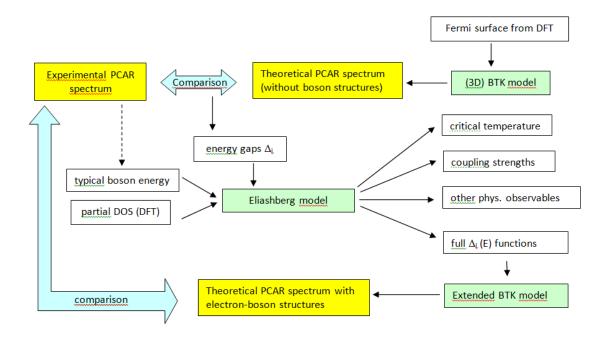
Fig 5.3 Linking of electronic models in *IRON-SEA* (Kazumasa Iida, Institute for Metalic Materials, DE)

5.1.2 Linking of electronic and atomistic models

Note that we have not included QM/MM in this chapter as this is using two models side by side; part of the atom coordindates are calculated using QM and part using MM. there is no transfer of information, the two models act on the basis of all atomic coordinates of all parts.

> *AMCOS uses DFT calculation to produce a force field for Molecular Dynamics and grand canonical Monte Carlo atomistic simulation.*
>
> *ATHENA combines electronic structure calculations at the level of DFT with model Hamiltonian schemes for simulating the thermodynamical properties of complex oxides and oxides interfaces. The electronic structure is then mapped onto model Hamiltonian via the rigorous Wannier function scheme. Then the model Hamiltonian is solved at the Monte Carlo level for extracting finite temperature properties of oxides and their interfaces. These properties include magnetic order, critical temperature for magnetism, conductivity, ferroelectric distortion.*
>
> *COMPNANOCOMP is using DFT to calculate electrical conductivity in functionalised carbon nano-tubes. This serves as input to Molecular Dynamics (MD) and Monte Carlo (MC) to study nanostructure, local segmental mobility and mechanical properties calculating chain mobility at interfaces (elastic constants, local electricity and thermal conductivity as function of filler functionalization).*
>
> *CONANOMET is using MD simulations to calculate atomistic configurations whose electronic densities of state were calculated with DFT.*
>
> *FEMTOSPIN uses ab-initio information (spin, exchange integrals, anisotropy) to parameterise atomistic and heat bath model calculations. A multiband Hubbard model is under development and will be used to improve the calculation of the exchange field in disordered systems and the introduction of longitudinal spin fluctuations.*

GRENADA used the electrical and structural properties of graphene (electronic interaction between graphene and its surroundings and in between graphene layers in multilayers) calculated with DFT in ab-initio molecular dynamics calculations to model mechanical, magnetic and electrical properties of materials

HIPERSOL is connecting DFT and molecular dynamics with a finite element model of the current transport from the silver finger to the silicon in a standard Si-based solar cell. The interfacial resistivities are obtained from Schottky barriers calculated with DFT based on atomic interface models optimised using empirical molecular dynamics.

HYPOMAP is using DFT and higher level ab –initio electronic calculationsto to develop force fields to assess adsorption at atomistic level (Quantum Liquid DFT or Grand Canonical Monte Carlo) and calculate proton conductance in polymeric proton exchange membranes.

IFOX uses electronic structure and transport characteristics of transition metal oxide hetero-structures and their interfaces calculated with DFT in Molecular Dynamics calculations for defects diffusion in oxides.

IMS & CPS models the ion transport percolation with statistical mechanics based codes that take the structure into account and calculate thermodynamic properties with data calculated from electron tunnelling quantum mechanical percolation models which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunneling between carbon nanotubes.

LEMSUPER used Gutzwiller and Dynamical Mean Field Theory to generate input for the ab initio molecular dynamics models whichwere used to simulate pressure induced metallization of potential high pressure superconductors and to study interactions, vibron properties and Jahn Teller effects.

MACADEMIA uses classical simulations Grand Canonical Monte Carlo and Molecular Dynamics to characterize the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures. Both Molecular Dynamics and Grand Canonical Monte Carlo are conducted using rigid or flexible force fields generated by quantum calculations (DFT-CC) describing the adsorption phenomena when specific interactions occur at open metal sites that cannot be treated using generic force field.

MINOTOR linked DFT and MD to compute the interface dipole at organic/organic interfaces; since this dipole is highly sensitive to the molecular packing at the interface, we have first generated realistic morphologies with MD simulations before computing the interface dipole at the DFT level on clusters extracted from the MD snapshots.

MODERN is using electronic models to describe ionisation potentials of building blocks in nanoparticles with these potentials MD calculates the thermodynamically most stable crystal structures.

The MONAMI project has done simulations of magnetisation dynamics. First the electronic structure is modelled with density functional theory and this is used as input for atomistic models for spin-dynamics.

MORDRED used parameters calculated with DFT and electronic drift diffusion models expressed as force fields fro dynamic charge transfer in atomistic MD models.

MUST uses the ab-initio quantum chemical calculation to determine some of the force field parameters for the molecular dynamic simulations of adsorption of polyelectrolytes during the layer-by-layer formation of thin film coatings and capsule shells.

NAMASTE has performed density-functional and microscopic tight-binding Anderson calculations of the band structure of ferromagnetic semiconductors. Results of these calculations served as a justification for the choice of an effective Kondo spin Hamiltonian and provided the values of the Kondo Hamiltonian parameters. The effective model Hamiltonian description served then as a basis for calculating a wide range of thermodynamic magnetic properties and magneto-transport properties with a special focus on spin-orbit coupling induced effects.

NANOPUZZLES used DFT to provide potentials for MD to calculate binding free energy. These are used to establish descriptors of nanoparticles and toxicity rules.

NANOSIM uses DFT calculations of enthalpy and activation energies in MD simulations to calculate the properties of reactive porous particles.

ONE-P used electronic quantum-chemical models for the evaluation of the molecular parameters defining the rate of charge transfer between molecules in organic conjugated compounds for applications in organic electronics. These were used in atomistic Molecular Dynamics simulations for the prediction of the bulk organization and in kinetic Monte Carlo models for the propagation of the charge and the evaluation of the charge carrier mobility.

ORAMA used parametrised electron density distribution obtained through ab initio quantum mechanical models to develop semi-empirical potentials. These were used in molecular dynamics simulation (atomistic model).

OXIDES is interfacing electronic and atomistic calculations through DFT calculations which will set the basis for the derivation of the appropriate effective Hamiltonians describing how the ferro-electric and anti-ferroelectric domain distortions couple to each other at the interface and what the relevant an-harmonic interactions are. The effective Hamiltonian should be able to capture the physical effects which dominate the behaviour of super-lattices.

QUANTIHEAT is using DFT to validate MD results on heat transfer and to prepare empiric potentials.SIMPHONY designs an environment to link electronic and atomistic codes.

RADINTERFACES used DFT and fitted many body potentials the project will quantify the energies required to activate diffusion (diffusion barriers). These were used in molecular dynamics models.

ROLICER uses DFT to calculate adhesion energy bonding and structure of interfaces and grain boundaries and uses this in MD calculations.

SMASH is using a multi-scale model where atomistic band structure calculation on a sub region is linked to a continuum drift-diffusion type electronic transport model.

SYNAPSE is developing interatomic potentials from a DFT database by fitting the data with the help of a Neural Network. The potentials will be used in the molecular dynamics simulations. The molecular dynamics simulations will calculate thermal conductivity and crystallization speed of chalcogenides.

SUPER-IRON calculated effective tight-binding Hamiltonians starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (Jc, Hc, Tc) This provided fundamental information on the superconducting transition, and its dependance on the critical temperature. This information is used in molecular dynamics models to calculate the the stability and energetics of thin film geometry and superlattices formed by different layers of various FeAs superconductors.

SURFUNCELL calculated forc fields for water-cellulose interaction in bulk water with DFT and used them in molecular dynamics simulations.

ULTRAMAGNETRON used electronic modelling to calculate the ultrafast laser-induced magnetization reversal based on the use of the Heisenberg formalism for the exchange interaction between atomic spins. This was then used in atomistic modelling of a ferrimagnetic material with magnetic compensation pointsLandau-Lifshitz-Bloch (LLB) equation.

Z-ULTRA uses electronic models to calculate diffusion coefficients and MD to calculate initial dislocation configurations.

5.1.3 Linking between electronic and mesoscopic models

DYNAMAG and MAGNONICS used ab-initio calculations are used to calculate the saturation magnetisation, the exchange stiffness and the anisotropy constants of magnetic materials and the strength of the exchange interaction and surface anisotropy at interfaces in composite magnetic materials. The parameters are then used in micro-magnetic simulations e.g. on the basis of the Landau-Lifshitz equations.

MULTIHY used electronic models for the energetics of hydrogen in bulk phases and around point defects hydrogen interactions with extended defects and used this as input to mesoscopic kinetic montecarlo simulations for hydrogen diffusion as function of defect distribution.

NANOPYME uses DFT to calculate electronic properties: critical temperatures (Curie temperature for magnetic systems and Verwey temperature for Co-ferrites systems) and magnetic anisotropy.

REFREEPERMAG used DFT models to calculate the magneto-crystalline anisotropy both full-potential and pseudopotentials methods and used this in micromagnetic simulations.

ROMEO calculates intrinsic magnetic properties with spin polarised DFT and these serve as input for mesoscopemodel simulations with micromagnetics codes. The electronic models give the lattice distortions near interfaces and compute the anisotropy as function of lattice constant. These models also give the magnetic reversal curves. Micromagntics models use these data to describe the magnetics at the nanoscale in domains and the outcome will be the macroscopic properties coercivity, remanence, max energy product and thermal stability (thermal dependance of coercivity). Elastic band method finds the optimal path where the gradient of energy points is everywhere parallel to the path.

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5.1.4 Linking between electronic and continuum models

AMON-RA uses diffusivities calculated with electronic drift diffusion models in electrical continuum models. Also the bandgap calculated with electronic k.p models was used in optical continuum models.
DEEPEN used device models with parameters extracted from electronic models

IMS & CPS has developed electrical models of carbon nanotubes at nano-scale to study electron displacements between nanotubes. In parallel, solid continuum mechanics models applied to macro-scale are performed to predict the mechanical behaviour of a composite part (a landing gear door of civil aircraft). When the optimal location of nanotubes in the composite is determined at nano-scale, the mechanic model applied at macro-scale is modified to add the carbon nanotubes in the analysis of the mechanical behaviour of the composite part.

IRON-SEA calculated characteristics of Josephson junctions fabricated from Fe-based superconducting films by the electrical circuit resistively and capacitively shunted junction (RSCJ) model using parameters calculated by the Eliashberg theory.

NEXT-GEN-CAT aims at linking DFT calculations with full scale catalytic converters simulation. Adsorption energies and reaction barriers obtained through DFT methods provide the basis to develop a surface reaction mechanism. This has to be included in continuum models of the non-isothermal, reacting flow bounded by catalytic surfaces, to simulate experimental activity measurements of different PGM-free catalysts.

ROLICER uses DFT to calculate constitutive eqs for micromechanics describing the relation between interface structure, point defects and adhesion. They also derived a fracture constitutive equation from DFT results and used this in micromechanics models.

SMASH used a multi-physics model where linear elasticity theory is coupled to electronic band structure calculation which itself is coupled to a drift-diffusion system. Within the drift-diffusion electron transport system, a k.p-method is coupled to take care of the regions where quantisation processes of carriers take place. The result of this model is then taken as input to calculate the electromagnetic problem for the extraction efficiency.

SOLARDESIGN calculated electronic charge transport within the solar cell with drift diffusion models and used these results to extract a diffusivit in the continuum models fro charge transport.

SSEEC calculates exchange couplings with DFT which were used in continuum models for magnetic cooling containing modules for thermal, fluid and magnetic switching behaviour.

SYNAPSE will use molecular dynamics simulations to calculate thermal conductivity and crystallization speed of chalcogenide and these will be employed as input in the finite-elements electro-thermal modelling of actual devices.

5.1.5 Linking between different atomistic models

AMCOS performed ab initio molecular dynamics (Car–Parrinello and Born–Oppenheimer) to develop force fields for the sub category of metal-organic frameworks, the ZIFs, to be used as input in the classical molecular dynamics computer experiments.

MINTWELD carried out ab-initio simulations molecular dynamics calculations to predict multi-component force fields and to provide an extensive configurational database for the energetics and dynamics of alloys in complex environments. These data will be used as input in Molecular Dynamics modelling. Molecular Dynamics modelling was then performed to explore the process of grain boundary formation under various conditions using results from micro-scale phase-field modelling as input data. The atomic-scale grain boundary structure and chemistry will be determined and this information will then be used in Ab-initio simulations and micro-scale phase-field modelling.

In NANOINTERFACE, the interaction parameters for Coarse Graining (CGMD) and Discrete Particle Dynamics (DPD) simulation of cross-linked epoxy structures are obtained from molecular simulations (MD).

5.1.6 Linking of atomistic and mesocopic models

AMCOS carried out atomistic molecular dynamics and kinetic Monte Carlo calculations providing sorption isothermes and diffusivities for the lattice gas cellular automata flow models, bridging atomistic to mesoscopic models.

ARTIVASC-3D uses atomistic MD models to calculate pore-size-dependant ion transport to input the optimal morphology into mesoscopic ion infiltration models.

CODICE used atomistic Molecular Dynamic simulations to identify the smallest bricks of cementious structures. Afterwards, these segmental pieces have been approximated by 4-5 nm-sized spherical particles which served as coarse grained particles in a home-made kinetic Monte Carlo scheme. This KMC scheme has enabled to describe larger structures of C-S-H gel and establish a linkage with a new continuous chemical model which provided microstructural information.

COMPNANOCOMP calculates nanostructure, local segmental mobility and mechanical properties with Molecular Dynamics (MD) and Monte Carlo (MC). This is used in CGMD and FTiMC applied to polymer network with included nanoparticles, DPD to predict filler dispersion in the polymer matrix (reference to chapter3.3), PFVD model to describe the mechanics on larger scales- within the coupling of the models part describing the influence of deformation on the mesoscale structure.

FEMTOSPIN used atomistic models to calculate temperature dependence of magnetisation, anisotropy and longitudinal and transverse susceptibilities for use by mesoscopic (micro-magnetic) models.

IFOX uses defects diffusioncoefficients calculated with Molecular Dynamics in corase grained Monte Carlo codes to evaluate thermodynamical properties for example critical temperatures.

M3-2S used coating deposition parameters calculated with MD in atomic lattice models to calculate dislocation generation and crack nucleation and growth in the coating materials.

MEMBRANENANOPART is using MD to calculate nanoparticle-nanoparticle binding energies, which are plugged into coarse-grained MD and used to predict the corona.

MEMBRANENANOPART also used MD to calculate potentials between nanoparticles and cell membranes for CGMD to calculate aggregation and how nanoparticles enter cells.

MODIFY calculated flow characteristics by using information from the atomistic simulations to parameterize a statistical mechanics model based on a particle- coarse-grained picture of the latex particles.

MORDRED used first principles simulations describing the atomic and electronic structure of the sources of fluctuations (discrete dopants, localised defects, interface roughness, body thickness, composition, strain, structure variation) in oxide interfaces to parameterise hierarchical device simulations in order to predict realistically intrinsic fluctuations in CMOS devices.

NAMASTE used some of the results of the atomistic calculations, including the magnetization, magnetic anisotropy constants, spin stiffness, and Gilbert damping parameter as inputs into the phenomenological Landau-Lifshitz-Gilbert micro-magnetic simulations of various magnetization dynamics phenomena of relevance to the devices studied in the project.

NANOSIM uses atomistic MD calculations to arrive at properties of reactive porous particles used in a mesoscopic chemical reaction model.

ONE-P modelled the charge mobility in the bulk of organic semiconductors. On the basis of a generated morphology, first the rate of charge hopping between two molecules is computed by evaluating at the quantum-chemical level the relevant parameters (transfer integral, reorganization energy, energetic disorder). In a next step, the rates are injected into Kinetic Monte Carlo simulations to propagate the charge carrier(s) and estimate the mobility from the total distance travelled during the time of the simulation.

In ORAMA the multifunctional oxides structures resulting from molecular dynamics simulations (atomistic model) have been fed into mesoscopic models that solve the Boltzmann transport equation for the description of gas flow phenomena by means of Direct Simulation Monte-Carlo (DSMC) techniques. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena.

SIMPHONY designs an environment to link atomistic to mesoscopic codes.

Z-ULTRA uses MD to calculate initial dislocation configurations which are used in mesoscopic DDD models to calculate the evolution of the dislocations.

5.1.7 Linking of atomistic models and continuum mechanics

AUTOSUPERCAP applied classical molecular dynamics model to calculate geometrical parameters (ion size and limiting pore size) of different ions, solvated and unsolvated in various solvents. These were used in continuum flow models for the infiltration of ions and electrons into the porous carbon structure during the operation of the energy storage device.

CODICE used the knowledge of the structure generated with atomistic MD models in micromechanics fracture model predicting the elastic modulus and tensile strength of cementitious skeletons.

GRENADA use mechanical, magnetic and electrical properties of materials calculated with ab-initio molecular dynamics in continuum mechanical modelling to find the morphological properties of graphene based flakes and to study the transport in multilayer graphene (with and without defects) in media of variable polarisability.

HIPERSOL has calculated diffusivities of Ag and other elements in different silver pastes (glasses) with first principles molecular dynamics and used this as input to a phase-field model (with Gibbs free energies taken from a thermodynamic database) of transport of silver through a glass layer.

HYMEC uses diffusivities calculated with atomistic statistical mechanics models in a continuum model simulating electrical characteristics of steady-state transport in the two different conduction states.

MACADEMIA used the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures calculated by the GCMD and MD in thermodynamic and flow models.

MINOTOR used outputs from quantum-chemical calculations to feed into electromagnetic models applied at very small scale (micro-electrostatic models) to determine the energy landscape of the charge transport levels in molecularly doped organic semiconductors.

In MINTWELD micro-scale Phase Field modelling is used obtain a complete picture of microstructure and defect (e.g. cracking) formation in the welding process, as illustrated in Fig 1. Atomistic molecular dynamics simulations provide the structure of the interface and its thermodynamics properties as input. The predicted results on transformation kinetics and interface morphology are fed to grain-scale models; the calculated chemistry and crystal orientation and stress can be used as input for molecular dynamics modelling.

MODIFY calculated flow characteristics with information from the atomistic simulations used to parameterize a continuum rheology model using the Pom-Pom tube constitutive equation. Furthermore non-equilibrium thermodynamics (phase fields) were applied to mixed systems consisting of bulk regions and interfaces where atomistic displacements of the interface calculated with atomistic models were taken into account which calculates molecular structural changes upon stretching, which computes the entanglement network. The outcome of this effort has been a new type of boundary condition for elastic polymers strongly adhered on hard substrates.

MULTIHY will employ novel constitutive equations for hydrogen diffusion and trapping that are informed by atomistic descriptions of the occupancy of different trap sites with respect to lattice

concentration and their effect on the overall diffusion rate, there by enabling use of atomistic results at the continuum level.

MUST used molecular mechanics for modelling of the limiting adsorption of organic anticorrosive or hydrophobizing agents. This information is then used as the boundary condition for the transport(diffusion) equation to determine the critical concentration of agents in capsules and of capsules in multifunctional coating necessary to achieve protection of the damaged surface. Similar methodology was used to predict surface activity (i.e. determine the hydrophilic-hydrophobic ratio) of selected compounds with silanol groups, which can be used to built the silica shell around the capsule core. In addition the MD simulations of the L-b-L formation of polyelectrolyte shells allow determination of its porosity, which enters as a parameter for prediction of the release rate of anti-corrosives from capsules.

NANOINTERFACE bridged length scales between atomistic and continuum by re-casting the data obtained from MD simulations within the framework of continuum cohesive zone model (CZM) to quantify the cohesive zone law. Atomistic simulations on the epoxy resin were conducted to compute its material properties, and interfacial interaction energy on its interfaces with copper and cuprous oxid and roughness. These were input to micromechanics models to establish cohesive/adhesive interfacial delamination criteria under external loading. The molecular dynamics model also gave material properties, including densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties and constitutive equations for interfaces between a 2D polymer network and copper as well as cuprous oxide.

NANOMODEL linked Molecular Dynamics and Continuum Mechanics models. They are closely connected, via forward and reverse mapping schemes.

NANOPUR uses Molecular Dynamics to simulate the interaction of functionalized polymeric membrane surfaces with water and small amounts of micro pollutants. The output is used to parameterize CFD boundary rheology models of water and continuum adsorption kinetics models of micro pollutants at meso-/macro-scales, used in a full simulation.

ORAMA used the Statistical mechanics (Boltzmann) transport equation for the description of gas flow phenomena as atomistic level and used the diffusivities extracted in the continuum fluid flow models.

POCO used MD to calculate constititutive eqs for elastic properties and interface energy and used this in continuum mechanical models
SIMBA is using the atomistic statistical mechanics Boltzmann kinetic gas equation to calculate plasma thermodynamic and transport properties needed in CFD simulations.
SMASH is linking micro solid mechanics, continuum drift-diffusion, kp band structure and electromagnetics for nanorod LED simulation. The data transfer mechanism between solid mechanics and kp band calculation is displacement data on a mesh. Kp calculation and drift diffusion is iterated self-consistently. Drift-diffusion hands over optical generation data to electromagnetics.
SYNAPSE uses thermal conductivity and crystallisation rates calculated with atomistic Molecular Dynamics models in continuum for coupled electrical and thermal behaviour.

*VINA*T *uses MD for dislocation dynamics an fro the determination of elastic properties of nTi used in continuum micromechanical models fro deformation behaviour of nanomaterials.*

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5.1.8 Linking of mesoscopic and continuum mechanics

COMPNANOCOMP calculates an elasto-visco-plasticity CE with mesoscopic models to be used in continuum micromechanics model.

DYNAMAG used the output of micromagnetics models (the spin wave spectra and dispersion in multilayer structures andf relative dynamics of different sublattices in antiferromagnetic and ferrimagnetic materials) in models of electromagnetic absorption and emission in magnetic nanomaterials.

ICMEg is developing standards to link discrete phase field models and continuum models. N NNNANOSIM uses the results of a mesoscopic chemical reaction model in CFD simulations to arrive at diffusion within porous particles.SIMPHONY designs an environment to link mesoscopic to continuum codes.

MAGNONICS micromagnetic simulations results describing the behaviour of thermally excited spin waves in planar one- and two-dimensional magnonic crystals have been used in the electromagnetics plane wave method (PWM) for the calculation of magnonic band structure and the calculation of magnonic spectra of thin slabs of 1D and 2D magnonic crystals consisting of arrays of dense magnetic elements (dots and stripes) and antidots (periodic arrangement of holes embedded into a continuous magnetic film).

In MINTWELD CFD modelling applied to macro-scale is taking into account a wide range of predicted thermal and grain structure information of welded interfaces to relate the process variables to the properties of the weld pool. The dynamics of welding interface evolution is being solved to give the local chemistry and the flow of molten liquid in the weld pool, through linking the models applied to macro-scale with the mesoscopic solidification model. Models applied to grain scale (mesoscale from cm to tens of μm) are being used to model grain structure evolution, such as grain size and distribution, and local solidification profile (e.g. mushy zone) for computational fluid dynamics (CFD) modelling of weld flow at macro-scale; predicted thermal and grain structure information is used as input for continuum modelling applied to micro-scale, as shown in Figure 1.

MUST uses the DPD modelling in parallel with the continuum modelling of transport of anticorrosive or protective agents in the cracked coatings to determine the values of effective parameters used in continuum approach. The solution of diffusion equation in inhomogeneous media, based on the lattice gas model and finite differences were elaborated. Finally the one dimensional diffusion equation describing water (or ions transport) in the effective medium was derived using the values of the effective parameters devised basing on the discrete 2D and 3D approach. In the model various triggering mechanisms of the release of inhibitor from containers as concentration thresholds of corrosive ions or corrosion products were considered. Single and multilayer coatings were simulated with the arbitrary distribution of water, ion traps and inhibitor containers.

NANOMODEL starts with coarse-grained Molecular Dynamics models and transfer s structural (thermo-mechanical and failure) information to continuum models. These CGMD models also provide metal-oxide-polymer adhesion properties describing the relevant dissipative mechanisms that affect adhesion, including the underlying microstructural mechanisms and these are use in continuum micromechanics and flow models.Also the mesoscopic transport equations Dissipative Particle Dynamics are used to provide input for these continuum models.

NANOPYME used micromagnetic modeling of thin films, bilayers and two-phase nanocomposites to study magnetisation processes like hysteretic behaviour. These are used in finite element simulations of devices (e.g., electric motors) to predict magnetic performance of NANOPYME magnets in operation conditions.

NANOSIM uses the results of a mesoscopic chemical reaction model in CFD simulations to arrive at diffusion within porous particles.

SIMPHONY designs an environment to link mesoscopic to continuum codes.

5.1.9 Linking between different continuum models

ARTIVASC-3D uses micro CFD to generate deposition rules to be used in macro CFD.

DISC-REGENERATION modelled vascular transport models using a poromechanical model coupled to a diffusive transport model to study the effect of mechanical and nutritional factors on the diffusion of two fundamental cell solutes, oxygen and lactate, strongly related with disc cell metabolism.

Within DYNAMAG and MAGNONICS, micro-magnetic simulations are run to determine magnetic response of nanostructured materials (mainly resulting from magnonic responses). The output is used to calculate magnetic susceptibility of the magnonic meta-atoms. Using appropriate homogenisation procedures, the susceptibility is then used to calculate the magnetic permeability of corresponding magnonic metamaterials, which is then used with Maxwell equations to explore how electromagnetic waves propagate in such metamaterials.

ICMEg is developing standards to link continuum models.

HIVOCOMP uses micromechanics models for mechanical deformation and shrinkage to get the description of resistance of the hybrid (carbon/self reinforced PP or PA) preform to deformation and shrinkage during thermoforming. The models will produce material constitutive equations to be used in the macro-modelling of forming.

LIGHT.TOUCH.MATTERS uses a hybrid of continuum mechanics (either solid or fluid) and electromagnetic models. The effective dielectric constant of a composite material is calculated and its dependence on different deformation modes of the composite (e.g. bending versus torsion, or bending versus compression) and the model will calculate which material shows this anisotropy.

LISSEN couples chemical and microstructural models to simulate battery cells. The morphological parameters of cathode and anode, needed for single-cell reactive-transport models (e.g. volume fractions of the components, volume-specific surface areas and phase boundaries) will be obtained by interpreting results from 3D microstructural modeling of the porous electrodes and by geometrical considerations of structural changes of individual pores, particles, or particle agglomerates.

MATRANS used effective thermomechanical properties calculated with continuum micromechanical models (modelling of wear, including shape evolution and coupling with oxidation) in continuum macromechanics models. These were transported as phenomenological constitutive equations for materials behaviour (processing induced thermal residual stresses and material damage; static and dynamic fracture; thermomechanical fatigue).

METACHEM is linking the response of structured media with equivalent parameters of homogeneous media. They link equivalent permittivity representations at bulk material level with full-wave continuous-domain simulations. Those in turn are linked with equivalent-parameter representations for structured media.

MMP is using continuum phase field models to calculate the microstructure which is input to photovoltacic device simulations.

MUST uses the continuum modelling of transport of anticorrosive or hydrophobizing agent to the damaged area in the protective coating together with statistical analysis to determine probability of achieving satisfactory corrosion protection at a given concentrations of capsules and agents in capsules (i.e. the technical risk analysis of "not performing").

NANOINTERFACE is linking solid mechanics with chemistry models to describe the thermo-mechanical and failure behaviour of epoxies, copper, copper oxides, and the respective interfaces. The data transfer mechanism involves thermo-mechanical and failure properties by means of sequential coupling.

NEXT-GEN-CAT is coupling fluid flow characteristics of exhaust gases within a real catalytic converter with the equations derived from the mass and energy balances.

SAVEME linked continuum equations for diffusion and biochemistry to describe biodistribution of nanoparticles in tissue and tumours.

SYNAPSE uses coupled electro-thermal models based on Poisson's equation for electrical conductivity and Fourier's heat law, which can be tailored to fit different materials (In-Sb/In-Te, In-Sb-Te) and architectures (confined cell PCM, free-standing NWs, confined NWs).

RADINTERFACES calculated micromechanics damage and hardening constitutive eq and used them in macromechanics models.

YBRIDIO will link electromagnetic, thermal, mechanical models at continuum level to predict Joule heating temperatures, thermal fields, cooling behaviour, pressure requirements for consolidation, magnetic fields, electric fields, Lorentz forces, thermal expansion/deflection of joined dissimilar materials. All physics equations are solved in a coupled model within each completely independent FEA code. There is no need for data transfer between the two codes.

5.1.10 Linking of flow models with thermo-mechanics

DISC REGENERATION coupled mechanical deformation of the disc with diffusion and convection of small solutes within the disc and vertebra.

FREECATS used a CFD code with kinetic equation results as boundary conditions and micro-model for heat conduction (mm scale) to resolve macroscopic heat, mass, momentum transport in boundary layers near catalytic surfaces.

5.2 Numerics

5.2.1 Solvers

Solvers are used to solve the physics equation. In this Review there is a strict separation between the two concepts "solver" and "model". Some aspects are highlighted but for a thorough review of solvers other texts should be consulted.

> Note: Discrete solvers use concepts like "fictitious particles" but these are not to be confused with real particles and one should keep in mind the physics equations to be solved and for which physical entities these are established.

Discretisation (FV and FE)

Discretisation methods are used to allow numerical solving of the governing equations and these include

- Finite difference methods (FD)
- Finite volume methods (FV)
- Finite element methods or analysis (FE, FEM or FEA or RVE)
- Spectral element methods (SEM)
- Boundary element methods (BEM)

In all of these approaches the same basic procedure is followed:

1. During preprocessing
   a. The geometry (physical bounds) of the problem is defined.
   b. The volume occupied by the material sample is divided into discrete points or cells (the mesh). The mesh may be uniform or non uniform.
   c. The physical modeling is defined – for example, the equations of motions + enthalpy + radiation + species conservation
   d. Boundary conditions are defined. This involves specifying the fluid behaviour and properties at the boundaries of the problem. For transient problems, the initial conditions are also defined.
2. The simulation is started and the equations are solved iteratively to converge to as a steady-state or to describe transient situations.
3. Finally a postprocessor is used for the analysis and visualisation of the resulting solution. Extraction of data for further model can be done.

> *CODICE developed a novel digitalization model that generates a 3D voxel structure of the virtual microstructure and can be used for information exchange within the run of each time step. This new model employs as input macroscopical processing variables, such as the cement grain size, the water/cement ratio, etc. and gives for each voxel relevant information like density, relative humidity, saturation, chemistry, etc.*
>
> *MODIFY developed a powerful finite-element code for the full three-dimensional (3-d) simulation of the deformation of acrylic adhesives. It is based on a consistent coupling of an elliptic-mesh generation methodology with domain decomposition and local mesh refinement around deforming and moving interfaces. The transport code can follow the large adhesive and*

bubble deformations inside the material (which lead to fibrillation); it can also trace the elastic boundary layers that form at the moving interfaces. It can therefore reliably simulate the force-deformation history of the material under industrially relevant conditions.

NANOINTERFACE has obtained interchange between Molecular Dynamics and continuum mechanics by creating a finite element "boundary" around the Molecular Dynamics boxes and defining so-called "anchor atoms" reaching into the "boundary". The anchor atoms are part of the polymer chains within the MD domain. In the continuum domain, they are coupled to the finite elements and moved along with their displacements.

NANOMODEL has developed numerical techniques for Molecular Dynamics models to do a coarse graining of the nanocomposit. . They impose stochastic boundary conditions with a dissipative particle dynamics thermostat on the grains. I information on forces and positions is then transfreed via fixed anchor points.

Discrete Element Method

A discrete element method (DEM), also called a distinct element method is any of a family of numerical methods for solving physics equations. The fundamental assumption of the method is that the material consists of separate, discrete particles. These particles may have different shapes and properties. He forces are given by the physics equation to be solved. An integration method is employed to compute the change in the position and the velocity of each particle during a certain time step.. Then, the new positions are used to compute the forces during the next step, and this loop is repeated until the simulation ends. DEM is very closely related to molecular dynamics, Today DEM is becoming widely accepted as an effective method of addressing engineering problems in granular and discontinuous materials, especially in granular flows, powder mechanics, and rock mechanics.

Statistical methods to solve different equations (kinetic Monte Carlo)

The kinetic Monte Carlo (kMC or KMC**)** solver is a Monte Carlo method computer simulation intended to simulate the time evolution of some processes occurring in nature. Typically these are processes that occur with a given known rate. It is important to understand that these rates (the physics equation) are inputs to the KMC algorithm, the method itself cannot predict them. Kinetic Monte Carlo (KMC) is a stochastic computational procedure that generates statistically correct state-to-state trajectories. It is based on the assumption that all transition pathways are known (input) and then generates a correct state-to-state trajectory (output) by randomly selecting pathways with a probability proportional to their rate.

Accelerated simulation methods and kinetic Monte Carlo have been used to calculate diffusivities of charge carriers, band structure calculations for up to 10000 atoms (HIPERSOL) and to calculate adsorption including quantum effects of light-weight hydrogen (HYPOMAP). Metadynamics will be employed to study slow migration processes or migration involving a large and complex energy surface in conducting oxides and oxide-based junctions (IFOX).

Kinetic Monte Carlo models have been used to calculate charge propagation and charge carrier mobility, to quantify the impact of different dielectrics on the charge carrier mobility and the exciton diffusion length (ONE-P); and to follow the evolution of individual defects in order to calculate irreversible processes at atomic scale under irradiation conditions (RADINTERFACES).

> *The Monte Carlo method was used in many body quantum mechanical models to evaluate the governing matrices by sampling the, then evaluating the energy expectation value and minimising it. The Quantum Monte Carlo method starts with a direct representation of the many-body wave function. The Hartree-Fock approximation can be used as starting point of the many-body wavefunction and then be multiplied by any symmetric function designed to represent the correlations ([GOFAST](), [MONAMI]()).*
>
> *Quantum Monte Carlo methods have been used to derive a DFT exchange-correlation functional which was used in molecular dynamics to calculate adsorption of light-weight hydrogen ([HYPOMAP]()) and to calculate thermodynamic properties of single and double perovskites many body Hamilton problem at finite-temperature problem ([ATHENA]()). Monte Carlo method was also used to solve the Boltzmann transport equation for the description of gas flow and plasma to calculate particle motion, interaction between phases, and transport proprieties in oxide based electronic materials ([ORAMA]()).*

Smooth Particle Hydrodynamics (SPH)

Smoothed-particle hydrodynamics (SPH) is a computational method used for solving fluid dynamics and structural dynamics equations. The smoothed-particle hydrodynamics (SPH) method works by dividing the fluid into a set of discrete elements, referred to as particles. These particles have a spatial distance (known as the "smoothing length") over which their properties are "smoothed" by a kernel function. This means that the physical quantity of any particle can be obtained by summing the relevant properties of all the particles which lie within the range of the kernel. The contributions of each particle to a property are weighted according to their distance from the particle of interest, and their density. Kernel functions commonly used include the Gaussian function and the cubic spline. The latter function is exactly zero for particles further away than two smoothing lengths (unlike the Gaussian, where there is a small contribution at any finite distance away). This has the advantage of saving computational effort by not including the relatively minor contributions from distant particles.

> *Smoothed-particle hydrodynamic model has been used to predict wall shear stresses at the vascular graft walls ([ARTIVASC-3D]()).*

Automata (Lattice Gas, Cellular and Movable Cellular Automata

Lattice gas automata (LGA) or lattice gas cellular automata (LGCA) solvers used to solve mechanics models used to simulate diffusion. I These Eularian models comprise of a lattice, where the sites on the lattice can take a certain number of different states. The various states are 'fictitious particles' with certain velocities (entities). Evolution of the simulation is done in discrete time steps. After each time step, the state at a given site can be determined by the state of the site itself and neighboring sites, before the time step. The state at each site is purely Boolean. At a given site, there either *is* or *is not* a particle that is moving up. At each time step, two processes are carried out, propagation and collision (model). In the propagation step, each particle will move to a neighboring site determined by the velocity that particle had. Barring any collisions, a particle with an upwards velocity will after the time step maintain that velocity, but be moved to the neighboring site above the original site. The so-called exclusion principle prevents two or more particles from travelling on the same link in the same direction.

In the collision step, collision rules are used to determine what happens if multiple particles reach the same site. These collision rules are required to maintain mass conservation, and conserve the total momentum; the block cellular automaton model can be used to achieve these conservation laws. Note that the

exclusion principle does not prevent two particles from travelling on the same link in *opposite* directions. When this happens, the two particles pass each other without colliding.

Macroscopic quantities like the density at a site can be found by counting the number of particles at each site. If the particles are multiplied with the unit velocity before being summed, one can obtain the momentum at the site. However, calculating density, momentum, and velocity for individual sites is subject to a large amount of noise, and in practice, one would average over a larger region to obtain more reasonable results. Ensemble averaging is often used to reduce the statistical noise further.

> *Kinetic Monte Carlo and lattice gas automata have been used to calculate diffusive transport and sorption of carbon dioxide (AMCOS). Lattice gas models have also been used to simulate the release of the healing agent from micro-containers and its propagation during self-healing action (MUST) and to calculate charge and mass transfer (SUPERLION).*

A Cellular Automaton (pl. cellular automata, is a discrete solver. Cellular automata are also called cellular spaces, tessellation automata, homogeneous structures, cellular structures, tessellation structures, and iterative arrays.A cellular automaton consists of a regular grid of cells, each in one of a finite number of states, identifying a physics parameter value. The grid can be in any finite number of dimensions. For each cell, a set of cells called its neighborhood is defined relative to the specified cell. An initial state is selected by assigning a state for each cell. A new generation is created according to the physics equation, which determines the new state of each cell in terms of the current state of the cell and the states of the cells in its neighborhood. Typically, the physics for updating the state of cells is the same for each cell and does not change over time, and is applied to the whole grid simultaneously, though exceptions are known, such as the stochastic cellular automaton and asynchronous cellular automaton.

The Movable Cellular Automaton (MCA) method is another solver used in computational solid mechanics based on the discrete concept used for direct simulation of materials fracture including damage generation, crack propagation, fragmentation and mass mixing. The automata are mobile and the new concept is "neighbours" is based on the introducing of the state of the pair of automata (relation of interacting pairs of automata) in addition to the conventional one – the state of a separate automaton. As a result of this, the automata have the ability to change their neighbors by switching the states (relationships) of the pairs. The automata are ruled by the physics equations to be solved, which give the dynamics by their mutual forces and rules for their relationships.

5.2.2 Accelerated simulations in molecular dynamics

The main problem of standard molecular simulations is that the time of the simulation sampling is often not long enough to ensure complete statistical sampling (ergodic theorem not valid, see Chapter 2). For example, "centuries" on their available supercomputer would be needed to simulate 1s of "a day in the life" of a polymer. For this reason, calculating free energy, reaction pathways and rare events may be not possible using standard molecular simulations. Advanced methods have thus been developed to increase the efficiency of the sampling and to obtain a more accurate answer in a limited amount of time, e.g. temperature accelerated molecular dynamics, metadynamics and kinetic Monte Carlo.

Accelerated Molecular Dynamics (AMD) and Metadynamics are methods to increase the sampling in Molecular Dynamics simulations. Accelerated molecular dynamics (AMD) tricks MD into reducing the separation of timescales between fast and slow components of the dynamics and renormalizes the MD-

time accordingly. Metadynamics is an artificial molecular dynamics method performed in the space defined by a few collective variables, which are assumed to provide a coarse-grained description of the system.

5.2.3 Post-processing and extraction of parameters (homogenisation)

Models will produce values at many points in space and time and these results might have to be reduced into values representing a larger area. Post-processing is concerned with homogenisation for further use of the data in coarser models and in visualising the results or in the generation of constitutive equations. Often simple volume averaging is not correct and homogenisation needs to take phyics/chemistry considerations into account.

> *DYNAMAG and MAGNONICS are using SEMARGL for post processing and data transfer, notably for covering the results of simulations performed in the time and real space domain to the frequency and reciprocal space domain.*
>
> *FEMTOSPIN Is developing interfaces to transfer ab-initio information from various packages into atomistic codes and to transfer atomistic information into mesoscopic codes*
>
> *METACHEM and NIM-NIL are calculating the EM field at many points in space and from these scattering, transmission and reflection parameters have to be extracted. Further processing is done into negative refractive indexes but the value of this notion is currently subject to debate.*
>
> *ROMEO creates a database with spin-polarised DFT results and will use high-throughput descriptors which will allow rapid screening of the database. The descriptors will help identify promising materials. Convex Hill diagrams will be used against the ICST database, which will establish whether or not a material is thermodynamically stable.*
>
> *SIMBA has developed software with which to describe nanopowder nucleation out of the gas phase. This is an aerosol model tracking the particle size-distribution and particle population in the reactor region and gives the precursor particle thermal history and trajectory prediction. The software then calculates the process yield.*
>
> *SYNAPSE is developing interatomic potentials from a DFT database by fitting with the help of a Neural Network approach.*
>
> *ThyssenKrupp in MULTIHY uses statistical models (mainly based on multilinear regression) to process data from the production process and relate the process parameters to the mechanical properties of the produced coil. The statistical models help to optimize the steel production processes and the properties of the produced strips.*

5.2.4 Databases

Models that are not worked up from quantum mechanical (ab-initio) principles need values for the parameters used in the model. Huge databases are created for each class of compounds in any medium (environment). These contain e.g. potentials parameters (e.g. for classic force fields) to use in electronic and atomistic models, polymer properties and thermodynamic phase diagrams for micromechanical modelling.

The creation and use of these databases is often a commercially sensitive topic and is not the subject of this document.

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Chapter 6
Model Development

6.1 Software engineering (Guidance on quality assurance for academic materials modelling)

In the introduction chapter the definition of models and of model development was given.
This chapter presents the advice of software owners, commercial and academic, on what academic software could do to generate better quality software, ready to be used by third parties. It can also be found on www.emmc.info.

Under Horizon2020, funding programmes have divided their scope by TRL levels

TRL 0: Idea. Unproven concept, no testing has been performed.
TRL 1: Basic research. Principles postulated and observed but no experimental proof available.
TRL 2: Technology formulation. Concept and application have been formulated.
TRL 3: Applied research. First laboratory tests completed; proof of concept.
TRL 4: Small scale prototype built in a laboratory environment ("ugly" prototype).
TRL 5: Large scale prototype tested in intended environment.
TRL 6: Prototype system tested in intended environment close to expected performance.
TRL 7: Demonstration system operating in operational environment at pre-commercial scale.
TRL 8: First of a kind commercial system. Manufacturing issues solved.
TRL 9: Full commercial application, technology available for consumers.

1. The European Research Council is addressing TRL1-3. They fund bottom-up research, usually in individual grants to support a group of a junior or senior principal investigator and the first priority is the development of an initial, promising idea.

2. The "Materials" (NMBP) programme is under the LEIT pillar (leading and enabling industrial technology) and is aimed at funding projects between TRL3-7. These are typically collaborative projects with a consortium with a mixture of academic and industrial partners to ensure that the goals have specific and realistic industrial relevance. In material modelling projects, the industrial partners could be either software companies or manufacturers or finished product sellers.

3. TRL7-8 is taken care of by companies who will customise the results and use them in commercial operations.

In this chapter all phases in materials modelling software engineering are briefly addresse and then the text concentrates on the software development done in the LEIT programme.

This guidance is meant to help guide the change from FP7 till H2020 and discuss how physics and chemistry PhD students can become ready to do the work in LEIT.

Introduction

The transfer of software developed in many universities to industry remains insufficient. Academic institutions do not target to provide fully developed software or materials models services.
For this a lot of effort is to be invested (corresponding to some 70% of the total software development) and for this spin-off companies are created or the software is transferred to existing commercial companies.

To stimulate this transfer to industry an inquiry is done into the requirements of commercial companies on the quality of software.
<u>Quality of the model</u> is the ability of the software to solve the initially defined problem.
<u>Quality of the software</u> is defined by:
- o   Code design.
- o   Stability and resilience.
- o   Modularity.
- o   Performance (CPU, memory, …)

and the software quality should lead to software which is easy to maintain, understand, improve and adapt, and deploy to the target users.

Cooperation forms

Most software houses do not adopt software in which they have not been involved. The continuum model vendors tend to develop the software themselves, while in the discrete world models are adopted by the commercial vendor. Most companies have standing relations with a university group where the PhD students change but the relation continues. And this allows the software to be adapted to later customer needs. Access to the original developers over the course of the software life time is important. EU projects are thus just a stage in this long-lasting relation.

<u>Licenses</u>
As the investment is large academics and companies agree licenses with their co-developers and customers that allow the return of profits.

Consideration of the advantages and drawbacks and pitfalls of different <u>licensing schemes</u> is important. Many commercial companies feel open licenses and viral licensing schemes like GPL are a blocking point when transferring or using software from academia to industry as they do not allow commercial exploitation. However other companies support Open Source code – like the many Linux support companies. Trends in main licensing schemes were mentioned during the discussion:

- o   One-to-one licensing. Service License Agreement/Contract can be limited in time (and thus cheaper) and allow "software (solutions provided) as service and/or on demand".
- o   LGPL is better than the "viral" GPL scheme, but poses a commercial constraint as only "dynamic linking" into commercial software is commercially viable – and dynamic linking has a performance disadvantage.
- o   BSD or Apache licensing schemes are most permissive in allowing to link technology building blocks of non-commercial R&D partners into commercial software in a performant manner.
- o   Dual licensing: Many academic institutions go for dual licensing which keeps the software free to academia but allows commercial protection and there is some ROI.

Commercial SWO recommend to use a permissive licensing scheme (as BSD or Apache) already for the R&D and prototyping phase of new methods and software tools, as the resulting technology blocks will be

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acceptable to commercial tool vendors downstream, which smoothens the procedure to get new software modules into industrial deployment (by leveraging on the installed base of commercial software at manufacturing industry).

Stages of software development

In the current situation, three phases of software development can be identified.

PHASE I Exploratory phase (modelling)

In this phase new models[3] are elaborated with new physics/chemistry, and the models are applied to one or two specific test cases. Exploratory model development takes place mostly in academia. Software developed in this stage is typically developed to test a scientific idea. ERC funding could be requested for this Phase. In this phase the science is important and the software is considered to be a side product. The ideas are often the basis for literature articles.

The software is not user-friendly and is often shared freely among specialists (mostly academics) through PhD and postdoc collaborations. IP protection is usually only covered by the academic code of conduct.

If a SWO becomes interested, this interest of the SWO is often based for 80% on the functionality and for 20% on the software quality.

Huge amounts of money and time are wasted on maintaining and developing a bad piece of software. (The PhD student is spending all their time on making a code converge or to restart the code when it crashes). If the commercial company rewrites the code then they either lose the benefit of future academic developments or have to spend their time re-implementing the ideas in their code.

PHASE II Bridging Phase: new material modelling software and software prototyping

New material modelling software has been validated on some test cases and has thus proven wider applicability and the software has the ability to solve new problem(s) of value for industry. The software is in a prototype phase and the software has to become validated trusted code during this phase. In this documents we do not address quality of the model and influence of boundary conditions, and solver technologies or coupling to other models. This will be addressed in another document to be issued by modellers.

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[3] Materials are complex systems and the equations that describe the physical and chemical behaviour of real systems are often too complicated to be solved easily. In order to save computer time, which is a precious and limited resource, the description of phenomena has to be simplified. Fortunately, often not all details need be taken into account in order to reproduce and predict experimental results. Key assumptions about reality can be made ignoring the complexity that is not necessary to describe the given situation. These approximations are called "models" (see "Review of Materials Modelling What makes a material function? Let me compute the ways…", 3rd edition, 2014, http://ec.europa.eu/research/industrial_technologies/pdf/modelling-brochure_en.pdf)

This phase can be subdivided further:

- Phase II a: Proof-of-concept phase. Techies from industrial R&D departments become interested in academic results or new models. Their drive is to find something new. In this phase they may work with software developers/ companies to develop software for proof of concept.

- Phase IIb: Visionaries in industrial context get involved. They are concerned in finding better solutions within a broader business context. Projects in this phase typically last 2-3 years and are used also in collaboration with software developers to solve particular useful problems, including validation and metrology.

Often, scientific/academic modellers work together with commercial software owners and follow their software habits. The academics will need to understand and respect standards, formatting, protocols etc. with regard to the existing software data structures and architectures.

Licensing: Academics often use open source licences like GPL. Alternative models are used like L-GPL and small commercial companies (spin-offs) may be involved at this stage to support the commercial development and exploitation. Alternatively, dual licensing models are used so that academics can continue to develop the code and commercial companies can explore those cases where potential industrial users/consumers are not yet clearly identified or the value of the results in the industrial setting is not yet established.

In the later stages of this phase, the software is used by a wider community and applied to a wider range of systems.

Versioning: Software versioning supporting tools are sometimes used but it's too often considered too cumbersome.

Additional software writing may also happen in this Phase, e.g.
> scripting, may be at the level of a material scientist (depending on the language and individual skills)
> automating and packaging (not usually in their expertise…)

Good software engineering practices will help in overcoming the so-called "CHASM"[4], where many new models fail to be introduced to the mainstream market.

PHASE III Commercial modelling software.

The main target is the commercial scale-up of software for more than a small community of end-users. In this phase "pragmatists" will need to become convinced that a new technology is worth their time, effort and money to get it deployed into their organisations. These pragmatists are managers which are primarily interested in the economics behind a new approach, they are reluctant to change, and will only decide on a change if they're convinced that it's worth it for their operational / ROI targets. Improvement in performance is only one factor in this phase, several other aspects are considered: investments already done, 'cost of change' (in training and process changes), ability to cope with potential demand for new products. It may be preferred to buy out the software in this phase.

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[4] "Crossing the Chasm" by G.A. Moore (1991)

The effort needed to rewrite the code for exploitation purposes is large as software developing skills by material scientist are often not sufficient (even when they can write codes for themselves that calculate useful things) and professional expertise might be necessary. Today this deployment step unfortunately often involves a complete rewrite of the code by software engineers and this phase amounts often to 70% of the total development effort and this is to be reduced.

Quality control

Quality control is performed using multiple quality targets that must be monitored and considered simultaneously for every software release. This allows avoiding 'waterbed effects': focusing intensively on improving 1 quality target will risk to reduce the performance of another quality target. For example, reducing the level of details provided to the user reduces the 'content' quality and accuracy, but increases the speed of calculation and result evaluation. Formal software quality management metrics are used e.g. **CFURPS[5].**

Commercial companies put a large effort into ensuring full validation, documentation, user-friendly interface, testing suites, durability long term support systems are developed since the life span of the successful models is many decades.

In order to get the software into an industrial framework the code need to be portable, well defined and documented APIs and product packaging on the one hand, and communication between developers on both sides on the other. In general, for commercial exploitation, a piece of software must be robust and relatively easy to use, with a good user interface. This can require a great deal of development in the:

1. Installer and licensing system,
2. Graphical User Interface,
3. Help system and manuals,
4. Updating system.

The software company will consider data and exchange standards. In case wrappers and homogenisation tools are needed also these need to be developed if they do not yet exist.

There could be a range of tasks required to be undertaken to get the software/data in a form ready for exploitation. Maintenance (adaptation to new IT) is an important issue as software is on the market for many years/decades and both the solution and the framework are not static in time, nor are the underlying hardware architectures. This development involves constant updating to changing environments (like Apple dropping the active support for Java on Mac).The company has to think about possibilities for service provision and training that can accompany the software.

Catalysts to facilitate the flow of innovation from model developers to mainstream end users use are:
- Bi-directional communication: awareness upstream at academia w.r.t. downstream industry needs, and vice-versa awareness downstream at industry w.r.t. promising academic methods.
- Availability of information: store material models/data, document best practice methods/tools, and demonstrate their impact on the basis of industrial use cases.

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[5] Compatibility, Functionality Usability Reliability Performance Supportability (CFURPS)

- Standardisation of data and interfaces to enable and facilitate the take-up of information by other actors in the industrial value chain, and with other tools that cover parts of this value chain. Note that multi-scale modelling in itself can, in simple cases, also be seen as an interface between different tools available at different simulation levels, which must be integrated to be able to deal with applications at a higher scale.

For making and selling new tools that operate within a standard "mainstream" process at the industrial end user, a shortcut may be found when the innovative component is implemented as a new "feature" (an integrated module) into the "mainstream software" that is deployed at the end user. This allows the design engineers at the end user company to use the new "content block" directly, without making any (disruptive) changes to the software tool chain, nor to the in-house process to use the tools, nor requiring too extensive training of the staff involved, nor requiring changes to the teaming and organisation. The "new content block" simply acts as a new / improved feature within a well-known process and tool chain, familiar to the users, hence there's a smaller chasm: there are less hurdles in the organisation to be overcome before deployment of the new feature within the tool chain that's already well known and broadly used.

Proposed guidelines on how material modelling software should be developed in EU-LEIT funded projects

The purpose of these guidelines is to make it more likely that models developed in LEIT projects are used in industry. The purpose of these guidelines is thus to ensure that the models/software are transferred to professional software owners (academic and commercial) who licence the code to third parties and maintain the code. After the code is fully developed we enter phase III and the code can be sold by (commercial) SWO who sell the codes to an end-user, or academic software SWO who transfer the code to other users , but also by new translator actors (e.g. spin-offs) who use the code themselves in R&D services done for industrial end users. In this document we only focus on Phase II, the completion of the software development up to TRL 7. The target of EU H2020 –LEIT research and innovation funding will be to support Phase II in the projects since it will bridge the gap over the software valley of death. Phase III is considered commercial and thus not part of EU funding.

The cost of developing code after the initial research on the functionality of the model can be substantial. It is certainly so when software funding is starting to demand small proof-of-concept or emerging technology software components to be developed. To optimize these investments, the following recommendations have been gathered:

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Proposed recommendations for phase II software development

- Prove wider applicability via validation on a set of fully documented test cases. (benchmark test and literature references, proof of some sort)- Documented results obtained in collaboration with industrial users solving specific industrial problems.

- Document accuracy/ functionality proven in high profile academic publications (especially important in some markets, e.g. Japan)

- Demostrate good numerical implementation, proven numerical stability (performance, boundaries on values of parameters for numerical stability), pragmatic approach to software engineering including the use of software metrics (e.g. Halstead (1977), Watson & McCabe (1996) (Kan, 2003).

- Provide good documentation of underlying equations and (justification of choice of) algorithms, validation cases, boundaries of validity, clear mapping of raw formula to code variables, manuals/tutorials explaining what the code can do.

- Include appropriate testing procedures and document the results in deliverables.

- Provide clear documentation of which version of the code was used to obtain what result and content of the next upgrades (not necessarily professional versioning).

- Provide documentation about IT requirements (operating system, compilers, MPI distribution, …) and how to compile the code.

- Adopt a licence allowing commercial industrial use

-Demonstrate interest of potential customer, and traction with potential future users

-Collaborate with SWO to drive the direction (mentor for software writing)

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In H2020 programmes under the "Leadership in Enabling Industrial Technologies" pillar, it is of crucial importance that proposals are led by industrial needs.

When the new model addresses a new and previously unaddressed problem in a "niche" market, reference cases are of paramount importance to generate new business, research grants should show the potential of the new method on an application case that is familiar to the target end user (at least in terms of having similar complexity and comparable workflow)

Developers in phase II should consider if the new model can be implemented as an innovative integrated component of the "mainstream software" that is deployed at the end user; this approach has a high ROI (return on investment) as a more effective industrialization can be achieved.

Licences
It is recommended that the guiding principle should be "Have an organized system of sequential licensing options, which would allow for commercialization under specific terms" and not only "Don't put any obstacles for future commercialization".
Licences should be chosen together with the mentoring SWO in the project who is likely to exploit the software. Although in the "prototype" phase II in principle any tool (and licensing scheme) can be used for the purpose of validating a methodology, we believe that it's wise to keep in mind future re-usability of code blocks in case an innovation moves downstream the innovation chain, as this reduces the hurdles to bring the innovation in position to provide value to the end users by solving their application challenges.

Education:
It is of utmost importance that academic software developers receive better information on alternative licensing models that do not preclude commercial exploitation.
Workshops on basic software writing schemes may be useful at this stage as well as workshops on versioning, software repositories and testing suites that can guide the development. Several existing activities are running in Europe and some documentation is available online. Academics should be informed about best software writing practises before starting to write any code – not just at the exploitation stage. The course should deal with issues like
- Code design. - This depends on the problem solved and on the parallelisation/load balancing concepts employed in the code - memory distribution, structures and communication patterns. There are multiple ways to achieve this. Best practices are about code neatness (file, modularisation, dependences, architectural design), cleanliness, testing, comments, keeping track of changes (repositories), test case to demonstrate performance and functionality, and documentation.
- Modularity. - Mentioned in code design as code neatness (file, modularisation, dependences architectural design), cleanliness
- Performance (CPU, memory, …). - also mentioned above
- Portability
- Numerical stability deviations from standard models with controlled termination when entering ill-defined problem input (rarely). There may be much more depending on the hardware architecture too.

6.2 Development of physics/chemistry equations

The following projects added physics and/or chemistry to existing models.

ARTIVASC-3D

This project developed of a new equation to describe clogging and deposition of blood platelets.

ATHENA

This project developed first–principle models for complex oxides:
DFT extended with variational formulation of the pseudo-self-interaction correction scheme (pSIC)
new version of DFT exact exchange model
new hybrid Hartree-Fock DFT
method combining DFT with dynamical mean-field theory (DMFT)< describing what?>

AUTOSUPERCAP

Fast charge and discharge behaviour in a new model for the behaviour of battery-super-capacitor (or battery only) power systems.

CODICE

This project developed a new micro-level model for individual hydration of cement grains (HYMOSTRUC-3D). Also a novel Monte Carlo growth scheme to calculate aggregation of dried C-S-H particles was created, which provides a better insight than the existing phenomenological models. The degradation model (CODICE_DEG) is a novel toolkit which solves the Nerst-Planck set of equations over a voxelized microstructal piece of cementitious material. By selecting sufficiently large voxels (but still within the nano-range) the code exploits the fact that the decoupling of the transport and chemical reaction equations is feasible. It enables to monitor the microstructural changes that take place along the degradation process.
A new fracture model enables virtual mechanical testing (e.g. tensile strength evaluations). It is based on a lattice beam formalism specifically adapted to the case of cement structures.

CRONOS

The project will make new descriptions of photo-energy conversion (combined electron-ion dynamics) and laser-induced ultrafast magnetisation dynamics. CRONOS will contribute to the development of TDDFT along four directions:
- o development of new DFT and TDDFT meta-GGA exchange and correlation functionals
- o development of new spin non-collinear DFT and TDDFT exchange and correlation functionals
- o development of method to combine non-adiabatic ionic dynamics with time-dependent DFT
- o development of optimal quantum control theory for TDDFT

DYNAMAG

Spintronic and thermodynamic aspects were added to an existing micro-magnetic model. Also the relative dynamics of different sub-lattices in ferri-magnets and antiferro-magnets and new spin-transfer torque mechanisms have been added to this existing model.

FEMTOSPIN

Optical spin manipulation and light induced magnetisation processes involving interactions between spin, conduction electrons and laser light have been developed in a new femto-dynamics model for exchange, spin-orbit coupling and spin-flip scattering, that can describe non-equilibrium spin-scattering (energy and spin transfer). The project developed a LLB equation for ferrimagnetic

materials and parameterisation using atomistic models the new version has two sublattices to represent ferrimagnets and antiferromagnets. The two sublatttices give very different dynamics and allow exchange modes which we believe explain the thermally driven magnetisation reversal. Development of an entirely new 'heat bath' approach, in which the thermally excited heat bath (for example, the conduction electron population) is simulated and coupled directly to the spin system. A model based on the multiband Hubbard Hamiltonian to calculate exchange in disordered systems is also developed.

GOFAST

The project will develop a model to describe the temporal evolution after being driven out of equilibrium by high-energy excitations (photo-injection by ultrafast laser pulses) in correlated materials (conduction in Mott insulators and superconductivity in cuprates.

HIPERSOL

HiperSol developed two completely novel schemes for the calculation of recombination rates. The first approach is based on Fermi's golden rule. Envelope functions are fitted to band structures obtained from first principles calculations of structures containing different kind of traps (e.g. strongly localised K-centres in the silicon nitride with Si atoms bounded to three N atoms instead of four). Also a model will be developed to obtain Auger recombination rates (the most important non-radiative process in semiconductors) from k-point interpolation of orbitals and eigen-energies using Gutzwiller techniques.

HYPOMAP

QLDFT (Quantum Liquid Density Functional Theory) was developed because there was no adequate modelling method for the adsorption calculations on the market that included the quantum effects of light-weight hydrogen. QLDFT is an atomistic model that can be used to describe physisorption and loading/unloading of physisorbed hydrogen including quantum effects and hence is a fundamentally higher-level treatment. It uses the same formalism than electronic DFT, but instead of electrons it describes H_2 molecules which obey a Boltzmann statistics (rather than a Fermi statistics that holds for electrons).

LEMSUPER

Many-body techniques for metal-insulator interfacesexist (e.g. Dynamical Mean Field Theory (DMFT) but generally assume spatial uniformity. The project will develop models able to describe inhomogeneous situations and will apply these to surface doping.
This may be done by assuming that the electron self-energy depends, besides on the frequency, also on the layer depth below the surface plane. Dividing the space below the surface into layers the self-energy will be calculated by solving an auxiliary impurity model for each layer in which the conducting bath depends self-consistently on the fully interacting impurity Green's functions not only of that given layer, but also of the nearby ones. The effect of many body interactions beyond mean-field levels in picene and similar molecular systems will be added to the models. Improvements to the modeling of new superconducting materials will include Gutzwiller correlations, applying a method recently developed (before Dynamical Mean Field Theory).

MONAMI

The project developed a theoretical technique for calculating the effect of electron-electron correlations. The developed models are an elaboration of existing models to make the theory general to treat complex crystal structures like that of V_2O_3.
Non–Newtonian dynamics (temporal evolution of a system of classical objects) are incorporated in UppASD package for spin-dynamics in order to describe the behaviour of nano-sized magnetic systems of particular symmetries.

Also an extension was made to allow accurate and fast calculations of ground state properties of solids by incorporating tail cancellation of orbitals. This is base on physical insight in how electrons move around in solids, and how to best describe their quantum mechanical equation of motion. In the model developed in *MONAMI*, several conceptual steps and mathematical derivations have been made to come to a set of equations which enable a numerical implementation.

MORDRED

Models have been developed for statistical impact of bias temperature instabilities and hot carriers on the electrical characteristics of CMOS transistors. Also a model for the impact of local defect generation on dielectric gate leakage current is developed.

NAMASTE

The project has implemented relativistic corrections (i.e. spin orbit coupling) to the band structure calculations of diluted ferromagnetic semi-conductors (DMS). (no codes to do so existed yet). They have subsequently used these tools to: a) describe the magnetic anisotropy of DMS, b) explore how magnetization and anisotropy change either varying the total electron carrier density or strain acting on the films/nanostructures; c) predict a new batch of antiferromagnetic metals with strong spin orbit coupling (antiferromagnetic materials for spintronics) and d) to describe single electron transistors.

NIM_NIL

A EM model was developed to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents, which is necessary to model metamaterials made from low-loss conducting materials. This model led to an identification of which conducting materials are useful for metamaterials. Silver was found to be the best conducting material at optical wavelength. Graphene was ruled out.

ONE-P

The project developed a methodology to model the triplet energy transfer in molecules from quantum-chemical calculations to end up with exciton diffusion length using Kinetic Monte Carlo.

OXIDES

This project has developed models using pSIC and B1-PW wave functions.

RADINTERFACES

Irreversible processes leading to material damage taking place under irradiation described by a new hybrid kinetic Monte Carlo-Molecular Dynamics model. This Object Oriented kinetic Monte Carlo (OKMC) method allows to follow the evolution of individual defects (i.e. vacancies, interstitials, He and their clusters) by listing all possible reactions and paths that a given defect could follow and choose the most probable one based on a statistical method (allowing the use of longer time step). All possible events are quantified using migration energies, formation energies (leading to binding energies). These energies are quantified using Nudged Elastic Band method in Molecular Dynamics.

A damage accumulation model is also developed based on differential equations to describe the thermodynamic and kinetic response of the synthesized materials to microstructural features. This is a 3 Dimensional Cluster dynamics model -where transport and reactions in the form of absorption and emission of defects are taken into account. In this model, rather than following individual defects within the nanloayered system, defect quantities are followed as densities. This leads to a great decrease in the amount of information (i.e. defects) to be followed which then allows the simulation of the evolution of defects over long time scales.

An existing model for plasma fluid-dynamics for nanoparticles production has been extended to simulate non-equilibrium plasma allowing low pressure operating conditions and strong temperature gradients due to the quenching system.

ULTRAMAGNETRON

Basic physics for opto-magnetic reversal process have been added to an atomistic Heisenberg model. These describe the thermal processes involved.
The single-macro spin Landau-Lifshitz-Bloch model was extended into a multi-macro spin model taking the exchange coupling as well as the dipolar interaction into account.

6.3 Development of of closure relations (constitutive equations, material relations)

Modelling of constitutive equations

MATRANS developed a new constitutive model defining the relationship between tensile strength of functionally graded materials (FGMs) and volume fraction of ceramic phase has been developed to simplify complicated mechanical behaviour of FGMs.
In oxidation modelling a new constitutive relation has been proposed between the oxide growth rate and the surface temperature. Since the calculated macro temperatures are too low to allow for the oxidation, only closer look at surface asperities can provide the mathematical model for the experimentally observed oxidation phenomena. A user-defined FORTRAN code for the developed constitutive relation has been added to a commercial FE software.

MODIFY developed new macroscopic constitutive equations capable of describing quite reliably the deformation equations (e.g. the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

MULTIHY has developed macroscopic models based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before.

POCO developed an electro-dynamics constitutive equation relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

ROLICER extended existing models that treat damage and fracture in silicon nitride to include under cyclic contact loading based on the behaviour of the solid phases and boundaries phases.

6.4 Phenomenological modelling

In nanoparticle research for health applications the situation is so complex that no physics/chemistry based model can yet fully describe what happens. Therefore relations are sought between "descriptors". Molecular descriptors play a fundamental role in chemistry, pharmaceutical sciences, environmental protection policy, and health researches, as well as in quality control. The "model" is then a rule that gives the quantitative structure–activity relationship (QSAR models). They relate a set of "predictor" variables (physico-chemical properties or theoretical molecular descriptors of chemicals) to the response variable (e.g. a biological activity of the chemicals). QSAR models are used to predict the activities of new chemicals.

QSAR models are supposed relationship between chemical structures and biological activity.
The model can use force field computed with Molecular Dynamics or experimental fits of the parameters in e.g. the Lennard-Jones potential for a molecule as entity to study the interactions between the structural domains of proteins This potential takes into account the steric fields (shape of the molecule), the hydrophobic regions (water-soluble surfaces),[13] and the electrostatic fields. The model is established by reducing data sets by feature extraction (see also dimensionality reduction). The learning method can be machine learning methods or multiple-instance learning. Feature selection can be accomplished by visual inspection (qualitative selection by a human); by data mining; or by molecule mining. A typical data mining based prediction uses e.g. support vector machines, decision trees, neural networks for inducing a predictive learning model. Typically QSAR models derived from non-linear machine learning is seen as a "black box" and it might be a while before physics based models can replace this approach.

> This situation also appeared in micromechanics, where the constitutive equations were purely phenomenological derived from experimental data. But now the CE start to be derived from simulated data generated with atomistic models.

The QSAR rules found might direct the future work of (physic based) mesoscopic modellers as this is often how models are used: to generate physics understanding of phenomena (when prediction is still not possible).

NANOPUZZLES developed new groups of descriptors such as: topological, constitutional, metal-ligand binding descriptors, simplex representations of molecular structure (SiRMS)-based descriptors, "liquid drop" model (LDM) derived descriptors as well as descriptors derived from quantum-mechanical calculations and from computational processing of microscopic (SEM/TEM) images were calculated. Simultaneously, a methodology how to investigate the size-dependent electronic properties of metal oxide nanoparticles that might be considered as potential nanodescriptors, vital for Nano-QSAR studies, was identified. In addition novel approaches for scoring the quality of nanomaterial physicochemical/structural and toxicity data were established. Finally, preliminary read-across and Nano-QSAR models for the selected endpoints were developed.

MODERN established nanodescriptors that take into account the size and shape calculated with MD of the actual particles, next to chemical composition. Machine Learnin) used as input the Conduction Band Energy and Ionic Index of metal cation and the output is the probability of toxicity.

However as this Review of Materials Modelling is only discussing physics law base models, QSAR modelling is not further discussed and only projects with the models described in Ch1-4 are included.

Chapter 7
Modelling applications

Modelling in the projects considered cover seven main areas of application: Energy, Information and Communication Technologies (ICT), Health, Environment, Construction, Manufacturing, and Transport. Projects have been defined cross-cutting if they can be applied to more than one sector.
The variety and frequency of models have been applied in each of the sector are illustrated in Fig. 7.1.
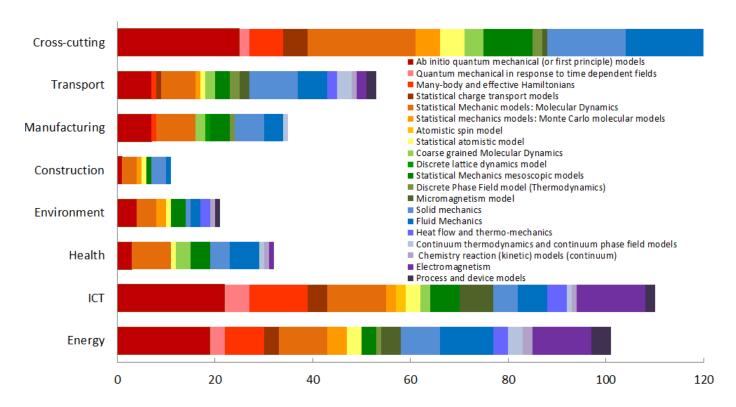

Fig. 7.1 Bar chart of the models used in the different application sectors
Each fragment corresponds to a model type and the color code is in the legend. The size of the fragments is proportional to the number of projects in that sector using that model type.

Fig.7.2 shows the number of projects per sector that are using the different models.

Fig 7.3 The number of projects developing linking of models describing the same entity (multiphysics) and for different entities (multi-scale) per sector.

Chapter 8

Impressions of Industrial modelling

The NMP Programme has as objective to support the industry. This chapter presents how companies involved in NMP Materials projects are using models.

> *Please note that these are impressions and <u>not</u> necessarily a complete account of what these companies do.*

8.1 Industrial areas

The responding industries are operational in the following industry sectors:

  energy (power generation, flue gas cleaning) (ANDRITZ Energy & Environment)
  chemical, materials research (BASF)
  chemical Industry, oil and gas exploration (BASF SE)
  transport (BMW)
  energy efficient, gas-free refrigeration and cooling technology (CAMFRIDGE)
  near net shape composite technologies for aeronautics (COEXPAIR)
  polymer manufacturing (DOW)
  aeronautic and space industry (EADS)
  automotive (FPK Lightweight Technologies)
  magnetic material (IMA)
  magnetic and optical systems, crystal growth (INNOVENT, magnetic and optical systems)
  chemicals, energy, catalysis, environment, manufacturing, health (JOHNSON-MATTHEY)
  chemicals and polymer manufacturing (LYONDELL-BASELL)
  chemistry (MERCK)
  automotive transmission systems (OERLIKON DRIVE SYSTEMS)
  manufacturing of ICT devices (OXFORD INSTRUMENTS)
  manufacturing of ICT devices (PHILIPS)
  risk technologies (RISK-TECHNOLOGIES)
  cutting tools for grinding, milling and drilling (SANDVIK COROMANT)
  data storage (SEAGATE)
  chemicals, processes, materials research (SOLVAY/RHODIA)
  chemistry (SOLVAY)
  solar energy (SOLARONIX)
  steel manufacturing (TATA STEEL)
  steel manufacturing (THYSSEN KRUPP)
  manufacturing of oxide nanoparticles for catalysts (TECNAN)
  energy, security (explosion), manufacturing (TOTAL)
  materials technology / chemistry / material sciences (UMICORE)
  car manufacturing (VOLKSWAGEN)

8.2 Type of models used

The models used span all classes of modelling (electronic to continuum modelling)

8.3 The reason why industry uses modelling

ANDRITZ Energy & Environment GmbH uses modelling as optimization of steam generators and air pollution control systems and their subdomains is crucial for the performance of plants!

BASF uses modelling as it offers unique insight and modelling is considered to allow for faster development cycles (guide to experiments, interpretation of experiments).

BASF SE is using modeling to speed-up and cost reduction of R&D projects by reduction of experiments, (2) Development of better or new products by enhanced understanding via modeling, (3) Design of new and optimization of existing manufacturing processes.

FPK Lightweight Technologiesis using modelling to have less development cost

BMW wants to reduce development time, development cost and hardware for testing.

CAMFRIDGE states that modelling helps them design their products more quickly.

COEXPAIR is using modelling to design composite parts for aeronautics applications by analytical and numerical calculations and models. They so ensure that the composite part can withstand the loads occurring during flight of the aircraft.

DOW uses modelling as it speeds up development of new products and provides insights into application properties of materials.

EADS wants to gain process knowledge, shorten lead time, replace time and cost expensive trials.

FPK Lightweight Technologiesis using modelling to have less development cost

IMA uses magnetic simulations to help them design prototypes for magnets and choose the optimum dimensions, materials.

INNOVENT uses modelling as it is often the only available mean to understand intrinsic properties and behaviour of magnetic, optical and semiconducting materials and it saves time and money when designing new device prototypes.

JOHNSON-MATTHEY uses modelling to aid understanding and guide experimental work. Simulation offers a faster and cheaper method of designing systems, than an experimental "traial and error" approach.

LYONDELL-BASELL predicts final product properties and performance with modelling. They also limit experimental cost and minimize time to develop new products, understand and control industrial processes.

MERCK predicts specific material properties as a form of pre-screening.

OERLIKON predicts the effect of the transmission system design on vehicle performance and energy efficiency with modelling.

PHILIPS uses models to understand the underlying physics of devices and processes; to optimize product designs and processes, to shorten development and qualification time and to decrease the time-to-market.

RISK-TECHNOLOGIES use multi-scale modelling of corrosion protection for new materials, testing and optimisation of new materials and new devices.

SANDVIK COROMANT uses models to gain deeper understanding of the materials properties of i.e. hard cutting tools and to enable faster development of new products. FEM modelling of the cutting tool process is used to save time in machining tests and to better understand the wear behaviour of the cutting tool. One common method is the prediction of phase diagrams (ThermoCalc), but also, the energetics and geometry of metastable compounds or compounds where no/little experimental data exists can be calculated by first principles software such as VASP, Phonopy etc. CFD and other methods are used to simulate synthesis processes in order to save time and improve understanding of these processes.

SEAGATE uses modelling as it reduces time to learning and allow them to determine if a design concept works without having to build it.

SOLARONIX states that modelling helps to optimize solar equipment. Modelling helps screening new materials by discarding the ones that are not compatible seen their energetic levels.

SOLVAY/RHODIA uses modelling to catalyse and support all stages of its innovation processes and to continuously improve the operational performance of its production technologies. Modelling is a key part in SOLVAY/RHODIA to understand, predict, design, optimize and control, which highly complements experiments.

SOLVAY is using modelling because it speeds up product development and helps fostering the understanding of physical-chemistry bahaviors. With the help ofacademic partners from our joint units (UMR CNRS/Solvay), we develop mesoscopic models on material properties (Barrier properties, mechanical properties, …)

TATASTEEL have been using modelling through the years in various R&D activities, such as materials design, processing route selection and optimisation. Recently, they have benefited from their weld modelling and simulation exercises in terms of understanding and control of weld induced residual stresses and distortion, as well as avoidance of formation of unfavourable microstructures in critical areas such as heat affected zone. They also use modelling to complement our physical experiments and generate inputs for engineering critical assessment work of structures in service.

TECNAN uses models to anticipate the properties of the materials to be created and reduce the time and materials spent on trials.

THYSSENKRUPP uses modelling as it improves the understanding of physical mechanisms and effects determining the materials' properties, for the optimisation of production processes and in order to provide improved material models describing the properties of new steels in industrial applications (i.e. forming, crash, etc.).

TOTAL uses modelling to understand the behaviour of certain materials under well-controlled conditions and to study physic-chemical properties of compounds, thermodynamics, CO_2 storage, new active compounds (polymers and lubricants, etc.) for interface activities.

UMICORE uses modelling as it can speed up considerably the design time for new processes (faster screening of alternative designs). It helps to optimize the efficiency and performance of processes by giving a more thorough insight in the physics involved, which will facilitate the debottlenecking. The use of modelling can also help to reduce the number of required experimental tests, thereby reducing the overall costs.

VOLKSWAGEN is using modelling to get a deeper insight into the battery cell behaviour.

8.4 Industrial use of models for new materials

ANDRITZ Energy & Environment GmbH uses continuum structural mechanics models for optimization and support in structural & thermal analysis as well as strength calculation.

BASF uses these models for rapid screening and simulated tests of quantum chemistry (reaction mechanisms, kinetics, photo-physics, new chemistries), complex liquid mixtures (formulations) and organic semiconductor properties (e.g. exciton or charge carrier mobilities).They are working on homogeneous and heterogeneous catalysis (mainly quantum chemistry) quite extensively! Also theoretical thermochemistry is an important topic (including high level methods like CCSD(T)). We are also using Hybrid-QM/MM-approaches for catalysis (mainly enzymatic reactions) from time to time and there is now some revival of these methods with respect to organic semiconductors. Besides that theoretical photochemistry/photo-physics is an important topic.

BASF SE uses modelling Chemical reactivity prediction (material synthesis and degradation behavior), Property prediction (solubility, interfacial and transport properties).

DOW uses materials modelling going from molecular structure to processing and end-use properties, and back. They do fundamental modelling of reaction mechanisms, rheology, interfacial behaviour and self-assembly; rational design of formulations.

EADS: newly developed alloys lack a proper description in terms of constitutive laws necessary for FE simulation studies. EADS uses new and self developed models to validate such new materials and get more insight into its behaviour during manufacturing operations.

FPK Lightweight Technologies uses modelling to calculate the fiber orientation and their mechanical properties due to the process, fatigue simulation in composites due to the process.

INNOVENT does simulations of static and dynamic behaviour of patterned magnetic films and magnetic nano-composites in order to understand the results of corresponding measurements and predict the properties of new magnetic materials. They also use (home-made) software for simulating dislocation dynamics in crystals.

JOHNSON-MATTHEY does simulations of new alloys for fuel cell and electronic applications. They also do modelling of chemical reactions to predict the reactivity of their catalysts. These models can locate molecules within porous materials and provide understanding of diffusion and adsorption. This is used for automotive emissions after treatment systems and emission control catalysts.

LYONDELL-BASELL calculates material parameters from rheological and other physical tests, predict rheological properties from chemical structure, compare theoretical predictions to experimental results.

MERCK uses materials models for the estimations of electronic energy levels (e.g. HOMO / LUMO) in molecules / polymers.

RISK-TECH uses dedicated Molecular Dynamics, Dissipative Particle Dynamics, Computational Fluid Dynamics, continuum mechanics, fluid-structure interaction software for simulated test of new materials and as the software allows optimising of the fitting parameters they can determine the optimal material characteristics. They e.g. analyse the effect of varying the nanocontainers fillings, particle-particle interactions, diffusivity parameter and the localization of the particles into the scratch. These findings provide guidelines for formulating nanocomposite coatings that effectively heal the surfaces through the self-assembly of the particles into the defects.

SANDVIK COROMANT uses electronic structure methods like VASP/VASP+phonopy to calculate thermodynamic properties, geometry and electronic structure of compounds used in the bulk and coating of the cutting tools. Empirical models based on large sets of measured data are used to predict mechanical properties of the cutting tool.

SEAGATE screens new device and material designs for perpendicular writers. New material properties and advanced geometries are entered into the simulation to and output magnetic fields are measured to determine the likely performance and reliability of the prototype structure. If successful in simulation, the new device design or material is processed in a real prototype to determine electrical performance.

SOLARONIX calculates the energy levels in new solar cell material.

SOLVAY/RHODIA is oriented toward a computer-aided rational design and optimisation of new highly functional materials and formulations for sustainable solutions in the fields of energy, consumer chemicals, electronics, automotive, ... Molecular modelling (ranging from electronic to meso-scopic scale) and empirical modelling are used to perform a virtual and high throughput experiment screening of new materials as well as to pinpoint the most important microscopic material properties which (qualitatively or quantitatively) determine the macroscopic performance and application properties. Also, they are a valuable tool to establish new design concepts that can enlarge the discovery process and help experimentalists in their daily work. End application behaviours are simulated (e.g. with Finite Elements) in order to optimise the solutions that are delivered. Process technologies used to produce these materials are also simulated (e.g. reaction kinetics, computational fluid dynamics, heat integration, dynamic process modelling) to design eco-efficient processes which minimize the environmental footprint and reduce associated CAPEX and OPEX.

SOLVAY uses mterials modelling to get good insight of the structure/property relationships at the microscopic (DFT, MD), mesoscopic (Most of the time house made programs) and macroscopic (continuum mechanics) levels

TATASTEEL uses materials modelling for thermodynamic and phase diagram calculations (during solidification and heat treatment) and microstructure prediction during thermo-mechanical processing of steels.

THYSSENKRUPP uses modelling to simulate phase transformations and recrystallization processes in the hot strip material and to predict the microstructural properties as well as the mechanical properties. They use modeling to establish phase diagrams of the steels.

TOTAL study materials properties and absorption capacity, enhanced oil recovery, polymers development, additives for lubricants or fuels, friction studies and corrosion.

UMICORE simulate the mechanical strength/service life of new materials in specific customer applications.

8.5 Industrial use of models for manufacturing

ANDRITZ Energy & Environment GmbH uses hey use CFD models for analysis and optimization of wet and dry SO2 scrubber design, duct design and baffle layout, fluidized bed combustion, over fire air nozzle layout, design of burners.

COEXPAIR is using visualisation models to generate and visualise the finite element model before and after calculation. They use analytical modelling and continuum mechanics models to calculate stress, deformations, displacements of composite parts such as T shape junctions or I shape beams up to the complete final part e.g. the landing gear door of an aircraft.
With these they do analysis of deformation and stress in the material loaded with a static or dynamic mechanic load, thermal load, thermo-mechanic load, vibration load for resonance and instability.

EADS uses Finite Element based software for process development to optimize part accuracy or process parameters during metal forming or machining.

FPK Lightweight Technologies uses modelling to analyse component performance and to simulate future production processes.

INNOVENT uses (home-made) software for simulating crystal growth and dynamics of point defects in crystals.

LYONDELL-BASELL: uses modelling for reactor engineering and process engineering, checking proper functioning of the reactor and predicting final product structure and material performance at customer-applications.

OXFORD-INSTRUMENTS models processes in order to optimise their design of new plasma etch and deposition hardware.

RISK-TECHNOLOGIES use two different modelling approaches for self-healing materials consisting of nano-containers. Simulation determines nano-containers fillings, particle-particle interactions, diffusivity parameter and the localization of the particles into the scratch.
The models are Dissipative Particle Dynamics, Finite Element Method and continuum mechanics.

SANDVIK COROMANT uses CFD-modelling as well as other internally developed methods to simulate manufacturing processes.

SOLVAY/RHODIA uses modelling for the sustainable improvement of the operational performance of its manufacturing units, looking for optimizing capital and operational expenditures. Computational fluid

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dynamics is used to troubleshoot, debottleneck, re-vamp process equipment and to optimize their overall efficiency. Heat integration is performed to make efficient use of energy. Advanced process control solutions are used to operate processes as close as possible to the optimum limits while satisfying safety constraints and ensuring that quality requirements are met. Statistical data mining is used to value plant historical production data coming from manufacturing execution systems so as to identify and optimize key process variables. Dynamic process modelling allows building Operator Training Systems to develop skills of manufacturing teams. Polymer processing technologies that are used by our customers are also simulated to bring them our knowledge of our materials.

SOLVAY uses CFD for the development of new reactors, improvment of curent process, …

TATA STEEL uses manufacturing models for loading and deformation prediction in rolling and pipe forming, characterisation of residual stress and distortion due to welding, prediction of microstructure and properties in thermo-mechanical processing of steels and assessment of in-service performance of steel products and Computational Fluid Dynamics.

THYSSEN KRUPP use continuum mechanics, thermo-mechanical models, CFD and statistical models to simulate casting and hot rolling processes. They also use welding models to simulate weldings for crash relevant parts including the description of the microstructure evolution and the residual stresses. The simulations are validated by comparison to experimental results. They also simulate precipitation forming which plays a crucial role during the development of new steels and the optimization of steel concepts.

TOTAL uses models for polymers compounds manufacturing processes.

UMICORE is simulating metallurgical and chemical processes ranging from a single operation to entire plants. It is used to debottleneck and troubleshoot manufacturing processes. The models are often used to reduce the number of measurements and to design efficient experiments. They also do verification of new designs of processes (i.e. ovens, gas treatment plants).

8.6 Industrial use of models for products and devices design

BASF uses modelling to optimization of device architecture, detailed design and scale-up of devices.

BMW uses computational fluid dynamics and crash, fatigue and stamping simulation to predict the behaviour of their cars.

CAMFRIDGE use software to optimise device architectures by optimising geometries for heat transfer, fluid flow, magnetic force maximisation, magnet design. The code is integrated with CAD design tools – "really it is our SWISS army knife".

COEXPAIR is using the same approach for product design as they do for material design (visualisation models and continuum mechanics models to analyse deformation and stress in a composite part loaded with a static or dynamic mechanic load, thermal load, thermo-mechanic load, vibration load for resonance of the part and instability).

INNOVENT uses models based on electromagnetic field theory and mesoscopic theory of ferromagnetic materials to optimise permanent magnets and current circuit configuration in order to achieve the desired magnetic field configuration.

OERLIKON uses Finite Element Analysis, CFD, general computing software and multi-physics modelling software for the design of the mechanical parts, the optimisation of the transmission internals (churning losses) and the evaluation of the impact of the transmission system design on the overall vehicle performance.

SANDVIK COROMANT uses FEM modelling to simulate the cutting tool process and predict wear behaviour at different process conditions. The utilization of first principles modelling to simulate the chemical interaction between the cutting tool and a work-piece material is at an early stage development.

SEAGATE uses models for simulation of writers for perpendicular magnetic recording. This writer technology forms the basis of all current hard drive products and is expected to do so for the next four years at least. Modelling involves creating new geometries with complex shapes and critical dimensions typically less than 100nm. Output magnetic fields are measured with geometric and material parameters varied to determine optimal writer designs.
They use models for plasmonic nanostructures for Heat Assisted Magnetic Recording (HAMR). Simulation experiments are carried out with various geometries and
Also thermomechanical modelling for coupled mechanical modelling of a recording head under various temperature conditions is done. This is critical for recording head designs which works at a given fly height and meet certain reliability conditions in the final drive product.

SOLARONIX uses solar illumination simulation software and device design software for the design of microwave wave guides and antenna's.

SOLVAY.RHODIA uses modelling tools to predict and validate relationship between parameters to prepare and synthesize product versus final properties.

SOLVAY uses modelling fro the improvement of macroscopic structure (shapes, local organization, …) to improve mechanical properties.

PHILIPS applies new and existing models to predict the physical behaviour of current and future devices thereby taking into account the processing history. After experimental validation, the models are applied to achieve optimized product and process design with respect to several failure mechanisms such as interface cracking and fatigue. The models deal with thermo-mechanics, fracture mechanics, multi-scale mechanics, heat transfer and multi-physics phenomena.

TATA STEEL carries out system design, optimisation and performance evaluation of a novel (mechanical) device (machine) for weld (hot) cracking susceptibility testing with the models.
RISK-TECHNOLOGIES develop the computational procedures and software for modelling of blood flow in micro-vessels and particle margination and endocytosis. A general scheme of the physical process involving blood microcirculation, nanoparticle motion, attachment and endocytosis is modelled using continuum-based methods

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TOTAL uses chemical engineering models for simulation of reactors and processes and apply this a.o. to multiphase-multi-fluid flows, flows in porous media and combustion.

UMICORE does design optimisation of new devices with respect to efficiency and /or mechanical strength/service life.

VOLKSWAGEN is using device modelling for battery pack optimisation.

8.7 Industrial research into modelling

ANDRITZ Energy & Environment GmbH is developing models for combustion modelling for fluidized bed boilers; grate fired boilers and burners; chemical reaction modelling for wet SO2 scrubber desulfurization

BASF is doing development of multi-scale modelling, both vertical (parameter estimation from chemistry to coarse graining) and horizontal (coupling of continuum mechanical modeling and particle based MD). Related to organic semiconductor research quantum chemical parameters for intermolecular interactions relevant to charge and exciton transport as well as drift diffusion models are focus of research. They participated in an EU-project QUASI, where they were co-developing the software Chemshell.

BASF SE uses existing models from literature whenever possible and adapts or enhances them for the specific R&D project needs. In very rare cases, specific software tools are / have been developed because not available on the market.

DOW does research into a large variety of simulation routines in polymer science.

FPK Lightweight Technologies does research into model development for fiber orientation and their mechanical properties due to the process, fatigue simulation in composites due to the process

LYONDELL-BASELL is developing reaction engineering and polymerization kinetics for their own processes in order to achieve process optimization

INNOVENT participates in research into numerical methods in micro-magnetics, in order to increase the efficiency of existing packages and to develop new packages for simulations of those classes of magnetic material which can not be simulated with the state-of-the-art software. They also do development of the software for simulations of the dislocation dynamics in crystals in order to understand the formation of equilibrium and non-equilibrium dislocation patterns in semi-conductors.

OERLIKON is doing simulations based on newly developed vehicle models and energy management system models, actuation system models, churning and windage losses models.

OXFORD INSTRUMENTS is developing new atomic and molecular chemical reactions sets to be added to their plasma modelling code.

PHILIPS is doing research into fracture and damage mechanics, multi-scale mechanics and thin film mechanics.

RISK-TECHNOLOGIES develop computational procedures and software for modelling of blood flow in micro-vessels and particle margination and endocytosis. They developed two different modeling approaches, DPD and FEM for self-healing materials, based on the nanocontainers healing concept.

SANDVIK COROMANT develops empirical/semi-empirical models of mechanical properties of hard materials and performs thermo-dynamical assessments of new materials ´systems. Models for manufacturing processes are continuously developed and improved.

SEAGATE does model development in micromagnetic and plasmonics. Micromagnetic modelling development takes place to improve modelling times and accuracy for reader and writer modelling in perpendicular recording heads. Modifications are made to a freely available modelling platform. This development is aimed towards products being developed for the next 4 years. Plasmonics modelling is carried out to compliment modelling capability. This is carried out to improve modelling capability for very small nanophotonic elements. This is targeted towards the Heat Assisted Magnetic Recording (HAMR) application which should be in product hard drives in around 2017.

SOLVAY/RHODIA has internal R&D activities and external partnerships in the modelling of catalytic reactions, reactive and multiphasic flows, multi-physics and multi-scale simulation of advanced materials, development of quantitative laws for predicting materials and blends properties.

SOLVAY does with the help of our academic partners from our joint units (UMR CNRS/Solvay), we develop mesoscopic models on material properties (Barrier properties, mechanical properties, …)

TATA STEEL is developing industrial scale modelling of welding for weld induced residual stress and distortion characterisation, incorporating the capabilities of defect prediction such as cracking using multi-scale modelling techniques.

TOTAL develops models for multiphase flows in risers (avoid Hydrates), and derives closure equations of "slug flows".

Chapter 9
Achievements of the models

Of course the results of all the models are very impressive and useful for industry.

In this chapter a subset of these results is presented, listing those achievements that <u>can NOT be achieved experimentally.</u> It is hoped that this can convince experimentalists of the value of modelling!

ADGLASS
The modelling revealed previously unknown details of an important process (hydrogen embrittlement of silicon crystals) widely employed for the fabrication of Silicon-On-Insulators (SOI) nanoelectronic devices. It also unveiled undiscovered mechanisms of brittle fracture in solid materials, including the precise chemomechanical role of defects (impurities, reconstructions, dislocations) and dynamical instabilities during the propagation of cracks in brittle materials. Moreover, the simulations explained the reasons for the previously observed, yet so far very poorly understood, binding specificity of certain peptide sequences to inorganic materials surfaces. They revealed an unknown adhesion driving force modulated by the local variations of water density at the solid/liquid interface.

AMCOS
Simulations can predict the sorption isotherms of pure and mixed gases in recently synthesized nanoporous materials (zeolites, metal-organic frameworks, polymers), or in hypothetical materials considered for synthesis. They can also predict the rates of diffusive transport through these materials.

AMON-RA
The model guides nanorod solar cell devices device development and clarifies the specific underlying physics by
Definition of suitable bandgap energies for single- and dual-junction nanowire solar cells
Definition of suitable device structure including doping levels and barrier layers
Definition of optimum configuration for wire length, distance and diameter in nanowire array
Understanding of optical and electrical loss mechanism in single- and dual-junction nanowire solar cells
Contribution to roadmap for assessment of III-V nanowire photovoltaics

ARTIVASC-3D
The hydrodynamic modelling will be able to predict wall shear stresses at the vascular graft walls. These stresses have to be within a certain range in order to stimulate the endothelial cells to perform e.g. neo-angiogenesis.. These wall shear stresses would be extremely difficult to measure for any possible graft geometry. Therefore, a modelling-based design approach is crucial for tissue engineering.

ATHENA

Identification of candidate materials and materials interfaces for future nano-electronics based on complex oxides. These included hetero-junctions, superlattices and multilayers consisting of doped magnetic perovskites (e.g. LaxSr1-xMnO3, PrxCa1-xMnO3), double perovskites (e.g. LaNi1-xMnxO3) and diluted magnetic ferroelectrics designed to exploit and manipulate the coupling of different order parameters at the two sides of the interface.

Prediction of the phase diagram of complex magnetic oxides MnO and NiO under pressure, Explanation of the extremely high antiferromagnetic ordering temperature in SrTcO3 and BaTcO3.

AUTOSUPERCAP

The battery-supercapacitor modelling and simulations allow selection of the best materials/supercapacitor for scaling up reducing experimental costs.

The molecular ion simulations guided the research for a pore size, maximising the specific capacitance for carbonaceous electrode materials and thereby increasing energy and power density.

CODICE

The developed toolkits revealed that there is a synergy in the hydration of alite and belite phases of cement clinker, which opens the door to new eco-cements.

While a priori one would expect that the larger the content of C_3S the better the resulting mechanical properties, the simulations have revealed that there is synergy in the hydration of C_3S and C_2S blends, and that there is an optimum C_3S/C_2S ratio around 70/30.

DISC-GENERATION

The modelling contributions are twofold:

The coupled transport-mechano model is able to predict the movement of solutes within the intervertebral disc and predicts the interactions between mechanical properties, fluid and solute transport, and cell viability. This is essential for a proper understanding of the mechanisms of disc degeneration and disc regeneration with the use of biomaterials as disc substitute.

Simulations of the effect of partial and complete disc nuleotomy on load transfer as a function of the biomaterial substitute used can be used to determine the surgical variability during nucleus removal.

Both contributions cannot be obtained experimentally and therefore are complementary to the experimental evaluation of the biomaterial performance.

DYNAMAG

The calculations pointed out samples that were until then simply not considered.

A novel magnonic logic architecture has been developed based on physics discovered by the models. The, until then unexplained, origin of the response experimentally observed in optical pump-probe studies of magnetic multilayers with strong perpendicular magnetic anisotropy, has been revealed via calculations in the discrete lattice model.Mechanisms behind unusually low magnetic domain wall depinning currents within spintronic devices have been revealed via full 3D finite element simulations.

FEMTOSPIN

Prediction efficiency of ultrafast spin dynamics in multiferroics excited by THz laser pulses

Prediction of the smallest stable domain structure in magnetic thin films

Prediction of the time and spatial scales of magnetic pattern formation

Identification of optimal materials for ultrafast optically induced magnetic switching

FREECATS

Heat transfer modelling guides the design of the foam materials and predicts the deposition of carbons during operation, (a phenomenon critical in oxidative dehydrogenation) and so reduce costs of trial and error developments.

Multi-scale modelling of reaction, surface-fluid interactions, heat transfer and hydrodynamics allow to predict from first principles the behaviour of the overall reactor system and to screen a large space of operating conditions prior to experimentation. This leads to better understanding of physical phenomena involved and dynamics of processes within the system, thus reducing the number of experimental trials required.

GOFAST

The model identified optimal correlated materials (composition, size, direction of the laser pulse versus surfaces, etc...) and excitation pathways (photon energy, intensity, polarization and temporal profile) for the production of controllable and reversible photo-induced transition between very distinct phases, e.g. metallic and insulating, or normal and superconducting.

HIPERSOL

The methods can predict contacting and recombination properties of nanostructured materials and complicated interfaces.

The model gave fundamental insight into nitrogen diffusion in silicon, into the nature of different recombination traps, into dissolution and transport of Ag during the firing process, and insight in how the current flows through the contacting region. Based on this optimal Ag crystallites geometries were gained.

HIVOCOMP

Prediction of structural properties to avoid unfeasible or expensive experimental tests.

The models also enabled screening of possible choices for the resins. The flow modeling shortened part of the design by predicting permeability and impregnation time of the different resins.

The model predicted structural behavior in function of the above properties and damage initiation by calculating the threshold and damage development parameters in the composite during different loading types

HYMEC

The electric field distribution of charged metal nanoparticles in organic matrices can be predicted, which allows identifying the switching mechanisms of memory cells. This, in turn, allows optimizing the morphology of devices.

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HYPOMAP

Computational modelling, in particular of the electron or atomistic type, allows the investigation of processes beyond the experimental scale. People often speak of the "computer microscope" that allows to monitor the motion of a single atom. It also provides understanding of an individual vibrational mode, or of the contributions of material fragments to an individual property. In this project modeling provide insight in the adsorption energy of hydrogen as function of the composition of the individual building blocks of a molecular framework. With this data it is possible to improve the performance of the target materials.

IMS & CPS

The "electrical conductivity" model predicts the electrical percolation and conductivity of CNT/polymer composites close to the experimental observations. The achievements beyond experiments include the positive effect of agglomeration and the transverse conductivity of the CNT/polymer composite with the CNTs only sprayed on the surface. In fact, nobody believed that there will be conductivity in the transverse direction when the CNTs are sprayed on the surface alone. In addition, this model correctly predicted that the addition of compatibilizers and copolymers has a significant effect on electrical percolation threshold and conductivity. These characteristics are experimentally proved and this is the only model which can predict this behaviour.

The toughness model will predict the effect of carbon nanotubes and their agglomerates on re-distribution of stresses and strains inside the composite and the threshold strain for the onset of damage on the micro-scale.

The model utilized for validation elements can predict the initial failure of the T junctions and of the I beams for the different used materials (with and without CNT). This will help to design the test jigs to be used in the project.

INNOVASOL

Trial and error synthesis costs were avoided by computing the energetics of inclusion of some anions (iodide and tri-iodide) in a layered solid analogous to hydrotalcite before the actual systems were synthesized. The calculations showed the limit concentration expected for anions in this environment.

The models could provide understanding of phenomena occurring, e.g. the excess of lead observed in certain conditions.

The calculations allowed to predict which surface passivant would help obtain particles of octahedral shape exposing (111) crystallographic faces, and this will guide the experiments.

IRON-SEA

The model determined the pairing symmetry and its evolution with doping, which is impossible to determine experimentally.

The model determined the characteristic energy of the boson that mediates superconductivity (examples: Co-doped Ba-122, Sm-1111) and of the coupling strength.

The model determined the effects of disorder, doping, lattice strain, etc on the superconducting properties.

The model determined the effects that are optimal or detrimental for device fabrication and optimization.

LEMSUPER

New correlation-driven mechanisms for superconductivity in light element systems were predicted long before they were validated. A superconductivity mechanism for fullerides was predicted, where electron-vibron coupling, orbital degeneracy, and strong electron correlations implying a nearby Mott transition all play a crucial role. Cesium fullerides validated this theory.

Identification of new electronic ground states in light element systems leading to superconductivity, potentially unveiling new light element molecule-based superconductors, something that cannot be done experimentally.

MAGNONICS

Numerical simulation of quasistatic magnetization processes explain measurements by MOKE and of spin-wave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of nanoscale magnetic dots and antidots. These simulations facilitate explaining the nature and spatial structure of magnons in the magnonic arrays.

MASTER

The model can predict the magnetization dynamics in an array of hetero-structures. These dynamics cannot be computed analytically. These simulations are used to optimize the design of spin devices as optimization by experimental means would be too costly.

MATRANS

Most of the modelling in the project is done to replace the experiments, which are usually complex and costly or, in other words, the modelling predicts the materials' properties/behaviour which will be observed in experiments and thus shortens the development process.

METACHEM

The model predicts whether the metamaterial can be described within effective media theory. The model extracts parameters not directly measurable.

The model can determine individual polarizabilities of a complex scatterer (electric and magnetic), surface susceptibilities of metasurfaces (electric, magnetic and magnetoelectric), efractive index of the wave in a lattice and wave impedance of the wave in a lattice.

MINOTOR

Modelling allows material design of multilayer devices with optimized proprieties as follows:

- The model has predicted the contributions to the discontinuity between the electronic structure at the interface and the bulk material
- The model explained the origin of the electronic level alignments at organic/organic interfaces as measured in short-circuit current and the open circuit voltage of solar cell devices, two key quantities that directly dictate the efficiency of those cells.
- The model has shown that modifying the surface of electrodes, can tune the charge or spin injection barriers in devices such as OLEDs.
- The model predicted the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties.

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MINTWELD

Manufacturing industry, metal alloys, welding, EAM (electric active materials) modeling

MODIFY

Modelling has explained the interplay between the chemical composition of the synthesized PSA samples and the degree, strength and life-time of the specific hydrogen forces developing in the polymer, which in turn governs the unique cohesive properties and strong elasticity of these materials. Models also explained the big role played by particle-to-particle transient forces on the elasticity-to-viscosity ratio which seems to be at the heart of the design task for new adhesives. Modelling explained the connection between bulk rheological properties in extension and shear and the debonding mechanisms during stretching of PSAs.

MONAMI

Modelling of materials properties allows the search for new materials or to make accurate interpretations of observed materials phenomena. An example can be found for magnetic materials where two properties are most important from an application point of view, namely the size of the saturation moment at room temperature and a large magnetic hardness (or synonymously, a large magnetic anisotropy energy – MAE). These two properties can be predicted for any material, with an accuracy that is needed to make the search for novel permanent magnetic materials much more efficient.

MORDRED

Predict defect character and density that causes device breakdown in realistic environments and over realistic performance times.
Characterize this for a variety of new, industrially untested materials.
Suggest routes for device design that should eliminate or reduce reliability problems

MULTIHY

Optimisation of the pulse-plating process used in the fabrication of the combustion chamber of the Ariane satellite delivery vehicle
Mechanistic understanding of the susceptibility of advanced high strength steels to HE by absorbed H
Prediction of the influence of H on the fatigue lifetime of wind turbine bearings.

MUST

The model can be used do give recommendation concerning optimal composition and structure of the coating to delay corrosion of metallic and polymeric substrates and structures, thus reducing development costs.
The model predicts service-life time via the probability of the scratch healing or inhibition based on the physico-chemical properties of the materials and realistic scratch geometries.

NAMASTE

Reproduction of the valence band nature of Fermi level states the archetypical ferromagnetic semiconductor (Ga,Mn)As. Prediction and explanation of the observed magnetic and magneto-

transport properties in ferromagnetic semiconductors.Understanding of the observed spin-torque effects which lead to the discovery of new ferromagnetic resonance (FMR) effects.

Based on the developed capabilities to model spin-orbit in metals, it was shown that appropriate antiferromagnetic materials could be employed as active layers in spintronic devices (GMR, etc), thus opening up the possibility of the new field of antiferromagnetic spintronics.

NANOINTERFACE

A set of design and reliability guidelines guidelines for microelectronic packages for microelectronic packages with respect to delamination risk has been elaborated, which can only be generated in a systematic way by accurate models.

A better, quantitative understanding of adhesion mechanisms at the very small to macroscopic scale and of the effect of surface roughening on adhesion properties has been provided. This was only possible via mesoscopic semi-analytical and numerical fracture mechanics models.

NANOMAGMA

The model predicted that the optical and magneto-optical response of complex structures where metals and magneto-optical materials are simultaneously present is proportional to the electromagnetic field in the magnetic material. This guided the design and now the whole structure is grown to try to maximize the field in that material.

NANOMODEL

The role of the interphase (structure and dynamics) is difficult to investigate experimentally. Only modelling can give access to the structure of matrix, nanoparticles and their interphases. Modelling revealed details how the interface is influenced by the chemistry.

NIM_NIL

Modelling allowed the optical properties to be calculated before the sample is fabricated, being essential for design and leaving room for optimization. Once a sample is fabricated and characterized, modelling gave results usually in excellent agreement with measured data, allowing to understand the underlaying physics and proving the sample high quality. It helped identify the EM properties of fishnets in the wedge configuration demonstrating the operation of a metamaterial in the visible regime.

NPMIMETIC

The study of the intervertebral disc (IVD) mechanical behaviour presents a high level of difficulty, due to intrinsic uncertainty on the quantification of real working loads (coupling compression forces, flections and torsion moments). Post-mortem analysis doesn't allow a full understanding of these phenomena, mainly due to the highly hydrated nature and the fact that the osmotic role of nucleus function is not achieved in those conditions. Modelling can overcome these restrictions and predict two fundamental situations:

i) degenerated IVD – stress/strain conditions due to nucleus degeneration (geometry, stress conditions, prediction of overstretched annulus' fibres)

ii) restored IVD – prediction of restoration conditions, annulus rupture state and/or failure risks on the nucleus 'refilling' process, influence of nucleus prosthetic materials characteristics on overall mechanical stability

OXIDES

Theoretical predictions to be further validated experimentally:

The unexpected possibility to induce multiferroism in epitaxially strained $CaMnO_3$

The unexpected possibility to achieve exploitable Tunnel Electro-Resistance (TER) in symmetric Ferroelectric Tunnel Junction (FTJ); for memory applications

The prediction of the unexpected appearance of a half-metallic ferromagnetic highly-confined 2-dimensional electron gas (2DEG) in $SrTiO_3/SrRuO_3$ superlattices

The unexpected role of oxygen rotation in shifting by 300 K the ferroelectric phase transition of $PbTiO_3$;

Joined theoretical-experimental breakthroughs

Improper ferroelectricity in oxide superlattices in which modelling identified a new microscopic mechanism (the so-called trilinear coupling of structural instabilites) as observed in parallel experimentally

Exchange bias in $LaNiO_3/LaMnO_3$ superlattices; modelling allowed the proper understanding of the unusual spin order giving rise to the experimental results

Compelling evidence of the intrinsic nature of the 2DEG at polar oxide interfaces; modelling of ideal interfaces was required to unambiguously distinguish between intrinsic and extrinsic effects

Confinement properties of the 2DEG at the $LaAlO_3/SrTiO_3$ interface; modelling provides key information on the electronic band structure, mandatory to interpret measured properties

POCO

Molecular models of functionalized CNTs and polymer matrices could predict the influence of the functional groups on the mechanical properties of the CNT and the interfacial shear strength (IFSS) of the nanocomposites. The influence of the functionalization of CNTs on the IFSS of the nanocomposite was demonstrated, something that would otherwise have cost many experiments.

The pull-out of CNTs from molecular matrices is difficult to analyze by experimental methods due to the scales involved. In this case, the process modelling of the pull-out was necessary to analyze the interfacial shear strength of the nanocomposites.

RADINTERFACES

The modelling is going to guide the appropriate tuning of interfaces within multi-laminate composite materials to obtain defect absorption materials with a self-healing mechanism.

REFREEPERMAG

The theory can pre-identify interesting materials prior to the actual synthesis and experiments and thus save time and resources.

ROLICER

The FEM simulations provide solutions for material stresses, which cannot be obtained experimentally. The fracture models describe crack nucleation based on traction-separation laws which provide a phenomenological lifetime prediction tool without the need for extensive experiments.

The result of models applied at microscale are homogenised to give thermoelastic properties and strengthening effects in ceramics. Such simulations provide information that cannot be obtained experimentally.

The ab initio models provide reliable properties of the bulk material and solid-solid interfaces as criteria for crack initiation, which are very difficult to obtain by experiments.

Molecular dynamics models are used in modelling hybrid steel-ceramic contact to study the interaction between additives in lubricants and bearing surfaces. Experiments that provide such information are not possible.

SIMBA

The modelling of the plasma flow dynamics and particle trajectories permitted to define the process at different scales and to predict the influences of the main process parameters (e.g. effects on nanopowder production yield when changing the reactor geometry and operating conditions). The model enabled the design of an optimum reactor chamber with increased flow of particles for collection thus avoiding an expensive try-and-fail approach, and saving time and effort in optimising the lab scale process and in transferring main results to an industrial ICP installation.

SIMUGLAS

Shape of moulds can be now predicted with the help of modelling of the glass shrinkages, which had to be done previously by expensive try-out experiments.

Index drop inside glass lens can be now predicted with the help of modelling of the structure relaxation behaviour of glass material, which was unknown only by pure experiments.

Material flow and temperature during forming process can be predicted, which cannot be observed and measured in the real moulding process.

SMASH

The modelling and simulation of GaN-based LEDs is able to guide the device design, by optimizing strain, polarization and quantum effects in order to improve the performance of the devices. Atomistic simulations can shed light on the effect of clustering in the alloy active regions.

SSEEC

The materials modelling of the overall system gave us invaluable feedback on experimental development, reducing the time that would otherwise be required to make multiple measurements or a full phase space of physical samples.The 2D model of an active magnetic regenerator (AMR) enabled accurate optimisation of geometry (packing density, absolute length scales), system operating parameters (frequency, flow rate) and identification of optimal (or ideal) refrigerant material properties (magnetocaloric effect and heat capacity) against overall efficiency and power requirements.

SUPER-IRON

Prediction of high-pressure phase transitions in Ba(Ca)Fe$_2$As$_2$ and of non-hydrostatic effect, confirmed by high-pressure XRD measurements.

Prediction of the peculiar structural and electronic modification upon doping with rare-earth metals in CaFe$_2$As$_2$.

Understanding of disorder, surface and interface effects.

Model calculations, joined with DFT calculations, were able to predict a tri-critical point in the phase diagram of iron-pnictides, now a hot subject for experimental confirmation.

SUPERLION

The model allowed shortened and better-informed selection of the most efficient cell architectures and geometries, and the optimal cell materials. Modelling can avoid excessive and often futile efforts to create more impressive micro-architectured electrodes, since these will often not result in improved battery performance.

SURFUNCELL

Modelling reproduced and predicted the strength and structured build-up of hydrogen bonds of water to the cellulose surface and inside the water layer as a function of the water layer thickness. This lead to suggestions for the design of the surface structure and charge distribution at cellulose surfaces.

ULTRAMAGNETRON

Materials with a compensation point are shown to be very promising media for magnetic recording. The magnetization reversal by a single circularly polarized laser pulse has been successfully simulated A phase diagram for opto-magnetic reversal was obtained, demonstrating a window of peak electron temperature and effective magnetic field pulse duration for opto-magnetic switching. A new mechanism of linear magnetization reversal was discovered. Experimentally the two sublattices of a ferrimagnetic alloy (GdFeCo) were found to demagnetise at different rates which was then confirmed by the model. The model predicted that the ferrimagnet transitioned into a transient ferromagnetic phase stable for only around 300femtoseconds which was found experimentally. The theoretical model predicted that the magnetisation of the ferrimagnet reversed spontaneously on application of a heat pulse, which was then experimentally verified.

Chapter 10
Conclusions

According to the stakeholders, the future of the European industry is associated with a strong modelling capacity. Their opinion is that an efficient modelling approach is needed to shorten the development process of materials-enabled products.

To predict properties of final products several models covering a wide range of physics and chemistry phenomena are used. This requires strong interaction between the different modelling communities and industry. Because of the complexity and long timescale of the code development and validation processes, the support of programmes such as NMP makes an important contribution.

This Review provides insight and helps the reader to see the models as more than mere "black boxes". It shows that:

- Industry is a very active player both in modelling for production and in modelling research areas
- Application areas of modelling span all industrial sectors. In each industrial sector all types of models are used except for Health where electronic modelling is underrepresented and except for mesoscopic models which are predominantly used in ICT and Energy and Transport.
- The majority of the projects performed modelling of the continuum type, corroborating the idea that modelling has reached a level of maturity that enables realistic simulation of macroscopic behaviour that can be used in industrial applications.
- Electronic and atomistic models have a much respected position in industrial use and they are a traditionally a stronghold of the Europe.
- Mesoscopic models are the least represented in this survey. This is probably due to lower level of maturity of these models which have to bridge the gap between the established concepts of "electrons" and "continuum". In the medical area they are slowly finding their place.
- Winners in frequency of use are: ab intio quantum mechanics, molecular dynamics and continuum mechanics (solid and fluid).
- The bulk of the projects are applying existing models to new materials, which shows that the current state of the art of modelling can be characterised as "mature".
- Model validation against a chain of experimental data of increasing complexity is an ongoing activity.
- Development of the physics and chemistry models seems to progress steadily and there is a significant number of research groups that is constantly pushing the boundaries by developing models based on theoretical physics and chemistry.
- Linking between models, especially through newly developed force fields and constitutive equations is extensive.

Industrial impact of modelling

The modelling discussed has lead to progress in many industrial sectors, such as energy, chemistry, ICT, healthcare and transport. Models can provide insights that experiments can not provide.

Predictive design of novel materials optimised for specified applications is heavily used by industry e.g. to add properties and functionality to new materials. The modelling has generated improved control of materials development and an improved control of concerned industrial products and processes, minimising the environmental impact, reducing risk of product failure and increasing service life-time.

Modelling offers unique insight into
- properties and in-service behaviour of materials,
- industrial manufacturing processes,
- provides understanding of the underlying physics of materials, devices and processes;

Modelling complements experiments by
- guiding experiments, replacing time and cost expensive trials,
- reducing cost and hardware for testing,
- interpreting the experiments;

THEORY → PRACTICE

Modelling helps design prototypes by enabling
- pre-screening, faster screening of alternative materials and designs,
- predicting final product properties and performance,
- determination if a design concept works without having to build it,
- optimisation of production processes;

Modelling reduce development time by
- shortening lead and qualification time,
- facilitating the debottlenecking,
- decreasing the time-to-market;

Fig 10.1 Industrial feedback on modelling use and benefits (see Ch. 8)

Future research needs

The community, contributing to this Review, highlighted that future research could target linking of models to extending the width and breadth of the models.

In parallel, it could be targeted to elaborate the physics and chemistry involved in existing codes to extend their application scales, especially an elaboration of mesoscopic would be welcome.

Interface design to facilitate the future implementation in larger and extendable framework architectures would be of added value.

Conclusions

We hope that the analysis in this Review of Materials Models illustrated by results of NMP projects bring insights. We hope that, with this insight, material behaviour and manufacturing processes across length and time scales can be better understood. This understanding of materials should then enlarge the application area and shorten the development process of materials-enabled products, which is key to increased global competitiveness of our industries.

Annex 1

Summary of the new Modelling Vocabulary

Summary of the new Modelling Vocabulary

From EMMC

This page attempts to summarise in a concise manner the Modelling Vocabulary of the EC Review on Materials Modelling by Anne de Baas and Lula Rosso. This excerpt tries to be as accurate as possible, but in case of doubt and for more information see the original at
http://ec.europa.eu/research/industrial_technologies/modelling-materials_en.html.

What are Models? What are Simulations?

Materials Models consist of "*physics or chemistry equations*" and "*materials relations*". Together they are called *governing equations*

> The "*physics or chemistry equations*" describe the behaviour of electrons, atoms, particles or finite volumes (the model entities). The physics or chemistry equations are generic and applicable to many situations.

> Physics or chemistry equations need to be complemented with information on the application (material). This information is given in relations applicable to a certain class of materials. These relations close the physics/chemistry equations and make them solvable. In many fields, especially in the continuum model world, they are called constitutive equations, but in order to harmonise all fields we opt for the name "*material relations*".

Materials Modelling is the establishing of governing equations (physics/chemistry equations and/or material relations) between physical or chemical quantities. These governing equations contain the key assumptions of the model. Modelling does not include fitting parameters in existing governing equations to (simulated or experimental) data.

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Simulation software is a computational code, which solves the governing equations by numerical methods and requires information about the application (boundary and initial conditions)

➔ Models are the Governing Equations of the physical and chemical entities, not the codes or simulation software. A code can contain the implementation of one or several models (toolkit/framework/workbench).

Material Model Types

A new way of building an overview of materials models consists in classifying the models according to the physics and chemistry included. Classification can be done via the **entity** whose behaviour is described by the model, namely: *electrons*, *atoms*, *nanoparticles/beads/grains* and *continuum finite volumes/elements.*

The model approximations might use concepts like density of entities (like e.g. in electronic or atomistic DFT), collective spectral behaviour of entities (e.g. in phonon models describing heat in atomic crystals), but this does not influence the classification.

The four natural categories consist of three **discrete** types and one **continuum** type of models:

Method	Entity whose behaviour is described	Number of units	Length scale	Time scale
Electronic models	electron	10-100	0.1 - 1 nm	-
Atomistic models	atom	102 -10^9 $10^2 - 10^9$	0.1 – 100 nm	fs - μs
Mesoscopic models	nanoparticle, beads, mesoscopic particles, grains	10^6-unlimited 10^6	100 nm - mm	ms - s
Mesoscopic magnetism models			1 nm - 100 mm	1 ps - 1000 ns
Continuum approaches	continuum finite volumes	unlimited	nm-m	s - ks

➔ ***Models are strictly classified according to the entity described by the model and not according to the size of the application or system!***

The reason for this is that classifying models according to the size (length -scale) of their application, rather than their entities, does not convey any meaningful information on the nature and hence the accuracy of the models. For example, a microstructure domain of some nano meters length can be modelled by considering either electrons, atoms, grains or finite volumes/elements. Thus calling the model after the application size   "a mesoscale model" does not reveal enough information for material

scientiststhat want to know whether the phenomena are described by the Schrödinger equation, Newton dynamics, conservation equations, or other physics equations.

Electronic models

These models describe the behaviour of electrons using quantum mechanical physics equations that calculate electronic structures from *first principles*. The physics equation is the Schrödinger equation with a set of approximations.

Examples of electronic Models (see the Review of Materials Models for more):

1.1 Ab initio quantum mechanical (or first principle) models
    1.1.1 Hartree Fock approximation
    1.1.2 Higher level ab initio methods
    1.1.3 (Electronic) Quantum Density Functional Theory
1.2 Many-body models and effective Hamiltonians
    1.2.1 Nearly free electron model
    1.2.2 Pseudopotentials
    1.2.3 Semi-empirical tight binding potential (TB) model
    1.2.4 Hubbard model
    1.2.5 k·p effective Hamiltonian
    1.2.6 Polarisable continuum model
    1.2.7 Envelope function approximation for continuous media
1.3 Quantum mechanical in response to time dependent fields
    1.3.1 TD-DFT and TD(Spin)DFT
    1.3.2 Time dependent k·p model
    1.3.3 Other time-dependent models
1.4 Statistical charge transport model
    1.4.1 Semi-classical drift-diffusion model 10^2 - 10^9
    1.4.5 Percolation models

Atomistic models:

These models describe the behaviour of atoms. They ignore the electronic degrees of freedom and use mechanics (forces and potentials) to describe the behaviour of atoms.

Examples of atomistic models (see the Review of Materials Models for more):

    2.1 Classical Density Functional Theory and Dynamic Density Functional Theory
    2.2 Molecular Mechanics
    2.3 Statistical mechanics models: Molecular Dynamics
        2.3.1 Classical molecular dynamics
        2.3.2. Ab-initio molecular dynamics
        2.3.3. Quantum mechanics/molecular mechanics (QM/MM)
    2.4 Statistical mechanics models: Monte Carlo molecular models
    2.5 Atomistic spin models
    2.6 Statistical atomistic models
        2.6.1 Langevin Dynamic method for magnetic spin systems
        2.6.2 Semi-classical non-equilibrium spin transport model
        2.6.3 Statistical transport model at atomistic level
    2.7 Atomistic phonon models (Boltzmann Transport Equation)

Mesoscopic models:

These models describe the behaviour of (part of) molecules, nanoparticles, bead, mesoscopic particles or grains, while what happens inside such an entity is considered to be frozen.

At the supra-atomic scale, uninteresting or fast details of the atomic motions can be averaged out or replaced by stochastic terms, and the mesoscopic models concentrate on essential motions of entities that are formed from more than one atom. The models describe the interactions between the beads.

Examples of mesoscopic models (see the Review of Materials Models for more):
- **3.1 Mesoscopic Density Functional Theory and Dynamic Density Functional Theory**
- **3.2 Coarse Grained Molecular Dynamics**
- **3.3 Discrete lattice dynamics model**
- **3.4 Statistical Mechanics mesoscopic models**
    - 3.4.1 Dissipative Particle Dynamics (DPD)
- **3.5 Discrete phase field model (thermodynamics)**
- **3.6 Micromagnetism model**

Continuum models:

These models describe the behaviour of a continuum entity called finite volume or finite element. At this level material is assumed to be continuously distributed throughout its volume. Continuum models disregard the discrete particle-based structures and smaller details.

Examples of continuum models (see the Review of Materials Models for more):
- 4.1. Solid Mechanics
- 4.2. Fluid Mechanics
- 4.3. Heat flow and thermo-mechanics
- 4.4. Continuum Thermodynamics
- 4.5. Chemistry reaction (kinetic) models (continuum)
- 4.6. Electromagnetism (including optics, magnetics, electrical)
- 4.7. Process and device modelling

Interoperability of models (multi-scaling) and databases

Linking models is running different models consecutively. (Sequential modelling)
Coupling models is running different models concurrently (Concurrent modelling)
A major issue in linking models is transfer of data from one model to another. The post-processing (reduction, extraction) of model output into input for the next model is called *homogenisation*. Homogenisation can be purely mathematical fitting data when the value of a parameter in a known materials relation is calculated. But homogenisation involves physics, when the modellers are looking ofr a new materials relation. Then they have to have an idea (assumption)for what physics relation they are looking. And this relation is then proven by the data. . In continuum modelling, often the results of continuum models applied at meso-scale (nm) are fed into the continuum model applied at macro-scale model (μm) in the form of constitutive equations – which in the language of the brochure are called material relations - or as boundary conditions. The establishment of such constitutive equations represents a big challenge in contemporary modelling. Another example of homogenisation is finding a new template relation for a force field including extra physics/chemistry processes

Finally, last but not least, often not only models are to be connected but integration of experimental data should also be done in a clever way.

Solvers

Solvers are used to solve the physics/chemistry equation. In the Review there is a strict separation between the two concepts "solver" and "model". For example, smoothed particle hydrodynamics (SPH) is a solver (used to discretise the fluid dynamics model equations) and not a model. Kinetic Monte Carlo is a way to solve mechanics equations.

> Solvers sometimes use concepts like "fictitious particles" but these are not to be confused with the entities whose behaviour is to be described.

Annex II
Projects fiches

The modelling done in some 70 materials projects in the NMP Programme is described in individual project fiches. The past tense is used for projects that have finished at the time of writing (January 2013) and the present tense for projects still on-going.

To show the value of modelling, the achievements of the models beyond experiments have been listed.

Modelling

in ADGLASS 229205

Subject of the modelling
Protein adhesion, interface cohesion and crack propagation in glasses

Models used
Atomistic: QM/MM

Simulation software and type of numerics used
QUIP, CP2K, Amber, with ad-hoc modifications
Plug-ins for other academic/industrial codes (e.g. LAMMPS, OpenKIM, VASP, Castep)
    extended buffer zone in QM/MM to mitigate the effects of its artificial surface

Achievements of the model beyond experiments
The modelling revealed previously unknown details of an important process (hydrogen embrittlement of silicon crystals) widely employed for the fabrication of Silicon-On-Insulators (SOI) nanoelectronic devices. It also unveiled undiscovered mechanisms of brittle fracture in solid materials, including the precise chemomechanical role of defects (impurities, reconstructions, dislocations) and dynamical instabilities during the propagation of cracks in brittle materials. Moreover, the simulations explained the reasons for the previously observed, yet so far very poorly understood, binding specificity of certain peptide sequences to inorganic materials surfaces. They revealed an unknown adhesion driving force modulated by the local variations of water density at the solid/liquid interface.

Application
Pharmaceutical and biomedical products
Optical and photovoltaic devices
Architectural panels

Relevant review articles
J. Schneider, L. Colombi Ciacchi, "Specific material recognition by small peptides is mediated by the interfacial solvent structure", Journal of the American Chemical Society 134, 2407-2413 (2012)
N. Bernstein, et al "QM/MM simulation of liquid water with an adaptive quantum region", Physical Chemistry Chemical Physics 14, 646-656 (2012)
F. Atrash and D. Sherman, "Dynamic Fracture Instabilities Generated by Phonon Emission: Experiments and Atomistic Simulations", Journal of the Mechanics and Physics of Solids 60, 844-856 (2012)
G. Moras, et al "Atomically smooth stress-corrosion cleavage of a hydrogen-implanted crystal", Physical Review Letters 105, 075502 (2010) (Featured in Physical Review Focus, vol. 26, 13th August 2010)

Summary of the project

The project target detailed knowledge of chemical and physical processes taking place at glassy interface systems and is devoted to improving the efficiency, functionality and reliability of glass products for pharmaceutical and photovoltaic applications.

Summary of the modelling

The project applied multi-scale a hybrid quantum-mechanical molecular mechanics (QM/MM), atomistic modelling method. Large length scales (many tens of thousands of atoms) are required to describe the systems of interest, and key physics have been added in quantum mechanical models, combining the highly accurate QM models with the fast MM dynamics. The QM calculations are performed on a limited portion of the system which includes an extended buffer zone to mitigate the effects of its artificial surface. The QM calculations are only carried out when the dynamic evolution of the system leads it out of the range of configurations which can be accurately simulated by the classical potential alone (e.g. during chemical reactions involving bond breaking or forming).

To aid the above applications, the electronic degrees of freedom of an explicit quantum mechanical model have been removed without sacrificing the accuracy of the atomistic potential, formally derived from quantum mechanical models. We gain speeds of many orders of magnitude. Novel quantum-accurate classical potentials have been created for carbon, silicon, water, tungsten, and various oxides.

This method is applied for example to the simulation of fracture experiments where the mismatch between the thermal expansion coefficients of frame and specimen generate normal and tangential strain fields at the specimen's boundaries that serve as the driving force for crack initiation and propagation.

We have extended the method so that it can handle liquids, which enables us to study solid/liquid interfaces.

The novel method has been applied to two scientific problems which require at the same time quantum precision and very large model system sizes. Namely, we have investigated (i) the adhesion of proteins at the interface between a glassy SiO_2 phase and a water solution, relevant to pharmaceutical applications and (ii) the cohesion between heterogeneous glassy interfaces (e.g. containing SiO_2 and TiO_2 phases) relevant to thin-layer-based conditioning of glass materials for applications in architectural glass and photovoltaic cells.

Modelling

in AIM4NP 309558

Subject of the modelling
Plastic injection into moulds with nanomechanical engineered surfaces

Physics/Chemistry models used
Continuum: Thermally coupled computational fluid dynamics CFD for plastic injection with flow to solid transformation

Constitutive equation for relation between surface roughness and friction at nano-level

Simulation software and type of numerics used
Continuum: SolidWorks Plastics, MoldFlow, Moldex3D, Click2Cast and Vulcan commercial software used for plastic injection simulation.
Personalised version of Vulcan, Autodesk CFD and Kratos to run subcycles of commercial software with a fine mesh to model FIB marks in the nanoscale domain

Achievements of the model beyond experiments
The AIM4NP machine can identify regions of maximum wear in a mould and thus identify where engineered surfaces might change.and where to do measurements. The simulation model will explain the results obtained by the experiments, andwill give clues on how to improve the surface finish and coating process, and will define the way to validate the mould performance from the measurements of the AIM4NP tool.

Application

Plastic injection moulding

Relevant review articles covering the topic (not necessarily their own):

- Jian-Yu Chen, Sheng-Jye Hwang, "Investigation of Adhesion Phenomena in Thermoplastic Polyurethane Injection Molding Process", POLYMER ENGINEERING AND SCIENCE—-2012, p.1571-1580
- I. Martínez-Mateo, F.J. Carrión-Vilches, J. Sanes, M.D. Bermúdez, "Surface damage of mold steel and its influence on surface roughness of injection molded plastic parts" Wear 271 (2011) 2512– 2516
- Garcia Granada, AA; Lacarac, V; Smith, DJ; Pavier, MJ., "A new procedure based on Sachs' boring for measuring non-axisymmetric residual stresses: experimental application." International Journal of Mechanical Sciences, Vol. 43 (12), 12.2001, p. 2753 - 2768.
- J. Fraxedas, et al., Nanoindentation: toward the sensing of atomic interactions, Proc. Nat. Acad. Sci.USA. 99 5228 (2002)

Summary of project

The project AIM4NP aims to develop a fast robotic metrology platform and operational procedures for measuring topography, morphology, roughness, micro- and nano-hardness and adhesive properties with nanometer resolution, in a traceable way. This should be developed for large samples in a production environment. Modelling is used to change the final injection method and thus to improve the surface of produced parts.

Summary of the modelling

A computer model will be developed to simulate the effect of mould surface roughness on the appearance of the final part. Current commercial CFD software can simulate the flow of the melt into the mould and this model will be elaborated with boundary conditions that include the effect of nano surface roughness. The relation between friction coefficients and nanoroughness will be investigated by combining experiments (atomic force microscopy, scanning electron microscopy, etc.) and simulations used as a tool to understand the underlying phenomena.

In the CFD model roughness is introduced as a parameter in the boundary condition on the wall of the mould in which the plastic flows. This CFD model with improved boundary conditions is expected to be able to reproduce the influence of the nanoroughness on the profile of velocities and consequently on the heat exchange with the mould and to reproduce the large friction results in an air film placed between solidified plastic and the mould changing the heat exchange parameters.

Then, velocities and pressures will be taken from simulations using commercial software for plastic injection. The problem of doing a simulation of a mould looking at meshes showing nanoroughness is a problem of mesh size, stable time step for explicit calculations and therefore large calculation times. These velocities and pressures will be taken as boundary conditions for a detailed nano/micro model that includes the equations of flow of hot plastic and adhesion of solid plastic to walls with several roughness patterns. The equations are the same but the detailed mesh will allow to picture weather the plastic parts copies the defects of the mould and how air film changes the heat exchange conditions.

The project addresses Knowledge-based Functionality to correlate nanomechanical properties of engineered surfaces to their functionality (electrical performance) in two target applications: high precision plastic injection moulding and organic solar cells. Such correlations will be investigated by combining experiments (atomic force microscopy, scanning electron microscopy, etc.) and simulation with the customised tools.

The goal here is to establish the empirically observed correlation between morphological parameters to the device performance in a CFD model. It is well known that the morphology of the involved organic/organic interfaces is critical for an efficient functionality of organic solar cells. In this task the correlation between roughness and efficiency will be determined and then an empiric relation will be derived.

The methodology will be based in current state-of-the art knowledge on dynamic mode AFM and experimentation on polymer samples first and harder samples later. The possibility to implement multifrequency AFM operation modes for AIM4NP will be analysed.

Modelling

in AMCOS 233502

Subject of the modelling
Advanced materials for selective sorption of carbon dioxide from gaseous mixtures (zeolitic imidazolate frameworks, hyperbranched aminosilicas, functionalised polymers)

Models used
Electronic: Density Functional Theory (DFT) for electronic structure calculations
Atomistic: Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) approaches
  Metropolis Monte Carlo in the grand canonical ensemble
  Ab–initio and classical Molecular Dynamics
Mesoscopic: Statistical flow simulation methods (Lattice Gas Cellular Automata)

Simulation software and type of numerics used
In house codes CPMD and CP2 for QM/MM
Numerical solution of initial value problems in ~ 105 unknown functions of time.
Stochastic sampling of rare events (activated processes) by Transition State Theory which includes multidimensional spaces spanned by ~ 105 coordinates according to prescribed probability density functions. This entails computation of minima and saddle points on complex potential energy hypersurfaces of the high dimensionality.

Achievements of the model beyond experiments
Simulations can predict the sorption isotherms of pure and mixed gases in recently synthesized nanoporous materials (zeolites, metal-organic frameworks, polymers), or in hypothetical materials considered for synthesis. They can also predict the rates of diffusive transport through these materials.

Application
Capture of CO_2 and CH_4 by novel classes of MOF materials for applications in Carbon Negative technology and storage of H_2 in the above materials.

Relevant review articles
Pantatosaki, E.; Pazzona, F.G.; Megariotis, G.; Papadopoulos, G.K. "Atomistic Simulation Studies on the Dynamics and Thermodynamics of Nonpolar Molecules within the Zeolite Imidazolate Framework-8", J. Phys. Chem. B 2010, 114, 2493-2503.
E. Pantatosaki, H. Jobic, D. Kolokolov, S. Karmakar, R. Biniwale and G. K. Papadopoulos J. Chem. Phys. 2013, 138, "Probing the Hydrogen Equilibrium and Kinetics in Zeolite Imidazolate Frameworks via Molecular Dynamics and Quasi-elastic Neutron Scattering Experiments

Summary of project

The objective of the EU-India collaborative research project AMCOS is to investigate newly synthesized and/or modified classes of advanced sorbents, such as the zeolitic imidazolate frameworks (ZIF), functionalized polymers (FP), and the new category of inorganic-organic hybrid sorbents known as hyperbranched aminosilicas (HAS). Thanks to their exceptional physicochemical properties and enhanced ability for adsorbing specific groups of molecules, these advanced materials have been used for environmental and energy-related applications, such as the selective separation of carbon dioxide from flue gases and natural gas.

Summary of the modelling

Computer modelling has been utilized mainly for the study of CO_2-sorbent interactions along with the mobility of a wider class of guest molecules in the various advanced materials host systems, such as hyperbranched aminosilica (HAS), zeolitic imidazolate frameworks (ZIFs), and functionalised polymers. A focus of the project is the selective separation of CO_2 from CO_2/CH_4 and CO_2/N_2 mixtures, which is important for CO_2 capture and CH_4 enrichment, respectively, for environmental and energy resource related applications.

The ZIF-8 crystal was modelled using rigid and flexible models, starting from conventional general-purpose force fields (Dreiding) and proceeding to more refined energy expressions that better represent specific interactions with the metal atoms. Quantum mechanical calculations have provided a new, more reliable input for the values of the partial charges of the ZIF framework atoms. DFT calculations on periodic structures were performed using BLYP and PBE functionals. We have found that the fluctuations of the atomic charges are almost negligible, hinting that using a simple point charge approximation for classical Molecular Dynamics simulations of ZIF-8 is sensible. Car–Parrinello and Born–Oppenheimer first principle Molecular Dynamics simulations were conducted for the calculation of the charge distribution in metal-organic frameworks. We have also applied an ab initio quantum mechanical model to calculate the force field of the ZIF-8. QM/MM models have been used with methods enabling the enhancement of the sampling of rare events (activated processes), such as the newly developed Transition State Theory. The QM/MM model was used for the computation of the Force Field of the novel MOF materials employed in the project, by calculating the charge distribution on the atoms of the frameworks, the bond and angle force coefficients, which eventually were used as input in the atomistic modeling. Using these improved tools for describing interactions, we have designed and implemented efficient Grand Canonical Monte Carlo stochastic scheme and Molecular Dynamics simulations for the prediction of the sorption thermodynamics, the distribution of guest molecules over the adsorption sites (singlet probability density), isotherms (equilibrium amount of gas sorbed per unit mass of nanoporous material at given temperature and pressure) and finally the diffusivities of hydrogen (H2), methane (CH4), and carbon dioxide (CO2) within the project materials.

Lattice Gas Cellular Automata has been used for the study of diffusive mass transport processes in zeolites occurring on very long time scales. The main input for the model comes from data:

(i) local density dependent mean-field potentials and transition probabilities obtained from atomistic simulations that will be used as the starting point to derive adsorption and diffusion properties.

(ii) Thermodynamic and kinetic data obtained from experiments and/or other simulation methods, used as the starting point of a fit procedure to trace which local behaviour causes the system to produce these

Predictions are generally in very good agreement with the measurements conducted by the experimental partners of the project, validating our predictive computational approach.

http://comse.chemeng.ntua.gr/amcos/

Modelling

in AMON-RA 214814

Subject of the modelling
III-V Semiconductor materials, devices and systems

Models used
Electronic models: k.p theory for band structure calculation, drift-diffusion
Continuum modeling: electrical and optical modelling (continuity equation and diffusion equation (CFD)
non-linear Poisson equation for the electrostatic potential)

Simulation software and type of numerics used
Electronic models
    QUATRA/CELS (used and developed): three-dimensional drift-diffusion model
Continuum modelling
    FDMAX (formerly lumi3) (used and developed)
      Finite Element solver for vectorial Maxwell equations in three dimensions;
    EtaOpt (used)
      Scattering Matrix Method for electromagnetics (used and developed)
    Sentaurus device (DESSIS) for electrical circuit modelling

Achievements of the model beyond experiments
The model guides solar cell development by
  Definition of suitable bandgap energies for single- and dual-junction nanowire solar cells
  Definition of suitable device structure including doping levels and barrier layers
  Definition of optimum configuration for wire length, distance and diameter in nanowire array
  Understanding of optical and electrical loss mechanism in single- and dual-junction nanowire solar cells
Contribution to roadmap for assessment of III-V nanowire photovoltaics

Application
IIIrd Generation Photovoltaics
Solar Cells
Nanowire Optoelectronics

Relevant review articles
J. Kupec, B. Witzigmann, 'Computational electromagnetics for nanostructured solar cells', J. Comp. El., 2012, invited review
B. Witzigmann, R. Veprek, S. Steiger, and J. Kupec, 'Comprehensive Modeling of Optoelectronic Nanostructures', J. Comp. El., No. 4, Vol. 4, pp. 389-397, 2009, invited

Summary of the project

The project AMON-RA targeted photovoltaic cells made from arrays of light-harvesting nanowires on silicon substrates made with hetero-epitaxy of III–V semiconductors. Two main architectures were investigated: The first, called "Light Guiding made from core-shell nanowires, in which the sunlight will be guided through materials with decreasing band gap. The second architecture, called "Effective Medium", consists of denser arrays of much thinner wires, where the light waves will experience an effectively averaged medium as they propagate downwards. The high degree of self-assembly and insensitivity to lattice parameters and the use of inexpensive silicon substrates made the production cheap.

Summary of the modelling

The optical and electronic properties of nanowire photovoltaic cells are modeled using a combination of existing and custom developed multi-scale simulation methods. Models combining optoelectronic and quantization effects in a heterojunction nanowire were developed within AMON-RA.
The optical generation in nano-wires is calculated by spectrally integrating the local optical power density times the material absorption (excitonic and phonon loss effects). The optical power density is calculated from the numerical solution of the vectorial Helmholtz equation (which is derived from [Maxwells equations](#)) with the electronic model CELS/QUATRA using as input the resulting EM field of the the three-dimensional Maxwells equation calculated with FDMAX. (FDMAX is a model originally for eigenproblems, but is extended to model scattering problems within AMON-RA.) Optical generation is then used as source term in the continuity equation for the electronic system. The project numerically solves the electronic system of equations consisting of a continuity equation for electrons and holes, with diffusion currents for bulk regions ([CFD](#)) and thermionic emission currents for hetero interfaces, coupled to the non-linear Poisson equation for the electrostatic potential.The electrical simulation of carrier transport in large diameter hetero-junction nanowires with tunnel junctions is described.
A continuum model [EtaOpt](#) calculates the efficiency of a solar cell dependent on the band gap. Band gap is an input parameter. Thus the optimum bandgap combination for multi-junction solar cells with two or more junctions is evaluated depending on the spectral conditions and calculates the thermodynamic efficiency limit for a given bandgap combination. The optical properties absorptivity of nanowire arrays are modelled with a transfer matrix method within EtaOpt.
The [continuum electrical modelling](#) of the Esaki interband tunneling diode the most critical part of the solar cell, is done by the commercial DESSIS software. The resulting current flow and resistance of different device architectures is calculated and analysed and the optimum wire configuration is determined.

Modelling

in ARTIVASC_3D 263416

Subject of the modelling

Blood and nutrient transport in vascularised biomaterials

Models used

Continuum: computational fluid dynamics (CFD):
  advection-diffusion equation for transport of nutritients and O2 (microscale)
  hydrodynamics model based on Navier-Stokes equations (macroscale)

Simulation software and type of numerics used

FEM code "Elmer" to simulate the transport of nutrients and O2
Smoothed particle hydrodynamics code "SimPARTIX" to simulate blood flow

Achievements of the model beyond experiments

The hydrodynamic modelling will be able to predict wall shear stresses at the vascular graft walls. These stresses have to be within a certain range in order to stimulate the endothelial cells to perform e.g. neo-angiogenesis. These wall shear stresses would be extremely difficult to measure for any possible graft geometry. Therefore, a modelling-based design approach is crucial for tissue engineering.

Application

Regenerative medicine, additive manufacturing of tissues

Summary of project

ArtiVasc 3D aims at developing a bioartificial vascularised skin which will, for the first time, allow tissue replacement with optimum properties in a fully automated and standardised manufacturing approach. This will be achieved through an innovative combination of hi-tech engineering such as micro-scale printing, nano-scale multiphoton polymerisation and electro-spinning with biological research on biochemical surface modification and complex cell culture and using a multidisciplinary approach which involves experts in biomaterial development, cell-matrix interaction, angiogenesis, tissue engineering, simulation, design and fabrication methods work.

This new bioartificial vascularised skin will be of great value in a vast array of clinical treatments, e.g. as a transplant in trauma treatment. In addition, it will be used as an innovative in vitro skin equivalent for pharmaceutical, cosmetics or chemical substance testing, which represents a promising method to reduce expensive, ethically disputed animal testing.

Summary of the modelling

The project develops and applies modelling techniques for the design a vascular system that effectively delivers O_2 and other nutrients from the circulating blood flow to the surrounding tissue. Experiments and simulations will be employed in order to develop design rules and 3D models of the artificial vascular system. The modelling in this project aims at providing the link between biological demands and the scaffold manufacturing and development.

An (microscale) advection-diffusion model is applied to predict permeation times of nutrients and O_2 depending on material type (e.g. polymer, hydrogel, fat), and vascular system parameters like porosity and wall thickness. The simulation model explicitly considers the local porosity structure and, thus, gives far more detailed results than simple calculations using Darcy's Law. Model parameters will be adjusted by reference to the experimental data. The model is used to calculate permeation times which are necessary for the nutrients/O_2 to reach the cells in the surrounding hydrogel matrix.

The avoidance of clogging of the vascular grafts is of paramount importance to the long-term functionality of the system. In order to account for this aspect, the smoothed particle hydrodynamics solver will be extended by a deposition model. This allows for the analysis of deposition of platelets on the vessel walls depending on systematically varied flow conditions. Based on these microscopic simulations deposition/clogging rules will be derived to be incorporate into the finite element modelling on the length-scale of the complete vascular system.

Fluid dynamics simulations (at larger scale) of pulsatile blood flow through elastic blood vessels will be conducted and compared with pressure-controlled experiments. For this purpose a fluid-structure-interaction scheme will be used within the hydrodynamics code.

The blood flow simulations will provide information on the local geometry. Design rules for the local geometry (e.g. bifurcations, diminutions) will be derived. These rules will ensure the avoidance of flow anomalies (recirculating flows) and the compliance with a reasonable range of wall shear stresses to provide an endothelium-friendly flow environment. Thereby, neo-angiogenesis will be stimulated and clogging of the vascular grafts will be avoided.

The numerical results will be used for the 3D design of the complete artificial vascular system. The modelling-based design will ensure biomimetic conditions for the endothelial cell layer which is the key to a functional vascularised system.

Modelling

in ATHENA 233553

Subject of the modelling
Transition metal oxides (magnetic perovskites, double perovskites, diluted magnetic ferroelectrics, piezoelectrics, magneto resistivity heterojunctions, superlattices and multilayers)

Models used
Electronic:
  First-principles density-functional theory (DFT) based methods
  Tight binding model

Simulation software and type of numerics used
High performance electronic structure codes based on density functional theory: highly parallelised versions of the LCAO-based SIESTA code, the PWSIC code, the developer version of VASP. Model Hamiltonian solved with a range on Monte Carlo technique, including the travelling cluster scheme for large-scale simulations.
Maximally localized Wannier function suit WanT, interfaced with the DFT codes to give parameters for the model Hamiltonian

Achievements of the model beyond experiments
The integrated multi-scale approach (DFT WanT MH) allows a full parameter-free description of thermodynamics properties of complex oxides and oxides interfaces ahead of experiments, or where experimental information are difficult/impossible to extract.
Identification of candidate materials and materials interfaces for future nano-electronics based on complex oxides. These included hetero-junctions, superlattices and multilayers consisting of doped magnetic perovskites (e.g. $La_xSr_{1-x}MnO_3$, $Pr_xCa_{1-x}MnO_3$), double perovskites (e.g. $LaNi_{1-x}Mn_xO_3$) and diluted magnetic ferroelectrics designed to exploit and manipulate the coupling of different order parameters at the two sides of the interface.
Prediction of the phase diagram of complex magnetic oxides MnO and NiO under pressure, Explanation of the extremely high antiferromagnetic ordering temperature in $SrTcO_3$ and $BaTcO_3$,

Application
Multiferroic devices (both single-phased multi-functional materials and heterostructures), non-volatile memories based on multiferroic materials

Relevant review articles
A. Filippetti, et al Variational pseudo-self-interaction-corrected density functional approach to the ab initio description of correlated solids and molecules, Phys. Rev. B 84, 195127 (2011).
T. Archer, et.al Exchange interactions and magnetic phases of transition metal oxides: Benchmarking advanced ab initio methods, Phys. Rev. B 84, 115114 (2011).
C. Franchini, et al. Exceptionally strong magnetism in the 4d perovskites $RTcO_3$ (R=Ca, Sr, Ba), Phys. Rev. B 83, 220402(R) (2011).

Summary of project

The overall aim of the project is the investigation of the properties and functionalities of transition metal oxides and their heterostructure, as these may be viable candidates as building blocks of future micro- and nanoelectronic devices. The project investigates the physics of strong-correlated materials, which includes charge and orbital ordering, polaronic formation, spin-charge separation, non-Fermi liquid behaviour, just to name a few.

Summary of the modelling

The modelling consists of a multi-scale approach merging parameter-free first-principles methods based on density-functional theory (DFT) with many-body model Hamiltonian calculations suited for exploring the temperature dependant properties of strong-correlated systems. On the one hand, first principles techniques allow one to describe at a quantitative level the electronic structure of perfectly crystalline materials at zero-temperature. In this case the description does not necessitate parameters as the underlying quantum mechanical problem is solved exactly, within well-controlled approximations. On the other hand, the model Hamiltonian approach is suitable for exploring effects connected to finite temperature and disorder. This however requires parameters, which usually are extracted from experiments, whenever possible, or simply inferred from chemical/physical intuition. Our research strategy combines the benefits of the two approaches as the parameters for the model Hamiltonians are rigorously extracted from our first principles calculations.

The project developed several methodologies for first principles calculations tailored to the specific class of materials comprising complex oxides and their interfaces and heterojunctions. This is a class of materials critical to standard electronic structure methods, which usually fail in describing even the most elementary properties as the electronic band-gap or are too expensive to use for interfaces. Our newly developed methods are based on DFT and include a completely novel variational formulation of the pseudo-self-interaction correction scheme (pSIC), a new version of the DFT exact exchange method, the hybrid Hartree-Fock DFT approach and a hybrid method combining DFT with the dynamical mean-field scheme.

The project formulated novel model Hamiltonians for describing the finite-temperature thermodynamic properties of single and double perovskites, with the possibility of including both A- and B-site doping/disorder. The parameters for the models are rigorously derived by a procedure in which the DFT-calculated electronic band-structure is mapped onto a tight-binding Hamiltonian model. Such a mapping is carried out by constructing the system's maximally localized Wannier function, which is a universal procedure applicable to any material, no matter its complexity. New interfaces between the consortium available first principles codes (SIESTA, VASP and PWSIC) and the maximally localized Wannier function suit (WanT) have been constructed and will be soon distributed.

Achievements of the project include 1) the description of the phase diagram of both MnO and NiO under pressure, 2) the explanation of the spectacularly high antiferromagnetic ordering temperature in $SrTcO_3$ and $BaTcO_3$, currently the two materials with the highest Neel temperature among the 4d series, 3) the demonstration of the possibility of the coexistence of a tunnelling magneto-resistance and tunnelling electro-resistance in a complex oxides heterojunction, $SrRuO_3/BaTiO_3/SrRuO_3$, and the tuning of the effect by intercalating a think $SrTiO_3$ layers at one of the junction interfaces. 4)The project designed a new heterojunction stack, $SrRuO_3/BaTiO_3/SrTiO_3/SrRuO_3$, displaying both tunnelling magnetoresistance (TMR) and tunnelling electroresistance (TER). Furthermore we demonstrated that the TER is fully tuneable by changing the $SrTiO_3$ layer thickness. This may have significant application as a 4-state non-volatile multifunctional random access memory element. Predictions on new devices functionalities are now possible.

www.athenacomp.eu

Modelling

in AUTOSUPERCAP 266097

Subject of the modelling

Battery-supercapacitor power system for an electric vehicle application
Ion transport in supercapacitors made of carbonaceous materials, e.g. activated carbon,
carbon nanotubes, graphene

Models used
Atomistic: Classical MD code for ion and electrolyte transport to calculate ion size and limiting pore
size
Continuum: flow model for ion and electron transport
Device model for optimal control of a battery-supercapacitors system

Simulation software and type of numerics used

Matlab Simulink for power system
Materials Studio v5.0 for molecular dynamics simulations
In house code for continuum flow modelling

Achievements of the model beyond experiments

The battery-supercapacitor modelling and simulations allow selection of the best
materials/supercapacitor for scaling up reducing experimental costs.
The molecular ion simulations guided the research for a pore size, maximising the specific
capacitance for carbonaceous electrode materials and thereby increasing energy and power
density.

Application

Supercapacitors for energy storage units

Relevant review articles:

A. Santucci, F. Markoulidis, M.K. Abbas, C. Lekakou, B. Martorana, M. Gosso and J. Perry "A
Model of a Battery-Supercapacitor Power and Energy Storage System for Electric Vehicle
Applications", submitted to International Journal of Powertrains, May 2012
C.Lekakou, F.Markoulidis, C.Lei, A.Sorniotti, J.Perry, C.Hoy, B.Martorana, I.Cannavaro,
M.Gosso "Meso-nano and micro-nano ion transport in porous carbon composite electrodes for
energy storage applications", Proceedings ECCM15 - 15TH European Conference on composite
materials, Venice, Italy, 24-28 June 2012

Summary of project

The project is aiming at developing supercapacitors which are essential in electric vehicles for supplying power during acceleration and recovering braking energy. High power and high energy density are required in the automotive industry for both an effective power system but also to reduce weight.

Summary of the modelling

The project works with computer simulations at device level to optimise the power system and the design of supercapacitor banks. An existing generic power system and electric vehicle computer model have been elaborated with a model for a battery-supercapacitor energy storage unit (ESU) or a battery only ESU. Input to the model is imposed driving time schedule, in terms of speed and requested power as functions of time, imposes power requirements to a dc bus and associated control system. charge cycles will also be incorporated in the model as a control sub-loop, including charging of supercapacitor and battery from combined energy sources, e.g. fuel cell, electricity sub-stations, braking energy during the deceleration phases of the driving schedule. The fast discharge and charge phases impose a requirement for reliable and optimum operation, especially in urban driving schedules. The computer code to simulate these processes will be produced in MATLAB Simulink environment.

This power system computer model has been incorporated in the test rig computer model and in a generic electric-hybrid vehicle model (for parametric studies) to decide on the specifications of a generic electric-hybrid vehicle model. With this model, parametric and optimisation studies will be carried out for different scenarios in automotive applications and different battery-supercapacitor load combinations in order to establish supercapacitor specifications for the different types of supercapacitors to be developed in this project.

The work will aim to establish the 'real world' working envelope of typical supercapacitor energy storage systems. This will lead to minimisation of system mass, a very important consideration for an electrical vehicle, and also the cost of the system.

The project designed and tailored optimum electrode material morphologies for the ion transport of certain electrolytes to achieve maximum power and energy densities.

In energy storage devices carbonaceous composite electrodes are a popular choice, consisting of activated carbon (ac), conductive additives and a polymeric binder matrix. The active electrode components are in the form of ac particles, ac fibres, or ac monolith combined with conductive additives such as carbon black. Activated carbon plays the most important role for storing a large amount of energy in the form of ions contained in the carbon nanopores.

The project applied classical molecular dynamics model to calculate ion size and limiting pore size. Molecular dynamics simulations (Materials Studio v5.0) have been performed to determine the values of the geometrical parameters of different ions, solvated and unsolvated in various solvents. This project used continuum flow models for the infiltration of ions and electrons into the porous carbon structure during the operation of the energy storage device. Depending on the pore size, ion size and solvent molecule size, ions may be solvated or unsolvated as they move, where ions are solvated in meso-pores for most cases. The ion infiltration model can calculate both steady state and dynamic conditions. The model is implemented into a computer code and it can run for various input parameters to optimise speed, extent of ion transport and capacitance in a porous material.

Linking between the models was achieved by using the pore-size diffusion coefficients determined by the MD models in the continuum ion transport model. There was no linking between the ion transport model and the device model.

![European Commission logo]

Modelling

in CERAWATER 280909

Subject of the modelling
Water flow through porous filtration elements

Physics/Chemistry models used

Continuum: CFD models used for description of the porous media

Simulation software and type of numerics used

Continuum, CFD and FEM software used,
Software used to find the most suitable size and shape of filtration elements with respect to the capabilities of a future production

Achievements of the model beyond experiments
- Modelling is faster and allows investigation of mass transfer (and stability) prior membrane coating and testing
- Modelling allows evaluation of membrane structures (intermediate and final layers) that are coatable not yet → important tool for membrane development

Application
Drinking and industrial wastewater treatment

Relevant review articles covering the topic (not necessarily their own):

Dolecek,Petr;

Mathematical-Modelling of permeate flow in multichannel ceramic membrane

Journal Of Membrane Science, 1995, Vol.100(2), pp.111-119

Dolecek,Petr; Cakl, Jiri;

Permeate flow in hexagonal 19-channel inorganic membrane under filtration and backflush operating modes

Journal Of Membrane Science, 1998, Vol.149(2), pp.171-179

Simulation of structural and permeation properties of multi-layer ceramic membranes
Kikkinides, Es ; Stoitsas, Ka ; Zaspalis, Vt ; Burganos, Vn
Journal Of Membrane Science, 2004 Nov 1, Vol.243(1-2), pp.133-141

Breitenbach, G.; Alexopoulos, S.; Hoffschmidt, B.;
Fluid flow in porous ceramic multichannel crossflow filter modules
Proceedings of COMSOL Conference, Grenoble, 2007

Optimization of the geometry of porous SiC ceramic filtering modules using numerical methods
Alexopoulos, S. ; Breitbach, G. ; Hoffschmidt, B. ; Stobbe, P.
Ceramic Engineering and Science Proceedings, 2008, Vol.28(9), pp.95-104

Rieck, R.; Bènard, A.; Petty, C.;
Reynolds number dependent porous media flow using the Brinkman equation
Proceedings of COMSOL Conference, Boston, 2009

Summary of project

In CeraWater honeycomb like ceramic nanofiltration membranes with increased membrane area were developed. Anti-fouling layers were developed and applied on these membranes. The membranes were extensively characterized and filtration processes in drinking and industrial wastewater treatment were successfully developed and demonstrated in half-technical scale.

Summary of the modelling

Continuum CFD models (solved with FEM) were applied to size and shape of filtration elements, additional parts (housing, inlet, outlet), with an experimentally determined coefficient of permeability for both support and membrane layer(s). With this model the flow behaviour (pressure and velocity distribution, mass and volume flow) and stress distribution were calculated in order to better understand the interaction between geometry and membrane layer of filtration elements
This allowed an evaluation of the influence of the cross-section geometry to the cross-flow from inside the channels to outside of the element for a variation of geometry, support material, type of active/final membrane layer.

Modelling

in CODICE 214030

Subject of the modelling

Cement, cement hydration

Models used

Atomistic: [Molecular Dynamics](#) (Garofalini force field) for hydration
Atomistic and Mesoscopic: Hierarchical [Statistical Mechanics growth model](#) for aggregation of
C-S-H particles and [grain based flow](#).
Continuum: [mechanical](#) (wear and fracture model) and [transport model for hydration](#)
(extended Nerst-Planck equations)

Simulation software and type of numerics used

HYMOSTRUC-3D for hydration
CODICE_HYD Monte Carlo growth model (based on C4)
CODICE_DEG and CODICE_MEC for wear and fracture (Finite Elements)

Achievements of the model beyond experiments

The developed toolkits revealed that there is a synergy in the hydration of alite and belite phases of
cement clinker, which opens the door to new eco-cements.
While a priori one would expect that the larger the content of C_3S the better the resulting
mechanical properties, the simulations have revealed that there is synergy in the hydration of
C_3S and C_2S blends, and that there is an optimum C_3S/C_2S ratio around 70/30.

Application

Eco cement for construction

Relevant review articles

Puertas F et al. A model for the C-A-S-H gel formed in alkali-activated slag cements; JOURNAL
OF THE EUROPEAN CERAMIC SOCIETY Volume: 31   Issue: 12   Pages: 2043-2056
DOI:10.1016/j.jeurceramsoc.2011.04.036   Published: OCT 15 2011 –
Dolado Jorge S.; van Breugel Klaas; Recent advances in modeling for cementitious materials;
CEMENT AND CONCRETE RESEARCH Volume: 41   Issue: 7   Special Issue: SI   Pages: 711-
726   DOI: 10.1016/j.cemconres.2011.03.014   Published: JUL 2011

Summary of project

CODICE brought producers and suppliers of cement-based materials together with universities and research institutes for the development of new and radically improved computational toolkits that monitor the formation and properties of cementitious materiales by starting from macroscopic processing variables: size of cement grains, water-cement ratio, temperature, grain composition.

Summary of the modelling

CODICE project has developed a serial parameter-passing multi-scale modelling scheme to predict the structural evolution and the mechanical performance of non-degraded and degraded cementitious matrices as a function of macroscopical processing variables to guide the design of cementitious materials

A1) Coarse macrolevel description in CODICE_HYD TOOLKIT

The coarser description of the cementitious skeletons is provided by a new and modified version of HYMOSTRUC-3D which is mesoscopic statistical model based on a mass balance concept for individual hydrating cement grains and distinguishes three independent phases, i.e. C3S, C2S and CH (E. A. B. Koenders et al.; A Density Model for Micro- to Nano-structures; under review). Moreover a novel digitalization mode has been implemented that generates a 3D voxel structure of the virtual microstructure and can be used for information exchange within the run of each time step. This new HYMOSTRUC-3D model employs as input macroscopical processing variables, such as the cement grain size, the water/cement ratio, etc and gives for each voxel relevant information like density, relative humidity, saturation, chemistry, etc.

A2) Refined nano-level description in CODICE_HYD TOOLKIT

The refinement of the coarse microstructure is performed by a Monte Carlo based algorithm named C4 (CODICE_Colloidal_CSH_Code) model. With the data flushed from the micro level simulations, each voxel can be refined. To this end, current implementation of C4 receives as input the density of the C-S-H voxel, and its water content (saturation index). Then the structure at the submicro level is conceived as a resulting from aggregation of dried C-S-H particles using an atomistic statistical model. The information about the size, density or water content of these basic dried-C-S-H units is based on the knowledge gained from intensive atomistic simulations. Afterwards the voxel structure is generated through Monte Carlo growth scheme which mimics the textural details provided by Jenning's model. This is possible by adjusting the growth parameters so as to reproduce the right density of the voxel, and the saturation index.

The atomistic MD with garolini force field model identified the smallest bricks of cementious structures. By employing Molecular Dynamic simulations CODICE has revealed that the main constituent of cement hydration (C-S-H) is nano-branched, with segmental pieces of 3x3x6 nm-sized. Afterwards, these segmental pieces have been approximated by 4-5 nm-sized spherical particles which served as coarse grained particles in a home-made kinetic Monte Carlo scheme used for aggregation. This KMC scheme has enabled to describe larger structures of C-S-H gel and establish a linkage.

B) CODICE_DEG TOOLKIT simulates the accelerated micromechanics degradation processes that occur when ammonium nitrate (NH4NO3) solutions pass into the cementitious pore network. In essence, it solves by standard Finite Element Model (FEM) CFD (the extended Nerst-Plank set of equations) by decoupling the transport and chemical reaction equations. Remarkably, CODICE_DEG is well suited to trace the degradation processes at the C-S-H level, and to the best of our knowledge, it is the first time that the calcium leaching can be visualized in 3D. This new tools will contribute not only to a better understanding of the phenomenon of calcium leaching but they will also help engineers to the design of safer structures with smaller amount of material.

C) CODICE_MEC TOOLKIT, a 3D lattice micromechanics fracture model, completes the "structure-performance" linkage by predicting the elastic modulus and tensile strength of cementitious skeletons starting from the knowledge of their structure. Finally, the outputs of the fracture process simulation are the load-displacement diagram and micro-crack propagation. The load-displacement diagram reveals the tensile behaviour of cement paste at micro-scale, from which the elastic modulus and tensile strength can be obtained.

Modelling

in COMPNANOCOMP 295355

Subject of the modelling
Structure, segmental dynamics, rheological and dynamical mechanical behavior of soft polymer-matrix nanocomposites

Models used
Electronic: DFT to calculate electrical conductivity in functionalised carbon nano-tubes
Atomistic: Molecular Dynamics (MD) and Monte Carlo (MC) to study nanostructure, local segmental mobility and mechanical properties calculating chain mobility at interfaces (elastic constants, local electricity and thermal conductivity as function of filler functionalization)
Mesoscopic: CGMD and FTiMC applied to polymer network with included nanoparticles with forces describing the freely jointed chain/nanoparticles as a slip-spring network solved by kinetic Monte Carlo methods for equilibrated melt configurations and for rheological behaviour (frequency and amplitude dependant mechanical response of nanofilled thermoplastcics) (Chapter 3.3).
DPD to predict filler dispersion in the polymer matrix (Chapter 3.3).
PFVD model accounting for the effect of imposed deformation on the glassy behaviour of the matrix confined between filler particles to describe the mechanics on larger scales- within the coupling of the models part describing the influence of deformation on the mesoscale structure (particles dynamics) and its resultant effect on the macroscopic stress.
Continuum: Model to calculate electrical conductivity, taking into account CNT features like tunnelling and contact resistance. Continuum micromechanics model with a non-isothermal finite-deformation elasto-visco-plasticity CE generated by the mesoscopic models (Fokker Planck equation following the GENERIC framework taking into account the system energy and entropy and matrix diffusion). The output is fracture and compression dynamics and morphology evolution under loading.

Simulation software and type of numerics used
Atomistic: LAMMPS, Gromacs for MD, Materials Studio to generate the initial polymer structures, self-written code for MC and for coarse-graining/reverse mapping to the atomistic representation.
Mesoscopic: self-written code for Field Theory-inspired Monte Carlo and for Brownian Dynamics coupled to kinetic Monte Carlo, self-written code for DPD
Continuum: Marc/Mentat for inhomogeneous cases, self-written code for homogeneous cases

Achievements of the model beyond experiments
Detailed understanding of the exact molecular mechanisms responsible for changes in properties of the matrix (e.g. mechanical reinforcement) could be achieved only with the help of modeling. This allows us to predict how the microstructure of a polymer nanocomposite affects its macroscopic properties and, therefore, to control the performance of polymer materials by adding rationally designed nanostructured fillers.
The replacement of the common ad-hoc mechanical constitutive relation by a mesoscopic dynamical model accounting for the discrete filler particles is applicable to general transient situations "and provides understandings which could not be easily obtained via experiments.

Application
Silica-filled natural and synthetic rubber nanocomposites for "green tire" applications

Relevant review articles covering the topic:

1. Vogiatzis, G. G. and Theodorou, D. N. "Structure of Polymer Layers Grafted to Nanoparticles in Silica–Polystyrene Nanocomposites" *Macromolecules* **2013**, *46* (11), pp 4670 – 4683.
2. Pandey, Y.G.; Papakonstantopoulos, G. J.; Doxastakis, M "Polymer/Nanoparticle Interactions: Bridging the Gap" *Macromolecules* **2013**, *46* (13), pp 5097 – 5106.
3. Gavrilov A.A., Chertovich A.V., Khalatur P.G., Khokhlov A.R. "Effect of nanotube size on the mechanical properties of elastomeric composites" // Soft Matter, **2013**, 9, P. 4067

Summary of project

The central goal of this project is the development of properties of polymer matrix nanocomposites. It employed a multiscale simulation approach for predicting the morphology (spatial distribution and state of aggregation of nanoparticles) and network formation by cross-linking. With this thermal (glass temperature), mechanical (viscoelastic storage and loss moduli, stress-strain relations), electrical (conductivity) and optical (scattering) properties of polymer matrix nanocomposites could be calculated.

Summary of the modelling

A multiscale simulation strategy has been designed for materials consisting of spherical nanoparticles dispersed within rubbery polymer matrices. This strategy encompasses four interconnected levels of modelling:

Electronic modelling with DFT of conductivity

Atomistic modelling included a detailed, systematic molecular-dynamics simulation study of a (1,4) cis-Polyisoprene (PI) melt confined between two amorphous silica surfaces. The orientational segmental dynamics was investigated through the analysis of the bond-vectors relaxation.

Different **mesoscopic** models were developed. In FTiMC simulations, polymer chains are represented as freely jointed sequences of Kuhn segments (consisting of a few monomers), and nanoparticles as single spherical entities. At the FTiMC level interactions are parameterized by experimental findings and atomistic simulations. Equilibrated configurations are then cross-linked. These configurations are provided as input for Brownian Dynamics simulations at the mesoscale network level. Topological constraints at this level are introduced via a novel kinetic Monte Carlo scheme, allowing the frequency and amplitude-dependent mechanical response of nanofilled rubbers to be captured.

A new parallel algorithm for large-scale dissipative particle dynamics (DPD) simulations of polymer nanocomposites was developed. In this mesoscale coarse-grained model the macromolecules are represented in terms of the bead-spring model, with particles interacting by a conservative force (repulsion), a dissipative force (friction), and a random force (heat generator). Each polymer chain is represented by a sequence of N beads connected by bonds of certain length. The nanotube model is made of rings (hexagons) which consist of number of beads. Each bead is connected to two neighbors on the same ring, two neighbors on the top ring and two on the bottom ring, forming six bonds of length b for each particle.

A PFVD model for vitrication accounts for the effect of imposed deformation on the glassy behaviour of the matrix confined between filler particles. The concept/output of this model was used/implemented for the description of the mechanics on larger scales- within the coupling of the models part describing the influence of deformation on the mesoscale structure (particles dynamics) and its resultant effect on the macroscopic stress

Continuum modelling to calculate electrical conductivity, taking into account CNT features like tunnelling and contact resistance. Continuum micromechanics model with a non-isothermal finite-deformation elasto-visco-plasticity CE generated by the mesoscopic models (Fokker Planck equation following the GENERIC framework taking into account the system energy and entropy and matrix diffusion). The output is fracture and compression dynamics and morphology evolution under loading.

Linking of the models

The results from fully atomistic molecular dynamics (MD) simulations are used to obtain and optimize material-specific coarse-grained (CG) potentials for large scale DPD-based mesoscopic simulation of structural and mechanical properties of nanotube-reinforced thermoset resins.
Friction coefficients and elementary event rates for the mesoscopic models were provided by the atomistic MD simulations, keeping the need for adjustable parameters to an absolute minimum.

Coupling of models

The initial particle arrangement is specified as initial conditions for the DPD model. For a given applied deformation, the change of the microstructure (particle arrangement) is simulated with this model. The simulation results are used in a CE for the second model, the continuum model. This CE has the form of a Fokker-Planck equations and is a thermodynamically derived constitutive relation for the stress tensor as function of the particle arrangement (accounting for mesoscale structure deformation and relaxation). This CE ensures thermodynamically consistency and expresses how the altered mesostructure results in unbalanced forces, which are felt on the macroscopic scale in terms of the stress tensor, hence achieving a relation between macroscopic imposed deformation and stress. The project employs the General Equation for the Non-Equilibrium Reversible-Irreversible Coupling (GENERIC) framework for this CE and this resulted in a set of evolution equations describing finite-strain non-isothermal elasticity, and on the mesoscale a new evolution equation for the distribution of particle-connector vectors, with corresponding elastic and glassy-viscoelastic interaction. By considering a single, effective particle pair, that is representative of the entire particle arrangement in the (representative) macroscopic volume element, a many-particle simulation is avoided.

Modelling
in CO-NANOMET 218764

Subject of the modelling
Multi-technique characterization of nanomaterials
Validation of materials models

Models used
Electronic: DFT
Atomistic: MD
Mesoscopic: Model for self-organisation

Simulation software and type of numerics used
DFT: ABINIT, Quantum Espresso, VASP, Siesta, Crystal, Atomistix Toolkit (from QuantumWise),
Tight-binding
Molecular dynamics: DL POLY & inhouse developed code
Self-organization: Code developed at the University of Sofia and tested by the partners in NPL (UK)

Achievements of the model beyond experiments
The inclusion of simulation can speed up the characterisation of models and can help
experimentalists fabricating and measuring nanoscale devices with numerical simulations
shortcutting device design cycles

Application
Characterisation of nanomaterials for tunnelling devices and graphene devices

Relevant review articles covering the topic:
1. A. Proykova, *Challenges of Computations at the Nanoscale*, Journal of Computational and
   Theoretical Nanoscience **7**, 1806-1813, 2010
2. *Modeling and Simulation: Nanometrology Status and Future Needs Within Europe,* Publication
   Date: January 2011, Ana Proykova, Markus Baer, Jorgen Garnaes, Carl Frase, Ludger Koenders
   http://www.euspen.eu/page1418/Resources/Modelling-Simulation-Proceedings (2011) (ISBN:978-
   0-9566809-6-9)
3. European Nanometrology Strategy Paper, pp. 121-132 "Modeling and simulations for
   nanotechnology" (21.12.2010)
4. A. Proykova, D. Nikolova, and R. S. Berry, Symmetry in Order-Disorder Changes of Molecular
   Clusters, Phys. Rev. B **65**, 085411 (2002)
5. A. Proykova, S. Pisov, R. Radev, P. Mihailov, I. Daykov, and R.S.Berry, *Dynamical Phase
   Coexistence of Molecular Nano-clusters: Kinetics versus Thermodynamics*, Nanoscience &
   Nanotechnolgy, pp. 18-20 (2001)

Summary of project

The aim of CONANOMET was to forge a closer link between the computer-simulation community and experimentalists (metrologists) working at a nanoscale level.The project worked on the three relations between modelling and characterisation:
1) simulation guiding measurements, 2) simulations interpreting measurements and
3) measurements validating models.

Simulation guiding measurements

The project developed a European strategy for nanometrology that integrates simulation into measurement workflows. The aim was to establish standards for the situations in which measurements have to be conducted. This included establishing temperature intervals for various nanostructures – conductors, semiconductors – that should be monitored in order to obtain reliable experimental results. Another important standard involved the shape and the size of the nanoparticles to be measured. Novel nanometrology methodologies including simulation and measurement of macroscopic physical, chemical, and biological quantities that reflect the underlying nanoscale properties of the samples were developed. Furthermore procedures to relate the different time-scale domains were established.

Modelling and simulations can focus nanometrology measurements by
- calculating the physical properties of nanoobjects (clusters, polymers) for bottom-up design of nanoobjects, so that the mesuarements can be focused on these value ranges
- calculating the range of operational parameters in which "the wanted" physical effect occurs, e.g. clusters of silicon atoms might become metallic only when subject to certain light pulses

Simulations interpreting measurements

The integrated simulation & measurement techniques can be used by researchers interested in particular materials or device configurations to analyse and interprete measurements.

Modelling and simulations can help develop nanometrology measurements by
- simulating measurement results obtained by a measuring device under variation of internal (probe, electronic) or external parameters (temperature, vibration, …); The measurement instrument can interact with the specimen and thus influence the measurements. The simulations should take this process into account in order to convolute/allign the instrumental measurements with the computed results.
- estimate measurement uncertainties (virtual instruments);

Simulation workflows for metrology of engineered nanocomposites, molecular electronics and spintronics, nanoparticle-based pharmaceuticals were developed.

Measurements validating models

Theorists developing analytical theory can use measurements to validate models

The new techniques can be used for software testing and verification, incl. general principles of software validation. As an example the electronic software: ABINIT and Quantum Espresso (QE) were tested and both were found to be reliable for predicting the electronic properties of nanostructure – both semiconducting and metallic. The atomic-scale geometry was determined with an atomistic MD simulation and then this geometry ("configuration") or rather this ensemble of many geometries are input for DFT/NEGF simulations of electronic structure, electrical conductance etc. This is called "switching", a common strategy when one studies the influence of the nanostructure on the conductivity – the configuration influences very strong the electronic density of state.

As this project was a coordinating and support action the project agreed and established nanometrology procedures ad supported this with
- Co-ordination of education and skills
- Exploitation and development of infrastructures
  Workshops and delivery of two scoping papers

http://www.co-nanomet.eu/

Modelling

in CRONOS 280879

Subject of the modelling

Energy photo-conversion and laser-induced ultrafast magnetization dynamics

Models used

Full first principles method: time-dependent density functional theory (TDDFT)

Simulation software and type of numerics used

Open-source OCTOPUS code
> OCTOPUS has a modular structure with a real-space grid as basis set.
> Extreme parallelization with sparse matrix linear algebra

Achievements of the model beyond experiments

Prediction of full time-evolution of ultrafast pump-probe dynamics and their spectroscopy measurements for new materials. Prediction of charge oscillations in the electron transfer process in supra-molecular light harvesting organic triads. Prediction of demagnetization and spin-dynamics in bulk Ni in the first few fs subsequent an intense laser irradiation.

Application

Solar cell, magnetic recording

Relevant review articles

Time dependent DFT (the main theoretical tool of the project)
Miguel A. L. Marques and E. K. U. Gross, Time-dependent Density
Functional Theory, Annual Review of Physical Chemistry 55, 427 (2004)

Dye sensitized solar cells
Anders Hagfeldt, Gerrit Boschloo, Licheng Sun, Lars Kloo and Henrik
Pettersson, Dye-Sensitized Solar Cells, Chem. Rev. 110, 6595 (2010)

Ultrafast spin dynamics
Andrei Kirilyuk, Alexey V. Kimel and Theo Rasing, Ultrafast optical
manipulation of magnetic order, Rev. Mod. Phys. 82, 2731 (2010)

Summary of project

The CRONOS project will go beyond the "static total-energy and mapping" scheme for materials modelling and develop a full time-dependent, fully atomistic theory of ultrafast dynamics in materials. The processes addressed are energy photo-conversion and laser-induced ultrafast magnetization dynamics.

Summary of the modelling

Photo-energy conversion and laser-induced ultrafast magnetisation dynamics both consist of describing how an electronic system reaches equilibrium after an initial perturbation pumps energy into it. This is governed by dynamics of materials at the femtosecond (fs, 1 fs=10-15 seconds) timescale and at the microscopic level. The modelling will address how the relaxation to the equilibrium can be driven towards a particular "useful" final state (for instance the separation of an electron-hole pair in a solar cell or the magnetisation reversal in magnetic recording).

Such dynamics are the result of the interplay between all the degrees of freedom involved, namely electronic, ionic and spin. Each one of them is characterised by a different timescale and by a characteristic interaction with the others. Furthermore the same degrees of freedom may evolve rather differently in different materials, so that fully atomistic modelling in the time-domain is necessary.

Time-dependent Density Functional Theory (TDDFT) will be the common theoretical/computational framework of the project. CRONOS will contribute to the development of TDDFT along four directions:

1) Development of new DFT and TDDFT meta-GGA exchange and correlation functionals
2) Development of new spin non-collinear DFT and TDDFT exchange and correlation functionals
3) Development of method to combine non-adiabatic ionic dynamics with time-dependent DFT
4) Development of optimal quantum control theory for TDDFT

The model will be parallelised so to ensure efficient scaling with system size.

Modelling

in DEEPEN 604416

Subject of the modelling
Future nanoscale electronic and photonic devices

Models used
Electronic: DFT plane wave and tight-binding (TB) models; Empirical TB model; DFT and empirical TB with Non-Equilibrium Green's Function (NEGF); **k.p** model; Drift-diffusion model; Continuum: Electronic Device models

Simulation software and type of numerics used
VASP, OpenMX, Wannier90; TiMeS (DFT and NEGF), OMEN (TB); Tyndall TB and **k.p** models; TiberCAD (TIBER) drift diffusion models; S-Device (Synopsys) device modelling (TCAD)

Achievements of the model beyond experiments
Photonic and electronic device design requires detailed properties of nanoscale regions that are difficult and expensive to obtain experimentally. DEEPEN will develop a library for material properties and also develop models incorporating how these material properties change on nanometre length scales. To this end, models will be linked and coupled which have already proved very effective in describing phenomena at different levels of approximation and at different length scales. The linked models can be used to provide new insights as well as improved device design capability.

Application
Nanoscale electronic and photonic devices, in particular advanced CMOS and LED design

Relevant review articles
Mathieu Luisier, "*Atomistic simulation of transport phenomena in nanoelectronic devices*",
Chemical Society Reviews, Volume 43, Issue 13, pp. 4357-4367 (2014)
Matthias Auf der Maur, Alessandro Pecchia, Gabriele Penazzi, Fabio Sacconi, Aldo Di Carlo, "*Coupling atomistic and continuous media models for electronic device simulation*", Journal of Computational Electronics, Volume 12, Issue 4, pp 553-562 (2013)
Matthias Auf der Maur, Gabriele Penazzi, Giuseppe Romano, Fabio Sacconi, Alessandro Pecchia, and Aldo Di Carlo, "*The Multiscale Paradigm in Electronic Device Simulation*", IEEE Trans. Electron Devices, 58, n.5 (2011)

Summary of project
DEEPEN addresses problems common to future nanoscale electronic and photonic devices, providing an atomic-scale description of selected critical regions e.g. in the channel of a nanoscale transistor or active region of an LED while using continuum-level electronic models to describe the full device structure. DEEPEN also addresses the considerable uncertainty in many critical parameters required for device optimization.
DEEPEN will develop an open multi-scale modelling environment to simulate electronic transport processes in nanoelectronic and nanophotonic devices. The simulations will treat critical device regions using *ab-initio* calculation techniques, or, for larger critical regions, using empirical (tight-binding) methods. The interface between models is designed to be open and re-usable with a wide range of existing codes. An open source Common Data Format (**CDF**) is being defined, and relevant metadata keywords will be defined in order to allow the exchange of data of different kinds (mesh associated or global quantities, physical and geometrical parameters).

The environment will be demonstrated by integrating a range of open source and proprietary codes (electronic and continuum),which have the well-established capability to calculate phenomena at different levels of description. Although demonstrated with specific codes, it is envisaged that the interface should also be usable across a range of other codes with suitable adaptation of the code linkages to the interface.

Summary of Modelling
DEEPEN will implement linking and coupling schemes for a range of different models from ab-initio through to empirical tight binding and charge carrier diffusion codes.

Linking models
Several models will be linked (i.e. loosely coupled), with the output from the lower level being used to determine the input for higher level models. First principles electronic structure calculations will be used to determine details of carrier localisation. These empirical local electronic structure calculations will then be incorporated into a generic tight binding model applied to vertical transport and will also form the basis for a hopping model to describe lateral transport in InGaN quantum well structures. Linked simulations of TB code OMEN and continuum (device) SENTAURUS will use parameters extracted from more detailed studies performed on smaller structures, including ab-initio calculations.

Workflow
In order to accurately describe selected nanoscale regions, model coupling will be implemented betweena first principles DFT code (TiMeS) and the Tight-Binding code OMEN applied to transport. Both "transport codes" will be set up to accept Hamiltonian input in a tight-binding DFT format e.g. directly from OpenMX or from VASP, with the VASP plane-wave output converted to a localised basis using e.g. Wannier90. The output from the transport codes will then be fed back to the DFT codes to allow self-consistent calculation of the electronic structure and transport properties. Coupled simulations of OMEN and Sentaurus Device will be used when feedback effects from the macroscopic level to the nanoscale (e.g. by electrostatic interactions) are important in electronic devices, and fully self-consistent simulation of the system may be required. Coupling of models will also be required to investigate carrier tunnelling between neighbouring quantum wells in a multi-quantum well LED structure. The electronic tunnelling models will be implemented by developing TiMeS to treat tunnelling through the barrier between neighbouring quantum wells. To investigate the role of inter-well tunnelling in determining the steady-state carrier distribution in a MQW structure, this tunnelling model will be tightly coupled to TIBERLab's software, TIBERCAD as an example of an existing drift diffusion code

Interfaces and Platform
TiberCAD as well as S-Device are closed-source commercial products. The general output format which we are developing should be adaptable for use with open source TCAD software, which could be used as a substitute. The interface developed in DEEPEN will be open source, allowing others to use existing commercial software or to adapt open source TCAD software for use with the DEEPEN platform. Together with 5 other NMP projects on multi-scale modelling (ICMEg, MMP, MODENA, NANOSIM and SIMPHONY) communication standards (metadata keywords and an overall data structure for file based information exchange) will be elaborated. These will be used in the DEEPEN platform. ICMEg will organise workshops to reach European endorsement. Once established, the platform will be widely applicable across a wide range of applications. The project's OS environment will be released under the GNU Lesser General Public License (GNU LGPL), ensuring that the core of the multiscale environment together with all its Application Programming Interfaces (APIs) can be distributed and even modified freely. It will also be available through TIBERLab's existing support environment.

Modelling

in DISC REGENERATION 213904

Subject of the modelling

Biomaterials, scaffolds, intervertebral disc, angiogenesis

Models used

Continuum:
  Poroelastic model
  Diffusive transport model

Simulation software and type of numerics used

Commercial software (Abaqus) with specific Fortran subroutines for non-linear material properties and coupling between diffusion, convection and structural analyses
Finite Element method with an implicit scheme
Parallelization for such non-linear model and such coupling between structural equations and thermodynamic equations

Achievements of the model beyond experiments

The modelling contributions are twofold:
  The coupled transport-mechano model is able to predict the movement of solutes within the intervertebral disc and predicts the interactions between mechanical properties, fluid and solute transport, and cell viability. This is essential for a proper understanding of the mechanisms of disc degeneration and disc regeneration with the use of biomaterials as disc substitute.
  Simulations of the effect of partial and complete disc nuleotomy on load transfer as a function of the biomaterial substitute used can be used to determine the surgical variability during nucleus removal.
Both contributions cannot be obtained experimentally and therefore are complementary to the experimental evaluation of the biomaterial performance.

Application

Biomedical implants

Summary of the project

The project seeks to provide a cure for lower back pain by developing injectable a-cellular and cell-loaded bioactive polymer-based scaffolds and technology which will repair a damaged intervertebral disc (IVD) by enabling its regeneration to a natural healthy state or better.

Summary of the modelling

This new generation of replacement devices are designed with a biomimetic approach which will confer the appropriate mechanical and biological properties and enable the inclusion of the requisite cell signalling factors to produce a bio-hybrid structure which closely resembles the human tissue in all its essential attributes.

This requires comprehensive numerical studies to predict their behavior under stress in the post-implantation period. Particular attention needs also to be paid to angiogenesis because in IVD tissue, vascularization must be carefully controlled, due to the unique anatomy and physiology of the intervertebral disc. Modelling studies within this project identified the key physical and mechanical properties of the natural IVD and the substitute materials, and provided an understanding of the physical aspects of the regeneration process.

1) Mechanical model

Complex computational models are required for explorative preclinical biomechanical investigations, as they can potentially account for the complex physics of the intervertebral disc environment, such as the fluid-solid interactions within the implant as well as the interaction between the implant itself and the surrounding intact biological structures, which involve the contact between nonlinear and nonhomogeneous multi-phasic materials. For that purpose different disc replacement configurations were evaluated on how they affect the response of a poroelastic finite element model of the intervertebral disc under complex physiological loads.

2) Vascular transport model (mechanics and fluid dynamics)

Using a poromechanical finite element (FE) model coupled to a diffusive transport model we studied the effect of mechanical and nutritional factors on the diffusion of two fundamental cell solutes, oxygen and lactate, strongly related with disc cell metabolism1. In our model crucial disc properties such as fluid content, osmotic pressure of the nuclear region, disc height, permeability, cell density, pH, were parameterized and their effect was studied on both the mechanical and solute transport response. Importantly, disc mechanical response to external compressive loads was simulated at the same time. External compressive loads affected oxygen and lactate contents within the disc. Sustained compression had its greatest influence on nutrient transport by decreasing diffusion distances diffusivity of solutes. We found that the more the disc was deformable, the larger was the effect. By comparing with in vivo literature data the model predicted similar oxygen and lactate patterns. A parametric study showed that the most important factors affecting the solutes' transport were: cell density, fluid content, disc height and nucleus osmotic pressure while other parameters had no effect. It is also important that a model should be able to account for the detrimental effect of acidic pH (due to lactate accumulation) which is the most relevant nutrient affecting cell viability.

http://www.disc-regeneration.eu

Modelling

in DYNAMAG 233552

Subject of the modelling
Dynamics in magnetic nano-materials and devices

Models used
Electronic: Ab-initio models for the exchange interaction, magnetic anisotropy and magnetization.
Mesoscopic: Micromagnetic models based upon the Landau-Lifshitz equation with ab initio parameters to calculate the spin wave spectra and dispersion in multilayer structures. Models of relative dynamics of different sublattices in antiferromagnetic and ferrimagnetic materials
Continuum: Models of electromagnetism: absorption and emission in magnetic nanomaterials

Simulation software and type of numerics used
Electronic: VASP and WIEN2k (DFT)
Mesoscopic: NMAG: Finite difference micromagnetic packages and parallel version of OOMMF
       A code based on the Dynamical Guiding Centre approximation (GCA)
       Dynamical matrix method (DMM) calculations
       Micromagnetic data processing software SEMARGL
       Utilities for data transfer between Nmag and OOMMF (SEMARGL);
Continuum ElectroMagnetism: Plane wave method (PWM) calculations
       Parallel versions, in particular for multicore desktop PCs

Achievements of the model beyond experiments
The calculations pointed out samples that were until then simply not considered.
A novel magnonic logic architecture has been developed based on physics discovered by the models.
The, until then unexplained, origin of the response experimentally observed in optical pump-probe studies of magnetic multilayers with strong perpendicular magnetic anisotropy, has been revealed via calculations in the discrete lattice model.
Mechanisms behind unusually low magnetic domain wall depinning currents within spintronic devices have been revealed via full 3D finite element simulations.

Application
Spintronics and magnonics, including magnonic crystals, spintronic and magnonic devices interconnected with more conventional photonic, plasmonic, and electronic devices.

Relevant review articles
S. - K. Kim, "Micromagnetic computer simulations of spin waves in nanometre-scale patterned magnetic elements", J. Phys. D – Appl. Phys. 43, 264004 (2010).

Summary of project

Dynamag is a modelling project that focusses on magnonic crystals, a sub-field of a wider field of research called magnonics, and also deals with nanomagnetism and more specifically spin dynamics in magnetic nanomaterials and nanodevices. The ability to accurately predict fundamental and functional properties of fabricated magnetic nanostructures and complete devices by theoretical means is based on a thorough understanding of the relation between their chemical and physical fine structures and the desired useful magnetic functionalities.

Summary of the modelling

Competition between long and short range magnetic interactions leads to inherent complexity of phenomena observed in magnetic structures with nanoscale features, and hence to dramatic difficulties in their analytical treatment.

DFT models have been used to calculate the exchange interaction, magnetic anisotropy and magnetization.

DYNAMAG has extended the mathematical formalism of numerical micromagnetic solvers beyond the classical Landau-Lifshitz equation by a rigorous account of spintronic and temperature dependant aspects of modelled phenomena occurring in multi-sub-lattice magnetic materials. DYNAMAG also developed new software applications to process and analyse large amounts of data produced by micromagnetic simulations, in particular those run using supercomputers.

The finite element micromagnetic package Nmag has been extended to explicitly simulate relative dynamics of different sub-lattices in ferrimagnets and antiferromagnets and to facilitate inclusion of various spin transfer torque terms within models of magnonic devices interconnected with those of magneto-electronics (spintronics). This inclusion has provided deeper insights into the dynamical performance of magnetic sensors and recording heads.

On the numerical side the dynamical matrix method (DMM) code has been further developed, in particular to facilitate the calculation of the Brillouin Light Scattering (BLS) cross-section from the DMM results. The complete 2D magnonic band structure (and the resulting magnonic dispersions) has been successfully reproduced and interpreted Also a new dynamic simulation code based on the guiding centre approximation (GCA) has been developed, which deals withslow-variable micromagnetism.

A micromagnetic code particularly for studying static magnetic configuration and time domain dynamics of magnetic vortices in arrays of magnetic discs has been developed.

For the data processing a new software tool called SEMARGL as been developed to facilitate comprehensive analyses of large volumes of data produced by micromagnetic calculations. A new methodology has been developed to use the tool for calculating the scattering parameters of spin waves from magnetic non-uniformities, the magnetic susceptibility and permeability of magnonic metamaterials, as well as the magneto-optical signal measured in optical pump-probe experiments. Also a new software utility for Nmag that allows one to convert its output into the OVF format of OOMMF.

For the continuous electromagnetic calculations the plane wave method (PWM) has been developed to calculate magnonic dispersion relations in samples that are currently in focus of experimental studies.

http://www.dynamag.eu/

Modelling

in ECO2CO2 309701

Subject of the modelling
photo-electro-chemical catalysis

Physics/Chemistry models used

Continuum: CFD, chemistry reaction model, thermodynamics

Simulation software and type of numerics used

Continuum: FLUENT

Achievements of the model beyond experiments
- Prediction of final device efficiency in function of efficiencies of different components.
- Determination of best design to avoid mass transport and thermodynamic constrains in the real system.

Application
Production of fine chemicals

Relevant review articles covering the topic (not necessarily their own):

[1] Bockris J.O.M.S.S., Fuel cells: their electrochemistry, in, McGraw-Hill, New York, 1969.
[2] Thampan T., Malhotra S., Zhang J., Datta R., Catalysis Today 67 (2001) 15–32.
[3] Barbir F., Solar Energy 78 (2005) 661–669.
[4] You L., Liu H., Journal of Power Sources 155 (2006) 219–230.
[5] Choi P., Bessarabov D.G., Datta R., Solid State Ionics 175 (2004) 535–539.
[6] Hernández S., Bensaid S., Armandi M., Sacco A., Chiodoni A., Bonelli B., Garrone E., Pirri C. F., Saracco G., Chemical Engineering Journal 2014, 238, 17-26.
[7] Hernández S., Saracco G., Alexe-Ionescu A. L., Barbero G., Electrochimica Acta 2014, 144, 352-360.
[8] Hernandez S., Barbero G., Saracco G., Alexe-Ionescu A.-L., The Journal of Physical Chemistry C 2015, DOI: 10.1021/acs.jpcc.5b01635.
[9] Hernández S., Tortello M., Sacco A., Quaglio M., Meyer T., Bianco S., Saracco G., Pirri C.F., Tresso E., Electrochimica Acta 131, 2014, 184-194.

Summary of project

The Eco2CO2 project aims at exploiting a photo-electro-chemical CO_2 conversion route for the synthesis of methanol as a key intermediate for the production of fine chemicals (fragrances, flavourings, adhesives, monomers,…) in a lignocellulosic biorefinery . The project will develop a PEC reactor in which catalytic reactions take place of methanol and furfural to produce perfuming agents via partial oxidation or methylation, as well as of lignin or lignin depolymerisation derivatives to produce adhesives or monomers (e.g. p-xylene).

Summary of the modelling

The project used fundamental continuum thermodynamic and kinetic equation models to simulate the reacting systems and carry out preliminary analysis of the Eco2CO2 system performance.

The influence of different cell designs, material components, performance of catalyst and sensitizer on the efficiency of a water-splitting device are discussed. For different set-ups, the efficiency of the cell and the extra potential (Bias) needed to perform the artificial water splitting reaction with a given catalyst were calculated. A more general toolkit that calculates the different quantum yield of catalyst (%) and estimates the efficiency of cell has been created. The so improved mathematical method, can calculate the turn-over frequency and/or number of layers of catalyst needed to increase the target's efficiency. In particular, the proposed model considers the membrane and the electrodes overpotentials, to predict the performance of the entire device. The project has developed new constitutive equations for anode, cathode and trans-membrane transport to be used in continuum CFD models.

A thermodynamic model for anode and cathode reaction processes, microporous electrodes, water permeation front, etc. will be established. This model is based on an existing CFD code and contains equations for reaction kinetics, mass balances, energy balance, mass transfer and thermal transfer profiles.

All models will be validated during the progress of the project via specific experiments on sub components or the entire system executed.

All sub-models will be gathered and incorporated in an overall device for the trans-electrode and inter-electrode transport. With this system model steady-state and dynamic simulations will be done.

Single system behaviour will provide information for a final prototype design and to set test bench specifications. Besides, CFD codes (Fluent) will be used to design the shape of the chambers facing the electrodes assembly from opposite sides.

Modelling

in FEMTOSPIN 3281043

Subject of the modelling
Heat-assisted or optically induced ultrafast reversal of magnetism

Models used
Electronic first principles method:
  Time-dependent spin density functional theory (TDSDFT) with spin scattering effects
  Tight Binding model with Hubbard Hamiltonian
Atomistic models: Atomistic spin model based on LLG model using Heisenberg formalism and Langevin dynamics which include thermodynamics with improved dissipation and energy transfer mechanisms for non-zero temperatures.
Mesoscopic models: Micromagnetic (macrospin) model including quantum effects based on the generalised Landau-Lifshitz-Bloch equation for ferrimagnets, antiferromagnets and magnetic semiconductors

Simulation software and type of numerics used
Budapest code based on the kkr code using spin-cluster expansion technique to calculate ab-initio parameters (spin, exchange integrals, anisotropy).
Uppsala code for TDDFT calculations to understand the origin of the optomagnetic field.
VAMPIRE (Visual Atomistic Massively Parallel Integrator Engine) for atomistic calculations of dynamic response to ultrafast laser pulses.
York code for heat bath models, used to understand the underlying processes of energy transfer between the excited conduction electrons and the spins.
Madrid/Konstanz code for micromagnetics with finite-difference discretisation for large-scale calculations for comparison with experimental data, especially imaging.

Achievements of the model beyond experiments
Prediction efficiency of ultrafast spin dynamics in multiferroics excited by THz laser pulses
Prediction of the smallest stable domain structure in magnetic thin films
Prediction of the time and spatial scales of magnetic pattern formation
Identification of optimal materials for ultrafast optically induced magnetic switching

Application
Magnetic recording with increased speed of logic and data storage devices with increased storage density, Novel ICT-devices based on spin manipulation

Relevant review articles
I Radu et al, Ultrafast magnetism as seen by x-rays, Proc. SPIE 8260, 82601M (2012); http://dx.doi.org/10.1117/12.907433

Summary of project

The project addresses spin dynamics for magnetic information storage technology, which is based on nanostructured magnetic materials, and for spin electronics in which the manipulation of the spin forms the basis of the device operation. Magnetic spins can be manipulated on the femtosecond timescale, while the actual switching by precessional motion lasts hundreds of picoseconds. The project investigates the physics of these multi-scale processes.

Summary of the modelling

The standard formalism used for materials and device simulations (micromagnetics) is a continuum formalism dealing with the spin precession timescale of 10ps upward. However, optical spin manipulation and magnetisation processes are intrinsically much faster than that of precessional switching e.g. complete demagnetisation happens on the timescale of hundreds of fs. Thus multi-scale models are required dealing with the timescales associated with exchange, spin-orbit coupling and spin-flip scattering. The project will investigate processes at the light-spin interaction level, electronic structure level, atomistic level and mesoscopic level.

The fundamental interactions between spin, conduction electrons and the laser light (excitation and demagnetization processes) that occur on very short time scales (atto- to femto-seconds) will be described and the beyond- linear-response real-time formulations shall be combined with ab-initio code on the basis of the time-dependent spin-density functional theory (TSDFT) to compute ultrafast magneto-optical response.

The inverse Faraday effect is at the origin of the laser-induced "optomagnetic" field and this mechanism is further investigated so that it can be implemented in the atomistic spin Hamiltonians used in electronic simulations calculating atomic properties. A model of non-equilibrium spin-scattering (energy and spin transfer) channels will be built that can predict ultrafast demagnetization. The aim is to develop a suitably parameterized form of demagnetization caused through hot electron transport that can be used and incorporated in the spin Hamiltonians used for atomic simulations. The temperature dependent ab-initio parameters of spin Hamiltonians can be used in the atomistic spin-dynamics simulations. The first-principle electronic structure will be mapped to a multiband Hubbard model, with realistic tight-binding and interaction parameters. Within the framework of the multiband Hubbard model, the effects of exchange interactions being different from those in equilibrium (non-adiabatic effects) will be studied.

The project will introduce the above mentioned physics into the atomistic lengthscale heat bath models which rest on fixed spin length and fixed model parameters. They will develop equations of motion beyond current Langevin dynamics to arrive at a better treatment of the coupling of the spin system to electronic and phononic degrees of freedom and hence a better modelling of the dissipation channels. Also a more realistic model for the energy transfer on the fs timescale will be included. The coupling between the atomic spins and the heat bath will be based on the ab-initio models developed. To identify optimal materials for ultrafast optically induced magnetic switching the relevance of the specific spin ordering in ferro-, ferri-, antiferro-magnetic and magnetic semiconductors will be studied.

The project will include quantum effects in macrospin models of ferrimagnetic and antiferromagnetic materials. These macrospin models are based on the micromagnetic approach with finite-differences discretization and use the input of the electronic structure and atomic models. The codes will be used for (granular and polycrystalline) materials design exercises for heat assisted magnetic recording. The atomistic and multi-scale spin models, developed within ULTRAMAGNETRON and FEMTOSPIN are providing important insight into the physics of Heat Assisted Magnetic Recording (HAMR), and the testing and validation carried out within those projects are leading to the point at which the computer models are ready to become predictive design tools.

www.femtospin.eu

Modelling

in FREECATS 280658

Subject of the modelling

Catalysis reactions and processes in foam structures

Models used

Continuum: Multi-scale model for mass ([CFD](#)) and [heat transfer](#), [reaction kinetics](#) and [hydrodynamics](#) in foam structures

Simulation software and type of numerics used

MODELICA, MATLAB custom systems of partial differential equations with commercial PDE solvers; ANSYS CFD based code with custom reaction code written in C++

Achievements of the model beyond experiments

Heat transfer modelling guides the design of the foam materials and predicts the deposition of carbons during operation, (a phenomenon critical in oxidative dehydrogenation) and so reduce costs of trial and error developments.

Multi-scale modelling of reaction, surface-fluid interactions, heat transfer and hydrodynamics allow to predict from first principles the behaviour of the overall reactor system and to screen a large space of operating conditions prior to experimentation. This leads to better understanding of physical phenomena involved and dynamics of processes within the system, thus reducing the number of experimental trials required.

Application

Catalysts, reactor design

Relevant review articles

Kambiz Chizari, et al Nitrogen-Doped Carbon Nanotubes as a Highly Active Metal-Free Catalyst for Selective Oxidation: ChemSusChem (2012) DOI: 10.1002/cssc.201100276

Summary of the project

This project is addressing catalysis for the sustainable production of chemicals and commodities. The FREECATS project deals with the development of new metal-free catalysts, either in the form of bulk nanomaterials or in hierarchically organized structures both capable to replace traditional noble metal-based catalysts in catalytic transformations of strategic importance. Metal-based catalytic processes are considered in the light of new tailored metal-free catalytic architectures designed and fabricated starting from appropriate nanoscale building blocks.

Summary of the modelling

The models to be developed will address the chemical reactions, heat and mass transfer, and hydrodynamics with the foam structure as a parameter.

Based on the data on catalysts characterisation and kinetic measurements an analytical mechanistic reaction kinetic model will be developed and validated against the available data. The code solving the equation will be developed in MODELICA, which is an open-code modelling environment. The code will later be transferred (as custom-routines coded in C++) into commercial software (ANSYS). The model will be used to detail surface reactions and adsorption processes of the new catalysts.

A micro-model of heat conduction through a foam material based on the solid mechanics package within ANSYS and using finite elements methods will be applied. For this the actual structure of the foam, obtained through electron tomography, and geometrical models of the foam structure, will be used.

Two process models will be applied:

In the first approach, the above described reaction kinetic MODELICA model will be coupled to MODELICA gas-solid, gas-liquid and gas-liquid-solid mass transfer models, heat transfer and hydrodynamics. These continuum models will ignore inertia effects. The MODELICA code will be used for process optimisation. The model will explore a wide range of operating conditions. The key part of the model will be the part of the code relating foam structure to heat and mass transfer characteristics. This will be a semi-empirical model, as ab-initio model is unnecessarily complex for the desired outcome.

In another approach to describe the total process a CFD code describing the foam geometry at a coarser level to represent the continuous fluid domain will be run. Information from the MODELICA reaction kinetics model will be fed in via boundary conditions detailing surface reactions and adsorption processes. The CFD model will take into account complex physical processes, resolving heat, mass and momentum transport in boundary layers and accounting for inertia. The purpose will be to resolve macroscopic heat, mass, momentum transport everywhere in the foam.

www.freecats.eu

Modelling

in GOFAST 280555

Subject of the modelling

Optical control by intense ultra-fast laser pulses of metallic phases in the prototypical Mott insulator V2O3 and of the superconductive phase in the high-temperature superconductor family BSCCO.

Models used

Electronic: DFT
  Models for correlated systems:
  Multi-orbital lattice models of the Hubbard type
  Time-dependent Dynamic Mean Field Theory (DMFT) for out-of-equilibrium evolution
  Time-dependent Gutzwiller variational approach

Simulation software and type of numerics used
LDA-DFT calculations with Quantum Espresso for realistic Hamiltonian parameters
DMFT model solved with continuous-Time Quantum Monte Carlo (CTQMC) and Exact Diagonalization (ED) and Iterated Perturbation Theory (IPT)
Gutzwiller model (time-dependent) with multi-dimensional optimization

Achievements of the model beyond experiments

The model identified optimal correlated materials (composition, size, direction of the laser pulse versus surfaces, etc) and excitation pathways (photon energy, intensity, polarization and temporal profile) for the production of controllable and reversible photo-induced transitions between distinct phases, e.g. metallic and insulating, or normal and superconducting.

Application

Switching devices based on the optical switching between phases with very different conducting properties.

Relevant review articles

Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, Antoine Georges, et al Mod. Phys. 68, 13 (1996)
The Out-of-Equilibrium Time-Dependent Gutzwiller Approximation, M. Fabrizio, arXiv: 1204:2175 (2012).
Non-equilibrium dynamics of the driven Hubbard model, A. Amaricci, et al, arXiv:1106:3483 (2011).
Time-Dependent Mean Field Theory for Quench Dynamics in Correlated Electron Systems, Marco Schiró and Michele Fabrizio, Phys. Rev. Lett. 105, 076401 (2010)

Summary of project

The aim of this research project is to develop femtoscale-modelling schemes to study electronic, optical and structural properties of correlated materials driven out of equilibrium. The possibility to optically switch on and off the metallic phase in a model Mott insulator (vanadium sesquioxide) and the superconducting phase in model high-temperature superconductors (cuprates) will be investigated and tested. The photo-excited phases are investigated experimentally by different time-resolved spectroscopic tools, like reflectivity or photoemission.

Summary of the modelling

GOFAST will extend techniques for correlated systems, i.e. Dynamical Mean Field Theory (DMFT) and the Gutzwiller variational approach, to model the temporal evolution after high-energy excitations are impulsively photo-injected by ultrafast laser pulses. DMFT is a quite accurate technique, although numerically very demanding. The Gutzwiller approach is less rigorous but very flexible, relatively easy to implement and to push towards long simulation times. An important step to be undertaken is finding the minimal models able to provide a reliable description of the materials under investigation, where minimal means the minimum amount of complexity.

These models aim at describing the properties of a subset of electrons that participate to conduction and where correlation effects are predominant. In transition metal oxides these electrons are commonly those that reside on the partially filled d-shell of the transition metal ions (as opposed to light elements where the p-shell electrons control the properties). If one assumes that all the other occupied shells, both of the transition metal ions and of the oxygen's, just provide an effective potential for the d-electrons that adds to the ionic one, then the effective Hamiltonian projected onto the d-like Wannier orbitals has generally the form of a tight-binding model of interacting conduction electrons. Besides a long-range part, the electron-electron interaction comprises also a short-range contribution that includes a charge-repulsion, so-called Hubbard U, and an exchange splitting responsible for the Hund's rules. In vanadium sesquioxide, each V donates three electrons to the oxygen's; hence there remain two electrons to accommodate into the t_{2g}–orbitals that derive from the original five d-orbitals split by a cubic field. In this situation, Hund's rules play an important role. In addition, a trigonal field further splits the t_{2g}–orbitals into a doublet and a singlet, e_{ng} and a_{1g}, respectively, and the phonon mode that controls such a splitting is known to play an important role in all physical properties. In BSSCO cuprates only one among the crystal field split d-orbitals is involved in the physics, which is a simplification with respect to V2O3. However, antiferromagnetic fluctuations are known to play an important role in these materials, hence these have to be taken into account either explicitly or via an effective bosonic mode. When needed, realistic Hamiltonian parameters will be extracted from ab-initio LDA-DFT calculations through the Quantum Espresso Density Functional package

The other crucial task is to extend DMFT and the Gutzwiller variation approach for studying out-of-equilibrium conditions provoked by an intense ultrafast laser pulse. The simplest models will be studied both at equilibrium and out-of-equilibrium and the results compared with experiments. If the agreement is not satisfactory, additional ingredients suggested by the experiments will be included in the models, which will be once again analysed at equilibrium and out of it. The procedure will continue till the modeling will compare well with experiments.

www.gofastproject.eu

Modelling

in GRENADA 246073

Subject of the modelling

Optical, electronic and structural mechanical properties of graphene and its growth

Models used

Electronic: Density Functional Theory ([DFT]) and ab-initio Molecular Dynamics ([MD])
Continuum: Solid mechanics model
    Computational Fluid Dynamics (CFD) of Chemical Vapor Deposition processes

Simulation software and type of numerics used

VASP, Abinit and Quantum Espresso (DFT as well as ABMD) for electrical and structural properties of graphene
COMSOL (morphology) to simulate the structural, thermal and mechanical properties of graphene inside the local environment of batteries and ultracapacitors (i.e. graphene inside ionic and non-ionic liquids)
FLUENT (CFD) to model fluid dynamics inside the CVD reactor used to grow graphene.

Achievements of the model beyond experiments

CFD modelling of the chemical vapour deposition reactor provides accurate temperatures, gas flow, heat and mass transfer - information that could not possibly be obtained empirically. The choice of optimum graphene growth conditions are guided by modelling of the CVD processes.

Application

Energy storage (batteries and ultra-capacitors).

Transparent conductive electrodes (OLED displays).

Relevant review articles
''Role of the gas phase in graphene formation by Chemical Vapor Deposition on copper''. P. Trinsoutrot, C. Rabot, H. Vergnes, A. Delamoreanu, A. Zenasni, B. Caussat. Submitted to Carbon
''Multi-scale modeling of silicon nanocrystals synthesis by low pressure chemical vapor deposition'' I. Zahi, P. Mur, Ph. Blaise, A. Esteve, M. Djafari Rouhani, H. Vergnes, B. Caussat. Thin Solid Films, Vol. 519, 7650-7658 (2011).

Summary of the project

The objective of GRENADA is to optimize the material synthesis techniques which provide high quality graphene with optimal properties and morphologies for target applications. Reduced graphene oxide is expected to provide a larger storage of energy than usual carbon based materials and graphene is a good candidate for the replacement of ITO electrodes as its intrinsic properties outperform those of ITO. Graphene materials are tested in-situ in configurations and environments typically found in energy storage and display applications. Formation and evolution of defects and their impact on integrated graphene properties will be studied.

Summary of the modelling

The morphology and physical properties of as-grown and modified graphene material will be modelled to understand dependence of properties on types of graphene defects. Especially interaction with local environment and in nanostructures multi-phase systems will be studied. Modelling will address unexplored area of graphene properties and mechanisms.

Density functional theory (DFT) calculations with the planewave code ABINIT, VASP and Quantum Espresso will be done in order to simulate the electrical and structural properties of graphene in its local environment. Especially, the electronic interaction between graphene and its surroundings and in between graphene layers in multilayers will be investigated.

We will use also ab-initio molecular dynamics (MD) calculations to model mechanical, magnetic and electrical properties of materials.

Continuum COMSOL mechanical modelling will be performed for understanding of morphological properties of graphene based flakes. The model will also be used to study the transport in multilayer graphene (with and without defects) in media of variable polarisability.

Modelling of the growth of graphene by Chemical Vapour Deposition has been performed with Computational Fluid Dynamics (CFD). This modelling provided insights into the growth kinetics and the flow of gases into the CVD reactor. The simulation revealed the precise influence of gas flow, temperature of gases, types of gases, and concentration profiles on the structural properties of graphene. These insights have been used to adjust the experimental conditions finally resulting in high quality monolayer graphene.

www.fp7grenada.eu

Modelling

in HIPERSOL 228513

Subject of the modelling
Resistance and recombination of charges at interfaces in solar cells

Models used
Electronic:
  First principle (DFT) method to construct inter-atomic potentials (up to 2000 atoms)
Atomistic:
  Classical Molecular Dynamics using DFT-constructed inter-atomic potentials
Mesoscopic:
  Phase field modeling of dissolution of Ag particles and transport of Ag through the amorphous glass layer to the bulk Si

Simulation software and type of numerics used
VASP and extensions for DFT based on matrix diagonalisation procedures for plane wave based Hamiltonians
DL-POLY used for classical molecular dynamics based on velocity and leapfrog Verlet integration schemes
LAMMPS used for classical molecular dynamics and energy minimization applying special-decomposition techniques
FactSage used for estimation of Gibbs free energies
COMSOL for transport model (conductivity) of current flow through the interface region and phase field model of the firing process based on solution of large sparce systems

Achievements of the model beyond experiments
The methods can predict contacting and recombination properties of nanostructured materials and complicated interfaces.
The model gave fundamental insight into nitrogen diffusion in silicon, into the nature of different recombination traps, into dissolution and transport of Ag during the firing process, and insight in how the current flows through the contacting region. Based on this optimal Ag crystallites geometries were gained.

Application
Optimisation of contacting and passivation schemes for solar cells

Relevant review articles
K.T. Butler, et al. Structural and electronic properties of silver/silicon interfaces and implications for solar cell performance. Phys. Rev. B 83, 235307, 2011
Keith T. Butler, et al. Molecular dynamics studies of the bonding properties of amorphous silicon nitride coatings on crystalline silicon. J. Appl. Phys. 110, 124905, 2011
G. Kresse et al. Optical and electronic properties of Si3N4 and α-SiO2. Phys. rev. B 85, 45205, 2012
M. Marsman, G. Jordan, L.-E. Hintzsche, Y.-S. Kim, and G. Kresse. Gaussian charge-transfer charge distributions for non-self-consistent electronic structure calculations. Phys. rev. B 85, 115122, 2012

Summary of project
The HIPERSOL project will address the improvement of solar cells (beyond bulk calculations of band gaps) via modelling reflecting the complexity of the real surfaces and want to include impurities and defects which determine the performance in practice. Included will be the effects of recombination (at the interface between base (passivation layer) and emitter (semiconductor) and resistive losses (at this interface and at the metal contact-emittor interface) as they are the major loss mechanisms for the light generated carriers (electrons and holes).

Summary of the modelling
HIPERSOL is to develop an integrated multi-scale modelling environment that is applicable to properties of real materials on length scales not accessible by ab initio modelling; and to use this environment to accurately describe and predict important parameters and properties of interfaces of contacting and passivation layers with silicon. HIPERSOL targeted to do fully self-consistent DFT band structure calculations for systems containing up to 10.000 atoms, as the typical extension of such interfaces easily stretches to hundreds of nanometres. This is done integrating ab initio calculations with empirical atomistic modelling and finite-element methods.
First the construction of inter-atomic potentials was derived from first principles DFT calculations (0.1-1 nm). These inter-atomic potentials were used in classical molecular dynamics performed on the most relevant and interesting interfacial regions of the contacting and passivation interfaces, accounting for strain and for misfit dislocations. The MD simulations provided input for DFT calculations of the contacting interface. The Si/Ag and Si/Ni interfaces have been generated using MD and based upon derived inter-atomic potentials. These structures have been used to calculate Schottky barriers from DFT. The passivation (Si/SiNx) interface has also been modelled with inter-atomic potentials developed. These simulations were used to investigate the influence of N content and gradients on the trap density at the interface.
To apply DFT at a much larger scale than done until now, semi-empirical pseudo-potentials (SEPP) (10-100nm) were created based on first-principles calculations on a smaller scale (density functional theory, hybrid functionals and the GW approximation). These screened potentials can be used within the framework of DFT to calculate the accurate electronic structure of large structures with up to millions of non-equivalent atoms and calculate life times of charge carriers
The atomic coordinates at quasi-equilibrium were transferred to, and formed the basis for the rest of the first principle modelling in this project. Diffusivities and surface energies were also extracted as input to the modelling of the metallisation process. Statistical temperature accelerated molecular dynamics and kinetic Monte-Carlo was needed to calculate diffusivities of charge carriers, band structure calculations for up to 10000 atoms.

In a following stage, results from classical MD and first principles calculations (such diffusion parameters and surface energies) were used as input to finite element method calculations for phase fields, reaching the size and time scales of real devices.

To support the above, numerical techniques were developed for accurate calculation of electronic band structures in sub-systems large enough to include macroscopically relevant features. This involved the integration of realistic band structures and first principles wave functions in the envelope function approach, which were used to calculate life times of excited charge carriers.

Calculations have been performed on novel stacked Si/SiNx structures and new model paste compositions for metallisation under different firing conditions to improve contacting and passivation schemes. The applicability of new pastes was assessed to industrial production. The transport of Ag from the finger through the glass layer to the bulk silicon was modelled with a phase-field model, based on Gibbs free energies obtained from FactSage (using a database developed for solar grade silicon) and diffusivities obtained from first principles molecular dynamics.

www.sintef.no/Projectweb/HiperSol

Modelling

in HIVOCOMP 246389

Subject of the modelling
Composites consisting of a matrix and textile fibrous reinforcement (woven carbon fabric).
Self-reinforced composites consisting of a matrix and the reinforcement of the same chemical nature (polypropylene or polyamide).

Models used
Continuum:
  Microscale model for Newtonian fluid flow in porous medium (formed by fibres inside the yarns)
  Mesoscopic (unit cell of the textile reinforcement) model for uncompressible fluid flow (resin) through the textile reinforcement (Navier-Stokes/Stokes and Brinkmann equations) resulting in calculation of the homogenized permeability
  Micro-mechanics models (elasticity and plasticity and fracture) to calculate the deformation resistance (compression, shear, tension, bending) of dry preform and stiffness and strength of the impregnated composite.
  The results of the micromechanics modeling are used in macro-level models for simulation of forming and impregnation and finally the structural behavior of the part.
  Geometrical description of the reinforcement is the starting point of all the models.

Simulation software and type of numerics used
PAM-RTM a Darcy solver to simulate flow of Newtonian liquid through a porous medium (impregnation of a composite part)
FlowTex for micro scale Stokes, Navier-Stokes and Brinkmann flow
WiseTex micromechanics software to compute the internal structure and deformability of textiles
PAM-family of ESI for macroscale forming
All flow models use finite difference and mechanical models use FE technology

Achievements of the model beyond experiments
Prediction of structural properties to avoid unfeasible or expensive experimental tests.
The models also enabled screening of possible choices for the resins. The flow modeling shortened part of the design by predicting permeability and impregnation time of the different resins.
The model predicted structural behavior in function of the above properties and damage initiation by calculating the threshold and damage development parameters in the composite during different loading types

Application
Composite parts for the transport industry

Summary of the project

HIVOCOMP focuses on improving two materials systems for high performance carbon fibre reinforced parts and their production. The materials systems are: 1) advanced polyurethane (PU) thermoset matrix materials (resin) reinforced with textile (carbon) fibres and 2) composites consisting of self-reinforced thermoplastic polypropylene and polyamide composites, incorporating carbon fibre reinforcements.

Summary of the modelling

HIVOCOMP uses CFD models for the flow of the novel low-viscosity resin impregnating the network of textile reinforcements at meso and macro scale which is performed with an existing finite difference model for Newtonian flows in porous media and Stokes, Navier-Stokes and Brinkmann flow in the network of fibrous reinforcements.

The modelling starts with a geometrical description of the textile. Micromechanics models for mechanical deformation and shrinkage will lead to the description of resistance of the hybrid (carbon/self reinforced PP or PA) preform to deformation and shrinkage during thermoforming. The models will produce material constitutive equations to be used in the macro-modelling of forming.

Novel, predictive micro-mechanics models of elasticity are used to model damage and toughness of the materials following two routes:

1. Micro-level mechanics/elasticity model of textile reinforced PU composite and self-reinforced PP/PA. To account for the specific adhesion behaviour of carbon fibres in PP/PA, special finite elements will be introduced in the calculations. Novel theory of distributed damage, based on Ladeveze-type damage parameters and Puck-type damage initiation criterion is implemented in the model. An alternative predictive approach suitable to crack initiation and growth and based on the existing nonlocal damage EWK (ESI-Wilkins-Kamoulakos) model will also be used and coupled to the MultiModel Coupling capability of PAM-codes to achieve immediately simulation capabilities of industrial dimension.

2. Fast simulation using method of inclusions (Eschelby and Mori-Tanaka) of strength and damage-induced deterioration of the stiffness of composite including strength analysis of the equivalent inclusions and degradation of the stiffness of the inclusions. The method of inclusions is based on Eshelby's transformation concepts, and uses a short fibre analogy to describe the mechanical behaviour of curved yarn segments, combined with a Mori-Tanaka or self-consistent scheme to account for interaction effects. The geometrical input from WiseTex consists of the yarn mid-line representations and cross-sectional dimensions. Yarns are split up into segments and replaced by a short fibre equivalent using the yarn orientation and the local curvature. The output of the model is full stiffness matrix of the homogenised unit cell. In the elasticity model the orientation and length distribution of the fibres are used to generate instances of the random placement of the inclusions. Monte-Carlo scheme is then used to calculate homogenised stiffness matrix

Deterioration of stiffness of the composite with increased loading is calculated in the form of non-linear stress-strain diagrams. This approach lacks the thoroughness of meso-FEA, but will allow integration into the macro-level structural analysis of the composite part.

Finally the developed micro-meso level results are implemented in macro-mechanics tools (PAM- family of ESI) to simulate forming.

http://hivocomp.eu/

Modelling

in HYMEC 263073

Subject of the modelling

Organic semiconductors

Models used

Electronic: [drift-diffusion models](), [(T)DMFT]() , [Hubbard model]()
Atomistic: [percolation model]()
Continuum: [electrical model]()

Simulation Software and type of numerics used

TIBERCAD (commercial, but developed in part by partner of HYMEC)
Statistical mechanics (Monte Carlo algorithm) to calculate percolation

Achievements of the model beyond experiments

The electric field distribution of charged metal nanoparticles in organic matrices can be predicted, which allows identifying the switching mechanisms of memory cells. This, in turn, allows optimizing the morphology of devices.

Application

Photonics and electronics

Summary of project

The goal of the project is to investigate all relevant properties of systems comprising inorganic metal nanoparticles embedded in matrices of conjugated organic materials (organic semiconductors) and demonstrate the potential of such material hybrids as non-volatile memory elements (NVME) that can be addressed electrically and optically. This will allow interconnection of future hybrid electronic and photonic circuitry. Moreover, we target implementing cost-efficient production routes, such as printing, as well as exploring the ultimate miniaturization of such memory elements by novel sublimation- and imprinting-based nanostructuring processes.

Summary of the modelling

The theoretical work consist in developing computational tools for the structure-property-function relationships for NVMEs based on metal nanoparticles embedded in organic matrices, with the view of expanding the functionality of NV-MEs towards optical addressing capability and allow cost-efficient fabrication methods (printing and nanostructure formation).
A continuum model will be used to simulate electrical characteristics of steady-state transport in the two different conduction states. The effect of optical addressing the device to induce charging and de-charging of the metal nanoparticles in the macroscopic device is included in the modelling tool. Improving an existing multiscale code called TiberCAD we will study recombination mechanisms.
An electronic drift-diffusion model has been already implemented with several submodels for recombination and charge mobility (in particular a field dependent mobility). It includes also a module to include a fixed charge background and is currently going on the development of a module to include trapping and de-trapping models, both for energy localized traps or for more extended band-tails (like in amorphous materials). This computational tool will be used to model the device in steady state conduction when it is in high conductivity state or low conductivity state, respectively. Experiments will provide information on adequate rate equations for trapping mechanisms and charge mobility. Experimental results on the electrode/organic matrix interface energetics will be used to model the boundary conditions as Schottky-barriers at the contacts.
A statistical mechanics model for percolation uses a random walk over a network of nodes, which each represent a metal nanoparticle and so a possible site for charges, connected to a certain number of other nodes. The problem is solved using a Monte Carlo method and solving a Pauli Master Equation.The main parameters for this model are related to the jump rate and the coordination numbers (substantially related to the density of nanoparticles) and can be determined phenomenologically with well-known methods of quantum field theory and the support of experimental measurements.
The most demanding part of the theoretical work is the inclusion of exciton creation, transport and recombination (including charging and de-charging of metal nanoparticles) to grasp optical addressing in the drift-diffusion model and the Statistical Mechanics random walk model.
The time-dependent mean-field theory (TDMFT) is used to caluclate transport properties.
The Hamiltonian of the system is described by a Hubbard model but with a strong correlation term between particles. We will solve the equations by density matrix renormalization group (DMRG) for the ground state properties.

A software package is developed to model transport through NV-MEs including the main physical processes which affect conduction, such as charge effects, trap and de-trapping processes.
When the simulation tool is well tested and established as being reliable, it will be used as a support for the further engineering of devices, and it will be instrumental for the development of array and integration efforts in order to find the best selections of materials and device architectures.

http://hymec2.physik.hu-berlin.de

Modelling

in HYPOMAP 233482

Subject of the modelling

Hydrogen storage materials (physisorption and chemisorption), ad- and desorption processes, and proton exchange membranes.

Models used

Electronic:
  Density-Functional Theory (DFT)
  Higher level quantum mechanical methods (MP2, CCSD(T))
Atomistic: QM/MM model for proton conductance
  Statistical Mechanics (Monte Carlo) simulations

Simulation software and type of numerics used

Electronic: Gaussian09, VASP, deMon2k, GPAW, TurboMOLE
  Various Order-N techniques are used, including (i) diagonalization methods, (ii) Fast Fourier Transform, (iii) Matrix-matrix linear algebra operations, (iv) solvers for systems of linear equations
Atomistic: in-house codes for newly developed model called Quantized Liquid Density-Functional Theory (QLDFT)

Achievements of the model beyond experiments

Computational modelling, in particular on the electron or atomistic scale, allows the investigation of processes beyond the experimental scale. People often speak of the "computer microscope" that allows to monitor the motion of a single atom. It also provides understanding of an individual vibrational mode, or of the contributions of material fragments to an individual property. In this project modeling provide insight in the adsorption energy of hydrogen as function of the composition of the individual building blocks of a molecular framework. With this data it is possible to improve the performance of the target materials.

Application

Hydrogen storage and fuel cells

Relevant review articles
R. B. Getman, Y. S. Bae, C. E. Wilmer, R. Q. Snurr, Chem. Rev. 112 (2012) 703-723, DOI: 10.1021/cr200217c.
S. S. Han, J. L. Mendoza-Cortes, W. A. Goddard III, Chem. Soc. Rev. 38 (2009) 1460-1476, DOI: 10.1039/b802430h.
S. A. Shevlin, Z. X. Guo, Chem. Soc. Rev. 38 (2009) 211-225, DOI: 10.1039/b815553b.

Summary of the project

Effective hydrogen storage and fuel cell systems are required for the implementation of a hydrogen economy. HYPOMAP uses computational approaches to predict hydrogen adsorption and proton transfer in new candidate materials for technological application.

Summary of the modelling

For hydrogen storage by physisorption, the weak interaction between the H2 molecules and the host structures need to be modelled in order to understand the thermodynamics of the system. For chemisorption, the critical steps are the loading and unloading, so the mechanism of catalysts on the storage systems needs to be modelled. For fuel cells, the proton conductance in the proton exchange membranes needs to be studied. In all cases, dependence on temperature and pressure are to be included.

Physisorption was modelled linking different models:

1. Band structure comes from experiment or from a DFT calculation (VASP, deMonNano) the Kohn-Sham equations of a bosonic system of hydrogen molecules are applied
2. a force field describing the host-guest interaction usually from high-level ab initio electronic calculations (MP2, CCSD(T)) or literature.
3. atomistic statistical mechanics many body method to calculate adsorption (QLDFT and Grand Canonical Monte Carlo)

Chemisorption has been modeled using electronic DFT calculations (for ammoniaboranes and protonated nanotubes), software: VASP or GPAW. Sometimes a hierarchical approach has been used (the interaction energy is refined with a higher-level electronic method). Molecular storage, such as functionalized linkers in MOFs and transition metal complexes have been modeled with a variety of electronic models (Gaussian09 and Turbomole).

For proton conductance a QM/MM hierarchical protocol, combining Born-Oppenheimer techniques in conjunction with transition state theory and molecular dynamics, is applied:

1. a DFT functional for proton hopping is calculated with the QM part of QM/MM
2. this functions is refined witht high-level ab initio model (CCSD(T))
3. development of a force field with the new functional
4. MD simulations (the MM part of QM/MM) using this force fields of proton transfer in the polymeric proton exchange membranes.

QLDFT (Quantum Liquid Density Functional Theory) is an atomistic Statistical Mechanics model that describes physisorption and loading/unloading of physisorbed hydrogen. Also Grand Canonical Monte Carlo atomistic simulations can be used for this purpose, but QLDFT includes the quantum effects and hence is a fundamentally higher-level treatment. Formally, it is similar to electronic DFT, but instead of electrons it describes H2 molecules, and those obey a Boltzmann statistics (rather than a Fermi statistics that holds for electrons). QLDFT was developed because there was no adequate modelling method for the adsorption calculations on the market that included the quantum effects of light-weight hydrogen. This was a considerable development effort, as (i) a physical method needed to be developed, implemented and validated; and (ii) a series of numerical techniques, treating very large sparse matrices (dimension of ~100,000) efficiently had to be implemented. Moreover, we implemented an efficient technique to account for London Dispersion (a weak interaction governing the interaction of hydrogen with host materials) within DFT and implemented it into deMon2k.

Modelling

in ICMEg 606711

Subject of the project
Standardization of data exchange between models and respective simulation tools in Integrated Computational Materials Engineering settings.

Physics/Chemistry models being considered
Electronic: DFT
Atomistic: MD
Mesoscopic: discrete Phase Field, discrete models for dislocation dynamics
Continuum: continuum Phase Field models, models for thermodynamics, thermomechanics, fluid-flow, crystal-plasticity model

Empirical models generated
Simulation chains will be able to calibrate existing or to generate new constitutive equations.

Simulation software
A thematically structured directory of available simulation software tools will be compiled.

Achievements of the model beyond experiments
Virtual description of entire evolution of microstructures, properties of materials, properties of components, prediction of life-cycle behavior.

Application
Materials development, process development, alloy design,

Relevant review articles covering the topic (not necessarily their own):
National Research Council: Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security; National Academic Press, Washington, D. C. (2008), ISBN: 0-309-12000-4.
G.J. Schmitz and U.Prahl (eds):
Integrative Computational Materials Engineering- Concepts and applications of a modular simulation platform Wiley VCH Verlag Weinheim, ISBN 978-3-527-33081-2 (2012)
TMS: Implementing ICME in the Aerospace, Automotive, and Maritime Industries (2013)
Downloadable for free from: http://www.tms.org/icmestudy/

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Summary of the project

ICMEg as a CSA is a networking project aiming to build and maintain a network of stakeholders in Integrated Computational Materials Engineering (ICME) and to define an ICME language in form of an open and standardized communication protocol. This can be used by third parties tocreate a "plug & play" type architecture which will
 · significantly facilitate the exchange of data between different tools
 · create new options and functionalities of the present tools
 · allow for easy integration between commercial and academic approaches
 · provide the pathway for life-cycle modelling of components/products
 · allow for global optimisation of process chains
 · stimulate many further new developments

Summary of the materials model communication standard activities
The project focusses on models to describe microstructure evolution as a central part of ICME. Microstructure properties depend on the entire process history as well as on shape of the component and on the actual alloy composition. Outlining a scale and process spanning modelling scenario and making it available for material-by-design is one of the key objectives of ICME.

This networking project will have workshops to reach European endorsement for communication standards being proposed and jointly elaborated within 5 other NMP projects on multi-scale modeling: DEEPEN, MMP, MODENA, NANOSIM and SIMPHONY.
These standards will include a generic and structured list of metadata keywords and an overall data structure for file based information exchange. These will be based on existing standards to the largest possible extend and will allow sequential i.e. file based interoperability. ICMEg will propose Communication Standards for a file based exchange of information between models describing the behaviour of
 • the components providing the boundary conditions for the evolution of the microstructure
 • the microstructure comprising multiple grains and multiple phases
 • the individual phases and their properties
The standards and interoperability scenarios developed in ICMEg will focus on coupling and linking 2D and 3D continuum models but data obtained from e.g. DFT, MD and other small scale models will be integrated into the scenario. ICMEg will also elaborate standards for inclusion of data from electronic/atomistic/mesoscopic models required for continuum model simulations. Discrete models will be linked to give effective values to continuum models. Discrete models could e.g. deliver thermodynamic data for the individual phases in complex alloy systems, data for thermal conductivities or anisotropic thermo-mechanical properties and also provide relevant data like critical nucleation undercoolings for the formation of phases. Homogenisation tools with interpolation schemes to calculate effective properties from model output can be included in the scenarios.

Based on the identified needs of the continuum models, missing functionalities will be identified and a roadmap for future developments in the area of discrete and continuum models will be proposed.

The communication standards to be developed will be extendable and also applicable to other applications. They will provide the basis for a future platform which will enable simultaneous (coupling) or consecutive (linking) execution of models. The actual development of platforms is however not part of ICMEg but takes place within the EU projects mentioned above and hopefully the standards and platforms will be adopted by a wide community in the future.

Modelling

in IFOX 246102

Subject of the modelling
Transition metal oxide hetero-structures and their interfaces

Models used
Electronic scale:
  Density functional theory (DFT) for electronic structure and transport
Atomistic scale:
  Molecular Dynamics for defects diffusion in oxides
  Coarse-grained Monte Carlo codes to evaluate thermodynamical properties for example
  critical temperatures

Simulation software and type of numerics used
Various DFT codes:
  FLEUR: Full-potential linearized augmented plane wave (FLAPW) method, linear scaling
  algorithms for the treatment of nanometer-thick heterostructures, Green-functions for the
  calculation of semi-infinite solids and of electronic transport under finite bias
  KKRnano: Korringa-Kohn-Rostoker Green-function code for large scale parallel calculations
  SMEAGOL: code for transport calculations
SIESTA: Molecular Dynamics
MC code (inhouse)

Achievements of the model beyond experiments
Ab-initio calculations based on Density Functional Theory provide the necessary link between
simple models used to interpret materials properties and the complex interplay between
electronics, the atomistic structure and magnetism found in experiments. These calculations
enable the correct interpretation of experiments and can lead to guide research. An example
for this process relevant to our field was the prediction and interpretation of huge tunneling
magnetoresistance in tunneljunctions with magnesiumoxide barriers which predated the
experimental findings for several years.

Application
Memory, programmable logic and sensors

Relevant review articles

Computational Nanoscience: Do It Yourself! edited by J. Grotendorst, S. Blügel, D. Marx, NIC
Series Volume 31, ISBN 3-00-017350-1, URL: www.fz-juelich.de/nic

Summary of the project

IFOX is to explore electronic and magnetic functionalities that result from the rich interplay of charge, spin and orbital degrees of freedom in transition metal oxide heterostructures and their interfaces. The project will grow oxide films on commercial substrates and establish oxide patterning and processing conditions to deliver novel device concepts for memory, programmable logic and sensors.

Summary of the modelling

IFOX addresses three major classes of oxide heterostructures:

- Ferromagnetic oxide heterostructures controlled by charge or spin-polarized
- Ferroelectric oxide heterostructures controlled by charge and electric fields
- Multifunctional multiferroic oxide heterostructures controlled either by charge or by spin and ultimately by ultrashort light pulses

The models will be applied to understand electronic reconstructions at the interfaces; spin tunnelling and transport across oxide interfaces; fundamental properties of nanoscale oxide elements with respect to the ionic and electronic contributions to the screening of polarization charges at the electrode -oxide interfaces; the interaction of redox-centers and extended defects with ferroelectric polarization charges and interface coupling between ferromagnetic and ferroelectric oxides in artificial multiferroics.

Density functional theory (DFT) will be applied using the earlier developed full-potential linearized augmented plane wave (FLAPW) method FLEUR. It can model non-collinear magnetism, electric fields applied to surfaces, electric polarization and the mapping of the electronic structure to tight-binding Hamiltonians. SPEX is a recent addition to the FLEUR model that will be used to determine quasiparticle properties including band structures and band gaps to much higher accuracy than is currently possible with DFT.The DFT-based methods available within IFOX are based on a pseudopotential and local orbital implementation of DFT, which allows for more rapid and larger scale simulations than those possible with all-electron plane wave codes.

Moving beyond perfect interfaces, a realistic interface model must include large and extended defects and needs modelling of thousands of inequivalent atoms. The massively parallelized Korringa-Kohn-Rostoker Green-function code will be used to solve the DFT models. The electronic structure of point-like defects in oxides is affected by the interplay between strong electron correlation and polaronic coupling with the lattice distortions. Accurate description requires both the correct determination of the electronic structure of the host oxides, including the band gap and an extremely accurate estimate of the defect total energy. To this goal, a range of orbital-dependent exchange and correlation functionals, such as DFT exact exchange, self-interaction correction and hybrid functionals will be applied.

Bias dependent electronic transport calculations for oxide heterojunctions can be performed with the SMEAGOL code. At present only the ballistic limit is accessible, although inelastic effects can be included at a phenomenological level and an algorithm has been recently finalized within SMEAGOL.

Molecular Dynamics (MD) methods will be applied to model the electrical hysteresis of conducting oxides and oxide-based junctions. Initially, defect diffusion will be studied without an external field either using classical force fields or fully ab-initio Car-Parrinello methods. Metadynamics will be employed in the case of slow migration processes or migration involving a large and complex energy surface. Similar MD schemes will be employed for defect diffusion at the interface between heterogeneous materials.

The Heisenberg spin-Hamiltonianare employed in DFT models and parameters like hopping parameters or exchange couplings are extracted. These are input to coarse grained Monte Carlo models to calculate thermodynamic properties such as the Curie temperature, or non-equilibrium properties such as kinetic growth, on the mesoscale.

www.ifox-project.eu

Modelling

in IMS & CPS 246243

Subject of the modelling
Textile carbon fibre/epoxy composites reinforced with carbon nanotubes (CNTs), damage resistance, electrical conductivity and lightning strike protection

Models used
Microscale damage initiation model in textile fiber/reinforced composites
Electron tunneling percolation models and ion transport statistical mecahnics models

Simulation software and type of numerics used
WiseTex, TexComp for the calculation of stress and strain fields numerically in the representative volume using geometrical modeller WiseTex and commercial FE packages (such as ANSYS and ABAQUS).
Random Microstructure Generation (RMG) algorithm e.g. for buckling of the I beam with classic eigenvalue analysis.

Achievements of the model beyond experiments
The "electrical conductivity" model predicts the electrical percolation and conductivity of CNT/polymer composites close to the experimental observations. The achievements beyond experiments include the positive effect of agglomeration and the transverse conductivity of the CNT/polymer composite with the CNTs only sprayed on the surface. In fact, nobody believed that there will be conductivity in the transverse direction when the CNTs are sprayed on the surface alone. In addition, this model correctly predicted that the addition of compatibilizers and copolymers has a significant effect on electrical percolation threshold and conductivity. These characteristics are experimentally proved and this is the only model which can predict this behaviour.
The toughness model will predict the effect of carbon nanotubes and their agglomerates on re-distribution of stresses and strains inside the composite and the threshold strain for the onset of damage on the micro-scale.
The model utilized for validation elements can predict the initial failure of the T junctions and of the I beams for the different used materials (with and without CNT). This will help to design the test jigs to be used in the project.

Application
Textile reinforced composites, transport, aviation, railway

Relevant review articles
Verpoest I and Lomov SV, Composites Science and Technology 65 (2005) 2563–2574.
Lomov, S.V., et.al. Meso-FE modelling of textile composites: Road map, data flow and algorithms. Composites Science and Technology, 67, 2007, 1870-1891
Weibang Lu, et.al. A three-dimensional model of electrical percolation thresholds in carbon nanotube-based composites. Applied Physics Letters, 96(22):223106, 2010.
Andriy V Kyrylyuk, Marie Claire Hermant, Tanja Schilling, Bert Klumperman, Cor E Koning, and Paul van der Schoot. Controlling electrical percolation in multicomponent carbon nanotube dispersions. Nature nanotechnology, 6(6):364 – 9, January 2011.

Summary of the project
IMS&CPS intends to gather innovations linked to carbon nanotubes based innovative materials and innovative composite processings for transport applications (aeronautics and railway applications).

Summary of the modelling
In order to achieve higher mechanical properties and higher electrical conductivities in multi-scale carbon fiber/epoxy composites, an important part of the IMS&CPS project is dedicated to the development of modeling methodologies and predictive tools. The goal of these tools is to help understand how to maximize the benefit of carbon nanotubes in the structural composites for the improvement of such properties as damage resistance, electrical conductivity and lightning strike protection. The success of this modelling lies in the geometric modeling of the CNTs, polymer chains and their interactions because the geometrical distribution of the CNTs in the representative volume has a significant impact on the electrical conductivity and the percolation threshold.

Representation of the sample
The software package WiseTex implements a generalised description of internal structure of textile reinforcements on the unit cell level, integrated with mechanical models of the relaxed and deformed state of fabrics. TexComp uses the geometrical input from WiseTex, which consists of the yarn mid-line representations and cross-sectional dimensions. Yarns are then split up into segments and replaced by a short fibre equivalent using the yarn orientation and the local curvature. The output of the model is full stiffness matrix of the homogenised unit cell. The representation is further refined using the random microstructure generation (RMG) algorithm to simulate a fiber distribution in the representative volume element. In the framework of the IMS&CPS it is proven this algorithm generates microstructures that are statistically equivalent to real microstructures (from the point of view of geometrical characteristics and mechanical performance). The modified version of this model is currently in the development, which goal is to simulate fibers and nanotubes in a single model without transferring parameters from simulations on one scale to another. This is mainly explained by numerical challenges that come from modeling objects that differ in dimensions by 1000 times (microscopic fibers and nanoscopic tubes).

Physics and chemistry
The above internal geometry and stiffness prediction is a necessary input for physics and chemistry modelling.
The damage initiation model is developed on the micro-scale. This model predicts transverse damage initiation in unidirectional fiber/polymer composites with and without carbon nanotubes.
The conductivity model for polymer/CNT composites predicts electrical percolation thresholds and electrical conductivity of polymers reinforced with CNTs. It can be applied to different kinds of CNT/polymer nano-composites. The model accounts for the two types of charge transport mechanisms with and without chemical bonding between CNTs and the polymer. In the first case creation of ions and charge transport through CNTs and polymer chain networks play a role, while in the second case charge transport through the physical contact between CNTs, through the electron tunneling between CNTs, through the electron tunneling between polymer chains and through the electron tunneling between CNTs and polymer chains are important.
To model the ion transport percolation models are used (statistical mechanics based codes that take the structure into account and calculate thermodynamic properties), which emphasize the importance of the interfacial interactions at the boundary between the individual filler particles and the polymeric host for the network formation. As a consequence, these models interpret the percolation phenomena as a phase separation process.
Electron tunnelling is described with quantum mechanical percolation models which assume the charge transport between carbon nanotubes are partly through physical contacts and partly through electron tunneling between carbon nanotubes.

Representation of the sample
Different calculations are done to find a representation of where the fibers are after the physics and chemistry have evolved. Statistical calculations of random placement during dispersion and further agglomeration of carbon nanotubes give networks of physically connected paths. This is further refined in geometrical calculations to obtain a representation of the fibres in different dry premixed and subsequently sintered mixtures of conductive and insulating powders. Structure oriented models based on the parameters that have to be determined from the micro level structure of the mixture after final processing step. A detailed substitution of the real material structure by a theoretical model structure is needed for the determination of such parameters.

Modelling

in INNOVASOL 227057

Subject of the modelling
Excitonic solar cell materials (QuantumDots, Transparant Conductive Oxides and solid electrolyte)

Models used
Elcetronic:
  Ab initio Hartree-Fock and Density Functional Theory for calculations of structures, electronic distribution and properties;
  Polarizable Continuum Model (PCM) for the simulation of solvent effects on molecular structures and energies

Simulation software and type of numerics used
Computational packages:
  Gaussian03, Turbomole 6.0 for DFT
  Crystal06 (for DFT with periodic boundary conditions)
  Gaussian03(for PCM)
  SCF Self-consistent differential equations for solvent effects with PCM
  MSINW07
  solution of Schroedinger equation in the mean-field approximation, with atomic expansion of molecular orbitals and periodic boundary conditions

Achievements of the model beyond experiments
Trial and error synthesis costs were avoided by computing the energetics of inclusion of some anions (iodide and tri-iodide) in a layered solid analogous to hydrotalcite before the actual systems were synthesized. The calculations showed the limit concentration expected for anions in this environment.
The models could provide understanding of phenomena occurring, e.g. the excess of lead observed in certain conditions.
The calculations allowed to predict which surface passivant would help obtain particles of octahedral shape exposing (111) crystallographic faces, and this will guide the experiments.

Application
Solar cells

Relevant review articles
Simona Fantacci, Filippo De Angelis "A computational approach to the electronic and optical properties of Ru(II) and Ir(III) polypyridyl complexes: Applications to DSC, OLED and NLO", Coordination Chemistry Reviews 255 (2011) 2704–2726
Walter R. Duncan and Oleg V. Prezhdo "Theoretical Studies of Photoinduced Electron Transfer in Dye-Sensitized TiO2", Annu. Rev. Phys. Chem. 58 (2007) 143–184

Summary of the project

INNOVASOL aims at developing nanostructured and molecular materials for photovoltaic (PV) excitonic solar cells. The first step is the substitution of the liquid electrolytes, currently used in dye-sensitised solar cells, with solid-state hole conductors. In parallel, semiconductor quantum dots (QDs) with tuned band gap, designed to enhance the photon capture efficiency, will replace the organic dyes as light absorbers.

Summary of the modelling

Most modelling results have been obtained with DFT with hybrid GGA functionals, though also Hartree-Fock and post-Hartree-Fock calculations have been performed. In some cases, periodic boundary conditions have been used; both finite cluster and infinite periodic models made use of Gaussian-type atomic orbitals to expand the molecular orbitals. The packages adopted were Gaussian03 and Turbomole 6.0 for finite cluster models and Crystal06 for periodic systems. When necessary, the solvent effects were included in the calculations through the Polarizable Continuum Model PCM, where the solvent reaction field is simulated by a set of apparent charges self-consistently determined on the basis of the electric potential generated by the solvated molecule(s). This approach, partially developed in the past by some participants to the project is presently implemented in several codes: during INNOVASOL the implementation in Gaussian03 was used.

In addition to ab initio and DFT methods, also semi-empirical were used to describe at a lower level the effect of surrounding micro-systems, weakly interacting with the molecules. The adopted semi-empirical method was MSINDO7, with some adjustment of the parameters to fit model post-HF calculations.

Suitable meta-procedures were developed to link DFT and semi-empirical calculations in an ONIOM-like scheme (in which the more expensive DFT calculations are limited to the central molecules, whose properties are to be determined accurately, while the cheaper semi-empirical approach is used to include at a lower level the interactions with the surroundings). Routines to link MSINDO7 and Gaussian03 codes were written.

This way, the formation energy of some inclusion complexes in layered magnesium oxides (HTLC) which is relevant for the synthesis of quasi-solid electrolytes to be used in solar cells was simulated. Also PbSe nanoparticles were modeled, with particular attention to the binding energy of the different crystallographic faces to organic passivants, and the simulation of organic dyes/PbSe nanoparticles adducts.

In summary, computational tools proved to be efficient and useful in the following project achievements.

- Limit concentration and best choice of reaction partners were predicted for the synthesis of quasi-solid electrolytes by means of ab initio periodic calculations.
- Structural properties of PbSe nanoclusters and best affinities of clusters for different organic ligands used in syntheses were computed with ab initio finite cluster approach.
- Light absorption spectra of squaraine molecules in different conditions (isolated, dissolved in liquid media, attached on top of nanoparticles) were computed with time-dependent DFT methods including solvent effects via PCM, indicating which anchoring groups are more promising for adding the dye to the nanoparticles, and how the absorption spectra can change upon addition.
- The structure of dye monolayers on TiO2 surfaces has been described with mixed ab initio – semi-empirical calculations, to estimate the binding energy as a function of anchoring groups and degree of surface coverage, i. e. the limit concentration of adsorbed dye.

Modelling

in IRON-SEA 283141

Subject of the modelling
Fe-based superconductors
Characteristics of Josephson junctions (junctions where a supercurrent can flow through a non superconducting medium between two superconductors)

Models used
Electronic: DFT electronic structure calculations
  Multiband Eliashberg models (development and application)
  Blonder-Tinkham-Klapwijk model (application and extensions)
Continuum: Electrical circuit model: (resistively and capacitively shunted junction model)
(application)

Simulation software and type of numerics used
DFT calculations using the FP-LAPW Code
  Systems of non linear singular integral equations solved numerically by using in-house developed code.
  Systems of second-order differential equations where standard solvers are used (i.e. Runge-Kutta)
  Elk code for the calculation of band-structure and Fermi surface.

Achievements of the model beyond experiments
The model determined the pairing symmetry and its evolution with doping, which is impossible to determine experimentally.
The model determined the characteristic energy of the boson that mediates superconductivity (examples: Co-doped Ba-122, Sm-1111) and of the coupling strength.
The model determined the effects of disorder, doping, lattice strain, etc on the superconducting properties.
The model determined the effects that are optimal or detrimental for device fabrication and optimization.

Application
Superconductors

Relevant review articles
P. Seidel, Supercond. Sci. Technol. 24, 043001 (2011)
D. Daghero and R.S. Gonnelli, Supercond. Sci. Technol. 23, 043001 (2010)
D. Daghero, M. Tortello, G.A. Ummarino, R.S. Gonnelli, Rep. Prog. Phys. 74, 124509 (2011)
G.A. Ummarino, Physical Review B 83, 092508 (2011).
P. Popovich, A.V. Boris, O.V. Dolgov, A.A. Golubov, D.L. Sun, C.T. Lin, R.K. Kremer, and B. Keimer, Phys. Rev. Lett. 105, 027003 (2010)

Summary of the project

The project will study iron-based superconductors in the form of thin films, which have been prepared by molecular beam epitaxy and by pulsed laser deposition. The goal is to find unique physical properties, which lead to exploring new kinds of devices and applications. Since the iron-based superconductors have a multi-band nature, comparative studies to MgB2, which is a two-band superconductor, are also carried out.

Summary of the modelling

Intrinsic physical parameters (e.g. the superconducting transition temperature, the penetration depth, the upper critical field, and etc.) of Fe-based superconductors can be calculated by solving the three or four band Eliashberg equation, once the relevant Eliashberg parameters for a given materials are fixed. The Eliashberg theory allows calculating many different observables related to the superconducting state. In Fe-based superconductors, the solution of multiband Eliashberg equations requires some input parameters that can be either determined experimentally or provided by DFT electronic structure calculations. DFT electronic calculations have been carried out for calculations of the bandstructure and of the Fermi surface for the compounds under study. The shape of the Fermi surface is needed as input for the 3D- Blonder-Tinkam Klapwijk model for the fitting of the experimental point-contact spectra. Eliashberg calculations require as an input the density of states projected on the different bands from DFT calculations. Some very basic parameters related to the superconducting state can be adjusted to reproduce given experimental results. After that, it is possible to calculate with the same parameters and no further assumptions many different observables that can then be compared to experimental results or trigger new experiments to test the predictions. The analysis of a given material within the multiband Eliashberg models, especially when it is possible to explore the phase diagram can help discriminating between the effects of disorder, lattice parameters, changes in the density of states in determining the critical temperature or other superconducting properties. This can help optimizing the quality of the samples or even suggest some alternative chemical compositions or substrates (in the case of films).

Conductance-Voltage characteristics of Fe-based superconducting films obtained from point contact Andreev reflection spectroscopy measurements will be fitted to extract the superconducting energy gaps by means of the Blonder-Tinkam Klapwijk model and its generalizations, for example to account for the real shape of the Fermi surface.

Characteristics of Josephson junctions fabricated from Fe-based superconducting films can be described by the electrical circuit resistively and capacitively shunted junction (RSCJ) model. These models (BTK and its generalizations and RSCJ) are explained and can fit experimental data. Some of the parameters that can be extracted from the fit are specific of the single junction or point contact. Others can be compared to the outcomes of other measurements (specific heat, superfluid density, ARPES and so on). In most cases, the results for a specific material turn out to be in good agreement with those provided by these other techniques.

Theoretical aspects of the tunnelling and Andreev reflection in unconventional superconductors will be studied. In particular, they shall concentrate on:
- the Josephson effect and its dependence on the pairing symmetry
- the possibilities to use the Josephson effect to gain insight into deviations from the standard BCS -like behaviour.
- the analysis of the results of the different spectroscopy measurements in the framework of multiband Eliashberg theory with the main purpose of shedding light on the pairing mechanism and the nature of the mediating boson in Fe-based superconductors.

http://www.IronSea.eu

Modelling

in LbLBRANE 281047

Subject of the modelling
Trans-membrane ion transfer in nanofiltration

Models used
Continuum: CFD with Nernst constitutive equation

Simulation software and type of numerics used
Continuum COMSOL

Achievements of the model beyond experiments
Solution-Diffusion-Electro-Migration constitutive equation used in a general purpose CFD code provides insight in pressure-driven rejection of ions from electrolyte mixtures in complex situations (ions with 3 different charges and external concentration polarization) which cannot easily be obtained experimentally.

A new model (constitutive equation) describes trends in experimental data that previously remained unexplained.

Application
Nanofiltration

Relevant review articles covering the topic (not necessarily their own):

Yaroshchuk A., Bruening M.L., Licón Bernal E.E., Solution-Diffusion–Electro-Migration model and its uses for analysis of nanofiltration, pressure-retarded osmosis and forward osmosis in multi-ionic solutions, J.Membr.Sci., 2013, 447, 463–476

Summary of project

LbLBRANE applies the layer-by-layer (LbL) technology to develop a procedure for the fabrication of low-cost, stable, chemical-resistant polyelectrolyte membranes for water reuse and metal/acid recovery.

The goal is to create highly performant, regenerable membranes which could be cleaned in-situ and hybrid membranes with extremely high flux with high perm-selectivity and mechanical robustness.

Summary of the modelling

Predicting membrane performance and behaviour is based on the extended Fick's diffusion equations with added terms due to electric-potential gradients (Solution-Diffusion-Electromigration model). These equations are constitutive equations used to close the conservation of mass equations to describe the electro-diffusion of charged chemical species in membrane materials.

The necessary parameters to describe a specific application are a.o. permeability for single ions. After determination of the ionic permeabilities the CFD equations are solved to establish quantitative correlations between the structural, chemical properties and transport properties of polyelectrolyte multilayers membranes.

The model is used to predict optimal operational conditions (trans-membrane pressure, cross-flow rate, feed composition) for various classes of solutes for example, positively or negatively charged micro-pollutants of various molecular weights, multiple-charge metal ions, hydrogen and hydroxyl ions, etc. Such models can be used for the theoretical optimization of membrane performance in the targeted applications, first of all, in the metal/acid recovery.

Modelling

in LEMSUPER 283214

Subject of the modelling

Light element superconductivity

Models used

Electronic: DFT for electronic structure of relevant materials
  Tight binding (TB) and Hubbard models built by direct inspection or by downfolding DFT
  electronic structure as relevant for actual or potential superconductors
  Gutzwiller and DMFT
Atomistic: Ab initio Molecular Dynamics models for pressure induced metallization of potential
high pressure superconductors, and interactions, vibron properties, Jahn Teller effects

Simulation software and type of numerics used

Kohn-Sham and related equations for standard DFT calculations and simulations with a variety
of hybrid functionals (HSE, B3LYP) and LDA+U
Gutzwiller projector technique calculations for the ab-initio codes
Single site cellular DMFT calculations of appropriately built Hubbard models, using Anderson
model methods as an ingredient
Existing Car-Parrinello-Rahman codes for MD

Achievements of the model beyond experiments

New correlation-driven mechanisms for superconductivity in light element systems were
predicted long before they were validated. A superconductivity mechanism for fullerides was
predicted, where electron-vibron coupling, orbital degeneracy, and strong electron
correlations implying a nearby Mott transition all play a crucial role. Cesium fullerides validated
this theory.
Identification of new electronic ground states in light element systems leading to
superconductivity, potentially unveiling new light element molecule-based superconductors,
something that cannot be done experimentally.

Application

Light element molecules superconductors

Relevant review articles

Capone et al. Modeling the unconventional superconducting properties of expanded A(3)C(60)
fullerides 10.1103/RevModPhys.81.943   Apr-Jun 2009
Kubozono, Yoshihiro et al Metal-intercalated aromatic hydrocarbons: a new class of carbon-based
superconductors PhysChemChemPhys 13/17 2011 pp: 16476-16493   DOI: 10.1039/c1cp20961b

Summary of project

This project addresses the design and understanding of light (and cheap, abundant, benign) element (B, C, O) cluster/molecule-based superconducting systems with higher transition temperatures. The project aims to develop new understanding of the electronic and crystal structures required for high Tc superconductivity in light element systems. Competing electronic ground states and pairing mechanisms are at the basis of superconductivity. In light element materials a fine balance exists between electron-phonon coupling and the electron correlations. This was recently identified as the potential of light elements as superconductors.In light elements superconductivity is controlled by p orbitals and the π-orbitals of C contribute to the LUMO (lowest unoccupied molecular orbital, filled by the electrons donated by the alkali dopants). Furthermore the Coulomb exchange interaction plays a role, and the C-C phonon modes bring about the molecular vibrations relevant for superconductivity. Alkali doped fullerenes, fullerides and polycyclic aromatic hydrocarbons near metal-insulator transitions, where they are likely to develop superconductivity, will be studied. Also the influence of external actions, such as doping, pressure, electric fields will be investigated. The simultaneous role of correlations, screening and disorder will be considered, with special attention to the role that disorder may play in enhancing the critical temperature at the transition.

Summary of the modelling

The electronic structure, magnetism, phonon structure will be obtained by density functional theory (DFT) calculations, even in strongly correlated systems. Insulating or metallic tendencies and the Fermi surfaces of candidate light element and molecular superconductors can be addressed with an initial DFT study. The DFT total energies and enthalpies generally provide a good indication of the relative stability of different crystal structures. Relativistic effects, including Rashba at interfaces, can automatically be included by means of DFT codes including spin orbit. The electron phonon couplings, key ingredients to BCS (Bardeen, Cooper, Schrieffer) superconductivity (standard theory of superconductivity, based on electron-phonon interactions driving ordinary metals unstable against electron pairing) in regular metals and also in Jahn Teller systems, can be reasonably obtained by DFT. In addition correlations can be built-in at the mean-field level through approximations such as LDA+U or equivalent. DFT with a variety of hybrid functionals (HSE, B3LYP) and LDA+U models will be applied to identify aromatic superconductor materials that show a conduction band which comprises multibands and a Fermi surface which is an interesting composite of surfaces having different spatial dimensionalities. We use a Gutzwiller projector technique to introduce approximately electron-electron correlations in the ab-initio density functional theory (DFT) based codes. In this approximation, the Kohn Sham equations of ordinary DFT are modified into new ones, where the electron hoppings are reduced by factors reflecting the renormalization caused by repulsive correlations.

Full many-body models such as Dynamical Mean Field Theory (DMFT) with the "downfolding" description of the Mott-Hubbard insulator will also be applied.

Many body techniques for metal-insulator interfaces able to describe inhomogeneous situations will be developed for application to surface doping. The effect of many body interactions beyond mean-field levels in picene and similar molecular systems will be added to the models. The models will then be available for materials exploration of the rich variety in molecular species (various aromatic molecules in the present project), orbitals and crystal structures in order to find materials with long-ranged electron-electron interaction, expected to substantially affect the mechanism of superconductivity.

The superconductor- insulator transition in lattice expanded alkali fullerides has properties not yet experimentally explored. Insulator-superconductor transitions obtainable under pressure and/or in other organic doped systems will be investigated to identify materials that are possible candidates.

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http://www.lemsuper.eu

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Modelling
in LIGHT.TOUCH.MATTERS 310311

Subject of the modelling

Piezoelectric composites and OLEDs

Models used

Continuum: mechanics (either solid or liquid)
electromagnetics

Simulation software and type of numerics used

Micromechanics and EM models: conventional software packages such as Matlab, Abaqus or Comsol

Achievements of the model beyond experiments

The model will greatly facilitate making trade-offs between e.g. cost and sensitivity, as well as streamline tests of material stacks;

Application

Touch sensitive luminous user-product interfaces for creative industries, electronic health care and consumer goods, but also the chemical, automotive and printing industries, as well as mechanical-, electrical-, packaging- and systems engineering.

Relevant review articles

Y. Benveniste 1987 Mech. Mater. 6, 147-157
M.L. Dunn, M. Taya 1993 Proc. R. Soc. A. 443, 265-287
C.Andrews, Y. Lin, H.A. Sodano 2010 Smart Mater. Struct. 19, 025018
C.P. Bowen, R.E. Newnham, C.A. Randall 1998 J. Mater. Res. 13, 205

Summary of project

In Light.Touch.Matters polymeric piezo materials (piezo-active particles in a polymeric matrix) and flexible OLEDs will be designed that combine touch sensitivity with luminosity. Manufactured on plastic substrates, these novel 'light touch materials' will be thin, flexible and formable.They will expand design freedom and allow new modes of product-user interaction, using touch sensitivity and luminosity to produce simple, affordable and intuitive user interfaces.

Summary of the modelling

[Micromechanical models](#) will be applied to piezoelectric composites to predict performance in a wide variety of load cases, e.g. under tension, compression, bending or torsion, either directly loaded or indirectly loaded. The composite will be part of a 'stack' of materials with other materials placed between the load and the composite.

Electromagnetic models will predict the effective dielectric constant (i.e. piezo-electric sensitivity) of the piezoelectric composite material in relationship to the composite's, composition and the electromagnetic field applied during composite formation.

The modelling work involved is a hybrid of continuum mechanics (either [solid](#) or [fluid](#)) and electromagnetic models, i.e. multi-physics. With this materials can be designed that meet the properties desired by designers to enable certain modes of product-user interaction. These specifications might include that this constant will be different for different deformation modes of the composite (e.g. bending versus torsion, or bending versus compression), and the model will calculate which material shows this anisotropy.

http://www.light-touch-matters-project.eu/

Modeling

in LISSEN 314282

Subject of the modeling

Sulfur-based battery cells

Models used

Continuum: A single-battery-cell reactive-transport models (1D continuum-based transport of mass and charge, elementary kinetic description of electrochemistry and heterogeneous chemistry)
3D microstructural models for cathode and anode (geometrical representation of experimentally obtained structures, simulation of material properties based on structure)

Modeling and simulation software and type of numerics used

DENIS, a C-based DLR modeling framework for single-cell reactive-transport calculations
GeoDict, a 3D microstructural modeling
Matlab

Achievements of the models

The models will be used to simulate the influence of physical parameters on key performance metrics and cell lifetime, therefore generating a deeper understanding of functional principles of the studied system. Based on the resulting findings, experimentalists can be advised and guided, speeding up the actual development of the envisioned "Lissen Battery".

Application

Lithium-Sulfur battery cells

Relevant articles covering the topic:

- K. Kumaresan, Y. Mikhaylik, R. White; A mathematical model for Lithium-Sulfur Cell, J. Electrochem. Soc., 155 (8) A576-B582 (2008)
- S. Gewies, W. Bessler; Physically based impedance modeling of Ni/YSZ Cermet, J. Electrochem. Soc., 155 (9) B937-B952 (2008)
- J. P. Neidhardt, D. N. Fronczek, T. Jahnke, T. Danner, B. Horstmann, W. G. Bessler; A Flexible framework for Modeling Multiple Solid, Liquid and Gaseous Phases in Batteries and Fuel Cells, J. Electrochem. Soc., 159 (9), A1528-A1542 (2012)

Summary of project
This project aims for the identification and development of nanostructured electrode and electrolyte materials as well as appropriate cell designs to promote the practical implementation of the very high-energy lithium-sulfur battery. In particular, the project will be directed to the definition and test of a new lithium metal-free battery configuration based on the use of lithiated silicon as the anode and a nanostructured sulfur-carbon composite as the cathode.

Summary of the modelling
3D microstructural models will be coupled to single-cell reactive-transport models in a unidirectional "offline" fashion: electrode properties will be calculated for a range of parameters with microstructural models, and results are used as input for reactive-transport models. A bi-directional online coupling of different numerical codes or the integration of analytical results obtained from microstructural models in cell-level models might be established where useful and feasible.
The models developed within the LISSEN project will improve the conceptual understanding of mechanisms governing the functioning and degradation of Lithium-Sulfur battery cells. To this end, the role of three main aspects of Lithium-Sulfur cells for key performance metrics and longevity will be investigated: 1) the involved multi-step redox chemistry, 2) the surface and internal structure of electrodes used, and 3) the overall cell design (type and composition of active materials in the electrodes, used electrolytes, etc.)
Single-cell reactive-transport models based on a 1D continuum approach will be used to investigate the role of involved chemical reactions. The model couples chemical reactions and continuum mass and charge transport equations and solves them simultaneously. The multi-species redox chemistry of sulfur to lithium sulfide via polysulfides (and vice versa) will be modelled at the cathode. At the anode, lithium deposition/intercalation into an anode material will be described. Parasitic side reactions (e.g. polysulfide reduction at the anode) will be implemented as appropriate. When useful and feasible, the intercalation induced volume changes of electrodes as well as pore size changes resulting from dissolution and precipitation of solids will be modeled. The transport equation will describe the transport in the liquid electrolyte. Experimental data (as e.g. polarization behavior, electrochemical impedance, and other kinds of in-situ measurement results available from the partners or appropriate literature data) will be used to validate the model. Interpretation of simulation results then provides insights into the role and influence of the involved electrochemical reaction network and the results will also form the basis for describing the cross talk between the two electrodes (e.g., shuttle mechanism).
For an assessment of the role of electrode structures, the morphological parameters of cathode and anode, needed for single-cell reactive-transport models (e.g. volume fractions of the components, volume-specific surface areas and phase boundaries) will be obtained by interpreting results from 3D microstructural modelling of the porous electrodes and by geometrical considerations of structural changes of individual pores, particles, or particle agglomerates. Simulation results based on various electrode-microstructures will be compared. Existing or newly developed single-cell reactive-transport models and morphological models will be applied to various cell designs. Simulated cell performance and longevity will be compared.
Experimentally determined parameters that can aid in the development of the single-cell reactive transport models include the diffusion coefficients, the ion transference numbers, the conductivity and the initial concentration of participating components (electrolyte, conducting salt, polysulfides), as well as kinetic reaction parameters derived from, e.g., impedance measurements and the analysis of discharge/charge curves. Information about the morphology of solid components (sulfur, carbon, Li-Sn, Li-Si), like density, volume fraction, specific surface area, and particle size, will help in the development of the microstructural models. Here, input from ex-situ characterization from experimental work packages (SEM, TEM, BET) is required.

Modelling

in M3-2S 213600

Subject of the modelling

Load bearing capacity of nano/micro-scale multi-layered films (TiN, CrN and NbN) for improving the wear resistance of tools (e.g. for cutting)

Models used

Atomistic: Molecular Dynamics for coating deposition
Mesoscopic: (called "Atomic") lattice modelling for the breaking and forming of atomic bonds for the prediction of dislocation generation and crack nucleation and growth in the coating materials
Continuum: Discrete dislocation plasticity modelling to link the crystal plasticity scale and the atomic finite element scale
    diffusion model at the component scale

Simulation software and type of numerics used

The combined system linking the scales was implemented in a novel surface load-bearing expert software system integrated with DEFORM FE software to predict the load bearing capacity of the multilayer coatings.
virtual grain structure generation by controlled Poisson Voronoi tessellation

Achievements of the model beyond experiments

The multiscale modelling system for multilayers can predict crack initiation based on nano- and micro-mechanics, in particular so-called ring cracking, consistent with what is observed in experiments under load bearing scenarios. These predictions can then be used to evaluate the load bearing capacity of a coatings system, allowing virtual design of multilayers. This is not feasible using experiments as it would require a very costly and time consuming trial and error design approach.

Application

Coatings, manufacturing, surface engineering

Relevant review articles

Z. Xu, Y. Li, D. Shan and B. Guo, Computational Materials Science, 20(2011), 1432-1436.
R.Neuge-bauer, R.Wertheim, U.Semmler, Journal of Multiscale Modelling, 3(2011), 91-107.
J. Feng, Y. Qin, Q. Zeng, E. Almandoz, G. Fuente, H. Dong, Raghavan and J. Michler, Journal of Multiscale Modelling, 3(2011), 1-22.

Summary of the project

Currently, the design of multilayered surfaces (MSSs) in engineering components is normally based on experience and surface modelling techniques are needed to explain and avoid surface related failures in engineering components. The aim of this project is to address an urgent scientific, technological and market need for consistently reliable high performance MSSs, by developing generic, robust multiscale materials and process modelling techniques for the design, optimisation and performance prediction of MSSs.

Summary of the modelling

The goal is to develop an integrated multiscale modelling approach to link molecular dynamics crystal plasticity and continuum mechanics modelling activities for the applications. Molecular Dynamics techniques have been applied to model atom deposition processes and the atomic structure and interfaces to achieve optimal coating microstructures. The MD method was used to simulate the formation of lattice structures of coatings and layer interfaces in thermo-chemical processes and the results was used as input for nano- and micro-mechanics modelling for defining material structures.

Continuum diffusion models are used to simulate such processes as plasma nitriding, plasma carburising and plasma nitrocarburising. These surface modification processes have been widely used in the design of multilayered surface systems to improve their load supporting capacity. The outcomes have been used to define material structures as inputs for mechanics analysis.

New physically based constitutive equations based on evolving microstructural state variables (e.g. dislocation density) were developed to predict damage, hence load bearing, in MSSs. These incorporated with the newly developed controlled Poisson Voronoi tessellation technique for generating virtual grain structures allows load bearing capacity of polycrystalline films and multilayers to be predicted.

In parallel, we have applied mesoscopic(called atomic) and crystal plasticity FE modelling capabilities and facilities for predicting deformation and failure of individual layers of nano-/micro-coatings. The "atomic" lattice model is solved by finite element methods. Elements are used like bars or trusses. The behavior of the bar is described by an interatomic potential. This enables an atomic lattice to be modelled by a truss-like assemblage of members that deform according to a prescribed interatomic potential, which governs their relative separations under applied loading. A key feature of the atomic finite element method is that it results in a finite element equation with displacement degrees of freedom, hence an atomic finite element mesh can be directly coupled to other element types and larger scales. Discrete dislocation models were also used to model at scales between the atomic and crystal scales, with concurrent coupling.The lattice structure of coatings, atomic mismatch and dislocations at layer interfaces modelled at the atomistic level is used for the FE models.

Therefore, an integrated technique to determine mechanical properties of nano- and micro-scale coatings has been developed. Application software packages will be developed and attached to commercial FE codes for the analyses.

www.m3-2s.bham.ac.uk

Modelling

in M3d 309589

Subject of the modelling
Micromagnetism in nanostructures

Physics/Chemistry models used
Mesoscopic: "macro-spin" models and "micromagnetism".

Simulation software and type of numerics used
Mesoscopic and Continuum: inhouse

Achievements of the model beyond experiments
Provide quantities not achievable experimentally: distribution of magnetization below the spatial or temporal resolution of existing microscopes; 3D distribution of magnetization, while relevant microscopes provide 2D maps; magnetic energies to estimate the most probable distribution (no experiment may measure a magnetic energy); compare a situation with defects from a perfect situation, and its impact on the behavior, to analyse experiments and decide whether the properties are determined/limited by defects or are intrinsic; quick analysis of expected behaviors before designing structures, to spare time in the development.

Application
Magnetization switching and the motion of magnetic domain walls under a magnetic field

Relevant review articles covering the topic

A convergent and precise finite element scheme for Landau–Lifschitz–Gilbert equation, F. Alouges, E. Kritsikis, J. Steiner, and J.-C. Toussaint, Numer. Math. pp. 1 24 (2014), ISSN 0945-3245, URL http://dx.doi.org/10.1007/s00211-014-0615-3

Summary of project
The project aims at developing material solutions for storing and reading data in a 3D medium, with a view to increase storage capacity beyond currently-used 2D media (hard disk drives, flash, optical disks). The project is concerned with magnetic materials organized in essentially one-dimensional, densely packed structures. Information may be recorded <code means sofwtre code in the modelling world>based on local changes of direction of magnetization along the 1D structures, for example magnetic domain walls in continuous wires. Modelling tackles the expected type of domain wall, their motion under e.g. magnetic fields, their interaction with defects and local notches to make a digital medium.

Summary of the modelling
The project is developing and using macrospin and micromagnetic models. Micromagnetism models based on the Landau-Lifshitz-Gilbert equation is used when the knowledge of the exact and continuous distribution of magnetization is required. Input are material magnetic parameters (magnetization, magnetic anisotropy, exchange stiffness, damping, gyromagnetic ratio), mostly based on text-book bulk values or measurements (eg for magnetic anisotropy). Other input is geometry (size and shape) and possibly stimulus (e.g. applied magnetic field).
Output is phase diagrams of domain wall and soliton type, mobility of domain walls and solitons, working parameters against external field. Wires of diameter in the range 20-200nm are modeled, possibly with local modulations of diameter, with open boundary conditions so as to act as infinite wires.
The micromagnetism model calculates the vectorial distribution of magnetization inside a system, and its associated properties such as energy. The project is modeling both static distributions and their temporal evolution, with a typical time scale ranging from some tens of ps to a few nanoseconds in order to determine which magnetization distributions and domain walls occur, and at which magnetic field they move, and with which speed. The output consists of phase diagrams of domain wall and soliton type, or graphs of mobility of domain walls and solitons, working parameters against external field.
With this it is possible to design robust schemes how the recording (stored information) may be propagated.

Modelling

in MACADEMIA 228862

Subject of the modelling
Metal organic frameworks (MOFs) for separation of gases and liquids
Catalysis

Models used
Electronic: Density Functional Theory (Kohn-Sham method) and post Hartree-Fock models
Atomistic: Molecular Dynamics, QM/MM and Grand Canonical Monte Carlo (GCMC)
Continuum: Thermodynamic models: multi-scale mass transfer models (bed/pellet/crystal scale) and
heat transfer models (bed scale) for adsorption.
process model: Simulated Moving Bed and Pressure Swing Adsorption

Simulation software and type of numerics used
VASP & TurboMol softwares for DFT
DL_POLY software for molecular dynamics
In-house & MUSIC software codes for Monte Carlo simulations (statistical techniques)
In-house numerical simulation packages with Matlab software:
Ideal Adsorbed Solution Theory (IAST), Real Adsorbed Solution Theory (RAST), Heterogeneous Ideal
Adsorbed Solution Theory HIAST and the Vacancy Solution Theory with different models of activity
coefficients: Flory-Huggins (VST-FH) and Wilson (VST-Wilson)
COMSOL and Matlab softwares for transfer models
PC-based clusters used for parallel computing under Linux Operating System
In-house numerical process simulation tools including the Linear Driving Force strategy.

Achievements of the model beyond experiments
The modeling avoided time consuming and costly experiments characterizing the adsorption
performances of a large set of MOFs and thus allowed the fast identification of promising novel MOFs for
a given application. For example, the simulations led to the discovery of a simple rule that allows quick
assessment if a MOF is suitable for xylene separations. This reduces the number of time consuming
experiments. Furthermore, a screening strategy was developed to predict the separation properties of a
large number of MOFs for N_2/CO_2 and CO_2/CH_4 mixtures.

Application
Industrial separation processes for gases, vapours and liquids as well as catalysis

Relevant review articles
Tina Düren, Youn-Sang Bae, Randall Q. Snurr "*Using molecular simulation to characterise metal-organic
frameworks for adsorption applications*", Chemical Society Reviews, 1237-1247, 2009
G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P.L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi & J.
S. Chang, "*Why hybrid porous solids capture greenhouse gases?*" Chemical Society Reviews 40, 550,
2011

Summary of the project

The project MACADEMIA addresses the development of specific, energy saving processes for separation of gas and liquids, and catalysis with reduced environmental impact. These processes are to be optimised via the use of improved Metal Organic Frameworks (MOFs).

Summary of the modelling

The material/process properties modelled in MACADEMIA are:
• Thermodynamic and kinetic selectivity of the materials for gas/liquid mixtures
• Catalytic activity of the materials for a series of reactions and the resulting mechanisms.

Density functional theory (DFT) is used to characterise the chemisorption processes occurring at the surface of open metal centres. Chemisorption is an adsorption process where at least one partially covalent bond is formed between the adsorbate and adsorbent. The particular functional to be used most will be described with the PBE exchange-correlation density functional corrected within the DFT/CC correction scheme.

The catalytic activity of MOFs is explored regarding reactions catalysed by Lewis acid sites, using either traditional post-Hartree-Fock methods (e.g. MP2 or CCSD(T) methods) on cluster models or periodic DFT calculations. For larger systems, a combined quantum mechanical/molecular mechanical (QM/MM) model will be also employed to give the reaction path and relative energies of stationary points on the reaction path.

Classical simulations including Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) are used to fully characterize the selectivity and transport properties of different MOF materials with respect to the different liquid and gas mixtures. Both MD and GCMC are conducted using rigid or flexible force fields. Output generated from quantum calculations (DFT-CC) are implemented in the classical Grand Canonical Monte Carlo simulations to more accurately describe the adsorption phenomena when specific interactions occur at open metal sites that cannot be treated using generic force field. Furthermore, equilibrium and non-equilibrium MD simulations provide additional information on the molecular diffusion mechanisms of the separation processes in both liquid and gas phases. To support the experimental high throughput screening complementary Monte Carlo computational screening tools were developed that allow to get a realistic, first assessment if a MOF is promising once its structure is determined and therefore whether the synthesis should be scaled up for further experimental tests.

Thermodynamic models such as ideal adsorbed solution theory (IAST) , heterogenous ideal absorbed solution theory (HIAST) or Vacancy Solution Theory (VST) are employed to predict the equilibrium adsorption of mixtures from single component isotherms and thus their selectivity for a series of gas mixtures.

Continuum modelling are used to evaluate the materials on the process scale and to predict material behaviour and ageing in real applications. Macroscopic modelling includes the Simulated Moving Bed and Pressure Swing Adsorption for different separation processes (propane/propene, acid gas....). It is possible to:
   1) predict the performance parameters of the process: productivity, product purity/recovery, energy consumption;
   2) size the pilot/industrial scale process for a preliminary technical evaluation;
   3) compare the experimental results provided by industrial tests with simulated data.

www.macademia-project.eu

Modelling

in MAGNONICS 228673

Subject of the modelling
Nanostructured magnetic (magnonic) metamaterials with GHz and THz dynamics and/or with unusual electromagnetic properties (negative permeability in certain frequency ranges, band gaps in magnonic dispersion etc).

Models used
Mesoscopic: Spin dynamics: micromagnetic simulations based on the Landau-Lifshitz equation for computing magnetization dynamics in the time-domain and band gap gap and effectively continuous properties describing excitations in magnonic metamaterials consisting of patterned magnetic nanoelements
Continuum: electromagnetics Plane wave method (PWM) for the calculation of magnonic Spectra for full Maxwell equations with account of ferromagnetic resonance phenomena

Simulation software and type of numerics used
Finite-difference (MicroMagus, OOMMF) and finite-element (Nmag)
Dynamical matrix method for dipole-coupled magnetic nanoelements and arrays of antidots
Simulations of ordered and disordered systems of single-domain fine magnetic particles taking into account the magnetodipolar interparticle interaction
MatLab based solution of Maxwell equations
Matrix diagonalization

Achievements of the model beyond experiments
Numerical simulation of quasistatic magnetization processes explain measurements by MOKE and of spin-wave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of nanoscale magnetic dots and antidots. These simulations facilitate explaining the nature and spatial structure of magnons in the magnonic arrays.

Application
Electromagnetic antennas (e.g. patch antennas), and signal conditioning devices (e.g. microwave filters); magnonic devices and logic architectures, including magnonic filters, logic gates, programmable gate arrays.

Relevant review articles
V. V. Kruglyak, S. O. Demokritov, and D. Grundler, "Magnonics", J. Phys. D – Appl. Phys. 43, 264001 (2010); S. - K. Kim, "Micromagnetic computer simulations of spin waves in nanometre-scale patterned magnetic elements", J. Phys. D – Appl. Phys. 43, 264004 (2010).

Summary of the project

The project aims at creation of materials with artificial structures - so called metamaterials – having the GHz and THz excitation spectra with prescribed features (peaks and band gaps in given frequency regions). With respect to long wavelength spin waves, the artificial nanostructures will behave as effectively uniform and have effectively continuous magnetic properties not seen in nature. For short wavelengths the material will show band gaps.

Summary of the modelling

MAGNONICS focussed on the comprehensive theoretical understanding of the band gap and effectively continuous properties of the created magnonic metamaterials.

The electromagnetics plane wave method (PWM) has been used for the calculation of magnonic band structure of thin slabs of 1D and 2D magnonic crystals and validated via comparison with experimental results. The PWM has been applied to the calculation of magnonic spectra of antidot lattices and used to interpret experimental data acquired using broadband microwave spectroscopy and BLS.

Thermally excited spin waves in planar one- and two-dimensional magnonic crystals have been studied using both conventional (k-vector resolved) and micro-focused (spatial resolved) BLS measurements in arrays of dense magnetic elements (dots and stripes) and antidots (periodic arrangement of holes embedded into a continuous magnetic film), and the results have been compared with calculations performed by micromagnetic simulations.

> The 3-dimensional (3D) version of the Fast Fourier technique (FFT) for calculating the magneto-dipolar interaction field in continuous ferromagnetic structures has been implemented, so that large-scale simulations of 3D micromagnetic problems have become possible.
> A numerical technique, the dynamical matrix method has been used to deal with dipole-coupled nanoelements and arrays of antidots and to evaluate the BLS cross section. It has been applied to systems experimentally investigated within the project: chains and 2D arrays of magnetic dots, square arrays of antidots.
> The combined Ewald-FFT method for the calculation of the magneto-dipole interaction field in ordered and disordered systems of fine magnetic particles has been applied. In particular, this method enables highly efficient numerical simulations of magnetization processes in magneto-ferritin-based crystals.

Numerical simulation of quasi-static magnetization processes measured by MOKE and of spin-wave excitations observed by FMR, BLS, and TRSKM techniques in 2D arrays of magnetic nanodots have been performed. These simulations allow to explain the nature and to find out the spatial structure of corresponding magnons in the nanodot arrays under study.

www.magnonics.org

Modelling

in MAO-ROBOTS 246274

Subject of the modelling

Methylaluminoxane (MAO) activator in catalytic preparation of polyolefins

Physics/Chemistry models used

Electronic: DFT and ab initio quantum mechanical (or first principle) models and higher level ab initiomethods

Simulation software and type of numerics used

Electronic: Turbomole and Gaussian

Achievements of the model beyond experiments

The structure of MAO activator is not known from experiments. Structure elucidation was made possible by quantum chemical calculations, systematically following the reaction steps involved in synthesis of MAO. The obtained understanding of the MAO structure also explained the need for hundred or thousand fold excesses of MAO with respect to the transition metal complex used as a catalyst in the process, as only certain types of sites in the MAO structure were demonstrated to show catalytic activity. The conclusions could not have been reached without the aid of electronic modelling.

Application

Catalytic process

Relevant review articles covering the topic (not necessarily their own):

Zurek, E.; Ziegler, T. *Prog. Polym. Sci.* **2004**, *29*, 107-148.
Ziljstra, H. S.; Harder, S. *Eur. J. Inorg. Chem.* **2015**, 19-43.

Summary of project

MAO-ROBOTS develops a molecular factory for industrial polyolefin (PO) production.
The objective is to create MAO building blocks with a narrow molecular weight distribution and optimum nanostructure in terms of their activation efficiency. The project wants to establish the basis for reproducible production of MAOs and newly designed molecular PO factories and to develop methods for quality control of the polyolefin production process in the molecular PO factories on a laboratory scale.

Summary of the modelling

The project employed quantum chemical calculations, which were carried out with higher level ab initio models (DFT and MP2), taking electron correlation into account. The high accuracy of the models was necessary due to the difficult electronic structure of the MAO activator. We systematically followed the reactions leading to the formation of the MAO, producing the structure and energy of the MAO as an output. The structure was used as an input for the next reactions. Repeating the process resulted in more than 5000 structures for MAO. The energies of the structures that were obtained as the output were compared to deduce the most likely structures for MAO. For the most likely structures we studied the catalyst activation reactions (DFT and MP2), giving reaction energetics as the output.

Modelling

in MASTER 212257

Subject of the modelling

Spin wave excitation by spin-polarized current and spin-diffusion effect in normal metal near a junction

Models used

Mesoscopic: [Micromagnetic model](#)

Simulation software and type of numerics used

Micromagnetic package SpinPM, a generalized Landau Lifshitz Gilbert solver based on 4th order Runge-Kutta scheme with INTEL MKL FFT acceleration. It integrates:

Plug&Play user-friendly GUI
FFT-accelerated magnetostatics
time integration using 4th order Runge-Kutta solver
time step auto-adaptation
very flexible system definition
Spin Transfer Torque with both Slonczewski and Field-like torques

Achievements of the model beyond experiments

The model can predict the magnetization dynamics in an array of hetero-structures. These dynamics cannot be computed analytically. These simulations are used to optimize the design of spin devices as optimization by experimental means would be too costly.

Application
Mobile and wireless telecommunication technology
Spin torque devices

Relevant review articles

A.V. Khvalkovskiy, KAZ, et al Phys. Rev. B. 80, 140401(R), (2009)
A. Chanthbouala, AVKh, KAZ, et al., Nature Physics 7, 626 (2011)
A. Dussaux, AVKh, KAZ et al., Nature Com. 1, 1 (2010)
A.D.Belanovsky, KAZ, et al, Phys. Rev. B 85, 100409(R), (2012)

Summary of the project

MASTER is to explore microwave signal generation for integrated microwave components and wireless communications systems. The so-called Spin Transfer Nano-Oscillator (or STNO), can provide solutions to miniturization and broad-range microwave detection due to their specific spin polarized transport properties. This project aims at exploiting the coherent coupling within and between devices developed in large array to improve the microwave performances in terms of phase noise, emission power and to operate in different frequency ranges.

Summary of the modelling

The application of existing [micromagnetic](#) packages allowed us to reveal the influence of geometry and structural defects upon the STO phase diagram, phase-locking performance, and line width, and to create a virtual prototype of the STO array with optimized properties. The role of the thermal fluctuations in the phase-locking mechanism has also been investigated within the framework of a full scale 3D micromagnetic model, allowing the optimization of the array. Magnetization dynamics have been investigated in polycrystalline films, with the parameters of magnetic materials being distributed randomly over the crystallites. The model has been elaborated with the Berger / Slonczewski transport term. The code SpinPM simulates spin current-related effects and an extension that includes spin transfer-induced torque has been developed.

The project also developed a simple theoretical framework for transport in magnetic multilayers, based on the Landauer-Büttiker scattering formalism and random matrix theory. A simple transformation allows one to go from the scattering point of view to theories expressed in terms of local currents and the electromagnetic potential. In particular, the theory can be mapped onto the well-established classical Valet-Fert theory for collinear systems. The scattering formalism as our starting point and develop a theory which fully captures Valet-Fert and (generalized) circuit theory. The theory, referred to as C-RMT (for Continuous Random Matrix Theory), can be tabulated by the same set of (experimentally accessible) parameters as Valet-Fert. C-RMT will be included in the micromagnetic solver.

The projects also enhanced the micromagnetic numerical solver.The code has been elaborated to be able to deal with high simulation volume (up to few micrometer big lateral sizes), non-regular structure (multilayered structures), non-regular dynamics (very short-wavelength modes are excited), and huge computational times (> 50 ns). Features to define the structures and to help the analysis of the magnetization dynamics of the system have been added. The most important improvements in the software SpinPM are:
New time integration algorithm based on an integration procedure that includes an adaptive time-step control with a 4th order Runge-Kutta method
New exchange energy calculation algorithm: a new, energy-conserving, numerical algorithm has been developed and implemented allowing very simulations on very long time range
Fine system specification allowing much better flexibility in object specification
Spectra calculations: This tool provides us with a possibility to calculate these spectra for a batch of projects

Modelling

in MATRANS 228869

Subject of the modelling
Properties and behaviour of metal-ceramic functionally graded materials (FGM) (alumina ceramics and copper or Ni-Al intermetallics) at the stage of processing and under service conditions

Models used
Continuum:
- macromechanics models with phenomenological constitutive equations for materials behaviour (processing induced thermal residual stresses and material damage; static and dynamic fracture; thermomechanical fatigue)
- micromechanical models (modelling of wear, including shape evolution and coupling with oxidation) for effective thermomechanical properties

Simulation software and type of numerics used
Abaqus, ANSYS AceFEM and FEAP for micro and macro-mechanics
FE^2 for multi-scale thermomechanics modeling
Numerics
  Finite elements with three dimensional automatic mesh generation (e.g. SCAN/IP SCAN/FE) coupled with micro-tomography digital images of real material microstructures
  Automation of finite element computations using symbolic algebra software (e.g. AceFEM)
  self-consistent method or the Mori-Tanaka method
  Multi-objective optimisation method to find the optimal composition

Achievements of the model beyond experiments
Most of the modelling in the project is done to replace the experiments, which are usually complex and costly or, in other words, the modelling predicts the materials' properties/behaviour which will be observed in experiments and thus shortens the development process.

Application
- Transport (aerospace and automotive), Energy

Relevant review articles
Y.C. Fung and Pin Tong. Classical and Computational Solid Mechanics, World Scientific, 2001.
P. Wriggers. Computational Contact Mechanics, Springer-Verlag, Berlin Heidelberg 2006.
G.W. Stachowiak (ed.). Wear - Materials, Mechanisms and Practice, John Wiley and Sons 2006.
R.M. Christensen. Mechanics of Composite Materials. Dover Publications, Mineola, New York 2005.
M.F. Ashby. Material selection in mechanical design, 4-th edition. Butterworth-Heinemann, Amsterdam 2011.
J. LLorca. Fatigue of particle-and whisker-reinforced metal-matrix composites. *Progress in Materials Science,* 2002 *(*47), 283
P.N. Bogdanovich, D.V. Tkachuk. Thermal and Thermomechanical Phenomena in Sliding Contact. Journal of Friction and Wear, 2009 (30), 153–163.
G.A. Maugin, Configurational Forces: Thermomechanics, physics, mathematics, and numerics. Taylor & Francis, NY, 2011.
S. Murakami, Continuum Damage Mechanics: A Continuum Mechanics Approach to the Analysis of Damage and Fracture. Springer, 2012.
L. Mishnaevsky Jr., Computational Mesomechanics of Composites, Wiley, England, 2007.

Summary of the project

MATRANS aims at developing novel metal-ceramic functionally graded materials (FGMs) for aerospace and automotive applications in exhaust and propulsion systems (e.g. thruster), power transmission systems (e.g. valves), and braking systems. The main objective is to enhance the mechanical properties of these materials through spatial variations of material composition and microstructure.

Summary of the modelling

Modelling of graded profile of FGMs (i.e. number of layers, their arrangement and volume fraction of metal and ceramic phases in individual layers) was approached as a transient thermo-mechanical problem of [continuum mechanics](#) with account of deformation and damage evolution depending on structural parameters variation.

Physical quantities involved in this analysis include temperature, stress, strain, yield and crack resistivity. The sample is subjected to different temperatures and mechanical loadings. As the outcome we obtain stress, strain and optimal ceramic phase distribution in the sample. The software used for numerical solution was AceFEM - a general finite element system for Mathematica, combining symbolic and numeric approaches.

The effective linear thermoelastic properties of the FGM constituent layers were modeled using the full set of conservation principles along with the constitutive equations that relate the mechanical and thermal properties of the individual (metal and ceramic) solid phases. Macroscopic properties of the heterogeneous material were derived from the phase and morphology data either analytically or numerically by using homogenisation techniques such as the self-consistent method or the Mori-Tanaka method.

To model nonlinear overall properties, the above micromechanical approaches were extended to a sequence of incremental problems, linearized using either tangent or secant stiffness moduli, and implemented numerically within the Mathematica package.

Calculated macroscopic properties depend strongly on the material composition. An optimal content of the ceramic phase was searched for, which would meet the required thermo-mechanical properties of the composite for the target applications. For this purpose, a multi-objective optimization problem of continuum thermomechanics was formulated and solved numerically. The relevant objective function expresses the distance between required effective properties and their micromechanical estimates.

Several existing constitutive models have been coupled in such a way as to assist in revealing the influence of various micro defects (pores, matrix cracks, debonding cracks at interfaces between matrix and inclusions) introduced during the manufacture of metal-ceramic functionally graded materials on their macroscopic properties. These models have been validated on Cu-Al_2O_3 metal-matrix composites and implemented as an external module in the commercial finite element code Abaqus.

A continuum model to calculate thermal residual stresses and damage in graded metal-ceramic composites, generated during the cooling phase of the sintering process, was developed and implemented numerically with FEM, making use of microstructural material data from micro-CT images and transforming it onto finite elements by means of SCAN/IP and SCAN/FE software. The material models used in the FEM computations are the three conservation equations with a linear elastic constitutive equation for the ceramic and an elasto-plastic constitutive equation for the metal phase. Numerical calculations of thermal residual stresses and the resulting material damage were done using FEAP and Abaqus programmes.

Processing-induced microcracking in metal-ceramic composites due to mismatch of thermal properties of the constituent materials was calculated by micromechanical models with configurational forces considered to be the driving forces of macroscopic cracks and defects. The parameters of the macroscopic constitutive equations were either obtained by measurements or by micromechanical modelling. The micromechanical models were solved on a grid of voxels representing either the metal or the ceramics phase of the composite with the microstructural data coming from micro-CT scans or from a randomly generated microstructure. A voxel based generation of three dimensional FE models based on Mishnaevsky (2007) numerical procedures was used in the computations.

A phenomenological model of contact wear has been formulated which provides a constitutive equation relating the local wear rate (wear volume per unit area and per unit time) to contact variables (contact pressure, sliding velocity, etc.) and material properties (e.g. hardness, composition of an FGM layer, etc.). The model is a generalization of the classical Archard wear model. The wear model is a part of the contact and wear problem in which the equilibrium equations (balance of linear momentum) are solved on a varying domain, and the evolution of the domain is determined by the wear model. Thus two problems are solved simultaneously: the deformation (contact) problem and the shape evolution problem. The main focus of the work is on development of a solution strategy based on an unconditionally stable implicit time integration scheme and on development implementation of efficient computational algorithms suitable for this class of problems. The finite element implementation and the computations are performed using the AceGen/AceFEM system. Efficient computational algorithms have been developed which are not part of the existing commercial FEM codes.

A phenomenological model of oxidation coupled with wear was proposed for the alumina-copper FGM developed for the brake disk application. The model gives the oxide mass evolution (the wear and oxide change rates) as function of temperature, contact stress and time. The model is based on experimental observations from Thermo-Gravimetric Analysis (TGA) at a given temperature, tribological wear test (ball on disk) and real surface topography measurement. The wear-oxidation process was solved using a two scale approach. The first scale is the macroscopic level, corresponding e.g. to the ball on disc test of a braking system, the second scale is the asperity microscale level. On the microscale Finite Element Analysis with thermo-mechanical coupling was used for the calculation of averaged wear-oxidation parameters. Finally, on the macroscale the evolution of shape, stress and temperature (affected by the wear-oxidation processes) was calculated using FEM (Abaqus).

Models of mechanical and thermal fatigue of the copper-alumina FGM intended for the thruster application were developed using micromechanical and continuum mechanics approaches. The low-cycle fatigue behaviour of composite is treated as a localized damage development phenomenon activated by applied cyclic loading. The modelling is based in part on the analytical analysis on the microscale of the representative cell, formed by a composite element of a specified size and particle volume ratio. The energy equations are formulated to describe the energy balance with account for the stress transfer between the brittle-particles and ductile-matrix with different possible scenarios of damage localisation. On the macroscale the numerical analysis by the FEM (Abaqus) is used in which the representative damage parameter is introduced affecting the stiffness moduli of the macro element. The predictive result of these models is a relationship between the number of loading cycles (fatigue life) and the critical stress/accumulated equivalent plastic strain sustained by the material.

A series of fully coupled linear thermoelastic models of brake disk demonstrator solved with FE techniques were developed and tested. The focus was on the optimal design of the brake disk and on simulation of mechanical strength. The effective material properties were used as input in phenomenological model.

A new constitutive model defining the relationship between tensile strength of functionally graded materials (FGMs) and volume fraction of ceramic phase has been developed to simplify complicated mechanical behaviour of FGMs.

In oxidation modelling a new constitutive relation has been proposed between the oxide growth rate and the surface temperature. Since the calculated macro temperatures are too low to allow for the oxidation, only closer look at surface asperities can provide the mathematical model for the experimentally observed oxidation phenomena. A user-defined FORTRAN code for the developed constitutive relation has been added to a commercial FE software.

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Modelling in

MembraneNanoPart 310465

Subject of the modelling
Nanoparticle toxicity, nanoparticle interaction with proteins and lipid molecules, cell membranes

Physics/Chemistry models used
Atomistic: Molecular Dynamics for nanoparticle interaction with protein and lipid molecules, and lipid membranes
Mesoscopic: Coarse-grained united-atom Molecular Dynamics for nanoparticles, protein molecules and lipids, Dissipative Particle Dynamics (nanoparticles, lipids, proteins), hybrid Lattice Boltzmann (solvent) + Langevin Dynamics (solutes – nanoparticles, proteins and lipids), Monte Carlo simulations.

Empirical models generated
Statistical (QSAR) model to calculate probabilities and concentrations of nanoparticles in different end states with respect to cell membrane

Simulation software and type of numerics used
Most simulations have been performed using the following packages:
Atomistic: Gromacs, MDynaMix (http://people.su.se/~lyuba/mdynamix/MDynaMix.html)
Mesoscopic: ESPResSo (http://www.espressomd.org) (LD, DPD, LB+LD), MOLSIM (www.fkem1.lu.se/sm) (Monte Carlo)
Software used to parameterize the coarse-grained model: MagiC: Software Package for Multiscale Modeling (https://code.google.com/p/magic/)

Achievements of the model beyond the scope of experiments
The following values can only be measured with difficulty, while modeling can give the answer:
- Prediction of the protein/lipid binding affinity for nanomaterials
- Prediction of protein orientation at the surface
- Prediction of the content of protein corona
- Prediction of nanoparticle adsorption energy at the cell membrane
- Prediction of nanoparticle uptake rates into the cell for different nanomaterials
- Prediction of nanoparticle end state upon interaction with the cell membrane

Application
nanomedicine to design nanoparticles for diagnostics and drug delivery; nanotoxicology;
complex fluids in food industry, pharmaceutics, or cosmetics

Relevant review articles covering the topic
1. A. P. Lyubartsev, Multiscale modeling of lipids and lipid bilayers, Eur. Biophys. J. 35, 53 (2005).
2. M. Praprotnik, L. Delle Site, and K. Kremer, Multiscale Simulation of Soft Matter: From Scale Bridging to Adaptive Resolution, Annu. Rev. Phys. Chem. 59, 545-571 (2008)
3. E. Brini, E. A Algaer, P. Ganguly, C. Li, F. Rodríguez-Ropero, N. F A Van Der Vegt, Systematic coarse-graining methods for soft matter simulations, Soft Matter 9, 2108–2119 (2013)
4. C. Peter and K. Kremer, Multiscale simulation of soft matter systems – from the atomistic to the coarse-grained level and back, Soft Matter 5, 4357-4366 (2009)
5. A. P. Lyubartsev, M. Karttunen, I. Vattulainen and A. Laaksonen, On coarse-graining by the inverse Monte Carlo method: Dissipative particle dynamics simulations made to a precise tool in soft matter modelling, Soft Materials, v. 1, 121-137 (2003)

Summary of the project
The central goal of our proposal is to describe and understand the molecular mechanisms of nanoparticle-cell membrane interactions, which is a crucial point in any predictive model of nanoparticle toxicity. The mechanisms of nanoparticle protein corona formation, the protective function of the membrane, nanoparticle uptake into the cell, and the effect of nanoparticles on the cell membrane will be simulated. From this information the toxicological impact will be deduced. The approach is applied to a range of common engineered nanoparticles, relating their physic-chemical properties such as size and shape, surface charge, hydrophobicity, and plasma protein binding affinity to the toxicological effects and develop a test suite allowing to make toxicity prediction on the basis of purely computational or limited in vitro screening tests.The prediction of the content of nanoparticle corona can be used in nanomedicine to design nanoparticles for diagnostics and drug delivery and in nanotoxicology to avoid adverse effects of nanomaterials.

Summary of the modelling work

<u>Nanoparticle interaction with biomolecules (blood plasma proteins, lipids)</u>

Atomistic
Application of atomistic Molecular Dynamics models will give binding energies describing the interaction of nanoparticles (of different types and sizes) with blood plasma proteins/aminoacids and lipid molecules and these binding energies will determine the formation of the NP corona.
These simulations will also give parameters for effective potentials for coarse-grained modelling expressed in the form of amino acid - NP and lipid – NP interactions. The "grains" in the mesoscopic models correspond to subsets of atoms appropriate for the selected scale of the model, in the simplest case residues/amino acids constituents of proteins and alkyl groups, phosphate or other headgroups of lipids. We will compute binding affinities of arbitrary proteins of known structure from computed energies of NP interactions with aminoacids in contact with NP surface. This model will be further verified by comparison with results of mean force potential calculations for a few selected protein types.
MD simulations also give protein-NP binding constants, which are plugged into more coarse-grained simulations, which are used to predict average composition of the corona for each NP type from the known concentrations of the different components of the blood plasma.

Mesoscopic
Coarse-grained **mesoscopic** models are also used to simulate, at a larger scale, the interaction between NPs and biomolecules (aminoacid and lipids) using the binding energies calculated by the atomistic models. Different levels of coarse-grained modelling, representing groups of atoms as unified objects, are possible depending on the length scales and associated quantities that

are of interest as mentioned above. At a relatively fine coarse-grained level, the entities may represent individual amino acids, while at a much larger length scale the individual object may denote a group of aminoacids or a complete folded protein or a nanoparticle, and with the associated effective force fields allow the investigation of particle size and surface curvature dependencies of adsorption of various components on the NP forming the corona.
We validate the mesoscopic models on formation of NP corona by carrying out large scale **atomistic** Molecular Dynamics simulations of a few selected proteins (albumin and globulins) in solution in contact with NP surface, and direct MD computations of the potential of mean force between the proteins and NPs. Successful test demonstrates validity of the approach of computation binding affinities of proteins from the interacting energies of constituent aminoacids. Further on, for simulation of NP corona formation with competition between the proteins, we use a mesoscale model with coarse-grained protein globules made with 1 to 5 hyperatoms to reflect the size and shape of the plasma proteins. We use the results of the LB–LD method: hydrodynamic radii and diffusion constants in the concentrated plasma and the results of the calculation of adsorption energies for parameterization of the mesoscale model.
We attempt to quantify the corona content for each particle types by two nanoparticle-plasma protein binding parameters: the fraction of surface covered with proteins in an equilibrium state and total molecular mass of the adsorbed protein per particle. We envisage these parameters to be useful in classifying the particles with respect to their biological activity. The developed model of NP-biomolecule interaction is being further verified by prediction of properties of corona: molecular weight of adsorbed

plasma protein for a few types of NPs, for which experimental data on corona composition, or protein adsorption rates are available.

NP-NP interaction and aggregation

Mesocopic
We will use a **mesoscopic** (CG Langevin MD) and Monte Carlo simulation of NP dispersion in plasma to calculate the potential of mean force for NP –NP interaction. The NP will be modelled as a single rigid body of finite extent, whose shape is approximated as being either a sphere or an ellipsoid or an appropriate polyhedron having a surface charge. Our model of the direct nanoparticle interaction will be based on the standard Derjaguin-Landau-Verwey-Overbeek theory and use only central forces. The dispersion medium in blood plasma and the cytoplasm will be modelled via implicit solvent, i.e. a continuous medium with the dielectric constant of water and the Debye length corresponding to physiological ionic strength. The protein interaction will be expressed via the potentials of mean force calculated with the MD models. The plasma proteins, including albumins and globulins and some smaller spherical globules, approximated as being fully folded, will be represented by (i) united atom bead-spring networks with one bead per aminoacid or (ii) proteins represented by rigid aggregate of 3-5 spheres parameterized to reproduce the dimensions and shape of the globule and the adsorption energy. This model will be able to include the most important interactions: electrostatic, van der Waals, and depletion forces between the nanoparticles. We will calculate the potential of mean force for a pair of nanoparticles as a function of centre-to-centre separation for spherical and ellipsoidal particles and as a function of separation and orientation for non-spherical ones using the standard technique: by fixing the particles at a certain distance/orientation and averaging the energy over the positions of the remaining particles.
We will use the mesoscopic model to further coarse-grain the system. A simulation of NP dispersion in blood plasma will be augmented with inverse Monte Carlo simulations to extract the potential of mean force between NPs. Once this is done also the NP aggregation and equilibrium cluster size distribution can be calculated. Depending on the dominating contribution to the NP-NP interaction, the NP dispersion can contain single NPs or their aggregates. We will be able to determine the stability criteria and cluster statistics and thus the most probable cluster size and cluster characteristics (size, shape and charge) for the main groups of NP at physiological (blood plasma) conditions.

NP interaction with cell membrane

Mesoscopic
We will perform a **mesoscopic** simulation of a NP interaction with a cell membrane in the plasma environment, represented by a surface with fixed lipid headgroups and grafted glycoproteins. The simplified cell membrane will consist of glycan chains bound to the lipids to reproduce the typical height of the polysaccharide layer, the grafting density and the molecular architecture, which includes the assortment of branched and straight chains. The lipid headgroups and glycans monomers will be represented at coarse-grained level as spheres (each denoting a residue) with neighboring residues (of the lipid) coupled by effective bonds, and other pairwise force field otherwise. At this point we will address in detail only the NP (considered as one entity) interaction with the membrane surface to estimate the kinetic barrier a NP would need to overcome to go through the glycocalyx and reach the lipid surface. The kinetic barrier will be used to calculate the resulting concentration of NPs that reach the lipid bilayer, given the concentration in the bulk. We will perform simulations for four main cluster size distribution representatives for each particle type at a set of fixed positions/orientations against the membrane and measure the potential of mean force for each NP type.
The final goal is to be able to predict the uptake of nanoparticles under prescribed biological conditions as a function of their physicochemical properties. A range of materials will be considered from the five main groups of NPs: carbon, metal, metal oxide, polymer, and semiconductors.
The mesoscopic coarse-grained model will be used to calculate the NP-membrane translocation kinetics, to assess the NP effect on the membrane, based on the observable properties: lipid pair distribution functions, bond order parameters, area per lipid, and mechanical properties of the membrane (compressibility and elastic moduli).
Two representations will be constructed of the (cell and cell nucleus) membrane including the essential mammalian cell membrane elements: saturated and unsaturated lipids (DMPC, DOPS), cholesterol, glycans, water, and membrane proteins:

a) bilayer composed of lipids and cholesterol only where the united-atom beads represent individual residues/amino acids. The simulation will be compared with the full atomistic model to validate the coarse-grained presentation and this simulation will use the improved lipid force field (S-lipids).

b) membrane including also the attached glycans and membrane proteins represented by three-segment hydrophilic-lipophilic-hydrophilic sphero-cylinders where each rigid body represent several adjacent residues.

NP translocation into the cell

Once the binding energies and properties of the membrane are known the penetration of small NPs through the cell membrane can be simulated to obtain statistics on penetration and the final state of the NPs after translocation (post translocation NP/Corona/Membrane restructuring).

Small NPs

First **atomistic** MD models will be used for the interaction and translocation of small NPs where the simulated system consists of NP, aqueous phase and the membrane. We will determine the potential of mean force (by pulling the NP through the membrane (calculating the force for each

position of the NP on a trajectory through the membrane) to verify that the observed trajectories are those leading to equilibrium NP states. This will be done for representatives of the five main groups of NPs. The result will help us to further validate the coarse-grained model.

We will perform simulation of the same systems with a **mesoscopic** Coarse Grained model using DPD method and compare the potentials of mean force. Corrections of the dynamic properties (DPD molecular friction coefficients and range) will be made if necessary.

To study the role of the membrane composition, we will perform all MD and CG simulations for three versions of the membrane:

> (i) purely saturated lipid bilayer (DMPC)
> (ii) bilayer composed of saturated and unsaturated PC (DMPC) and PS (DOPS) lipids with cholesterol molecules and
> (iii) without cholesterol.

In all of these cases, the coarse grained level of descriptions is the same, where each grain represents an individual residue/aminoacid. At an MD level, the description is fully atomistic.

Where the appropriate NP corona is relatively small we will simulate translocation including the NP corona and any hydration both spontaneous and driven, obtaining a full picture of small NP membrane effects as well as the final state of the NP following translocation and subsequent equilibration. In this way we will attempt to probe any post translocation NP/Corona/Membrane restructuring to compare with Task 4.3.

Large NPs

The energetics and time scales associated with systems consisting of large NP/corona/membrane interacting systems will be addressed using only the mesoscopic CG method.

We will model the approach of large NPs from the main five groups using the representative particle states for each group and particle size: the typical cluster sizes including the protein corona. The clusters will be set against the membrane with the attached glycans and inserted membrane proteins. At this point, we are planning to address only clathrin and caveolin-independent endocytosis, although the receptor-mediated or caveolin-mediated endocytosis might play an important role in the uptake of engineered NPs. In this case, the entities of the coarse-grained description represent at the finest level several adjacent residues/aminoacids, to that of entire folded proteins.

We will perform two types of simulations: a forced translocation at a fixed force and measurement of the potential of means force. One of the most intriguing questions that can be answered more easily at this level of modelling is the final state of the NP/NP cluster after it is brought into contact with the membrane.

We envisage the following main end states:

> 1. NP outside the cell in an unbound state
> 2. NP attached to the outer surface of the bilayer
> 3. NP included into the bilayer with a contact to the hydrocarbon parts of the lipids

4. NP penetrated the bilayer unchanged (preserving the same cluster configuration and corona)
5. NP lost the corona or changes the cluster state
6. NP enveloped by the lipids and enclosed in a liposome

The data for the potential of mean force for the NP-membrane system during the translocation process will then be used to construct the predictive kinetic models of NP penetration models. By comparing the free energies of different final states of the system, we will be able to predict the probabilities and calculate the concentrations of particles in each state using the Boltzmann distribution. Moreover, the calculation of the kinetic barriers will allow us to predict the fluxes, the state-to-state transition rates provided that the starting concentration – NP concentration in plasma just outside the membrane is known.

Modelling

in METACHEM 228762

Subject of the modelling

Characterisation of electro-magnetic properties of thin-film metamaterials with well-defined boundaries

Extraction of optical constants from measured optical data (variable angle spectroscopic ellipsometry, transmission, reflection, phase.)

Models used

Continuum: electromagnetism models:

Maxwell equations with boundary conditions and different types of sources (plane wave; wave port; Gaussian beam; point dipole, etc)

Models developed for extraction of bulk properties of the materials (mainly real and imaginary parts of permittivity)

Generalized Mie Model (GMM) of scattering by clusters of simple and core-shell spheres

Simulation software and type of numerics used

Ansoft HFSS

CST Studio Suite

Original analytical method of dynamic homogenization for so-called Bloch lattices

Original analytical method of dynamic homogenization for so-called metasurfaces

Fresnel modelling using commercial WVASE software, a corrected Sivukhin-Debye model

Integral equation approach and discretization of the surfaces with the help of GMSH,

Accelerations:

- Exponentially converging (and tabulated) periodic Green's functions.

- Compression of matrix of system of equations using the incomplete-QR approach

- Matrix reduction using multiple-scattering Macro Basis Functions

Achievements of the model beyond experiments

The model predicts whether the metamaterial can be described within effective media theory.

The model extracts parameters not directly measurable.

The model can determine individual polarizabilities of a complex scatterer (electric and magnetic), surface susceptibilities of metasurfaces (electric, magnetic and magnetoelectric), refractive index of the wave in a lattice and wave impedance of the wave in a lattice.

Application

Optical devices

Characterization of metamaterials

Relevant review articles

http://ec.europa.eu/research/industrial_technologies/pdf/metamaterials-review_en.pdf

Summary of the project

The objective of the METACHEM collaborative project is to use the extreme versatility of nanochemistry and the physical-chemistry routes of self-assembly to design and manufacture bulk meta-materials exhibiting non-conventional electromagnetic properties in the range of visible light.

Summary of the modelling

ElectroMagnetism theory and numerical simulations provide guidance for designs by calculating which materials, shape of particles and range of sizes can provide new metamaterial properties. The aim is also to understand the consequences of disorder (in size and position). The models will give the effective optical parameters of the metamaterial (refractive indices, thickness, bi-anisotropy, etc.).

Plane wave models are used for the extraction of bulk properties of the materials (mainly real and imaginary parts of permittivity).

The generalized Mie Model (GMM) is used to study scattering by clusters of simple and core-shell spheres and also for the study of gain media, in combination with appropriate periodic Green's functions.

Ansoft HFSS and CST Studio Suite are used for infinite-array simulations of periodic meta-volumes and meta-surfaces in combination with plane-wave models (see above) for the extraction of material parameters.

Integral-equation approaches are used for the accelerated analysis of large finite structures and structures made of complex inclusions (systematic reduction of complexity with "macro basis functions"). It easily allows for the computation of "point spread functions" (response of a metamaterial to a nearby localized source). This approach is used for fast infinite-array response of magnetic nano-particles, point-spread function of arrays of nanorods, and study of disorder in large finite arrays.

The transmission, reflection and ellipsometry spectra measured at different angles of incidence (ellipsometric data) are used to extract values of optical constants of metamaterial. The spectroscopic data will be also analyzed with the help of the Sivukhin-Debye approach, which has a much better accuracy than effective medium theories in case of small film thickness.

https://www.metachem-fp7.eu/

Modelling

in MINOTOR 228424

Subject of the modelling

Electronic phenomena at interfaces in organic-based electronic devices

Models used
Electronic:
  Hartree-Fock methods, DFT methods
Atomistic:
  Molecular Dynamics (MD), QM/MM, Monte Carlo algorithms,
Continuum:
  Classical electromagnetism (microelectrostatic models)

Software code and type of numerics used

Gaussian, Ampac, Fireball, VASP, SIESTA, Gromacs, Materials Studio, Tinker, NAMD

Achievements of the model beyond experiments

Modelling allows material design of multilayer devices with optimized proprieties as follows:
- The model has predicted the contributions to the discontinuity between the electronic structure at the interface and the bulk material
- The model explained the origin of the electronic level alignments at organic/organic interfaces as measured in short-circuit current and the open circuit voltage of solar cell devices, two key quantities that directly dictate the efficiency of those cells.
- The model has shown that modifying the surface of electrodes, can tune the charge or spin injection barriers in devices such as OLEDs.
- The model predicted the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties.

Application
OLEDs, transistors, sensors and storage devices, solar cells

Relevant review articles

"Electronic structure and geminate pair energetics at organic - organic interfaces: the case of pentacene/ C60 heterojunctions". S.Verlaak, D.Beljonne, D.Cheyns, C.Rolin, M.Linares, F.Castet, J.Cornil and P.Heremans. Advanced Functional Materials 2009, 19, 3809-3814
"Electronic Processes at Organic-Organic Interfaces: Insight from Modeling and Implications for Opto-Electronic Devices". D.Beljonne, J.Cornil, L.Muccioli, C.Zannoni, J.L.Brédas and F.Castet. Chemistry of materials 2011, 23, 591-609
"Barrier Height formation for the PTCDA/Au (111) interface" J.I.Martinez, E.Abad, F.Flores, J.Ortega, G.Brocks Chemical Physics, 2011, 390, 14-19.

Summary of the project

The main goal of MINOTOR is to develop a multiscale theoretical approach to model the interfaces in organic-based electronic devices and the electronic phenomena taking place at these interfaces in order to optimize the device efficiency. Organic electronics and spin-based electronics use organic conjugated molecules and polymers in multi-layer devices. Many key electronic processes (such as charge injection from metallic electrodes, charge recombination into light or light conversion into charges, spin injection) occur at interfaces and predictive models need to be developed to reproduce and fine tune new materials characteristics.

Summary of the modeling

The project applied modelling approaches to investigate electronic and structural properties at organic-organic, organic-metal, and organic-inorganic interfaces, in close conjunction with corresponding experimental measurements.
MINOTOR aimed at a multi-scale modelling approach ranging from the atomistic to the mesoscopic scale. In particular, the modelling could predict and explain:

- Changes in the work function of metal electrodes upon deposition of self-assembled monolayers or organic semiconductors using DFT calculations with Periodic Boundary Conditions (as implemented in VASP, SIESTA, FIREBALL)
- The nature of interface dipoles formed at organic/organic interfaces by modelling the morphology at the atomistic level with Molecular Dynamics simulations and by computing the electronic properties of model systems or aggregates extracted from the MD snapshots using semi-empirical Hartree-Fock techniques or DFT calculations validated against highly correlated CASSCF and MP2 approaches.
- The nature of the dipoles at interfaces between organic semiconductors and oxide layers (ZnO, TiO2) and the resulting shift in the workfunction of the oxide layer at the DFT and tight-binding DFT levels; realistic morphologies have also been generated at the MD level.
- The mechanism of free charge carrier generation in organic solar cells by computing the energetic profile of the charge carriers around the interface with a classical microelectrostatic model with all relevant parameters provided by quantum-chemical calculations.
- The mechanism of chemical doping of organic layers to yield enhanced conductivities by determining the energy landscape of the charge carriers with a classical microelectrostatic model. The goal of the calculations is to find the energy of a positive charge or negative charge localized on each individual molecule of a large cluster. To do so, classical electrostatic laws were used to estimate the dominant interactions (charge-induced dipole and charge
permanent quadrupole moment) with all relevant molecular parameters (polarizability tensor, molecular charge distribution, and quadrupole moment tensor) provided by quantum-chemical calculations In a next step, the charge carriers are propagated in the doped layer by means of Monte-Carlo simulations relying on hopping transfer rates (with all molecular ingredients provided by quantum-chemical calculations and the energetic disorder by the microelectrostatic model) in order to evaluate the density of free carriers.

Modelling

in MINTWELD 229108

Subject of the modelling
Welding processes of metal alloys

Models used
Atomistic: Ab-initio molecular dynamics (MD) with plane wave pseudo potential
Born-Oppenheimer molecular dynamics (BOMD), classical MD simulations, by using the abinitio
fitted EAM potentials, Molecular dynamics simulation of solid-liquid interfaces with newly
developed force fields.
Mesoscopic: Phase fields model
Continuum:
Thermodynamic modelling
computational fluid dynamics modelling

Simulation software and type of numerics used
Quantum-Espresso software
Potfit force-matching code to fit a new EAM potential to ab-initio forces
Finite Element Analysis
Front-Tracking method
Adaptive interpolation scheme that is suitable for phase field simulations of relevant systems

Achievements of the model beyond experiments
The software predicted the failure of components under in-service loading conditions. By
doing so, it accelerated the development of new welding fillers and processes and it thus
reduced costs.

Application
Manufacturing industry, metal alloys, welding, EAM (electric active materials) modeling

Summary of the project

The ability to weld a metal to itself (similar welding) and to other materials (dissimilar welding) strongly depends on the chemical segregation and morphology of the advancing solidification interfaces, in particular at grain boundaries where individual crystals meet near the weld centre. The advancing solidification interfaces and the resulting grain boundaries have critical nano- and sub-micron scale features. These boundaries have different alloy concentrations due to chemical segregation during solidification, and are the regions where failure most probably occurs by cracking during solidification of the weld pool (hot cracking) or by cracking in service (cold cracking), an example is hydrogen embrittlement. Cracking is the most common failure mode in welds, and many expensive failures have occurred in welded components. This project aims at producing an integrated suite of modelling software, with special emphasis on the solid-liquid interface evolution in industrially relevant systems, such as steel/steel and steel/nickel-based alloys.

Summary of the modelling

The computational aspects of this project aim at incorporating the realistic effects of alloy chemistry and process parameters in modelling the interface evolution during welding and the in-service failure of weld components. Multi-scale approaches which link atomistic ab-initio and Molecular Dynamic models (interface properties and issues of chemistry in the crack) with micro/nanoscale Phase-Field Models (grain boundary and interface chemistry and structure), and continuum Computational Fluid Dynamics models (heat and mass flow) are required to go beyond the current single scale model. The current challenge facing modelling of weld hot cracking is the use of existing models to describe the formation of the weld pool, the advance of the solidification interface, element segregation at the grain boundary and the influence of the welding process parameters and mechanical constraints that arise from the geometry of the work-piece. The project will use models for fluid flow, solidification, phase field and front tracking to provide thermodynamic, kinetic and element segregation information relevant to the solidification interface evolution and resulting grain boundaries. Ab-initio and molecular dynamics studies will provide surface and interface energies and develop new interatomic potentials of selected EAM. For the representation of the sample mesoscope Front-Tracking calculations (crystal growth, grain size distribution) are used.
This information will be combined within the framework of the variational principle to predict component life time.
Validation of the predictions will be ensured by novel experiments at each scale, including realtime synchrotron imaging to observe morphological evolution of the welding fronts, electron probe micro-analysis and atom probe to characterise alloy chemistry near grain boundaries.
Strategies for intelligent design of new weld materials with improved properties of the nanoorganized interfaces and grain boundaries will be developed and passed on to the welding industry.
Multi-scale structure integrity analysis is taking advantage of the continuum CFD, mesoscope grain structure modelling, micro-scale phase field modelling and atomistic modelling to provide thermodynamic, kinetic and element segregation information relevant to the properties and failures in welded components. It is hoped that this new approach can provide us a better understanding of physical process during welding and the welded components in use.

http://www2.le.ac.uk/projects/mintweld

Modelling

in MMP 604279

Subject of the modelling
Materials processing of copper-indium-gallium-selenide type thin film photovoltaic (PV) cells and of phosphor converted lighting systems (phosphor LEDs)

Physics/Chemistry models used
Continuum:
- Fluid Dynamics (CFD)
- Continuum mechanics and thermal models
- Computational thermodynamics
- Phase field models
- Optical models (scattering, ray-tracing)

Simulation software and type of numerics used
Continuum
- X-stream: Multi-physics CFD (finite volume)
- Comsol multiphysics (finite element)
- MICRESS: phase field software (finite differences)
- Optical modelling software: VTT in-house scattering code
- HOMAT (finite element)

Database
- CALPHAD thermodynamics database and interpolation software
- Thermo-Calc software package for thermodynamic calculations

Achievements of the model beyond experiments
The development and design of materials and systems for solid state lighting (SSL) and photovoltaics (PV) requires a structured product design methodology. Such multi-objective and multi-disciplinary optimization can only be realistically achieved by a combination of dedicated numerical approaches addressing proper physics at the proper length scales combined with some experimental input.

Application
Solid state lighting and photovoltaic applications in diverse fields, including ambient lighting, healthcare, textile integration and PV power plants.

Relevant review articles covering the topic (not necessarily their own):
Schmitz, G. J.,Prahl,U., ed. (2012). Integrative Computational Materials Engineering- Concepts and applications of a modular simulation platform. Weinheim: Wiley VCH Verlag. ISBN 978-3-527-33081-2.
J.R. Stewart, H.C. Edwards: A framework approach for developing parallel adaptive multiphysics applications, Finite Elem Anal Des, 40 (12) (2004), pp. 1599–1617
S.G. Parker, D.M. Beazley, C.R. Johnson: Computational steering software systems and strategies, IEEE Comput Sci Eng, 4 (4) (1997), pp. 50–59
J. R. Frisvad et al., Computing the scattering properties of participating media using Lorenz-Mie theory, ACM Transactions on Graphics, Vol. 26, Issue 3, Article No. 60, 2007
Hong Du, Mie-scattering calculation, Applied Optics, Vol. 43, No. 9, 1951-1956, 2004

Summary of project

MMP develops an open source platform for linking of continuum materials models applied to different scales and including multiphysics phenomena. The MMP platform interfaces to the computational tools and their libraries and to data repositories through dedicated modules. The platform design is generic, even though its use will be demonstrated on case studies involving only continuum based models. Its design allows to link and couple different models. The object-oriented design of platform uses metadata representations of properties, fields and functions, naturally hiding internal representation behind a common interface.

The strategy is to equip existing software and databases with general application interfaces (APIs). These APIs ensure compatibility with the MMP-platform and allow for data exchange and control. The API definition will be open, thus any software provider can build an API for their solution to achieve compatibility with the MMP platform. The general application interface of the MMP-platform will be based on the Multi-Physics Integration Framework (MuPIF); a prototype, open source integration platform.

In order to achieve a sustainable and flexible platform design, standardisation of metadata keywords and data structures is essential. Collaboration with other funded projects should ensure agreement on these keyword and standard interface definitions.

The MMP platform will enable the user to automatically execute simulation scenarios, i. e. problem specific process flows of the desired multiscale-multiphysics simulation. It sequences the required simulation services and specifies the timing of the individual simulation processes. This is especially important for parallel computing, and for iterative schemes required for convergence and optimization. Code linking is handled through dedicated algorithms embedded in the MMP-platform. These operations can be called in the simulation scenario.

Two case studies will be considered: the materials processing for photovoltaic cells and phosphor converted LEDs. These applications require linking of codes for the microstructure (phase-field methods) to continuum models for the macro and device scale. < you link codes, not results; microstructure is the result of a phase field model) Also the project involves multi-physics coupling of thermal and optical modelling.

Homogenisation and scale transitions

An embedded toolbox will be developed and implemented which enables the required scale transition relations, e.g. spatial mapping, interpolation and homogenization algorithms that transform spatially resolved information provided by models at lower scales of resolution to properties for models at upper resolution levels.

The homogenization and scale transition techniques will be integrated in the platform as additional applications. Such an abstract concept retains the plug-and-play design, allowing the combination of different simulation tools, scale transition algorithms, etc. In this sense the scale transitions are independent of the (numerical) solution technique (e.g. FEM, phase field, molecular dynamics, etc.) used to resolve one scale. The homogenization facilitates the calculation of an effective property based on a field in a finite volume, where interpolation generates a continuous field based on values defined in a finite number of points only. The sequencing of the analysis of the different scales is flexible in the platform, e.g. a fully nested solution can be obtained where the two scales are solved simultaneously, but also a consecutive approach where for example first the large scale and then the fine scale is resolved.

In order to achieve a sustainable and flexible platform design, standardisation of metadata keywords and data structures is essential. Collaboration with other funded projects should ensure agreement on these standard interface definitions.

In order to promote and diversify plug-in possibilities, the MMP platform will be distributed under an Open Source public license (for instance, GNU Lesser GNU Public License (LGPL)) that allows a broad distribution of MMP but protects the intellectual property encoded in the APIs (or glue codes) and service modules. The license should also facilitate the interfacing with commercial (or non-public) software, without disclosing the source code or intellectual property of this software, even in case a direct interfacing based on direct access to data fields and libraries is required.

Modelling

in MODENA 604271

Subject of the modelling
Multiscale modelling of polyurethane foams

Physics/Chemistry models used
Electronic: Density Functional Theory
Atomistic:
- Molecular Mechanics and Dynamics
- Molecular interactions model based on quantum chemistry derived charge density surface of molecules. The interaction model underlies a thermodynamic relationship for predicting chemical potentials in liquids (COSMO).
Mesoscopic:
- Dissipative Particle Dynamics
- Classical density functional theory applied to coarse-grained molecules
Continuum:
- Mean field statistical mechanics of polymer reactions, describing concentrations and molecular weight distributions as a function of time
- CFD (Navier-Stokes) for rheology and solidification
- Continuum Mechanics of liquid/particle mixtures to simulate foam walls
- Solid Mechanics to determine mechanical properties of foam
  The project makes extensive use of materials relations (closure relation)

Simulation software and type of numerics used
Electronic: Turbomole, Gaussian (DFT)
Atomistic:
- Materials Studio Forcite+ with COMPASS forcefield (MD)
- In house code to perform Monte Carlo simulations
- Cosmologic COSMO-RS to determine thermodynamic relations from the interaction model.
Mesoscopic:
- DPD in Materials Studio
- In house classical density functional theory code
Continuum:
- Predici: for polymerization kinetics.
- OpenFoam CFD software
- LAMMPS/LIGGGHTS (DEM)
- Abaqus FEM software and Hypermesh meshing (pre-processing) software
- TFEM (toolkit for the finite element method)
- In house CFD and Continuum Mechanics multiphysics codes with new constitutive equations describing foam bubble growth, rheology, heat transfer and acoustics of foams.

Achievements of the model beyond experiments
The design and production of industrial products based on polyurethane (PU) foams is still largely based on an extensive educated trial-and-error approach. As a result of the development and integration of models in the MoDeNa project, industry should achieve a significant reduction of costs, mainly by substituting experimental efforts by computing but also by integrating currently separate disciplines and knowledge basis. Key to achieving that goal will be the ability to search for appropriate production recipes based on a multiscale approach, but with feasible computational loads. The software will thus enable the development of better and new products and materials as well lead to more efficient production methods, whilst enhancing insight through the knowledge in the form of models and data.

Application
Polyurethane foams for a wide range of applications, such as automotive, coatings, construction, footwear, furniture and thermal insulation.

Relevant publications
Geier, S., Piesche, M. Coupled macro and micro-scale modeling of polyurethane foaming processes, Journal of Computational Multiphase Flows, 2014 6 (3), 207-220.
Geier, S., Winkler, C., Piesche, M. Numerical simulation of mold filling processes with polyurethane foams, Chemical Engineering and Technology, 2009, 32 (9), 1438-1447.
Toth, R., Santese, F., Pereira, S.P., Nieto, D.R., Pricl, S., Fermeglia, M., Posocco, P. Size and shape matter! A multiscale molecular simulation approach to polymer nano composites. J. Mater. Chem., 2012, 22, 5398-5409
W. Li, A.J. Ryan, I.K. Meier: Morphology Development via Reaction-Induced Phase Separation in Flexible Polyurethane Foam, Macromolecules 2002, 35,5034-5042.
Y. Zhao, M.J. Gordon, A. Tekeei, F.-H. Hsieh, G.J. Suppes: Modeling Reaction Kinetics of Rigid Polyurethane Foaming Process, J. Appl. Polym. Sci. 2013, 13,1131–1138.

Summary of project
Polyeruthanes are systems that are characterized by structures formed on many scales ranging from nano to macro, all of which make their contribution to the properties of the final product. There are multiple interactions between the various scale-related phenomena, which can be described by the linking of discrete and several continuum models applied to different scales. A typical industrial product design problem will require workflows encompassing a correspondingly wide range of models at different scales forming an intrinsically complex network of computational activities. The network models the material over the full width of scales with the higher-scale models recursively utilising models of the lower scale. Seen from the higher scale, the lower-scale models are usually computationally expensive and thus are replaced by simpler models as surrogates. These approximate models are preferably identified for the complete application range, or are constructed locally on the fly. Both approaches require the passing of information across the scales, which when going upwards is referred to as forward mapping, whilst performing the lower-scale computational experiments is called backward mapping.
The mathematical structure of the surrogate model is usually a parameterised phenomenological constitutive materials relation. The parameters of the surrogate model are obtained by fitting the surrogate model to input/output data obtained from the computational experiments on the original, complex model. The experiments are designed such that the surrogate model delivers optimal information with respect to the target physics/chemistry model.

The surrogate model approach also goes hand in hand with a meta-data approach for information exchange and a system-theory notation for the models, based on state, input, output and parameters as the theoretical basis. This is supported by an ontology, i.e. the information framework, that is needed to give meaning to the exchange, storage and handling of physics information implemented in the basic IT infrastructure. In this context, the project aims to contribute to a process of standardisation for multiscale materials modelling.

To handle the workflows, an open-source software-suite is constructed that links the different materials relations used for the design of polyurethane products according to a given computational recipe. The suite of software components consist of adaptors, instantiated models and solvers. The adaptors manage the input and output to the solver for a given numerical problem, which is the instantiated mathematical model with the model in coded form and the solver is instantiated to solve the specific mathematical problem. The event-driven software orchestrator then executes a given workflow, where the events, such as "start", "complete" the execution of a module, but also "request for application of new surrogate model" or "unable to locate solution" etc., provide the triggers for the computational tasks in the workflow.

The orchestrator is being built on Fireworks using the nonSQL database MongoDB. Fireworks is a product of the MIT/Berkley Materials project. The platform is generic within the context of event-driven co-ordination of tasks, i.e. can be extended and applied to other applications.

Modelling

in MODERN 309314

Subject of the modelling
Nanotoxicity

Physics/Chemistry models used
  Electronic: DFT
  Atomistic: MD

Empirical models generated
  QSAR and Neural Networks

Simulation software and type of numerics used
  Electronic: TURBOMOLE, MOPAC2012 and Gaussian09
  Atomistic: LAMMPS
  Software used to find an empirical model: "In house" developed code in R, MATLAB as well as Scientific Workflows such as RapidMiner and KNIME

Achievements of the model beyond experiments
  The benefits of the modeling approach in MODERN are twofold. First, the use of electronic and atomistic models provides estimates of the structure and properties of new nanoparticles without requiring their synthesis. Second, empirical models use the information above, together with experimental data for a reduced set of nanoparticles, to predict the bioactivity profile of new nanoparticles. The use of models allows going beyond the experiments by facilitating their optimal design (i.e., intelligent testing strategies) and by paving the way towards safe-by-design nanoparticles. The achievements of the models developed in MODERN can be summarized as:

- Electronic models: Trend analysis of properties related to electronic structure (e.g., HOMO, LUMO, IP, EA) relative to NP building blocks of increasing complexity.
- Atomistic models: Development of 40 size-dependent nanodescriptors (e.g., constitutional, related to potential energy, based on coordination numbers, based on lattice energies) suitable for QSAR modeling.
- Empirical models: Development and validation of QSARs for the cytotoxicity (endpoint data obtained via high-throughput screening) of metal oxide nanoparticles.

Application
Safe-by-design nanoparticles

Relevant review articles covering the topic (not necessarily their own):
- Liu R, France B, George S, Rallo R, Zhang H, Xia T, Nel A, Bradley K, Cohen Y. (2014) Association Rule Mining of Cellular Responses induced by Metal and Metal Oxide Nanoparticles. Analyst, 139: 943-953
- Gómez S, Fernández A, Granell C, Arenas A. (2013) Structural Patterns in Complex Systems Using Multidendrograms. Entropy 2013, 15(12): 5464-5474
- Liu R, Zhang HY, Ji ZX, Rallo R, Xia T, Chang CH, Nel, AE, Cohen Y. (2013) Development of Structure – Activity Relationship for Metal Oxide Nanoparticles. Nanoscale, 5(12): 5644-53
- Liu R, Hassan T, Rallo R, Cohen Y. (2013) HDAT: web-based high-throughput screening data analysis tools. Computational Science & Discovery, 6: 014006

Summary of project
The project focuses on the understanding of the processes governing the interactions of nanoparticles with biological systems and their associated mechanisms of toxicity, which are essential for eNP safety assessment. The main goal of MODERN is to establish new modelling approaches suitable for relating nanotoxicity with the intrinsic molecular and physicochemical properties of engineered NPs at environmental exposure levels and to implement safe-by-design nanoparticle design strategies. This implies three specific objectives: (i) To apply computational models for the characterization of the structural and physicochemical properties leading to QNPRs and safe-by-design strategies for engineered NPs; (ii) to develop in silico models (QNAR) of biological activity of eNPs in the body and in the environment; and (iii) to establish a categorization and hazard ranking protocol for eNPs based on structural similarity principles and in the analysis of their toxicological profiles.

Summary of the modelling
- Physics/Chemistry based models
  Type: Electronic model
  Input: Geometrical and chemical description of the building block.
  Output: Ionisation potential, electron affinity, chemical hardness, electronegativity, electrophilicity and the number of electrons the molecule would have to donate or to accept for an optimal level of electronic saturation
  Summary: Given the fact that whole nanoparticle systems are hard to model using pure quantum chemical methods we have developed a new approach based on the division of the whole nanoparticle structure into smaller building blocks. At startup, calculations for very small building blocks of nanoparticles (Fe_2O_3, Al_2O_3, TiO_2, SiO_2) being previously described in the literature were reproduced. As a starting point, initial calculations were performed with the DFT method B3LYP/def2-TZVPP for the smallest molecular building blocks of these nanoparticles. The performance of several methods employing different levels of theory has been compared including semi-empirical methods (PM6, PM7), ab initio Hartree-Fock-Theory (UHF), and second-order Møller-Plesset perturbation theory (MP2).

  Type: Atomistic model
  Input: x-ray crystal structure, ionic radii, radius of NP, interatomic potentials (Buckingham)
  Output: thermodynamically most stable crystal structures
  Post-processing:nanoparticle properties into nanodescriptors.
  Summary: MD models calculate the thermodynamically most stable crystal structures of various metal oxides. With these nanoparticle properties a number of nanodescriptors have been developed that take into account the size and shape of the actual particles, rather than just their chemical composition. The formalism has been currently implemented based on the LAMMPS software using Buckingham potentials for the calculations.

- Empirical model
  Type: Machine Learning (Support Vector Machine)
  Input: Conduction Band Energy and Ionic Index of metal cation (model for metal oxide NPs)
  Output: Probability of toxicity
  A classification nano-SAR was developed for metal oxide nanoparticles with a toxicity class definition derived based on both dose–response analysis and consensus Self-Organizing Map clustering. A nano-SARs was developed using a dataset of twenty-four metal oxide nanoparticles that provided a multiparametric toxicity profile for two different cell lines and seven different toxicity assays over a concentration range of 0.39–100 mg/L and exposure time up to 24 h. The nano-SAR (built with support vector machine model) was based on two descriptors, namely conduction band energy (EC) and ionic index (Z2/r), had a high classification accuracy of 93.74%.

Modelling

in MODIFY 228320

Subject of the modelling

Stress-induced deformation of pressure sensitive adhesive materials (PSAs) consisting of complex formulations of acrylic polymers

Models used

Atomistic: All-atom molecular dynamic models using force-fields from quantum-mechanics calculations and parameterization on the basis of experimental data.

Mesoscopic: Statistical Mechanics rheology model (in-house)

Continuum: Closed-form differential constitutive equation for the rheology of highly elastic polymer-based materials.

Non-equilibrium thermodynamics model for interfacial phenomena.

Simulation software and type of numerics used

LAMMPS software for MD

Molecular Dynamics structural code using the NPxxPyyPzzT statistical ensemble, where N denotes the number of interacting atomistic units in the system, Pii the normal pressure in the i-direction, and T the temperature

Mesoscopic (network) geometry representation based on particle-to-particle transient forces and chain-to-chain entanglements

In-house Statistical Mechanics mesoscopic rheology model

CFD rheology: In-house finite element code to solve the set of partial differential equations describing transport phenomena during the stretching deformation of acrylic adhesives at macro-scale accommodating several boundary conditions (slip, no-slip, generalized slip, etc).

The deformation equations were solved using (a) the mixed Galerkin/finite element method for the velocities, pressure and location of mesh nodes, and (b) the DEVSS-G with streamline upwinding method for the stress components.

Phase field formulations (in-house thermodynamics codes)

Achievements of the model beyond experiments

Modelling has explained the interplay between the chemical composition of the synthesized PSA samples and the degree, strength and life-time of the specific hydrogen forces developing in the polymer, which in turn governs the unique cohesive properties and strong elasticity of these materials. Models also explained the big role played by particle-to-particle transient forces on the elasticity-to-viscosity ratio which seems to be at the heart of the design task for new adhesives. Modelling explained the connection between bulk rheological properties in extension and shear and the debonding mechanisms during stretching of PSAs.

Application

Pressure sensitive adhesive materials for cosmetics, food, paints, and coatings

Summary of the project
MODIFY has developed a hierarchical modelling framework for soft nanostructured adhesives based on acrylic polymers. These codes address a multitude of phenomena governing the performance of PSAs in real applications: cavitation, diffuse particle-particle interfaces that can transfer stress, adhesion on hard substrates and slip at high levels of stretching, elasticity-versus-viscosity, density of hydrogen bonds versus density of chain entanglements, and degree of chain cross-linking.

Summary of the modelling
The modelling framework of the MODIFY project consists of the following components:
a) The GENERIC framework of non-equilibrium thermodynamics (phase fields) was first utilized and extended to handle mixed systems consisting of bulk regions and interfaces based on a specific treatment of interfacial fields built on the concept of gauge invariance to atomistic displacements of the interface. The outcome of this effort has been a new type of boundary condition for elastic polymers strongly adhered on hard substrates.
b) For the solution of equations of motion at the atomistic level in the presence of a flow field, a generalized non-equilibrium molecular dynamics (NEMD) algorithm was developed, capable of predicting nano-scale structural changes both in the bulk of an acrylic PSA and at the interface with a substrate. The LAMMPS software was equipped with potential energy functions of relevance to the chemistry of the PSA materials.
c) Information from the atomistic simulations was used to parameterize a continuum model describing the bulk rheology of the PSA systems specifically synthesized in the course of the MODIFY project using the Pom-Pom tube constitutive equation, and a mesoscopic statistical mechanics transport model based on a particle-based coarse-grained picture of the latex particles. The tube-based model enabled accurate empirical fits both of the linear and of the non-linear extensional rheology of the synthesized adhesives. The particle-based coarse-grained model enabled semi-quantitative predictions of their linear and non-linear rheology, using input parameters which were estimated from experiment, statistical reasoning, or more detailed (atomistic) simulations.

Constitutive equations
A macroscopic constitutive model was developed capable of describing quite reliably the deformation equations (e.g., the shear and elongational behaviour) of the synthesized PSA materials. The new equation utilizes generalized expressions for the strain energy density as a function of the three invariants of the conformation or deformation gradient tensor. In limiting cases, it reduces to known laws widely used to describe hyper-elastic materials, such as the Rivlin-Saunders and Hart-Smith theories.

Representation of the sample
An advanced geometrical code was developed to monitor moleculare structural changes upon stretching at the atomistic level; this code can compute the entanglement network, and provide information to higher-level models for the response of polymer acrylics to elongational deformation fields.

Numerics
A powerful finite-element code was developed for the full three-dimensional (3-d) simulation of the deformation of acrylic adhesives. It is based on a consistent coupling of an elliptic-mesh generation methodology with domain decomposition and local mesh refinement around deforming and moving interfaces. The transport code can follow the large adhesive and bubble deformations inside the material (which lead to fibrillation); it can also trace the elastic boundary layers that form at the moving interfaces. It can therefore reliably simulate the force-deformation history of the material under industrially relevant conditions. This is one of the biggest achievements of the MODIFY project.

<div align="center">http://modify.chemeng.upatras.gr/</div>

Modelling

in MONAMI 233513

Subject of the modelling
Molecular- and nano-magnetism, spintronics and magnonics
Quantum transport through materials at nano-scale
Magnetism

Models used
Electronic: [Density Functional Theory](#) and [quantum chemistry models](#) with exchange-correlation
  (XC) energy density functional for excited states and time-dependent phenomena
  [Dynamical Mean Field theory](#) to study material dependent properties of strongly correlated systems
  like high temperature superconductors
  [Tight-binding model](#)
Atomistic: simulation of physical properties of nanostructured materials, using [coarse-grained](#)
[models](#) with effective soft potentials: stochastic terms for essential motions and large-scale
structures

Simulation software and type of numerics used
RSPt: Matrix diagonalization and invertion, quantum Monte Carlo simulations
NMTO Wannier-like functions for bonding in intermetallic systems
VASP plane wave pseudopotential treatment, Fourier analysis
DALTON quantum chemical first principle theory

UppAS: Stochastic differential equation, Fokker-Plank equation

Achievements of the model beyond experiments
Modelling of materials properties allows the search for new materials or to make accurate
interpretations of observed materials phenomena. An example can be found for magnetic
materials where two properties are most important from an application point of view, namely
the size of the magnetic saturation moment at room temperature and a large magnetic
hardness (or synonymously, a large magnetic anisotropy energy – MAE). These two properties
can be predicted for any material, with an accuracy that is needed to make the search for
novel permanent magnetic materials much more efficient. The MONAMI project has also led to
a soft-ware which enables simulations of magnetization dynamics, where the dynamical
movement can be followed for each atom in the simulation, an ability which goes way beyond
experimental possibilities.

Application
Electronic and spintronic devices, sensors
Nuclear Magnetic Response probes of electrons in nanoscale system

Relevant review articles
Review of Modern Physics, 82, 1633 (2010); Nature Commun. 105, 1109 (2010); Analen der
Physik 523, (2011); Phys. Rev. Lett. 93 27203 (2004) and Phys. Rev. Lett. 96 037205 (2006)
Computational Materials Science 55, 295 (2012)

Summary of the project

The project develops novel techniques and paradigms concerning theoretical modelling of nano-scale advanced materials. An important aspect here is the ability to carry out this development all the way from idea and concept to working computer softwares. The project has made contributions to the application of a quantum mechanics - molecular dynamics response approach and made applications for calculations of large solvated systems (including more than 10,000 atoms) on their magnetic properties, EPR, NMR parameters, solvatochromism, and non-linear optical properties, like hyperpolarizability and two-photon absorption. In this methodology, the full quantum mechanical interactions are accounted for in the evaluation of a given property. Underlying structures and trajectories are obtained by molecular dynamics or Car-Parrinello methods. Results on protein environments have been obtained and a new technique for parameterization of the electrostatic and polarization interactions in such environments has been developed.

Summary of the modelling

The project did a study of V2O3 to validate a DFT model that was developed within MONAMI, and is a theoretical technique for calculating the effect of electron-electron correlations. The developed models are an elaboration of existing models to make the theory general to treat complex crystal structures like that of V2O3. To be specific, testing of models have been executed to see which one describes the measurements best: a so called N-th order Muffin-Tin Orbital (NMTO) software, with features like massive down folding, generation of Wannier combined, and dynamical mean field theory (DMFT) for the study of strongly correlated system, has been used to investigate the electronic structure of V2O3. Also, the development of a full-potential software with incorporation of DMFT has been completed. These theoretical analysis methods are geared towards calculations of spectral properties, which are important when analysing and interpreting the data now emerging from synchrotron radiation facilities and x-ray free electron lasers.

The development of an overlapping muffin-tin approximation (OMTA) transport code has involved replacing the condition of "tail cancellation" of muffin-tin orbitals (MTOs) with "kink cancellation" in an existing tight-binding MTO (TB-MTO) model so as to make maximum use of all of numerical features such as the extensive use of sparse matrix algorithms. The tail cancellation of orbitals goes long back to a paper by O.K.Andersen, in the 70'ies. It provided new physical insight in how electrons move around in solids, and how to best describe their quantum mechanical equation of motion. In the model developed in MONAMI, several conceptual steps and mathematical derivations have been made to come to a set of equations which enable a numerical implementation. The model now allows accurate and fast calculations of ground state properties of solids.

Non–newtonian dynamics was discovered to be necessary for nano-sized magnetic systems of particular symmetries. This was a discovery and/or a numerical result of a simulation tool which was developed under MONAMI, i.e. the UppASD stochastical simulation package for spin-dynamics. Simulations of nano-magnetism and the dynamical response of small magnetic clusters have been completed and revealed several unexpected phenomena.

http://www.iacs.res.in/monami/Home.html

European Commission

Modelling

in MORDRED 261868

Subject of the modelling

Nanoelectronic devices, oxide interfaces

Models used

Electronic: Density functional theory (DFT), electronic drift diffusion (DD) and non-equilibrium
  Green's function (NEGF) for electron transport
Atomistic: MD using force fields for dynamic charge transfer,
Mesoscopic: Statistical models: Monte Carlo (MC)
Continuum: compact models for electrical circuit behaviour

Simulation software and type of numerics used

VASP (DFT), CP2k (DFT)
GARAND (DD, NEGF, MC)
Pysic (Molecular Dynamics)
Mystic and RandomSPICE (for compact modeling)
Numerics: genetic algorithms, Bayesian statistics

Achievements of the model beyond experiments

Predict defect character and density that causes device breakdown in realistic environments
and over realistic performance times.
Characterize this for a variety of new, industrially untested materials.
Suggest routes for device design that should eliminate or reduce reliability problems

Application

Nanoelectronic devices, transistor and memory design, semiconductors.

Relevant review articles

Nature Insight: Silicon electronics and beyond, Nature 479, 309 (2011).

Summary of the project

Building upon fundamental analysis of the structure and electronic properties of relevant materials and interfaces at the quantum mechanical level, we will construct mesoscopic models to account for defect generation and impact on Complimentary-Metal-Oxide-Semiconductor (CMOS) transistor and circuit performance and yield. The models will provide detailed understanding of the common reliability issues and degradation routes of next generation devices. Results will be supported by comprehensive experimental characterization techniques.

Summary of the modelling

The project is performing calculations and characterisation of oxide/semiconductor interfaces in stacks and films.
First principles (e.g. DFT) calculations are used for calculation of interface electronic structure and the impact of defects.
Semi-empirical (classical) MD codes are used for e.g. dynamic charge transfer atomistic simulations, for calculations of the structure of large models of the oxide interface.
Statistical charge transport models are used to calculate statistical variability of electrical impact of defects and their behaviour as a function of applied bias and time. These are supported by NEGF and drift diffusion simulations directly modelling current within interfaces. The NEGF formalism provides a powerful conceptual and computational framework for treating quantum transport in nanodevices. It goes beyond the Landauer approach for ballistic, non-interacting electronics to include inelastic scattering and strong correlation effects at an atomistic level.
Electrical circuit compact models are semi-physical/phenomenological models of an active circuit component designed to perform high level circuit simulation. There are several variations of the models generally with over 100 Parameters, often tied to a specific simulation methodology.

This results in a realistic description of interfaces in gate stacks, based on combinations of high-k oxides with III-V (GaAs, InGaAs, InP) and IV semiconductors (Si, SiGe, Ge, graphene) and gate metals (TiN, TaN, Ru).
Schottky barrier performance and defects in new gate stack materials are calculated with these models with the goal of improving the reliability of CMOS devices. The thermal stability of defects in different charge states, gap states, optical, electron spin resonance and vibrational properties are calculated. The empirical defect potentials have been optimised using the output of DFT calculations (energy levels, adiabatic potentials, metastable states, vibrational properties). The main defects are associated with oxygen deficiency, interdiffusion of cations, hydrogen and dopants.
The calculated properties of grain boundaries in polycrystalline films, which serve as sinks for vacancies and impurities are used to calculate stress-induced leakage current breakdown mechanisms. Also the dynamic behaviour of the defects and impurities creation and annealing has been studied, in particular the most common defects as oxygen vacancies in their various charge states, dangling bonds at the interface, hydrogen bridges, K centres, etc.
Models and corresponding drift diffusion (DD), monte carlo (MC) and non-equilibrium Green's function (NEGF) simulation tools have been developed that can describe the statistical impact of bias temperature instabilities and hot carriers on the electrical characteristics of CMOS transistors. The simulations are 'frozen' in time. At a particular stage of the degradation process the areal density of defect states and trapped charges is transformed in random defect states and trapped charge distribution that will be introduced in DD, MC and NEGF simulation tools in addition to the initial variability sources. Methods to capture the impact of local defect generation in the gate dielectric on the statistical variation of the gate leakage current have also been developed.

https://webhotel2.tut.fi/fys/mordred

Modelling

in MULTIHY 263335

Subject of the modelling

Microstructure and mechanical properties of materials under the effect of hydrogen embrittlement

Models used

Electronic: First-principles DFT calculations for calculations of the energetics of hydrogen in bulk phases and around point defects
Semi empirical Tight Binding (TB) and Bond Order Potential (BOP) models for hydrogen interactions with extended defects
Mesoscopic: kinetic Monte Carlo simulations for hydrogen diffusion as function of defect distribution finite element models of hydrogen diffusion at the continuum, specimen and component levels
Continuum: Fluid Dynamics models of hydrogen diffusion at the continuum

Simulation software and type of numerics used

DFT (self-developed codes employing mixed-basis pseudopotential approach, VASP)
TB and BOP codes (self-developed), ElectricActiveMaterials-Potentials (LAMMPS)
Kinetic Monte Carlo (self-developed codes) for diffusion
Continuum mechanics (Abaqus, Comsol, Marc, self-developed codes) finite element for diffusion

Achievements of the model beyond experiments

Optimisation of the pulse-plating process used in the fabrication of the combustion chamber of the Ariane satellite delivery vehicle in a fast and efficient way.
Mechanistic understanding of the susceptibility of advanced high strength steels to HE by absorbed H that could not be provided by experiments alone.
Prediction of the influence of H on the fatigue lifetime of wind turbine bearings enabling the choice of materials.

Application

Materials for manufacturing, wind turbine, automobile industry, plates for rocket combustion chambers

Relevant review articles

S.M. Myers, M.I. Baskes, H.K. Birnbaum, J.W. Corbett, G.G. DeLeo, S.K. Estreicher, E.E. Haller, P. Jena, N.M. Johnson, R. Kirchheim, S.J. Pearton, M.J. Stavola, *Rev. Mod. Phys.*, 64 (1992) pp559-617
A. Pundt, R. Kirchheim, *Annu. Rev. Mater. Res.*, 36 (2006) pp555-608
I.M. Robertson, H.K. Birnbaum, P. Sofronis, in *Dislocation in Solids*, J.P. Hirth, L. Kubin (Eds.), Vol. 15 (2009) ch91

Summary of project

The aim of the project is to develop a modelling framework to predict the susceptibility of materials and components to hydrogen embrittlement (HE) under conditions representative of those actually occurring in the aerospace, automobile and wind energy industries. To achieve this, the description of H transport in modern advanced materials with complex microstructures is created, through a multiscale modelling framework.

Summary of the modelling

The key aspect of this project is the incorporation of atomistically-derived diffusion barriers for critical H trapping sites into continuum and component level models, and their application to real industrial problems involving HE.

The project is applying density functional theory (DFT) to the evaluation of energy barriers and binding energies of H in normal interstitial sites and around point defects, based on quantum-mechanical effects. Semi-empirical tight-binding models and classical potentials for the evaluation of H trapping at extended crystal defects such as grain boundaries and dislocations are employed.

The results will be used in mesoscopic kinetic Monte Carlo (KMC) simulations to evaluate the effective H diffusivities under different strain conditions and trap densities. The ultimate aim of the atomistic-KMC calculations is to develop a database of H diffusivities as a function of defect distribution, stress/strain and temperature. This database would serve as the input for continuum diffusion equation (solved by FE) of H diffusion that could be applied to full components. The models will be applied at the continuum, specimen and component scales using boundary conditions furnished by data collected in-service and from experimental measurements.

The continuum models will be based on novel set of constitutive equations for H diffusion capable of exploiting the information being derived from the atomistic calculations. The equations are more generalised than those commonly used in the literature, enabling the description of hydrogen diffusion under a broader range of conditions (e.g. temperature variations, trap occupancies) as before. The equations are being implemented on a number of platforms, including as bespoke codes and as subroutines in commercial fluid dynamics packages, e.g. ABAQUS. Possibilities for the licensing or commercialisation of these codes will be evaluated during the course of the project.

The modelling will be validated at all levels using advanced experimental techniques (in situ hydrogen permeation tests, thermal desorption spectroscopy, fractography).

The effectiveness of the proposed simulation framework will be demonstrated by investigating the role of microstructure in three contrasting industrial problems, which have been specified by companies involved in the development and application of advanced materials.

www.multihy.eu

Modelling

in MUST 214261

Subject of the modelling
Inhibitor release, self-healing mechanisms and nanocontainers, formation of containers with
membrane emulsification, multifunctional coatings

Models used
Atomistic: QM/MM
Mesoscopic: Dissipative Particle Dynamics (DPD) lattice gas model of the inhibitor/healing
agent
   release under mechanical impact.
Continuum: Multi-phase diffusion equations for water, ions, corrosion products and inhibitor
   particles in a multilayer anticorrosive film

Simulation software and type of numerics used
Software for MD calculations, force field Amber 99 – Hyperchem v.8.0, Crystal Maker
Gaussian 03 for QM/MM
Monte Carlo simulations – lattice gas algorithm for statistical mechanics
Finite Elements and Finite Differences simulation of diffusion
Mathcad 14.0

Achievements of the model beyond experiments
The model can be used do give recommendation concerning optimal composition and structure
of the coating to delay corrosion of metallic and polymeric substrates and structures, thus
reducing development costs.
The model predicts service-life time via the probability of the scratch healing or inhibition
based on the physico-chemical properties of the materials and realistic scratch geometries and
thus enables an optimal material choice without having to do extensive service-life tests.

Application
Coating and surface treatment of metallic and polymeric substrates and structures

Relevant review articles
Z. Tabor, et.al. .Water Diffusion In Polymer Coatings Containing Water-Trapping Particles,
Part 1. Finite Difference - Based Simulations, Progress in Organic Coatings. 75 (2012) 200– 206.
Małgorzata Krzak et. al. . Water diffusion in the polymer coatings containing water-trapping
particles, Part 2. Experimental verification of the mathematical model, Progress in Organic Coatings,
75   (2012) 207–214.
N. Filipovic A. Jovanovic et. al. . Modelling of self-healing materials using discrete and continuum
methods, Surface Coatings Int., 95 2012 74-79.

Summary of the project

The project MUST developed new active multi-level protective self-healing coatings and adhesives for future vehicle materials that improve the long-term performance of metallic and polymeric substrates and structures. These materials are based on "smart" release nanocontainers incorporated into the polymer matrix of current commercial products.

A nanocontainer (or nanoreservoir) is a nanosized volume filled with an active substance confined in a porous core and/or a shell which prevents direct contact of the active agent with the adjacent environment. The purpose of nanocontainers is to release the inhibitor before corrosion has happened (e.g. in case of presence of aggressive environment) or just after the corrosion has started. The role of traps is to delay corrosion agents reaching the protected surface.

Summary of the modelling

Two basic mechanisms of corrosion have been modelled. First, the diffusion of corrosive species (e.g. water, chloride ions) through the intact coatings containing traps and inhibitor nanoreservoirs has been modelled atcontinuum level by diffusion equations. Second, the release of inhibitor/healing agent from the microcontainers and its propagation upon the mechanical impact during formation of mechanical defects is modelled at mesoscopic with the analytical geometry representation and the DPD lattice gas model .

Constitutive equations for the active feedback and self-healing processes have been based on the experimental results obtained on nanoreservoirs and the nanocontainer-containing coatings providing the conditions of effective self-healing (self-healing rate higher than corrosion rate). This has been used to develop new nanocontainers. The constitutive equations can be used to determine the probability of successful healing, i.e. for evaluation of technical risks of application of multilevel protective coating.

Numerical approach for simulation of the layer-by-layer encapsulation process has been developed using combination of QM and MD calculations (QM/MM). Surfactants and polyelectrolytes in solution, their interactions, adsorption at interface and formation of the polyelectrolyte membrane has been simulated according to the following steps:
- Quantum molecular computations for single surfactant molecules and polyelectrolyte monomers for determination of partial atomic charges and electric dipoles.
- Molecular dynamics simulations of polyelectrolyte chains to determine their average conformations, chain stiffness and degree of counterion condensation using AMBER99 force field with corrected van Waals interaction parameters for polyelectrolites in the aqueous medium.
- Molecular dynamics simulation of formation of surfactant-polyelectrolyte complexes and adsorption of single polyelectrolyte chains.
- Molecular dynamics simulation of formation of polyelectrolyte multilayer.

The mean porosity of the polyelectrolyte multilayer membrane was determined taking into account the sum of the solvent accessible volumes of polyelectrolyte chains.

A phenomenological constitutive equation of formation of liquid emulsion cores by membrane emulsification has been developed. It is based on the balance of hydrodynamic, capillary and buoyancy forces, taking into account the hydrodynamic instability at the formation of droplet at the mouth of the membrane pore. Key parameters for the constitutive equation have been identified, estimated and verified by measuring the interfacial tension in the system pertinent for emulsification.

Modelling of the release of corrosion inhibitor based on the solution of the multiphase diffusion equation (in spherical geometry) was developed and applied to the release of 2-mercaptobenzothiazole from the emulsion based nanocapsules.

Modelling

in NAMASTE 214499

Subject of the modelling

Magnetic and magnetotransport properties of magnetic materials (diluted magnetic semiconductors and transition metal ferromagnets) manipulated by electric fields and strain.

Models used

Electronic: Ab-initio density functional theory band structure calculations, damping based on the band structures from the ab-initio, tight-binding, and k•p kinetic-exchange effective Hamiltonian models for Band structure calculations in ferromagnetic metal nanostructures
Atomistic: Statistical mechanics model for magneto-transport in nano-devices
Mesoscopic: Micromagnetic Landau-Lifshitz models for magnetisation and magneto-crystalline anisotropies
Continuum: micromechanics elastic theory

Simulation software and type of numerics used

Revised k-space integration schemes

Landauer-Buttiker approach for the strongly SO-coupled transition metal systems and for the diluted magnetic semiconductors.

Prague Library of codes suitable for solving these numerical problems

Achievements of the model beyond experiments

Reproduction of the valence band nature of Fermi level states the archetypical ferromagnetic semiconductor (Ga,Mn)As.
Prediction and explanation of the observed magnetic and magneto-transport properties in ferromagnetic semiconductors
Understanding of the observed spin-torque effects which lead to the discovery of new ferromagnetic resonance (FMR) effects.
Based on the developed capabilities to model spin-orbit in metals, it was shown that appropriate antiferromagnetic materials could be employed as active layers in spintronic devices (GMR, etc), thus opening up the possibility of the new field of antiferromagnetic spintronics.

Application

Spintronic and magneto-electronic devices using control and manipulation of the
nanoscale magnetic properties through the application of local strain or electric fields.
Antiferromagnetic materials for spintronics
Single ElectronTransistors and Fast Precessional Switching Devices

Relevant review articles

"Spin-orbit coupling induced anisotropy effects in bimetallic antiferromagnets: A route towards antiferromagnetic spintronics", Shick A. B et al., PhysRevB. 81 212409 (2010)
"Magnetocrystalline anisotropies in (Ga,Mn)As: Systematic theoretical study and comparison with experiment", Phys Rev. B 80, 155203 (2009)
 "Semiclassical framework for the calculation of transport anisotropies", K. Výborný et al,   Phys. Rev. B, 79, 045427 (2009)

Summary of the project

The NAMASTE project aimed to control and manipulate the nanoscale properties of magnetic materials which have strong spin-orbit coupling by local strain and electric fields. This should make possible new types of magneto-electronic and spintronic devices. The project explored two parallel complementary strands based on ferromagnetic semiconductors and ferromagnetic metal materials.

Summary of the modelling

The project made detailed microscopic theoretical descriptions of the interrelated structural, magnetic, and electrical properties and their dependencies on a large number of degrees of freedom ranging from the choice of semiconductor host and doping densities to the geometry and arrangement of the nanostructures and spintronic nanodevices.

The spin-orbit band structure was calculated by electronic models
a)   ab-initio density functional theory
b)   multi-orbital tight-binding theory
c)   k•p kinetic-exchange effective Hamiltonian models

Spin-orbit (SO) interaction is at the heart of the materials physics involved and the majority of physical quantities relevant to the experimental work can be derived directly from the SO-coupled band structure of the considered systems. The relevant microscopic micromagnetic parameters include the magnetisation, relativistic magneto-crystalline anisotropy constants, Gilbert damping coefficient, and extraordinary MR coefficients. These have been calculated for metals (ferromagnetic and antiferromagnetic metal alloys), diluted magnetic semiconductors and metal/semiconductor hybrid structures.

Magneto-crystalline anisotropies, e.g., reflect the dependence of the system total energy on magnetization orientation and are sensitive to changes in electron concentration (charge accumulation/depletion in conventional field effect transistor structures) or lattice strains (electrical voltage on piezoelectric transducers). Magneto-crystalline anisotropy then represents the key microscopic input parameter for the micromagnetic Landau-Lifshitz simulations to be employed to describe the magnetization dynamics experiments explored within the project.

Another quantity that can be directly derived from the SO-coupled band structure is the dependence of the position of the chemical potential, at a fixed electron density, on the orientation of the magnetization. The chemical potential anisotropy influences the magnetization reorientation induced Coulomb blockade oscillations, a property exploited in a ferromagnetic Single Electron Transistor and modelled with micromagnetism.

Statistical mechanics based atomistic transport anisotropies in tunnelling or ohmic regime employed the Boltzmann or Kubo transport theories for uniform systems, whereas Landauer-Buttiker and Green's function formalisms were employed for spatially non-uniform nanogeometries and non-equilibrium conditions.

Finally, the magnetic and magneto-transport properties of ferromagnetic semiconductors nanostructures were successfully modelled by combining continuum micromechanics elastic theory and the microscopic relativistic band structure modelling.

http://namaste-project.net/

Modelling

in NANOINTERFACE 214371

Subject of the modelling
Metal-oxide-polymer adhesion and interface fracture

Models used
Electronic: many-body models for (band) structure based on interatomic potentials
Atomistic: classical molecular dynamics
Mesoscopic simulations; statistical mechanics particle-based models (coarse-grained molecular dynamics and DPD) for cross-linked epoxy structure
Continuum: mechanical models to describe delamination behaviour

Simulation software and type of numerics used
Electronic models for (band) structure /interatomic potentials: Forcite (universal and COMPASS forcefields) and Gulp (EAM) modules within Materials Studio (Accelrys), as well as LAMMPS (open source code)
Cross-linking algorithms for epoxy moulding
Materials Studio incorporating Mesocite and COMPASS & EAM for atomistic modelling
Implicit finite local arc-length methodes element for delamination

Achievements of the model beyond experiments
A set of design and reliability guidelines for microelectronic packages with respect to delamination risk has been elaborated, which can only be generated in a systematic way by accurate models.
A better, quantitative understanding of adhesion mechanisms at the very small to macroscopic scale and of the effect of surface roughening on adhesion properties has been provided. This was only possible via mesoscope semi-analytical and numerical fracture mechanics models.

Application
Prevention of delamination phenomena in microelectronic packages

Relevant review articles
Chen J, Bull SJ (2011) Approaches to investigate delamination and interfacial toughness in coated systems: an overview. J.Phys.D: Appl. Phys. 44: 034001.
DeVries KL, Adams DO (2002) Mechanical testing of adhesive joints. In D.A. Dillard, A.V. Pocius (Eds.) The Mechanics of Adhesion, Elsevier.
Hutchinson J, Suo Z (1992) Mixed mode cracking in layered materials. Advances in Applied Mechanics 29: 63–191.
Litteken CS, Dauskardt RH (2003) Adhesion of polymer thin-films and patterned lines. International Journal of Fracture 119/120: 475-485

Summary of the project

In the NanoInterface project a multi-scale modeling approach (electronic, atomic, mesoscopic, continuum scale) has been applied to describe the failure behaviour of metal-oxide-polymer materials systems. In addition, micro- and nano-scale characterization techniques have been developed and applied. The project focused on the simple and complex carrier systems, defined and processed by industrial partners.

Summary of the modelling

Large scale molecular statics and dynamics simulations were conducted on Cu-Cu tilt grain boundary interface, results of which are used as input to develop interfacial constitutive laws at larger scale. We have used Coarse Graining Molecular Dynamics (CGMD) and Discrete Particle Dynamics (DPD). The interaction parameters are here obtained from molecular simulations. Both of the methods have been used in the project to generate a cross-linked epoxy structure. Such models are paramount in developing predictive capabilities related to reliability and failure of microelectronic components. Molecular simulations were conducted on two Cu-Cu tilt grain boundary structures using ElectricActiveMaterial potential and open source LAMMPS MD simulation code. After obtaining relaxed equilibrium structure (using the coincident-site lattice theory to get the GB interface and conjugate gradient algorithm for energy minimization), it is subjected to Nose-Hoover NPT molecular dynamics with modified Hoover equation of motion under constant strain rate loading. An intergranular crack is introduced and local traction and crack opening displacement data is extracted from the simulation results. To bridge length scales between atomistics and continuum, the data obtained from MD simulations is re-casted within the framework of continuum cohesive zone model (CZM) to quantify the cohesive zone law. Atomistic simulations on the epoxy resin were conducted to compute its material properties, and interfacial interaction energy on its interfaces with copper and cuprous oxide.

To take into account the influence of roughness on adhesion properties, semi-analytical micromechanics models solved by FE at the micro-scale on Cu/Polymer interface are also developed to establish cohesive/adhesive interfacial delamination criteria under external loading.

A crosslinking procedure consisting of cyclic molecular dynamics simulation/energy minimization and covalent bond creation between reactive sites based on close contact calculation is developed to simulate polymer network formation of the epoxy resin. The cross-linked structure was then fully relaxed to achieve geometry optimization and equilibrated to get rid of artifacts introduced during crosslinking simulation. Subsequent molecular dynamics/molecular statics simulation predicts well material properties, including densities, glass transition temperature, volumetric coefficient of thermal expansion and isotropic mechanical properties, indicating the validity of the adopted polymer network formation methodology. Using the same crosslinking approach, constitutive equations for interfaces between a 2D polymer network and copper as well as cuprous oxide were constructed and subjected to energy minimization. Using energy minimization calculations based on force fields, the interfacial interaction energy for both systems was extracted by the energy difference between the total energy of the entire interface system and the sum of energies of individual components. The system was also subjected to external tensile loading and results related to the interfacial debonding strength are also reported. Interfacial excess energy computation methodology and results for Cu-Cu and Cu-Cu2O interfaces are also presented. Appropriate interatomic potential (IP) formalism is very important to conduct any molecular simulations, as it should be able to capture the correct physics at those loading and environmental conditions. The project also details the IP development framework and results for copper oxide system which is of paramount importance in addressing the failure behavior of the copper/polymer interface which encompasses a thin layer of copper oxide (both, CuO and Cu2O) and invariably influences its failure characteristics. The micromechanical delamination model at macroscopic level used to predict delamination in a microelectronic device is called the cohesive zone model. This is a model that describes the degradation process between 'crack surfaces' from initially closed to entirely open (i.e., a true crack). The input is interface strength and interface toughness (collected in a so-called traction-separation law, the constitutive equation for this model). The output is a transient crack path.

Modelling

in NANOMAGMA 214107

Subject of the modelling

Magneto-plasmonic nanostructures

Models used

Continuum: [Maxwell equations](#) in dipole approximation (coupled)

Simulation software and type of numerics used

Generalized Scattering Matrix Methods to solve Maxwell's equations in presence of magneto-optical effects. In various situations it involves a nonlinear eigenvalue problem that, in this case, has been solved by a linearization procedure. The linearization involves an increase in the dimension of the problem. A direct solution would be convenient.
Finite Difference Time Domain solvers, it would be desirable to extend this technology to cope with non-diagonal dielectric tensors for dispersive materials.

Achievements of the model beyond experiments

The model predicted that the optical and magneto-optical response of complex structures where metals and magneto-optical materials are simultaneously present is proportional to the electromagnetic field in the magnetic material. This guided the design and now the whole structure is grown to try to maximize the field in that material.

Application

Non reciprocal devices (Information Technologies devices), Magneto-optical Surface Plasmon Resonance Sensors.

Summary of the project

The goal of this project was the study development and application of a novel concept of nanostructured materials formed by the combination of components with plasmonic and magneto-optic (MO) activity, in order to produce "magneto-plasmonic" nanomaterials tailored on the nanoscale. Both bottom-up and top-down approaches were applied to obtain the desired magneto-plasmonic materials. The goal was to develop films, nanoparticles and core-shell structures. Also proof of concept for applications based on magneto-plasmonic activity is provided including identification of applications for microelectronics and information technology. Testing for specific applications in the field of chemical sensors and biosensors has taken place.

Summary of the modelling

The project modelled the optical response of MO-plasmonic nanostructures using two different approaches: analytical modelling (including the use of approximate methods) and quantitative numerical simulation. Both approaches are complementary and necessary in order to reach the main objectives.
Using the procedure described above the project explored the mechanisms that would allow:
i) Investigate the correlation between the optical, magnetic, magneto-optical and magneto-plasmonic properties.
ii) Controlling the plasmon (either surface or localized) using an external magnetic field.
iii) Analyzing the interplay between plasmon excitation and MO response.
iv) Amplifying the MO response from local field enhancements

The project performed electromagnetic studies:
• Numerical calculation of the MO response of continuous trilayered structures solving the Maxwell equations using transfer and scattering matrix techniques (layer thickness optimization for maximum sensor signal in Au/Fe/Au structures).
• Analysis of magneto-plasmonic periodic arrays of small particles coupled to a multilayer structure described by the Maxwell equations in the dipole approximation.
• Analysis of the MO properties of a random dispersion of magnetic nanoparticles (using the coupled dipole method).
• Comparison between SNOM measurements and calculations of near-field signals on magneto-plasmonic structures.
• Numerical study of field enhancements on magneto-plasmonic structures for molecular sensing.
• Quantitative study of single-molecule fluorescence control by magneto-plasmonic structured substrates or nanoparticles.

Modelling

in NANOONSPECT 263406

Subject of the modeling/method
On-line inspection of materials processing

Models used
Emperical: Artifical Neural Network Technology for signal processing during material fabrication.

Simulation software and type of numerics used
A software implementation of an Artificial Neural Network (ANN) has been developed with its own user interfaces in order to carry out on-line numeric correlations of desired off-line parameters values in compound processing industry.

Achievements of the model/method beyond experiments
In depth understanding of materials and processing is achieved as well as shortening of material development cycles and formulation changeovers. This will improve product quality, allow the reliable production of Polymer Nano Composites with tailored functions and reduce waste production.

Application
On-line inspection methods for materials processing

Relevant review articles covering the topic (not necessarily their own):

1. [F.A.N Fernandes, L.M.F Lona] Neural Networks applications in polymerization processes. Brazilian journal of chemical engineering Vol 22, No 3, pp401-418, July-September 2005

2. [Helps S C.R G, Strong A.B, Al-Zubi, R, Hawks, V.D Kohkonen K.E]. The use of Artificial Neural Networks in the prediction of machine operational settings for injection moulded parts. The journal of injection molding technology, 3 (1999) 201-211.

3. [Rigol, J.P Jarivs, Stuart N] Artificial Neural Networks as a Tool for Spatial Interpolation. Inf: Sci, (2011) 15,323-343

4. [Moonyong Lee, Sunwon Park] Process Control Using a Neural Network
 Combined with the Conventional PID Controllers ICASE: The Institute of Control, Automation and Systems Engineers, KOREA Vol. 2, No. 3, September, 2000.

5. [Ming Chang, Jen Cheng Chen, Jui Wen Chang, Jia Sheng Heh] Advanced Process Control Expert System of CVD Membrane Thickness Based on Neural Network. Material Science Forum Vols 505-507 (2006) pp 313-318.

Summary of project

NanoOnSpect project aims to optimise polymer nanocomposites manufacturing, combining online sensor technology for characterisation, artificial intelligence-based signal analysis and real-time process optimisation.

The characterisation tool and process control technique to be developed will allow precise adjustment of the composite properties (e.g. dispersion-dependent properties) during production. The characterisation technology will be tested on the material systems carbon nano-tubes (CNT) and nanoclay based composites.

Summary of the empirical modelling

NANOONSPECT will develop an Artificial Neural Network and Expert System (ES) module to analyse sensor signals (pressure, temperature, thermal conductivity, rheology, optical, ultrasonic and microwave sensing output) in order to predict the complex quality of the polymer nanocomposites and calculate new input parameters for the compounding line. The sensor signals of the new sensors will form the basis for the analysis via the artificial neural network for the prediction of complex properties not directly measured by the sensors.

The characterisation technology will provide the correlation between processing parameters and final composite properties and will approach this in three steps
1. Analysis of the influence of the different parameters involved in the compounding process: temperature profile, screw design, share rate, residence time, etc.
2. Evaluation of these impacts for two different types of nanoparticles namely nanoclays and CNTs.
3. Definition of the properties to be characterised for each type of nanocomposites to correlate material properties with process parameters
4. Data interpretation and feedback to process parameters to optimise the dispersion

The material systems for which the system will be developed are fillers in a matrix. Functionalised nanofillers with polymer matrices– one black CNT nanofiller and a colourless nanoclay filler --will be considered. Due to their different chemical and morphological properties and colour differences a broad spectrum of potential nanoparticles can be addressed. As polymer matrix, semi-crystalline polar, semi-crystalline a-polar and amorphous resins will be considered.

Modelling

in NANOMODEL 211778

Subject of the modelling
Mechanical, thermochemical and viscous flow behaviour of nano-filled polymeric materials

Models used
Atomistic: Coarse grained MD (CG-MD) for nanostructure and nanomechanics
Mesoscopic: statistical mechanics Monte Carlo model (Fti-MC) for nanostructures
  Dissipative Particle Dynamics (DPD) for nanostructures
Continuum: Micromechanics model and viscous flow models for behaviour of nano-filled
  polymeric materials

Simulation software and type of numerics used
FEM for micromechanics
Coupling schemes between Molecular Dynamics and Continuum Mechanics, based on modified
Arlequin algorithm
Integrated software product Culgi to model and visualize nanocomposites

Achievements of the model beyond experiments
The role of the interphase (structure and dynamics) is difficult to investigate experimentally.
Only modelling can give access to the very structure of matrix, nanoparticles and their
interphases. Modelling revealed details how the interface is influenced by the chemistry. In
particular, the glass transition temperature (Tg) was reported in the literature to depend
strongly on the nature of the fillers. This effect was not found (experimentally) in our systems
where Tg was not much affected (within the error bars). The reason for this could be
rationalized computing the structure and dynamics of the grafted silica particles by means of
MD (atomistic, CG, DPD) which showed there is now pronounced interface, at least not an
overlap of the interfacial area. From the modelling it was argued that in order to incease Tg
(or lower Tg), the mobility of polymer units has to be modifed. We saw this is the case close
(very close!) to the surface of the NP, but this effect was not long range. However, with only
1-2 wt% NP in the polymer, there is no macroscopic effect,

Application
Reinforcement of polymeric material
Surface modifiers ensuring stable particle dispersion under melt mixing conditions

Relevant review articles
Attinger, S., Koumoutsakos, P. (Eds.), Multiscale Modelling and
Simulation, Lecture Notes in Computational Science and Engineering Vol. 39
(Springer, Heidelberg, 2004)

Summary of the project

The project targets the reinforcement of polymers via the decrease of viscosity through a mixture of nanoparticles. The project has studied the detailed structure of matrix, nanoparticles and interface region. By detailed comparisons of computed structures and experimental ones, new composites were explored.

Summary of the modelling

The project used coupled [continuum fluid](#) and [micro-mechanics](#) (CM) models and particle based Molecular Dynamics (MD) methods.

The CM and MD part have been adapted as follows: in the MD part, the necessary number of degrees of freedom has been reduced by [coarse graining](#), i.e. groups of atoms are considered as single super atoms. Furthermore, the periodic boundary conditions (PBC), which avoid surface effects in the MD simulation box, have been replaced by stochastic boundary conditions (SBC), combined with a DPD thermostat. Using a certain probability function in the boundary domain, a part of the super atoms in that region is tethered via a harmonic interaction potential to so-called anchor points. These additional artificial particles transfer information (forces and positions) from the MD region to the FE domain and vice versa. The main advantage of this approach is the spatial fixing of the anchor points during the MD run, thus there is no dynamic coupling to FE required. The rigid frame of anchor points enclosing the MD domain is coupled to the FE domain by using the Arlequin method which is based on an energy blending of the different domains.

A coupling algorithm between MD ([Molecular Dynamics](#)) and CM allows for the computation of forces externally exerted on a nanocomposite. The multiscale approach to study the structure and dynamics of e.g. silica-polystyrene nanocomposite systems consisted of four levels of description: an atomistic one, several coarse grained ones where each "superatom" or bead represents e.g. a monomeric unit or a meso or racemo diad of styrene monomers, parametrized using Iterative Boltzmann Inversion ([Coarse Grained Monte Carlo (CG-MC)](#)), or [DPD](#), and a third one describing the system at a length scale comparable to that of the Kuhn length, by exploiting the polymer mean field approximation ([Field Theory – inspired Monte Carlo](#), FT-i MC), and a micromechanical approach based on mesoscale morphologies. The first two levels of modelling are closely connected, via forward and reverse mapping schemes. Initial configurations have been subjected to CG-MC simulations, where polymeric chains were e.g. treated as chains of diads and nanoparticles as solid spherical Hamaker interaction sites. Based on atomistic molecular dynamics trajectories of the equilibrated structures, local packing and dynamics were addressed by calculating pair distribution functions, bond orientational autocorrelation functions and H-NMR spectra. The third level of modeling at mesoscale (FT-i MC) has enabled simulations of micrometer-sized domains of the nanocomposite system, wherein the nanofillers are represented as solid spheres (interacting via Hamaker integrated potentials) and the polymer chains as freely jointed sequences of Kuhn segments.

The protocols developed for the model Polystyrene systems were applied to other systems identified by the consortium as interesting for applications, such as PMMA, Nylon 66, and PBT SiO2 based nanocomposites. A pseudo core-shell model to account for interface phenomena in the multiscale procedure was developed and tested on unmodified spherical and cylindrical nanoparticles based nanocomposites.

https://nanomodel.eu/

Modelling

in NANOPIGMY 280393

Subject of the modelling

Adsorption behavior of different molecules in porous solid multifunctional ceramic pigments

Models used

Atomistic: Monte Carlo simulations for molecular adsorption

Simulation software and type of numerics used

Materials Studio 5.0 (molecular modeling software form Accelrys): Sorption module (specific to study adsorption of molecules in solids through Monte Carlo Methods)

Achievements of the model beyond experiments

The use of Monte Carlo simulations can help to select the more suitable conditions for adsorption (pressure and temperature) and to perform successful experiments at the laboratory. It is also helpful to select the kind of molecules that can be adsorbed (type of functional groups and sizes of the molecules) and preferred adsorption sites.

Application

Pigment applications in automotive and construction

Relevant review articles

EJ Maginn et al. J. Phys. Chem., 99 (7), pp 2057–2079 (1995)
J. Phys. Chem , 100, 17573-17581 (1996)
H-J Son et al. Chinese Journal of Chemical Engineering, 16(1) 108—111 (2008)
I Daems et al, J. Phys. Chem. C, 111, 2191-2197 (2007)

Summary of the project

NANOPIGMY project seeks to produce cost-efficient multi-functional ceramic pigments to give to the automobile and construction materials (plastic, paint and concrete) additional functionalities apart from colour (such as antibacterial, anti-corrosion, self-cleaning, self-healing, energy efficiency). The aim is to avoid changes in manufacturing processes.

Summary of the modelling

In order to help in the design and development of the multi-functional pigments, computer modeling tools are used. Adsorption sites of Phase Change Materials (PCMs) molecules inside the pigment will be analysed using Monte Carlo molecular simulations of molecular adsorption at different pressures and temperatures. The interactions between nanoparticles/pigment surfaces will be analysed by studying the interaction energies between inorganic coatings and Phase Change Materials (PCMs) as well as pigment PCMs interaction energies.

http://www.nanopigmy.eu/

Modelling

in NANOPUR

Subject of the modelling
Functionalized polymeric membranes for water purification

Physics/Chemistry models used
Atomistic : molecular dynamics
Mesoscopic : pollutant models described by Langevin equations (statistical mechanics)
Continuum : CFD Navier Stokes, boundary rheology models and adsorption kinetics models of membrane surfaces.

Simulation software and type of numerics used
NAMD for the molecular dynamics
GeoDict platform for meso- and continuum modelling with integrated explicit jump finite volume flow solver

Achievements of the model beyond experiments
The modelling provided a basic understanding of the interplay between water rheology and micro pollutant uptake of functionalized polymeric membranes as a function of the specific functionalization.

Application
Water purification

Relevant review articles covering the topic (not necessarily their own):

- G. Keir, V. Jegatheesan: A review of computational fluid dynamics applications in pressure-driven membrane filtration, Ref. Environ Sci Biotechnol 13:183-201 (2014)

- H. Boroudjerdi, Y.-W. Kim, A. Naji, R.R. Netz, X. Schlagberger, A. Serr: Statistics and dynamics of strongly charged soft matter, Physics Reports 416:129-199 (2005)

Summary of project
NANOPUR aims to develop functionalized polymeric membranes for water purification in a bottom-up approach in order to remove micro pollutants, like pharmaceuticals and viruses, from water streams. Starting from two technology pathways, nanostructured membranes with enhanced permeability and low fouling and functionalized membranes for sub-micro-pollutant capturing, are integrated in one module for water purification, which will be tested at the pilot scale level.

Summary of the modelling
Molecular Dynamics is used in order to simulate the interaction of functionalized polymeric membrane surfaces with water and small amounts of micro pollutants. The output is used to parameterize CFD boundary rheology models of water and continuum adsorption kinetics models of micro pollutants at meso-/macro-scales, used in a full simulation. These models use representative volume elements at micro scales to solve the Navier Stokes water flow models (continuum) with embedded pollutant models describing pollutant diffusion in the water flow and surface reaction kinetics at mesoscale. The behavior of the pollution can also be modelled mesoscopically by Langevin equations for nanoparticles. The capturing of i.e. pharmaceuticals during water permeation through a membrane is simulated this way.

Combined with empirical models for the production costs of the membrane, the best possible compromises of performance and cost measures of polymeric membranes are identified (Pareto optimality). This principle understanding of quality and cost is presented in a graphical decision support system which is designed to browse the best possible compromises between membrane cost and performance. The GUI component of the decision support system may be used during trade off discussions of decision makers; a prototype of the complete system is already delivered to the project partners.

Modelling

in NANOPUZZLES 309837

Subject of the modelling
Toxicity of engineered nanoparticles

Physics/Chemistry models used
Electronic: DFT
Atomistic: MD

Simulation software and type of numerics used

Electronic: Gaussian, MOPAC, DRAGON, GaussView
Atomistic: Amber, AutoDock
Software used to find an empirical model: QSARINS, MATLAB, R, KNIME

Achievements of the model beyond experiments
Modelling allows the industry to design nanomaterials in an environmentally friendly way that will be of low risk for human health and the environment while being competitive on the market (according to the idea of "green marketing"). Models generate understanding of behaviour in physical processes in the environments, possibly without necessity of performing extensive animal testing. Employing computational techniques should significantly reduce the time and cost of risk assessment for novel engineered nanoparticles.
Information on the properties and toxicological activities of various types of chemical compounds, including engineering nanoparticles, is required under multiple regulatory documents, including REACH (Registration, Evaluation, Authorisation and Restriction of CHemicals). Taking into account the cost-effectiveness and the principle of the 3Rs (Replacement, Reduction and Refinement) of animal use, the missing data should, if possible, be obtained *via* alternative (non-animal) testing approaches. A great advantage of presented methods is the fact that they do not require a large number of experimental data. Thus in the light of the different regulatory frameworks and guidance published in the EU, USA, Canada, Japan, and Australia the proposed methods open new opportunities to support the risk assessment of nanomaterials without necessity of performing time consuming and costly experimental studies on large set of engineered nanomaterials.

Application
Risk and safety of engineered nanoparticles

Relevant review articles covering the topic (not necessarily their own):

- Puzyn T., Rasulev B., Gajewicz A., Hu X., Dasari T.P., Michalkova A., Hwang H.M., Toropov A., Leszczynska D., Leszczynski J. (2011): Nature Nanotechnol. 6, 175-178.
- Gajewicz A., Schaeublin N., Rasulev B., Maurer E.I., Hussain S., Puzyn T., Leszczynski J. (2014): Nanotoxicology. Doi:10.3109/17435390.2014.930195.
- Sizochenko N., Rasulev B., Gajewicz A., Kuz'min V., Puzyn T, Leszczynski J. (2014): Nanoscale 6: 13986-13993.
- Gajewicz A., Cronin M.T.D., Rasulev B., Leszczynski J., Puzyn T. (2014): Nanotechnology, 26, 015701.

Summary of project

Some types of engineered nanoparticles can be toxic for living organisms and exhibit negative impact on the environment. Thus, the design of new nanomaterials must be supported by a rigorous risk analysis. The main objective of the ^{Nano}PUZZLES project is to create new computational methods for comprehensive modelling of the relationships between the structure, properties, molecular interactions and toxicity of engineered nanoparticles.

Summary of the modelling

The project is to deliver a package of algorithms for phenomenological modelling relationships between the structure, properties, molecular interactions and toxicity of engineered nanoparticles that can be applied by the industry to design safe and environmentally friendly nanomaterials. The package includes:

- tools for evaluating quality of the experimental data (physicochemical properties and toxicity),
- database containing experimental data of high quality for further modelling,
- tools for calculating descriptors of nanoparticles' structure,
- workflows for simulating the interactions of NPs with biological systems,
- new classifications (grouping) schemes for nanoparticles, based on their structure, physicochemical properties, and toxicity, basis for quantitative modelling the relationships between the structure and physicochemical properties and toxicity of NPs as well as preliminary Nano-QSAR models for the selected endpoints.

The phenomenological methods will be based on the Quantitative Structure - Activity Relationship approach, chemical category formation and read-across techniques which will be adapted for nanoparticles. This approach is based on defining mathematical dependencies between the variance in molecular structures, encoded by so-called molecular descriptors, and the variance in a given physicochemical property or biological (e.g. toxicity or fate) property in a set of compounds ("endpoints").

Phenomenological QSAR and read-across modelling

A strategy for work to develop grouping, read-across and Nano-QSAR models, based on the results of data collection and evaluation was developed. New groups of descriptors such as: topological, constitutional, metal-ligand binding descriptors, simplex representations of molecular structure (SiRMS)-based descriptors, "liquid drop" model (LDM) derived descriptors as well as descriptors derived from quantum-mechanical calculations and from computational processing of microscopic (SEM/TEM) images were calculated. Simultaneously, a methodology how to investigate the size-dependent electronic properties of metal oxide nanoparticles that might be considered as potential nanodescriptors, vital for Nano-QSAR studies, was identified. In addition novel approaches for scoring the quality of nanomaterial physicochemical/structural and toxicity data were established. Finally, preliminary read-across and Nano-QSAR models for the selected endpoints were developed.

Materials Modelling of interaction

A computational protocol (workflow) for the calculation of the properties of large interacting systems, involving nanoparticles (NPs) and biological molecules (BMs) was developed using atomistic and electronic models. Specific rules (workflows) have been proposed for the computation of the interaction properties of small, medium and large size systems.

Modelling

in NANOPYME 310516

Subject of the modelling

Magnetic properties of thin polycrystalline magnetic films

Magnetic properties of bulk nanocomposite materials consisting of several magnetic phases

Characteristics of permanent magnets made of magnetic nanocomposites

Models used

Electronic model: DFT calculations for thin film systems (single layers and bilayers)

Mesoscopic: micromagnetic models applied to thin films and nanocomposite magnets

Continuum: modelling of magnetic performance of macroscopic magnetic components

Simulation software and type of numerics used

Electronic: SIESTA and Quantum ESPRESSO fro DFT calculations

Mesoscopic: OOMMF and MicroMagus

Continuum: Infolytica

Achievements of the model beyond experiments

Electronic properties (critical temperatures and magnetic anisotropy) calculated by DFT will allow exploration of the influence of the electronic correlations at the interface in hybrid metal/oxide-based magnetic bilayers in a nanocomposite system. The model will allowa systematic investigation on the exchange coupling phenomena between metal and oxide-based magnetic phases based on large scale density functional theory calculations and provide information that experiments can not give.

Application

permanent magnets which do not contain rare-earth elements.

Relevant review articles

D. Goll, Micromagnetism–Microstructure Relations and the Hysteresis Loop.

Summary of project

The NANOPYME project addresses the design and development of permanent magnets without rare-earths but instead with hybrid nanostructures of metals and metal ferrite oxides. The metallic nanostructures offer high magnetization values while the ferrite oxide ones provide high anisotropy. NANOPYME intends to design and process novel permanent magnets based on traditional hard ferrites and additional new magnetic phases combined with a soft magnetic phase to achieve high magnetic performance through effective exchange-coupling of both magnetic phases

Summary of the modelling

In the NANOPYME project, numerical simulations performed on the electronic scale (density functional theory (DFT)), on the mesocale (micromagnetic simulations) and on the macroscale (modeling of magnetic performance for magnetic components) will be carried out.

Input to the DFT calculations will be the experimental crystal structure coordinates, while the output will be the electronic properties: critical temperatures (Curie temperature for magnetic systems and Verwey temperature for Co-ferrites systems) and magnetic anisotropy. In order to understand the coupling phenomena between different magnetic phases at their interface, DFT calculations will be done to gain a fundamental insight into these phenomena at the atomistic level.

Next, micromagnetic modeling of thin films, bilayers and two-phase nanocomposites (composed by magnetically soft/hard grains coupled through the grain boundaries) will allow to evaluate which magnetisation processes take place in these systems and which structural and magnetic parameters (characteristics) determine the hysteretic behaviour of such materials. In addition, we shall study how the exchange coupling through the interphase boundary affects magnetisation processes. This information is expected to be crucial for optimizing the preparation of two-phase nanocomposite magnets.

At the final stage, device models solved by finite element techniques for e.g. electric motors will allow us to predict magnetic performance of NANOPYME magnets in operation conditions. Particularly important will be predicting any possible performance decay of these magnetic components due to temperature and demagnetisation effects under operation conditions.

www.nanopyme-project.eu

Modelling

in NANOSELECT

Subject of the modelling

Fluid behavior in nano-pores

Models used

Atomistic models: Classical density functional theory ([DFT](DFT))

Simulation software and type of numerics used

In-house code

Achievements of the model beyond experiments

Analysis the interaction between fluid and wall as well as their effect on the fluid behavior in nano-pores.

Application

Industrial and domestic water treatment

Relevant review articles covering the topic (not necessarily their own):

Monson, P. A. Understanding adsorption/desorption hysteresis for fluids in mesoporous materials using simple molecular models and classical density functional theory, microporous and mesoporous materials, 160, 47-66, 2012

Summary of project

NanoSelect aims to design, develop and optimize novel bio-based foams/filters/membranes with high and specific selectivity using nanocellulose/nanochitin and combinations thereof for decentralized industrial and domestic water treatment. Functional external stimuli sensitive filter surfaces for reduced bio fouling and enhanced filter cleaning or intelligent design of membrane modules allowing selfcleaning will be attempted for antifouling and to increase the service-life of the membranes. NanoSelect focuses on the removal of toxic chemicals, heavy metal ions, pesticides, fertilizers etc from contaminated industrial water.

Modelling is used as a supporting tool in the project to understand adsorption mechanisms and transport of water through nanopores.

Summary of the modelling

The developed hybrid model is based on the density functional theory and perturbed-chain statistical associating fluid theory equation of state. The input of the model is the parameters for fluids in perturbed-chain statistical associating fluid theory, the parameters for porous materials (pore-size) as well as the interaction between the fluid and porous material. The output of the model is the density profile of fluids and the excess adsorption of fluids.

A hybrid statistical mechanical code as developed by coupling density functional theory with perturbed-chain statistical associating fluid theory (PC-SAFT). In the developed model, the modified fundamental measure theory was used for the hard sphere contribution; the dispersion free energy functional was represented with weighted density approximation by averaging the density in the range of interaction, and the chain free energy functional from interfacial statistical associating fluid theory was used to account for the chain connectivity. The pore walls were assumed to be infinitely thick, and the solid-fluid interaction was represented by an external field, which can be Lennard-Jones, Square-well or other interactions. The parameters of fluids were obtained from the fitting of their properties in the bulk phase, and the parameters of solids were obtained from the fitting of the experimental results.

Simulation results of the density profile were compared with the prediction of the developed model, and the considerable agreement reveals the reliability of the proposed model in representing the confined behaviours of chain molecules in an attractive slit. The developed model was further used to represent the adsorptions of methane and carbon dioxide on activated carbons, in which methane and carbon dioxide were modelled as chain molecules with the parameters taken from the bulk PC-SAFT, while the parameters of solid surface were obtained from the fitting of gas adsorption isotherms measured experimentally. The results show that the model can reliably reproduce the confined behaviours of physically existing substances in nanopores.

It is expected that the can be further extended to describe charged molecules.

Modelling

in NANOSIM 604656

Subject of the modelling
Nano-structured reactive porous particles

Physics/Chemistry models used
Electronic: DFT for reaction enthalpy and activation energies
Atomistic: Classical molecular dynamics (MD) to simulate diffusion processes (e.g., through metal oxide layers) and statistical mechanics of elementary chemical reactions.
Mesoscopic: Statistical mechanics of elementary chemical reactions.
Continuum:

- CFD 1 level: CFD solved by particle dynamics (DEM) and intra-particle continuum models to simulate temperature and concentration profiles within and around porous particles.
- CFD 2 level: Multiphase Euler-Euler CFD to simulate particle clustering
- CFD 3 level: Multiphase Euler-Euler CFD to simulate full-scale equipment
- Process model: Phenomenological models to simulate full-scale equipment and systems

Simulation software and type of numerics used
Electronic: VASP (Plane-wave DFT)
Atomistic: SPPARKS (KMC), LAMMPS (MD), kinetic Monte Carlo solvers
Mesoscopic kinetic Monte Carlo solvers
Continuum:

- Classical finite-volume CFD sw: NEPTUNE_CFD, ANSYS FLUENT, OpenFOAM
- Particle dynamics sw: LIGGGHTS (DEM) and CFDEMcoupling (DEM+CFD)
- Finite-difference sw for reactive intra-particle diffusion & heat conduction:ParScale
- Finite-difference sw for full-scale conservation equations: PHENOM

Application
Chemical Looping Reforming (CLR) for hydrogen production with integrated CO_2 capture. Moreover, the NanoSim methodology can be applied to any (reactive) gas-particle contacting processes involving heat & mass transfer (catalytic or non-catalytic). Examples for such processes would be (i) biomass reactors, (ii) drying processes, (iii) coating processes, as well as (iv) other processes in the food/pharmaceutical/chemical/energy industries.

Achievements of the model beyond experiments
Modellig will allow fast and efficient virtual prototyping of new process concepts at full industrial scales and significantly accelerate the traditional scale-up and demonstration process of promising new reactor concepts.

Relevant review articles covering the topic
1.   Adanez, J., et al., Progress in Chemical-Looping Combustion and Reforming technologies. Progress in Energy and Combustion Science, 2012. 38(2): p. 215-282.
2.   Norskov, J.K., et al., Density functional theory in surface chemistry and catalysis. Proceedings of the National Academy of Sciences of the United States of America, 2011. 108(3): p. 937-943.
3.   Sundaresan, S., Modeling the hydrodynamics of multiphase flow reactors: Current status and challenges. AIChE Journal, 2000. 46(6): p. 1102-1105.
4.   Van der Hoef, M., et al., Numerical simulation of dense gas-solid fluidized beds: a multiscale modeling strategy. Annual Review of Fluid Mechanics, 2008(40): p. 47-70.

Summary of project

A key objective of the NanoSim project is to create an efficient and cost effective multi-scale simulation platform which incorporates of a set of interconnected free and open-source codes. To support the information flow and data sharing between different simulation packages, the NanoSim project will develop an open and integrated framework for numerical design (i.e., a common software environment) called Porto. Specifically, Porto is the key software tool which handles data and associated meta-data, and has an application programming interface (API) to ensure extensibility. This software will be used and distributed in terms of the GNU Lesser General Public License (LGPL).

The NanoSim project develops coupling (concurrent modelling) for which a co-simulation platform (COSI) is developed as well as linking (sequential modelling) methods. In the linking scheme information will be exchanged offline between different continuum models via newly developed constitutive equations. The different formats and interfaces used in the NanoSim project will conform to industrial standards (e.g., ECMA-404's JSON format) to enable the future implementation in a larger and extendable framework architecture.

A data centric strategy for linking and coupling of models is adopted. In Porto, a database of meta-data is built that describe the models and their applications in terms of entities and relationships supporting (correctly, safely and maintainable) sharing data between multiple in-house and commercial tools (proprietary and open). The strength of this framework lies in the code management and maintenance as requirements change and the platform grows with new tools and methods.

A new homogenisation tool called REMARC will be used in the linking between 1) electronic and atomistic models (DFT and atomistic and mesoscopic statistical mechanics for reaction chemistry solved by KMC and MD), as well as 2) between atomistic and continuum models. The newly developed tool *CPPPO*, for homogenisation of Computational Fluid Dynamics (CFD) data, will link continuum models applied to different scales. The novelty is that the workflow for homogenisation using these tools will be largely automated through the use of *Porto*.

The statistical reaction chemistry models are fed by distribution functions determined from first principles

calculations, typically DFT.

To link the continuum models, constitutive equations for drag, heat, and effective reaction rates taking key phenomena (e.g., particle clustering) into account will be developed based on small-scale simulations results, and will be validated with experimental results.

Semi-automated reversibility checks will be performed to guarantee model consistency. The approach will allow one to compare the "fine scale" and "coarse scale" simulation results and tune the model if necessary. The novelty of Porto is that the tool will offer an automated workflow for the generation of new closures (constitutive equations) for continuum models.

Model coupling (or concurrent modelling) in NanoSim involves the coupling of particle dynamics models (i.e., using the Discrete Element Method, DEM), classical Computational Fluid Dynamics (CFD) flow models, and intra-particle continuum models to predict reaction-diffusion processes within a porous particle. Specifically, the Co-Simulation (COSI) platform will enable coupled simulations of reactive gas-particle flows, in which relevant intra-particle data (e.g., the reaction rate within a particle) is passed to the CFD flow model during a single simulation run. In addition, intra-particle processes may change particle properties (e.g., the size and density of a particle). COSI will also be able to hand over such data to the particle dynamics model, and hence enable fully coupled gas-particle simulations.

Modelling

in NEAT

Subject of the modelling
Thermoelectric transport in nanocomposites containing nanoparticles

Physics/Chemistry models used

Electronic: DFT
Atomistic: Phonon-models

Simulation software and type of numerics used

Electronic: Quantum Espresso VASP, Our own codes for calculating thermoelectric coefficients
Atomistic: own codes for phonon scattering via atomistic Green's function calculations, and thermal transport.

Achievements of the model beyond experiments
Predicting optimal nanoparticle sizes for thermoelectric alloys, something that would take much longer time and would cost much more if done with experiments

Application
Energy harvesting

Relevant review articles covering the topic (not necessarily their own):

"Role of Surface-Segregation-Driven Intermixing on the Thermal Transport through Planar Si/Ge Superlattices" P. Chen, N. A. Katcho, J. P. Feser, Wu Li, M. Glaser, O. G. Schmidt, D. G. Cahill, N. Mingo, and A. Rastelli, Phys. Rev. Letters, 111, 115901 (2013)

"Composite thermoelectric materials with embedded nanoparticles"
J Mater Sci (2013) 48:2767–2778 Yi Ma • Richard Heijl • Anders E. C. Palmqvist

Summary of project

NEAT is addreessing energy scavenging from waste heat in car engines. There is a lot of heat wasted that can be put to good use in power generation. For cars, this can help reduce emissions. NEAT targeted a bulk alloy nanocomposite approach capable of increasing the thermoelectric figure of merit, ZT of solid solutions of compound semiconductors at high and medium temperatures by considerably decreasing the material thermal conductivity. The project developed two types of nanocomposites, for the medium (300-600°C) -based on Mg2SiSn matrix-, and high (600-1000°C) temperature –based on SiGe- matrix, suitable to harvest energy in the KW range. These materials, based on eco-friendly materials (. SiGe is not toxic and this is different from the typical Pb, Bi, Sb containing compounds used in thermoelectric materials.) were tested to operate in high thermal gradient such as the ones of automotive engines or industrial systems.

Summary of the modelling

NEAT employed a space independent steady state solution of the Boltzmann transport equation for electrons and phonons. NEAT developed new Green's function approaches to compute phonon scattering cross sections by nanoparticles and thin planar barriers. For the electronic properties, parabolic and non-parabolic band models were employed.
DFT codes like Quantum Espresso VASP and in house codes were used to calculate thermoelectric coefficients.

Modelling

in NEXT-GEN-CAT 280890

Subject of the modelling

Catalysts consisting of transition element metal nano-particles without Platinum Group Metals (PGM)

Models used

Electronic modelling: [ab initio quantum mechanical model](#) and [DFT](#) for surface energies and activation energies of the catalytic nanoparticles
Continuum modelling: models for the species concentration in the gas and [the kinetics of the reactions](#) and a [process model](#)

Simulation software and type of numerics used

Home made codes (on Matlab etc) and a process simulator like ASPEN and CFD simulator will be used. Additionally commercial/open source codes include Cantera, CHEMKIN, DETCHEM, Comsol
Commercial and/or academic programs Gaussian 03/ Vasp/ Quantum Expresso/ ADF

Achievements of the model beyond experiments

Improved understanding of catalytic reactivity on non-PGM catalysts

Application

Nanoparticles of transition elements based catalysts for automotive sector

Relevant review articles

L.L. Raja, R.J. Kee, O. Deutschmann, J. Warnatz, L.D. Schmidt, A critical evaluation of Navier–Stokes, boundary-layer, and plug-flow models of the flow and chemistry in a catalytic-combustion monolith, Catalysis Today 59 (2000) 47-60.
Paolo Giannozzi, et al. "QUANTUM ESPRESSO: a modular and open-source
software project for quantum simulations of materials" J. Phys. Cond.
Matter, 21 (2009) 395502.
H. Santos and M. Costa "Modelling transport phenomena and chemical reactions in
automotive three-way catalytic converters" Chemical Engineering Journal 148 (2009) 173–183.

Summary of the project

The main objective of NEXTGENCAT proposal is the development of novel eco-friendly nano-structured automotive catalysts utilizing transition metal nano-particles (Cu, Ni, Co Zn, Fe etc) that can partially or completely replace the PGMs.

Summary of the modelling

The project addressed physicochemical phenomena concerning nanostructured catalysts.
The project will apply existing models and the aim of the modelling activities within the NEXT-GEN-CAT is to check initially the validity of the current available models and /or to adjust their parameters in order to comply with the experimental data obtained either by the literature or by experiments performed by the consortium. After the validation of the models certain runs will be performed in order to predict the behaviour of a catalytic system without the need to perform the experiments. Therefore, only selected catalyst will be evaluated using real feed conditions. The results of the nano-scale modelling will be used later for the process engineering and the optimization of the catalytic performance.

Materials at nanoscale
The surface of the catalysts will be calculated at the atomic level in order to understand the interaction between the gas phase molecule and the catalyst. The stability of all exposed surfaces will be computed from first principles calculations. It will be possible to modify the composition of the surface to determine the most promising catalysts. These studies will the focus on the active phase composed of catalysts. The computed surface energies will be used to build the most probable shape of the nanoparticles.The chemical properties of the surfaces will be computed using the quantum formalism (Schrödinger Equation). Due to the size of the system model, DFT approach (Kohn- Sham equation) will also be applied.
In a second step, the reaction mechanism will be calculated as well as the activation energies that can be used latter in kinetic models for the process simulation of the catalysis.
The equilibrium shape of crystals can be predicted from the Wulff construction, which in turn is obtained from the surface energies of the most stable surfaces of the material.

Process Simulation
The models to be applied will simulate the performance of the catalytic converters and predict the concentration distribution of the chemical species in the gas and the temperature profile inside the converter as well as the velocity profile. More specific the models will enable the:
- simulation of the species concentration in the gas (near and far from the catalytic surface, along the flow direction), on the surface, and the corresponding temperature, pressure and velocity variation along the converter.
- tuning of a kinetic submodel, including detailed surface chemistry and possibly gas-phase reactions, able to make simulation consistent with experimental data. Initial kinetic parameter will hopefully be provided within the project dedicated to more fundamental approaches (nanoscale modelling).
The equations governing the simulation are the kinetic equations, and the equations produced from the mass balances of the chemical species, the heat balance and the momentum balance, will be applied. Furthermore, material, energy and momentum balances, in differential form and at any direction where gradients are expected (along and across the flow) will be considered using ordinary differential equations (ODEs) or partial differential equations (PDEs)

Modelling

in NIM_NIL 228637

Subject of the modelling
Characterisation of electromagnetic metamaterials

Models
  Application
Electromagnetic wave theory for characterisation, Maxwell's equations coupled to constitutive equations for material response; constitutive equations are dispersive models (Drude, Drude-Lorentz) or experimentally obtained material constants; Rigorous Coupled Wave Analysis (RCWA) method is used to calculate transmission and reflection and field distributions inside the metamaterial structures.
  Development
Models for losses

Simulation software and type of numerics used
Commercial software, DiffractMOD (RSoft inc.), Reticolo and RCWA solver
Self-written Mathematica and Matlab codes for implementation of Berreman formalism for oblique incidence retrieval and visualization purposes
Finite-difference time-domain method, finite-elements method (COMSOL), finite integration technique (CST Microwave Studio), retrieval procedure based on scattering parameters.
RCWA method solving Maxwell's equations for stratified structures like gratings and metamaterials
Simulated structures are assumed periodic in lateral dimension and the accuracy can arbitrarily be increased by taking a higher number of Fourier harmonics and better discretization

Achievements of the modelling beyond experiments
Negative refractive indices cannot be measured directly but need to be carefully derived from measurements.
Determination that silver is the best conducting material for use in optical metamaterials
Design and optimization of 3D metamaterial structures
Unambiguous demonstration of negative refraction with wedge configuration for designed negative index metamaterial in the visible regime

Application
Optical devices for communications and imaging

Relevant review articles
http://ec.europa.eu/research/industrial_technologies/pdf/metamaterials-brochure_en.pdf
C. M. Soukoulis and M. Wegener, "Past achievements and future challenges in the development of three-dimensional photonic metamaterials," Nature Photon. **5**, 523-530 (2011).
G. W. Hanson, J. Appl. Phys. 103, 064302 (2008).
J.W. Weber et al., Applied Physics Letters 99, 061909 (2011)
Oates et al., Optics Express 20(10) 11166 (2012)

Summary of project
The aim of NIM_NIL is the development of a production process for 3D negative refractive index materials in the visible regime combining UV-based nanoimprint lithography (UV-NIL) on wafer scale using the new material graphene and innovative geometrical designs. A micro-optical prism will be fabricated to directly verify and demonstrate the negative refractive index.

Summary of the modelling
[Electromagnetic characterisation tools](#) are used to interpret the measured reflection and transmission by spectroscopic ellipsometry to determine the region of negative refractive index and its dispersion as a function of wavelength. Dependence on the wave vector is also investigated. During the characterization stage ellipsometry and normal incidence responses of the models were compared with post fabrication measurements to calculate effective parameters of the product. Then necessary feedback was given to the fabrication team for further optimizations.

The optical properties of graphene are not completely characterized experimentally, especially in the infrared and Terahertz frequency regions. Relations between the density of free carriers and the frequency dependent conductivity as a function of the temperature and the Fermi level (which may be influenced by external bias) are established. The relation is based on the Drude model using the Kubo formula. We used these formulas as input to the dielectric functions to fit our infrared ellipsometry measurements. We used the Airy-Fresnel formulas to create a layer model of the substrate and graphene layer, and fit the optical conductivity (dielectric functions) in the range from 600-4000 cm-1. In this way we could estimate the Fermi level shift due to chemical doping from atmospheric exposure.

We also characterized the plasmonic modes of silver fishnet metamaterials fabricated using nanoimprint lithography. Coupling of obliquely incident radiation to surface plasmon polaritons (SPPs) at a metal-dielectric interface is affected when the incident wave vector matches an SPP wave vector. We used the SPP formulas coupled to the grating formulas to show the angular dependence of the SPP modes in spectroscopic ellipsometry data.

Full-wave simulations are used for the calculation of scattering parameters of metamaterial structures. The scattering parameters can subsequently be used to determine the effective material constants of the metamaterials. The models were used for the design of the metamaterial samples. Full-wave simulations were performed for metamaterial wedges. This effort used our existing numerical simulation capabilities, but it was scaled up to accommodate the large computational problem involved. Wedges contain many circuits and require resolving the electromagnetic on both the microscopic and macroscopic scales. Possible candidates for optical metamaterials with negative index of refraction were identified. The improved wedge configuration shows unambiguous phenomenon of negative refraction with designed optical metamaterials. Single and multiple functional layer Fishnet metamaterial in IR and visible regions were designed and simulated using ab-initio Maxwell solver (RCWA).

A EM model was developed to describe the dissipative loss in resonant electromagnetic metamaterials. The model takes into account the radiation damping of the resonant currents, which is necessary to model metamaterials made from low-loss conducting materials. This model led to an identification of which conducting materials are useful for metamaterials. Silver was found to be the best conducting material at optical wavelength. Graphene was ruled out.

Modelling

in NPMIMETIC 246351

Subject of the modelling
biomaterials, biomimetic nano-polymer gel, synthetic scaffolds

Models used
Continuum: Model for hyperviscoelastic behavior in biomaterials
Multibody system dynamics model (MBS) for intervertebral disc loading conditions incorporating local (biomaterial) physics

Simulation software and type of numerics used
Partial differential equations for finite element methods (model for hyper viscoelastic materials) and multibody system dynamics
Algorithms for image analysis (denoising, segmentation, smoothing, sampling and visualisation)

Achievements of the model beyond experiments
The study of the intervertebral disc (IVD) mechanical behaviour presents a high level of difficulty, due to intrinsic uncertainty on the quantification of real working loads (coupling compression forces, flections and torsion moments). Post-mortem analysis doesn't allow a full understanding of these phenomena, mainly due to the highly hydrated nature and the fact that the osmotic role of nucleus function is not achieved in those conditions. Modelling can overcome these restrictions and predict two fundamental situations:
i)degenerated IVD – stress/strain conditions due to nucleus degeneration (geometry, stress conditions, prediction of overstretched annulus' fibres)
ii) restored IVD – prediction of restoration conditions, annulus rupture state and/or failure risks on the nucleus 'refilling' process, influence of nucleus prosthetic materials characteristics on overall mechanical stability

Application
Biomedical implants for intervertebral discs

Relevant review articles
Cavalcanti, C; Alves, JL, Mechanical behaviour and constitutive modelling of the annulus fibrosus: a literature review, ESB-2012, 18th Congr. European Society of Biomechanics, Lisbon, Portugal, Jul. 2012

Araújo, A; Peixinho, N; Marques Pinho, AC, Stress characterization of intervertebral disc on radial direction: an experimental approach, ESB-2012, 18th Congr. European Society of Biomechanics, Lisbon, Portugal, Jul. 2012

Summary of the project

The NPmimetic project will develop a biomimetic nano-polymer based gel for minimally invasive disc regeneration treatment: Electro-spinning technology will be exploited to design and develop a nano-fiber based, biocompatible, biodegradable, synthetic scaffold that will mimic the mechanical properties of the native nucleus pulposus (NP) for immediate and short term treatment. Anti-inflammatory drugs will be carried by the biodegradable nano-fibers to be gradually released in situ for healing and preventing inflammation.

Summary of the modelling

The continuum mechanical models applied are focused on
1. prediction of the mechanical behaviour of an undamaged intervertebral discs, and possible geometrical/mechanical effects of a NP pathology
2. the behaviour of bio-mimetic gels withstanding loads and behaviour characteristics under working conditions.

A hyper-viscoelastic mechanical model for bulk material, with an almost-incompressibility assumption was used in a non-linear finite elements model (FEM) approach to mimic Nucleus pulposus (NP) behaviour within the intervertebral discs.

Intervertebral disc loading conditions were simulated with a multibody system mechanical model. This can, with a much lighter computational effort than FEM, simulate the dynamic behaviour of the mechanical phenomena inside the intervertebral discs, either under endogenous or exogenous actuations, and a detailed analyse of the localized deformation on intervertebral disc's soft tissues can be achieved.

Combining all these aspects, a hybrid model can be developed, using the multi body system tool to predict the motion of the segment and the FEM tool to detail the localized deformation on IVD's soft tissues. The kinematics, stress distribution and its effects can be analysed simultaneously, allowing a more precise definition of the loading state of the different parts in different situations, as well as the prediction of the overall behaviour of the set under 'real' use.

Image –processing: Intervertebral disc geometry definition involved the development of an automated image-based procedure, capable of making an identification of soft tissues and substrate bone (i.e., capable of distinguishing between muscle and ligaments, tendons and bones, cortical and trabecular bone, fibrous and pulpous regions, etc.), extracted from 2D high resolution MRI or other available technique images. A subroutine was created to build up geometrically consistent boundaries/regions, through analysis, parameterization and high-degree regression of 2D topographic curves, in order to produce suitable 3D meshed 'solid' entities.

With these models assistance in the evaluation of eventual different proposals for the therapeutic modalities and/or techniques of regeneration can be given.

Modelling

in ONE-P 212311

Subject of the modelling
Electronic processes occurring in organic-based devices (charge transport, light conversion into current, charge injection) and their dependence on system morphology.

Models used
Electronic: Ab initio or semi-empirical [Hartree-Fock methods](#), [DFT methods](#)
Atomistics: [Molecular Dynamics](#), [Molecular Mechanics](#)

Simulation software and type of numerics used
Gaussian, Ampac, ADF, SIESTA for DFT
Gromacs, Materials Studio, Tinker, NAMD for MD with the numerical Kinetic Monte Carlo procedure

Achievements of the model beyond experiments
Material design targeted to the optimization of physical properties and to yield devices with enhanced efficiencies. Modelling allowed the fast screening of candidate molecules for electron transport in devices, IR emitters and lasing applications. It predicted organic semiconductor crystal structures and explained the influence of lattice mismatches at the interface between two crystalline organic semi-conductors on the interfacial electronic properties; and predicted its implications for charge separation in organic solar cells.

Application
OLEDs, field-effect transistors, sensors and storage devices, solar cells

Relevant review articles
"An Atomistic Description of Polymer Dielectrics/Pentacene Interfaces: Influence of Electrostatic Interactions on Charge Mobility Values". N.G. Martinelli, M. Savini, L. Muccioli, Y. Olivier, F. Castet, C. Zannoni, D. Beljonne, and J. Cornil. Advanced Functional Materials 19 (2009) 3254-3261.

"Control of the Mutual Disposition of Cyclometalated Ligands in Cationic Ir(III) Complexes: Synthesis, Spectroscopy, and Device Efficiency of the Different Isomers". J.M. Fernandez-Hernandez, C.H. Yang, J. Beltran, V. Lemaur, F. Polo, R. Frölich, J. Cornil, and L. De Cola. Journal of the American Chemical Society 133 (2011) 10543-10558.

Photoinduced Work Function Changes by Isomerization of a Densely Packed Azobenzene-Based SAM on Au: A Joint Experimental and Theoretical Study". N. Crivillers, A. Liscio, F. Di Stasio, C. Van Dyck, S. Osella, D. Cornil, S. Mian, G.M. Lazzerini, O. Fenwick, E. Orgiu, F. Reinders, S.

Braun, M. Fahlman, M. Mayor, J. Cornil, V. Palermo, F. Cacialli, and P. Samori. Physical Chemistry Chemical Physics 13 (2011) 14302-14310.

Summary of the project

ONE-P developed new functional organic materials for organic electronics and photonics and some applications such as organic light-emitting diodes, photovoltaics and active matrices. These materials provided enhanced properties in electron transport, conversion of photons into electrons and/or conversion of electrons into photons and can be printed in a continuous process.

Summary of the modelling

ONE-P applied electronic and atomistic modelling approaches in order to investigate electronic and structural properties of the next generation of organic conjugated compounds for applications in organic electronics. The project combined quantum-chemical models (a.o. by means of Non-Equilibrium Green's Function DFT calculations) for the evaluation of the molecular parameters defining the rate of charge transfer between molecules and Kinetic Monte Carlo numerical algorithms for the propagation of the charge and the evaluation of the charge carrier mobility and Molecular Dynamics simulations for the prediction of the bulk organization,

The project developed a methodology to model the triplet energy transfer at the molecular scale from quantum-chemical calculations to end up with exciton diffusion length using Kinetic Monte Carlo.

Results: with these models the project could
- model realistic donor-acceptor interfaces (such as polymer-fullerene) using Molecular Dynamics simulations and then extract by means of quantum-chemical calculations the dipole at the interface between organic layers.
- design functional molecules for SAMs for application in molecular electronics
- predict the changes in the work function of metal electrodes upon deposition of self-assembled monolayers or organic semiconductors using DFT calculations with Periodic Boundary Conditions (as implemented in SIESTA) to tune the charge or spin injection barriers.
- find a relationship was found between the structural organization of polymer chains (modelled by Molecular Dynamics) and the solid-state optical properties (described by phenomenological models).
- elaborate a design rules for improving the charge transport properties of n-type as well as ambipolar organic semiconductors.
-study the impact of the nature of the insulating layer in field-effect transistors on the electrostatic disorder at the interface between the dielectric layer and the organic semiconducting layer. We have used here a combination of Molecular Dynamics simulations to generate realistic interfaces between the insulating layer and the organic semiconductor at the nanometre scale, quantum-chemistry and Kinetic Monte Carlo approaches to quantify the impact of different dielectrics on the charge carrier mobility.

http://www.one-p.eu/public/

Modelling

in ORAMA 246334

Subject of the modelling
Multifunctional oxides (Active Semiconductor Oxides (ASO))
Passive n-type amorphous Transparent Conducting Oxides (a-TCOs) and p-n type junctions thereof

Models
Electronic: First principle modelling (DFT) of oxide materials for the electronic structure of oxides
Atomistic: Generalized Boltzmann Transport Equations models for plasma and thin film growth
Continuum: Computational fluid dynamics for droplet formation

Simulation software and type of numerics used
Own codes: BEM for electric field computation by Poisson's equation
PICMC Parallel Particle-in-Cell Monte-Carlo code including routines for particle motion (DSMC)
BEM for electric field computation by Poisson's equation
RIG-VM for computation of magnetic fields using the Boundary Element Method
CFX Ansys (CFD)
Commercial software: Advanced, Essential Macleod, Code and OptiLayer
Scripting language used for scheduling of parallel simulation tasks, for specialized post-processing and for optimization issues.
Direct Simulation Monte-Carlo (DSMC) techniques.
Optical analysis codes

Achievements of the modelling beyond experiments
Using modelling, we understood the relevance of the grain boundaries for shallow acceptor levels which are the prerequisite for p-doping in ZnO films with substantial resource savings compared with an experimental approach. Similar savings are achieved for the layout of deposition chambers and coating processes. Our modelling allows for an in depth understanding of the plasma parameters and growth conditions particular in PVD processes. The modeling of particle fluxes and energies allows for substantial time savings and deeper understanding compared to experiments.

Application
Electronic devices (automotive),thin film photovoltaics, Displays, LED and OLED technology

Relevant review articles
B. Szyszka et al., Development of new transparent conductors and device applications utilizing a multidisciplinary approach, Thin Solid Films 518 (2010) 3109
B. Szyszka et al., Recent developments in the field of transparent conductive oxide films for spectral selective coatings, electronics and photovoltaics, Current Applied Physics 2012, in press, doi: 10.1016/j.cap.2012.07.022
W. Körner et al., First-principles density functional study of dopant elements at grain boundaries in ZnO, Phys. Rev. B 81 (2010) 085324
M.Putti, et al., "New Fe-based superconductors: properties relevant for applications" Supercond. Sci. Technol. **23** (2010) 034003
K. Tanabe and H. Hosono "Frontiers of Research on Iron-Based Superconductors toward Their Application" Japanese Journal of Applied Physics **51** (2012) 010005
G. R. Stewart "Superconductivity in iron compounds" Reviews of Modern Physics, **83** (2011) 1589

Summary of project

Orama deals with the development of multifunctional oxide based electronic materials, processable at low temperatures, including flexible substrates. Orama will address the potential of oxides as electronic materials in the automotive industry. It will achieve this by addressing the four key elements being essential for building up the new era of oxide based electronic industry: 1st principle material modelling, synthesis of new materials, development of low temperature and damage free deposition and patterning techniques and novel characterization methods.

Summary of the modelling

The materials modeling in Orama aims at understanding of semiconductor properties for realistic life materials including doping and defect related phenomena. An important issue is the understanding of p-conductivity in doped ZnO films and novel p- and n-type oxide materials. Another important issue is the suppression of plasma damage due to high energetic species impinging on the substrate.
A multiscale model for coating processes is used. To achieve this, we use different approaches to model electronic structure, plasma process and thin film growth phenomena and for continuum modelling of ink-jet processes.
First principle modeling of the electronic structure of oxides
Own code developments or source codes available for academic purposes were utilised to solve the Kohn-Sham equations of density functional theory for the first principle modelling of the electronic structure including defect effects, such as doping and grain boundary related issues.
Plasma and thin film growth related phenomena
For these areas, codes developed earlier were used. Monte-Carlo techniques Direct Simulation Monte-Carlo (DSMC) were used to solve the statistical mechanics (Boltzmann) transport equation for the description of gas flow phenomena. With self-consistent electric field computation that approach is extended to Particle-in-Cell Monte-Carlo Techniques (PIC-MC) for plasma phenomena. The simulation environment is entitled "picmc". RIG-VM is used for scheduling and parameterization of the parallel computing jobs. Further, it can be used for specialized post-processing and optimization issues. Besides PIC-MC simulation, RIG-VM comprises a module for optical simulation of multilayer stacks.
Computational fluid dynamics (CFD) modelling is used for various tasks in the optimization of Ink-Jet and Sol-Gel processes. Here, we use commercial software, from suppliers such as CFX / Ansys.
Optical analysis
Here, we use also the RIG-VM code to analyse optical spectra and X-ray reflectometry data besides several commercial products in this field (such as Advanced Fit by Sentech, Essential Macleod, Code or OptiLayer.An important application is the analysis code of RF-superimposed DC-sputtering of TCOs serving as front contact for thin films LEDs where intense bombardment reveals plasma damage (due to release of N from the GaN substrates) which increases the operation voltage of the device.

www.orama-fp7.eu

Modelling

in OXIDES 228989

Subject of the modelling
Oxide interfaces and nanostructures (structural, electronic and functional properties)

Models used
Electronic models:
First-principles description within the Density Functional Theory formalism
Second-principles modeling: Tight-binding Hamiltonians for electrons, Effective Hamiltonians for the lattice-related properties at finite temperatures
Bloch-Boltzmann theory for transport and thermoelectric properties

Simulation software and type of numerics used
Standard packages for first-principle simulations (SIESTA, ABINIT, CRYSTAL, VASP) and home-made/open-source codes (BoltzTraP) for second-principles simulations. Iterative resolution using either a variational formulation and a minimization method or a diagonalization procedure. In house arallelised code

Achievements of modelling beyond experiments
  Theoretical predictions to be further validated experimentally:
The unexpected possibility to induce multiferroism in epitaxially strained $CaMnO_3$
The unexpected possibility to achieve exploitable Tunnel Electro-Resistance (TER) in symmetric Ferroelectric Tunnel Junction (FTJ); for memory applications
The prediction of the unexpected appearance of a half-metallic ferromagnetic highly-confined 2-dimensional electron gas (2DEG) in $SrTiO_3$/$SrRuO_3$ superlattices
The unexpected role of oxygen rotation in shifting by 300 K the ferroelectric phase transition of $PbTiO_3$;
  Joined theoretical-experimental breakthroughs
Improper ferroelectricity in oxide superlattices in which modelling identified a new microscopic mechanism (the so-called trilinear coupling of structural instabilites) as observed in parallel experimentally
Exchange bias in $LaNiO_3$/$LaMnO_3$ superlattices; modelling allowed the proper understanding of the unusual spin order giving rise to the experimental results
Compelling evidence of the intrinsic nature of the 2DEG at polar oxide interfaces; modelling of ideal interfaces was required to unambiguously distinguish between intrinsic and extrinsic effects
Confinement properties of the 2DEG at the $LaAlO_3$/$SrTiO_3$ interface; modelling provides key information on the electronic band structure, mandatory to interprete measured properties

Application
Nanostructures for electronic and spintronic applications, ferroelectric and multiferroic memories, thermoelectric devices for energy conversion and energy harvesting

Relevant review articles
ABINIT: first-principles approach to material and nanosystem properties X. Gonze et al.Computer Physics Communications 180, 2582 (2009)

Summary of the project

The OxIDes project develops advanced techniques for the atomic scale modelling of the most relevant types of oxide interfaces and uses these tools to design a new generation of layered materials with unique experimentally-confirmed properties.

Summary of the modelling

OxIDes addresses the physics of three types of interfaces: (i) insulating interfaces between insulating oxides, where coupling between lattice modes can lead to unusual phenomena; (ii) conducting interfaces between insulating oxides, where an interfacial 2-dimensional electron gas (2DEG) might exhibit large thermoelectric power; and (iii) interfaces between metallic and insulating oxides, for a deeper understanding of screening.

OxIDes relies at a first level on advanced electronic modelling based on first-principles Density Functional Theory (DFT) techniques where the study of highly-correlated electron sytems and/or specific interfaces (like metal/insulator interfaces) requires going beyond the usual approximations. Significant methodological advances concern the use of pseudo self-interaction correction local density functional method pSIC and B1-WC hybrid functional techniques for these interfaces. The pSIC method removes in complex systems the spurious self-interaction repulsion present in local or semilocal density functionals (LDA, GGA). The B1-WC functional was introduced only recently and implemented in CRYSTAL code during the project. Hybrid functionals are well known but this is a new functional that was adjusted to properly describe at the same time the lattice dynamics and electronic properties of functional ferroelectric and related perovskites. Previous hybrid functionals were not satisfactory for those systems.

A variational pSIC extension was developed within Oxides allowing atomic relaxation at the pSIC level. In the VPSIC approach, the atomic forces formulation follows from the usual Hellmann-Feynmann procedure. It is obtained as the LSDA expression augmented by a further additive contribution due to the atomic-site dependence of the SI projectors.

The first-principles techniques have been used to study single- and poly-domain structures of ferroelectric capacitors and various $ABO_3/A'BO_3$ superlattices, the origin and confinement of the 2DEG at the $LaAlO_3/SrTiO_3$ interface or in $SrRuO_3/SrTiO_3$ superlattices, the magnetic properties of nickelates, etc.

The second-principle modelling includes a tight-binding Hamiltonian for electrons to determine the equilibrium distribution of the conduction charge in 2DEG, extended effective Hamiltonians for finite-temperature simulations of ferroelectric-related properties, an approach based on Bloch-Boltzmann theory for the prediction of thermoelectric properties and the Brinkman-Dynes-Rowel relation for the determination of electronic transport properties (The voltage dependent tunneling conductance has been calculated using two extreme models of the WKB approximation)

OxIDes developed a totally new effective Hamiltonian approach, that properly includes all ionic degrees of freedom, for the study of structural phase transitions with temperature, implemented a method including a temperature-dependent relaxation time for the description of the transport properties within the Bloch-Boltzmann approach, proposed a simple electrostatic model properly including incomplete screening for the description of ferroelectric capacitors in zero and finite bias and also realized the first ever ab initio simulation of a realistic ferroelectric tunnel junction under finite bias, combining DFT and non-equilibrium Green's function formalism.

http://www.oxides.ulg.ac.be/

Modelling

in PMJOIN 309993

Subject of the modelling
Polymer-metal laser joining

Models used
Continuum: heatflow and thermodynamical models ; electromagnetic models

Simulation software and type of numerics used
Simulation software: Comsol Multiphysics / Matlab/ABAQUS
Type of numerics: Analytical / Finite Elements/Monte Carlo

Achievements of the model beyond experiments
Thermal modelling of joining of parts will help to determine the viable parameter space and provide thermal cycles at all points of the part. Structuring modeling will assist to numerically evaluate the generation and the effect of different patterns on the joint. Finally mechanical modelling will clarify the constitutive behaviour and the nature of breaking of the joint interface.
All these models save precious resources and provide in-depth understanding of the underlying physical processes, as opposed to a purely experimental approach.

Application
Polymer-metal joined structures for automotive industry

Relevant review articles
Farazila,Y.; Miyashita, Y.; Hua, Wang; et al, YAG Laser Spot Welding of PET and Metallic Materials,
Journal of Laser Micro Nanoengineering, Volume 6, Issue 1, Pages: 69-74
- A.P. Mackwood, R.C. Crafer, Thermal modelling of laser welding and related processes: a literature review, Optics & Laser Technology, Volume 37, Issue 2, March 2005, Pages 99-115, ISSN 0030-3992, 10.1016/j.optlastec.2004.02.017.
- Giuseppe Casalino, Elhem Ghorbel, Numerical model of CO2 laser welding of thermoplastic polymers, Journal of Materials Processing Technology, Volume 207, Issues 1–3, 16 October 2008, Pages 63-71, ISSN 0924-0136, 10.1016/j.jmatprotec.2007.12.092.
- Bappa Acherjee, Arunanshu S. Kuar, Souren Mitra, Dipten Misra, Effect of carbon black on temperature field and weld profile during laser transmission welding of polymers: A FEM study, Optics & Laser Technology, Volume 44, Issue 3, April 2012, Pages 514-521, ISSN 0030-3992, 10.1016/j.optlastec.2011.08.008.
- M. Ilie, E. Cicala, D. Grevey, S. Mattei, V. Stoica, Diode laser welding of ABS: Experiments and process modeling, Optics & Laser Technology, Volume 41, Issue 5, July 2009, Pages 608-614, ISSN 0030-3992, 10.1016/j.optlastec.2008.10.005.
- Experimental and Numerical Investigation of Laser Welding of long Fiber Thermoplastic Composites, M. Oumarou, J. Renard, D. Jeulin, W. Knapp, S. Clément, ICALEO 2011, Orlando, Florida, USA, 2011.

Summary of project

The projects targets lightweight structures for the automotive industry to replace metal parts and to achieve reduced energy consumption. As metals cannot fully be replaced by plastics in many applications, many products are made of multi-components consisting of several types of materials. The present project aims to develop a new innovative joining concept for Plastic and Metal materials using a direct non-contact laser joining process without extra filler, adhesive bonds or mechanical union.

Summary of the modeling

Thermal modeling will provide thermal gradients, weld seam geometry and thermal distortions, as a function of laser parameters, material properties and clamping conditions. A finite elements model (FEM) commercial thermodynamics package, COMSOL Multiphysics, will be used for fast heating and joining while ZEMAX will be the tool to model the scattering behaviour of the laser beam through the polymer, via ray tracing and Monte-Carlo methods. With this, the laser input parameters will be predicted that yield the required polymer melting temperature independently of the required joining configuration (through the polymer or the metal). Possible joint distortions (generated during the cooling of both materials) will be also determined.

Structuring modelling of the micro-structured pattern geometry in the metallic part will identify the most appropriate structure facilitating anchorage of the melted polymer during the joining operation. The code COMSOL is used. This modeling does not describe the physical phenomena in laser ablation but it links the laser processing parameters for the structuring to the resulting structures and the subsequent joining process. It will be a MIMO (Multiple Input/Multiple Output) matrix relation definition in order to obtain a starting point in a process development and to better understand the complete process chain. In terms of the structuring model the approaches from the laser material interaction model known from laser drilling applications will be adapted to the structuring process.

Process descriptions for manufacturing technologies in terms of correlating manufacturing parameters e.g. laser power, feed rate with the joining results e.g. tensile strength. These relations follows the approach of RSM (Response Surface Model) which is utilized in DOE (Design of Experiments) methods to link process results to input parameter using Statpoint Statgraphics Centurion.

Mechanical modeling with ABAQUS will clarifying the behaviour and the nature of breaking of the joint interface and how to obtain the best rigidity and weld seam strength. Generally, the joint interface has a complex behaviour and depends on the loading condition and rate. The variables (internal variable) written at meso or macro scales for structural calculation, are directly linked to the physical mechanisms occurring in the material at microscopic scale. We obtain the constitutive law of the welded zone thanks to our testing system, which is able to test the assembly in 3D. By this way we get the real behavior of the in situ seam. Concerning the link with the physical mechanisms, we are able to perform tensile and shear tests through a scanning microscope and then to observe the microstructure. By this way we don't get a mechanical characterization because the tested volume is too small to be representative, but we can understand the evolution of the microstructure. That means that we identify the domain of elasticity and then damage, the type of damage and its evolution till breaking of the join.

Modelling

in POCO 213939

Subject of the modelling
Interactions of functionalised carbon nanotubes with polymer matrices and influence of processing parameters on different properties of the nanocomposites

Models used
Atomistic: Molecular Dynamics for interfacial interactions between CNTs and polymeric matrices.
Continuum: Solid mechanics to describe the elastic behaviour of the nanofilled composites as whole i.e matrix+CNTs.

Simulation software and type of numerics used
Materials Studio (Molecular Dynamics)
ANSYS Finite Elements method (FEM) for continuum mechanics
  Minimization algorithms (Steepest descents, Conjugate gradient, Newton)
  Ewald summation method, Finite Differences method (Verlet integrator) with Andersen numerical thermostat and barostat to simulate the NVT and NPT statistical ensembles

Achievements of the model beyond experiments
Molecular models of functionalized CNTs and polymer matrices could predict the influence of the functional groups on the mechanical properties of the CNT and the interfacial shear strength (IFSS) of the nanocomposites. The influence of the functionalization of CNTs on the IFSS of the nanocomposite was demonstrated, something that would otherwise have cost many experiments.
The pull-out of CNTs from molecular matrices is difficult to analyze by experimental methods due to the scales involved. In this case, the process modelling of the pull-out was necessary to analyze the interfacial shear strength of the nanocomposites.

Application
Polymer composites filled with CNT for automotive, aeronautics, building, aerospace, wind power generation (blades), ship building and biomedicine applications

Relevant review articles
Molecular dynamics modelling for the analysis and prediction of miscibility in polylactide/polyvinilphenol blends; de Arenaza, et al Polymer 2010 51-19 pp4431-4438
Molecular dynamics study of the influence of functionalization on the elastic properties of single and multiwall carbon nanotubes. Coto, B.et al. Comp Mat Science 2011 50-12 pp.
Poly(ethylene oxide)-b-poly(L-lactide) Diblock Copolymer/Carbon Nanotube-Based Nanocomposites: LiCl as Supramolecular Structure-Directing Agent. Meyer et al Biomacromolecules 2011 12-11 pp4086-4094

Summary of the project

POCO develops innovative polymer composites filled with CNT, a nanostructured material with tailor made and superior properties. This involves development of CNT confinement strategies.

Summary of the modelling

CNTs/Polymer matrices were modelled with the following approaches for the different properties:

The influence of the functionalisation on the mechanical properties of the CNTs was analysed using a Molecular Dynamics approach and by calculating the stress-strain slopes with mechanics models.

The interfacial interactions between CNTs and polymer matrices were analysed using Molecular Dynamics pull-out simulations, where the interaction energy between the CNT and the polymer matrices is monitored while the CNT is being pulled-out from the matrix. This energy can be related to the interfacial shear strength. Analytical relations were developed from the analysis of the curing of the thermosetting polymers (kinetic, chemo-rheology) and used Ozawa's and Avrami's models to study the crystallization of thermoplastics semi-crystalline matrices both pure and with CNTs. For the alignment of CNTs in viscous media under electric fields, POCO developed an electro-dynamics constitutive equation relating the polarisability of the CNTs, the electric field applied and the viscosity of the polymer with the torque.

The mechanical properties such as Young's modulus, shear modulus and Poisson's ratio of nanofilled systems have been obtained by a macromechanical model using stress-strain constitutive equations, which was solved with a finite element approach implemented in a dedicated simulation code called ANSYS.

The project has proven that a moderate degree of chemical functionalization of the CNTs can increase the interfacial shear strength up to a 300% (depending on the functional groups used) when compared to pristine CNTs.
The influence of functional groups on the properties of the CNTs has been proven to be detrimental for the mechanical properties of the SWCNTs. This detrimental effect is less critical in the case of MWCNT.

http://www.poco-project.org/home.asp

Subject of the modelling
Coatings for supercritical steam power plants

Physics/Chemistry models used
Continuum: Structural Mechanics for mechanical and thermal properties

Simulation software and type of numerics used
Continuum: ABAQUS and Thermo-Calc Dictra and MatCalc and MTDATA databases and interpolation software and FatSage software and SigmaPro software

Achievements of the model beyond experiments
The modeling can prevent expensive experiments and give understanding of phenomena

Application
Power plants and materials for extreme environments

Relevant review articles covering the topic (not necessarily their own):

1. Andersson J.O., Helander T., Höglund L., Shi P.F., and Sundman B. (2002) Thermo-Calc and DICTRA, Computational tools for materials science. Calphad, 26, 273-312.
2. Andersson J.-O. Fernandez Guillermet A., Hillert M., Jansson B., and Sundman B. (1986) A Compound Energy Model of ordering in a phase with sites of different coordination numbers. Acta Metallurgy, 34, 437-445.
3. Andersson J-O., Höglund L., Jönsson B., and Ågren J. (1990) in Purgy G.R. (Ed.) Fundamentals and Applications of Ternary Diffusion, Pergamon Press, NY, pp. 153-163.
4. Ansara I. and Sundman B. (1986), in Glaser P.S. (Ed.) Computer Handling and Dissemination of Data, Elsevier Science Publ., CODATA, pp. 154-158. Borgenstam A., Engström A., Höglund L., and Ågren J. (2000) DICTRA, a tool for simulation of diffusional transformations in alloys. Journal of Phase Equilibria, 21, 269-280.

Summary of project

The overall objective is the development of new coatings for supercritical steam power plants for efficient and clean coal utilization. The project develops advanced coatings for steam environments which can resist the chemical attack of steam and fireside corrosion. Ferritic–martensitic steels will be considered as substrate materials for up to 650º C and austenitic steels will be explored for higher temperatures. A significant reduction of emissions is expected by increasing efficiencies

Summary of the modelling

Continuum materials modeling using FE analysis is done to calculate scale deformation and scale fracture allowing prediction of scale integrity. Development of microstructural models to predict the initial stages of scale formation and scale growth (nucleation and growth) in steam and oxy-combustion containing environments. The software using is ABAQUS.

Constitutive equations describing formation of oxide scales and material loss are used to model the scale growth kinetics. This CE is based on continuum damage mechanics describing mechanisms that cause deviation from the parabolic behavior.

Continuum diffusion modeling for diffusional transport of the substrate elements is done with CFD models and the Darken CE using the software DICTRA. This calculates diffusion profiles for optimalisation of compositions of coatings.

Databases are used to calculate relationship between new possible coating compositions and substrates and to calculate thermodynamic stability of the phases using MTDATA and Thermo-Calc to determine phase stability in the coatings.

- Thermo-Calc, to model the substrates phases design and coatings design related to chemical composition; Stable and meta-stable heterogeneous phase equilibria, Amounts of phases and their compositions, Thermochemical data such as enthalpies, heat capacity and activities, Transformation temperatures, such as liquidus and solidus, Driving force for phase transformations, Phase diagrams (binary, ternary and multi-component), Solidification applying the Scheil-Gulliver model, Thermodynamic properties of chemical reactions.
- Dictra, to model, Microsegregation during solidification, Homogenization of alloys, Growth/dissolution of carbides, nitrides and intermetallic phases, Coarsening of precipitate phases, Interdiffusion in compounds, e.g. coating systems, Austenite to ferrite transformations in steel, Carburization, nitriding and carbonitriding of high-temperature alloys and steels, Post weld heat treatment, Sintering of cemented-carbides.
- MatCalc: constrained and unconstrained phase equilibria, precipitation kinetics, long-range diffusion, simultaneous diffusion and precipitation, phase transformations/moving phase boundaries, lattice Metropolis and kinetic Monte Carlo by diffusion equations.

Also LCA calculations were done and Life time and remaining lifetime modeling by combining all results on diffusion and thermodynamic modeling as well as mechanisms on scale growth prediction of lifetime for different environmental conditions can be made.

Modelling

in QUANTIHEAT 604668

Subject of the modelling
Heat transfer, thermal and thermomechanical properties from nano to macroscale

Materials Models used for charge and energy transport
Electronic:	Density Functional Theory
Atomistic:	Ab-initio and Molecular Dynamics simulations, atomistic BTE
Mesoscopic:	Quasiparticle transport: mesoscopic Phonon Boltzmann Transport
		Equation (BTE); fLuctuation-Dissipation Theorem based equations for computation at carrier's wavelength size: High-frequency fluctuational acoustics (continuum elasticity) for heat conduction in the ballistic regime
Continuum:	Fluid mechanics, heat conduction and convection; Thermomechanical, rheological couplings
		Fluctuational Electrodynamics (Maxwell's equations) for radiative heat
		transfer Landauer formalism

Simulation software and type of numerics used
Electronic:	Fireball, VASP (Vienna Package) and Quantum Espresso when needed.
Atomistic:	In-house codes, LAMMPS for MD when needed.
Mesoscopic:	Phonon BTE: Monte-Carlo statistical method, Deterministic method such
		as Ballistic-Diffusive Equations (BDE) and Discrete Ordinates Method (DOM)
Continuum:	Finite element method: COMSOL, SfePy. Finite Element Analysis models
		of thermomechanical response of layered nanostructures. GSvit software
		for Finite Difference Time Domain (FDTD) electromagnetic calculations

Achievements of the model beyond experiments
The systematic analysis of heat transfer phenomena from macroscale to nanoscale should bring new design rules for nanomaterials and for measurement tools. The models will bring insight into the physics and the chemistry leading to typical phenomena that take place when investigating heat transfer at nanoscale. Beyond experimental results, data such as spectral distributions or atomistic architecture impacts can be obtained thanks to the simulations tools.The availability of calibrated numerical modelling tools will facilitate the rapid "digital" thermal design of new nanosystems without the need for extensive prototyping.

Application
Scanning thermal microscopy; nanoimprint lithography; atomic-layer deposition (ALD); thermoelectric devices.

Relevant review articles
- P. Heino, Simulations of nanoscale thermal conduction, Microsyst Technol, 15, 75–81, (2009)
- J. Murthy et al., Review of Multiscale Simulation in Submicron Heat Transfer, International Journal for Multiscale Computational Engineering, 3, 5-32 (2005)
- S. Sinha and K. E. Goodson, Review: Multiscale Thermal Modeling in Nanoelectronics, International Journal for Multiscale Computational Engineering, 3, 107-133 (2005)
- Thermal Nanosystems and Nanomaterials, Topics in Applied Physics, 118, S. Volz (Ed.), Springer, 2009
- D.G. Cahill, Nanoscale thermal transport. II. 2003–2012, Applied Physics Reviews, 1, 011305 (2014)

Summary of project
The project will develop an integrated physics-based experimental and modelling effort to be used in nanometrology and will define a common terminology for nanothermal measurement, realise standard materials and devices for measurement and calibration of nanothermal measurements, calibrated and validated thermal models covering the range from atomic to macro-scale, reference measurements and documented procedures. All these outputs should become standards of measurement including their traceability and reproducibility.

Summary of the modelling
Tools for modelling the proximal and contact thermal interaction between nanoprobes and samples are being developed, as well as heat transport inside nanomaterials. Heat conduction through electrons, vibration modes such as phonons and air molecules in materials and at interfaces are computed. Thermal radiation at close-contac is also calculated. A separate task deals with macroscopic thermomechical properties of polymers.

• Thermal conduction effective properties in nanomaterials using:
- Molecular dynamics to calculate heat transfer in nanoscale and microscale systems, both in bulk materials and across microscopic junctions. This involves effective thermal conductivities and thermal boundary resistances. Density Functional Theory is used to validate classical molecular dynamics calculations and to prepare empiric potentials for some structures and their combinations.
- Boltzmann transport equation for phonons. The goal is to calculate the heat flux that propagates from localized heat sources, mostly in the stationary regime. Monte-Carlo statistical sampling techniques and deterministic techniques such as the Discrete Ordinate Method (DOM) or the Ballistic-Diffusive Equations (BDE) are used to solve the Phonon Boltzmann Transport Equation for both atoms and molecules. Continuum elasticity is also used to calculate the phonon band structures, which allows computing the effective thermal conductivity.
• Thermal radiation in and between nanoscale to macroscale objects such as nanoprobes to samples using Fluctuational Electrodynamics, that is the mixing of wave theory (Maxwell equations) with the Fluctuation-Dissipation Theorem (FDT). Maxwell equation calculations based on Finite Difference in Time Domain (FDTD) to estimate electromagnetic field-related phenomena in Scanning Thermal Microscopy
• Heat conduction in air between probe shapes and flat samples with Ballistic-Diffusive Equations (BDE) and Direct Simulation with Monte Carlo (DSMC) method
• Thermal transfer and flow in polymeric materials during their fabrication process in order to assess the link between the shape and macroscopic structure and their thermomechncial properties.

All these simulations are compared to experiments for validation and the developed tools can provide guidelines for optimization.

Modelling

in RADINTERFACES 263273

Subject of the modelling

Damage mechanisms and effects on mechanical properties for novel crystalline materials with large interfacial areas

Models used
Electronic:
  DFT and fitted many body potentials for calculation of diffusion barrier
Atomistic:
  Molecular Dynamics (MD)
  Hybrid kinetic Monte Carlo-Molecular Dynamics
Continuum:
  Mechanical modeling for interface defect and dislocation mechanics

Simulation software and type of numerics used
LAMMPS Molecular Dynamics Simulator for fast and precise modelling of multilayer systems and nanostructured systems
Micromechanics model: Dislocation Dynamics Simulator solved by FE methods for interface motion and damage

Achievements of the model beyond experiments

The modelling is going to guide the appropriate tuning of interfaces within multi-laminate composite materials to obtain defect absorption materials with a self-healing mechanism.

Application

Nuclear reactors, radiation damage

Summary of the project

Radiation damage is known to lead to materials failure and thus is of critical importance to lifetime of and safety within nuclear reactors. The purpose of the project is to create self-healing materials using nanoscience in the design and control of nanostructures and complex defect structures. The materials should self-heal radiation-induced defects and avoid impurities that can yield radiation impervious (inpenetrable) materials.

Summary of the modelling

This project aims at developing general modelling tools to predict the effect of interface composition (monophase, heterophase) and structure (geometry, roughness) on its propensity to resist radiation damage (both via defect localization and creep) using a multiscale multiphysics approach. Model validation will arise through direct comparison with materials testing for a wide array of materials systems (metal/metal, metal/oxide, oxide/oxide).

First using DFT and fitted many body potentials the project will quantify the energies required to activate diffusion (diffusion barriers). For the sake of simplicity, diffusion of vacancies will be studied first. The simulations will be conducted on bilayer interfaces for the Cu/Nb system in the Kurdjimov Sachs orientation, for the Zr/Nb system in all three Burgers, Potter and Pistch Schraeder orientations such as to extract their excess energy and structure. Comparison with experimentally observations will serve as a validation. Based on experimental observation and ab initio simulations of the different interface structures -such as those in the Zr/Nb system, inter-atomic potentials will be developed and improved.

Atomistic models of interfaces representing bi-material interfaces (e.g. metal/metal, oxide/oxide, metal/oxide) and substrate/layer interfaces will be developed based on molecular dynamics (MD). The code will be based on LAMMPS. A hybrid kinetic Monte Carlo-Molecular Dynamics (Object Oriented kinetic Monte Carlo) model will be developed aiming at studying the irreversible processes taking place in the irradiation conditions at the atomic scale and in cascade events. This is done by listing all possible reactions and paths that a given defect could follow and by then choosing the most probable one based on Monte Carlo statistical method. All possible events are quantified by migration energies, formation energies (leading to binding energies). These energies are quantified with the numerical Nudged Elastic Band method in MD. It will be based on a newly developed synchronous parallel kinetic Monte Carlo algorithm capable of reaching longer times in larger systems and will allow following the evolution of individual defects (i.e. vacancies, interstitials, He and their clusters).

At the continuum scale, a damage accumulation constitutive equation for macromechanical modelling will be developed based on a micromechanical model (differential equations) to describe the thermodynamical and kinetic response of the synthesized materials to microstructural features. This micromechanical model is 3-D cluster dynamics model -where transport and reactions in the form of absorption and emission of defects are taken into account in constitutive equations. Here rather than following individual defects within the nanolayered system, defect quantities are followed as densities. This leads to a great decrease in the amount of information (i.e. defects) to be followed which then allows to simulate the evolution of defect for long time scales.

Discrete dislocation dynamics simulations (micromechanics), accounting for the symmetry of the crystals considered, will be performed to predict the mechanical response of layered systems and to extract latent hardening parameters. To describe phenomena in the interface regions a constitutive equation based on point defect and dislocation mechanics concepts capable of accounting for interface morphology, diffusive processes, radiation-induced hardening, and the effect of dislocation/vacancy interactions will be developed. For example, the effect of defect penetration on the presence of disconnections (i.e. interfacial defect with both dislocation and step characters) will be considered.

A continuum mechanics model incorporating the above constitutive models will be implemented capable of accounting for coupled diffusion-mechanical bulk and interfacial phenomena. Numerically this is going to be implemented with the Finite Element method. The code will be based on a two level approach in order to account for the coupling between interfacial motion and defect diffusion, and at each finite element time step, driving forces for interfacial motion will be calculated.

Modelling

in REFREEPERMAG 280670

Subject of the modelling

Magneto-crystalline and shape anisotropy in RE-free magnets

Models used

Electronic: Density functional theory (DFT) for crystalline anisotropy
Mesocale: Micromagnetics dynamics for shape anisotropy

Simulation software and type of numerics used

WIEN2k, Elk, muffin-tin orbitals (EMTO) pseudopotential approaches with plane waves (VASP) or numerical local orbitals (SIESTA, OpenMX) for DFT calculations
Most of these codes provide MPI-parallel versions suitable for large-scale computations. MAGPAR, FEMME will be used for micromagnetics together with finite element discretisation codes (GID, Salome)

Achievements of the model beyond experiments

The theory can pre-identify interesting materials prior to the actual synthesis and experiments and thus save time and resources.

Application

Magnets

Relevant review articles

Gilleien and Dronskowski • Vol. 31, No. 3 • Journal of Computational Chemistry, 2011
J. Buschbeck, et al, PRL 103, 216101 (2009)

Summary of the project

The project REFREEPERMAG aims at developing new permanent magnets (PM) with high energy product without use of rare-earths or platinum. High-aspect-ratio nano-structured materials with large magnetic moments will be studied theoretically and synthetized in environment-friendly ways.

Summary of the modelling

Two different kinds of magnetic anisotropies, namely the magneto-crystalline anisotropy and shape anisotropy are investigated. Due to their inherently different nature, they will also be studied with two different approaches. The magneto-crystalline anisotropy will be studied by first-principles electronic structure calculations with DFT using both full-potential and pseudopotentials methods. The project will use various basis sets, e.g., augmented plane waves with local orbitals.   High-throughput algorithms will be employed to search the parameter-space of ternary compounds. An additional alloying element will be added to these selected systems to obtain additional degrees of freedom and the modeling will determine whether this improves the system. For alloys, some of the DFT codes implement the coherent potential approximation, which was shown to be the best single-site approximation for alloys.

The shape-anisotropy will be studied with a micromagnetics code solved with a finite element discretization approach in order to study the influence of realistic microstructures on the magnetic switching behaviour of nano and mesoscopic structures in order to predict optimised structures and packing densities for a nanocomposite PM. In every iteration step the contribution of the Zeman field, the anisotropy field, and the stray field components of the particles/grains are calculated by the hybrid finite element method with boundary element method. Energy barriers for thermal switching are calculated by the implemented nudged elastic band method,which calculates the minimum energy path, i. e. the saddle point between two local energy minima of the system. Starting from an initial guess a highly probable path is found moving the points along the path according to an algorithm which resembles tensioning an elastic band across maximum energy range. Micromagnetics can predict the hysteresis properties of mesoscopic magnetic structures including the coercive field and switching times and their thermal stability depending on the geometry and the size of the magnetic volumes.

The ultimate aim is to compact powders of magnetic nanostructures with intrinsic large coercivities.

http://refreepermag-fp7.eu/project/what-is-refreepermag/

Modelling

in ROLICER 263476

Subject of the modelling

Damage and degradation of ceramics (silicon nitride, mechanical and thermal loading)

Models used

Electronic: DFT and Mixed-Basis PseudoPotential (MBPP)
Atmoistic: Molecular Dynamics (MD: based on inter-atomic empirical potentials)
Continuum: micromechanical models for thermoelasticity, plasticity, sliding interaction, cohesive interfaces and dynamic analysis) and an elastohydrodynamic lubrication (EHL) model (Reynolds equation)

Simulation software and type of numerics used

Quantum Espresso for ab initio QM DFT
LAMMPS for MD
EHL (Fourier analysis)
ABAQUS, ANSYS (FEM) and numerical methods of homogenization for continuum mechanics
        SIMPLEWARE for 3D microstructure generation

Achievements of the model beyond experiments

The ab initio models provide reliable properties of the bulk material and solid-solid interfaces as criteria for crack initiation, which are very difficult to obtain by experiments.
Molecular dynamics models are used in modelling hybrid steel-ceramic contact to study the interaction between additives in lubricants and bearing surfaces. Experiments that provide such information are not possible.
The micromechanical and macroscopic models calculate stress distributions in undamaged and damaged regions of components, which cannot be obtained experimentally. The fracture models describe crack nucleation based on traction-separation laws which provide a phenomenological lifetime prediction tool without the need for extensive experiments.
The microscale models results are homogenised to arrive at thermoelastic properties and thermomechanical homogenisation of strengthening effects in ceramics. Such simulations provide information that cannot be obtained experimentally.

Application

Metalforming tools; hybrid bearings

Relevant review articles

J. Wippler, T. Böhlke, Structure and fracture property relation for silicon nitride on the microscale, Computational Materials Science, DOI 10.1016/j.commatsci.2012.02.042

Wippler, J., Fünfschilling, S., Fritzen, F., Böhlke, T., Hoffmann, M.J.: Homogenization of the thermoelastic properties of silicon nitride. Acta Materialia 59, 6029-6038 (2011) DOI:10.1016/j.actamat.2011.06.011

I. Khader, A. Hashibon, J.-M. Albina, A. Kailer,Wear and corrosion of silicon nitride rolling tools in copper rolling, Wear 271 (2011) 2531-2541.

A. Hashibon, C. Elsässer, Approaches to atomistic triple-line properties from first-principles, Scripta Materialia 62 (2010) 939-944

J.H Beynon, Finite-element modelling of thermomechanical processing, Phil. Trans. R. Soc. Lond. A, 357 (1999) 1573-158.

J.H Beynon, Tribology of hot metal forming, Tribology International 31 (1998) Pages 73-77

Summary of project

RoliCer relies on multiscale predictive models to assess damage and simulate degradation mechanisms in engineering ceramics under realistic working conditions. This will include tribology, damage analysis and lifetime predictions. The project aims at a systematic tailoring of ceramic materials for new applications, where modelling is supported by measuring techniques. The project concentrates on silicon nitride ceramics which are wear corrosion and contact fatigue resistant materials and potential materials for high temperature metal-forming tools and rolling elements for bearings

Summary of the modelling

RoliCer develops multiscale simulations based on continuum [mechanics](#) (finite-element FE numerics and numerical homogenization) and elastohydrodynamic lubrication (EHL) to predict time-dependent mechanical, tribological and thermal material stresses arising in contact. The micromechanical models use coupled thermal-mechanical analysis techniques to obtain material stresses as a function of material properties and realistic working conditions. Within the homogenization schemes, efficient numerical estimates of the failure probabilities depending on microstructural parameters are obtained. The modeling focuses a reliable failure prediction also for non-proportional and cyclic loading. The EHL simulations provide information on the lubrication film thickness, local stress, pressure distribution, temperature and deformation and factors affecting the breakdown of the lubrication films on real rough surfaces in mechanical contacts; the applied methodology is based on Fourier analysis of the harmonic components of the surface microgeometry to predict stresses and the induced lubricant film.

Continuum models depend on the availability of material parameters suitable for describing the behaviour of the bulk material, and in RoliCer they are partially provided through electronic and atomistic simulations. These include the elastic constants, physical and mechanical properties of the materials involved.

First, an electronic model based on [density functional theory (DFT)](#) calculations will be conducted to investigate the adhesion of relevant metal-ceramic interfaces, and internal grain boundaries. The adhesion energy will provide direct information on the tribological aspects which relate to the degradation mechanisms. Additionally, the influence of the environment on the degradation mechanisms will be investigated. This will be achieved by considering the effects of impurities and point defects on the bonding and structure of both metal-ceramic interfaces and grain boundaries. The main assumption here is that impurities are correlated with the environment, such as (i) temperature, which enhances the diffusion and leads, for example, to higher concentration of point defects; (ii) foreign impurities originating from the metal or lubricant. As a result, the role of DFT calculations will be twofold: to investigate the correlation between the interface structure, point defects and adhesion and to provide input to the microscale simulations through constitutive equations, hence enabling the simulation of realistic working conditions.

The second atomistic method describes the interactions between atoms with semi-empirical potentials, which allow performing large-scale [molecular dynamics](#) and static relaxation. Such methods can be used to study large scale defect structures in the ceramics, such as dislocations and general incoherent grain boundary models. The effect of temperature, or thermal stresses will be studied large-scale molecular dynamics and static relaxation; two distinct approaches will be tackled, by inducing large thermal gradients, or via coupling to statistical physics (fluctuation-dissipation theorem) where one can estimate via statistical mechanics the rate of [thermal transport](#), and its effect on the degradation of the materials, for example, through the interaction of dislocations and phonons (which are the means by which the thermal energy is transported in the system).The initiation and propagation of cracks will be investigated efficiently using molecular dynamics and static (relaxation of atomic positions at absolute zero temperature) simulation techniques. Such simulations require reliable interatomic potentials. [Constitutive equations](#) will also be derived from the results of the interatomic potentials, which would have the advantage of dealing with incoherent interface models, and take temperature effects into account as well.

Modelling

in ROMEO 309729

Subject of the modelling

Magnetic material with reduced content of critical raw materials

Models used

Electronic: spin-polarized [density functional theory](#) to predict new phases that exhibit ferromagnetism and to compute the magneto-crystalline anisotropy as function lattice constant in permanent magnetic materials

Mesoscopic: [micromagnetics dynamic models](#) based on Landau-Lifshitz-Gilbert equation to calculate magnetization reversal in permanent magnets as function of microstructure and intrinsic magnetic properties

Simulation software and type of numerics used

Ab-intio packages VASP and WIEN2K for spin-polarized density functional calculations
Micromagnetic software FEMME for the calculation of magnetization reversal
     Hybrid boundary element / finite element method for micromagnetic simulations

Achievements of the model beyond experiments

Fast database screening combined with spin-polarized density functional theory can be used to find candidate materials for new permanent magnets and this saves a huge amount of time.

Application

Permanent magnetic stuctures for energy automotive and wind power applications

Relevant review articles covering the topic (not necessarily their own):

Schrefl, Thomas, Gino Hrkac, Simon Bance, Dieter Suess, Otmar Ertl, and Josef Fidler. 2007. "Numerical Methods in Micromagnetics (Finite Element Method)." In *Handbook of Magnetism and Advanced Magnetic Materials*. Helmut Kronmüller, Stuart Parkin (eds) John Wiley & Sons, Ltd.

Summary of project

Currently, magnets are based on the rare earth elements neodymium and dysprosium, which are predominantly mined in China (>95%). ROMEO targets to remove, or greatly reduce, the need for heavy rare earths in permanent magnets, by developing several novel microstructural-engineering strategies that will dramatically improve the properties of magnets based purely on light rare earths elements, especially the coercivity, which will enable them to be used for applications above 100°C. ROMEO's second goal is to develop a totally rare-earth-free magnet.

Summary of the modelling

Inter-granular phases of sintered RareEarth-TransitionMetal-Boron magnets create a lattice distortion in the hard magnetic grains. The role of the specific structural distortion near grain boundaries on the magneto-crystalline anisotropy and magnetization will be determined by means of first principles DFT calculations using the WIEN2K package. The project will perform ab-initio calculations of the magnetic properties of Pr2Fe14B, Nd2Fe14B and tetragonally-distorted tetragonally distorted FeCo-compounds. The computed intrinsic magnetic properties (magnetization and anisotropy) serve as input for mesoscopic simulations.

Using non-zero temperature micromagnetics based on the elastic band method. The project computes the influence of the local change of intrinsic magnetic properties near grain-boundaries in grain-boundary engineered magnets. The minimum required thickness of the layer that contains heavy-rare-earths will be computed. Magnetic properties will be computed as a function of grain size. Magnets containing a grain boundary phase that is anti-ferromagnetically coupled to the main phase may lead to high coercive field at the expense of remanent magnetization. The optimal structure (grain size versus boundary phase thickness) with respect to specific requirements of key applications (EV, HEV, wind power) will be searched for using numerical optimisation techniques combined with micromagnetic simulations The results will be compared with temperature dependent measurements of the coercive field..

Analytical expressions will be sought for the relations between parameters and results. Micro-magnetic and global relations between the coercive field and the activation volume will be compared to find analytical relations expressing the role of various structural and physical parameters. The relation expressing the coercive field for different superferrimagnetic structures (for example $Nd_2Fe_{14}B$ in a $GdFe_2$ matrix) and nanostructures will be used to find an optimum solution. The relations will be compared with experimental data.

First a database will be created of electronic structures of 50,000 existing and new Heuslers by performing spin-polarized DFT calculations for prototype compositions. This will be used in a search for materials exhibiting specific intrinsic properties such as magnetization and anisotropy with a ground-state crystal structure which is uni-axially distorted (tetragonal). The experimental data will be used to develop the database and to improve the predictive power.

http://www.romeo-fp7.eu/

Modelling

in SaveMe 263307

Subject of the modelling
Nanoparticle and drugs transport and uptake in tissues and tumours

Physics/Chemistry models used
Continuum: Chemical (pharmacokinetic) model; Fluid mechanics: Advection-Diffusion equation; Darcy's law; Dual Porosity model for flow and transport

Simulation software and type of numerics used
Tumour growth model (in-house developed code based on the boundary element method)
Dual porosity model for flow and transport through tissue (in-house developed code based on the meshless RBIE)
Physiologically based pharmacokinetic model (in-house developed code)
COMSOL multiphysics software platform

Achievements of the model beyond experiments
The physiologically based pharmacokinetic (PBPK) model was used to analyse the effect of the permeability of the blood capillary membrane on the biodistribution of nanosystems. The model was also used to conclude on the in-vivo toxicity of nanosystems based on in-vitro toxicity results.

Application
Analysis of biodistribution of nanosystems in the living organisms
Dose determination of nanosystems for diagnostics and therapy
Analysis of accumulation of nanosystems in tumours and other tissue, binding to targets, and delivery of localized treatments
Analysis of tumour response to therapy

Relevant review articles covering the topic (not necessarily their own):
1. Nestorov I (2003) Whole-Body Pharmacokinetic Models. Clinical Pharmacokinetics, 42:235–249.
2. Erbertseder K, Reichold J, Flemisch B, Jenny P, Helmig R (2012) A Coupled Discrete/Continuum Model for Describing Cancer-Therapeutic Transport in the Lung. PLoS ONE, 7, e31966.
3. Cristini V, Lowengrub J, Nie Q (2003) Nonlinear simulation of tumor growth. J. Math. Biol. 46, 191–224.

Summary of project

SaveMe project addresses pancreatic cancer diagnosis and treatment by the design and development of novel modular nanosystems platform integrating new functionalized nano-core particles and active agents. For diagnostics, superior tracers are developed for molecular MR/PET and gamma camera imaging, enabling efficient diagnosis and guided surgery, respectively. Novel functionalized nano-core systems were conjugated with semi-confluent active shell layer. For therapeutics, active nanosystems are developed to deliver (1) therapeutic siRNAs or (2) anti-MP-inhibitory-scFVs. To facilitate the above diagnostics and therapeutic effects, advanced tumour targeting and penetration active agents are linked to nano-core functionalized groups, including a biocompatible PEG layer linked to tumour selective MMP substrate molecules and highly safe and potent novel somatostatin analogue peptides targeting SSTR overexpression.

Summary of the modelling

Two different physiologically based pharmacokinetic (PBPK) models and software tools were developed (a blood flow restricted (perfusion rate limited) and a membrane-limited model) for biodistribution of nanoparticles in living organisms. The model equations are based on principles of mass conservation, fluid flow, and biochemistry. The model parameters, e.g., partition, diffusion and clearance coefficients for different organs or tissue systems are determined through calibration using data on concentration change with time in plasma and organs. It was found that the permeability of the blood capillary membrane has significant effect on the transport of larger nanosystems between blood and tissue. The membrane-limited model would be more accurate than the blood flow restricted model in predicting accumulation of smaller nanosystems with large binding affinities, amplified by multivalent interactions. These nanosystems will accumulate in the first cells they encounter after extravasation. The model was also used to conclude on the toxicity of nanosystems based on in-vitro toxicity results.

A tumour growth model and a software tool was developed which determines the sharp interface between the tumour and the surrounding tissue. The model starts with a certain size and shape of the tumour and depending on the parameters/conditions determines its growth. The model is based on the CFD equations for diffusion of nutrients and Darcy's law for cell movement. A number of constitutive equations provide the required links between blood-tissue transfer rate and concentrations in blood and tissue; cell velocity depending on pressure (constitutive equation based on Darcy's law); Laplace-Young interface condition linking interface pressure, surface tension related to cell-to-cell adhesive forces and local total curvature; and several other equations related to characteristic tumour cell mitosis rate and tumour cell apoptosis rate. The cell-to-cell pressure is solved in the tumour as well as the pressure in the surrounding tissue to increase accuracy. The application domain includes the presence of necrotic core viable tumour tissue and surrounding healthy tissue. The system of equations is non-linear and represents a moving interface problem. The numerical implementation has been based on the boundary element method. The model provides a tool for analysis of the effects of therapeutic drug on tumour growth through the effect of the drug on the characteristic tumour cell mitosis rate and the tumour cell apoptosis rate.

A model for transport and uptake of nanosystems in tissue was developed based on the CFD equations for dual porosity approach. The field variables in the model are fluid pressure for the flow, which is described by the Darcy law, and the solute concentration for the transport, which is calculated using the advection-diffusion equation. According to the dual porosity approach the tissue is considered to consist of two overlapping porous systems representing the interstitial and the vascular space and that there is exchange of fluid and solute through the walls of the blood vessels. The model and software tool is developed in-house and is calibrated and validated using COMSOL Multiphysics software platform. The model for transport and uptake of nanosystems showed the significance of the time within which the therapeutic drug is released on the drug transport in the tumour due to its influence on the concentration gradients.

Modelling

in SIMBA 229034

Subject of the modelling
Synthesis of silicon nanopowders in Inductively Coupled Plasma (ICP) systems

Models used
Atomistic: statistical mechanics transport model (kinetic gas equation) for plasma thermodynamic and transport properties
Continuum: Computational Fluid-Dynamics (CFD) for plasma physics, precursor evaporation and nanopowder transport and growth

Simulation software and type of numerics used
Commercial CFD code ANSYS FLUENT extended to take into account plasma physics, precursor evaporation and nanopowder synthesis.
Numerical routines written in C for the Chapman-Enskog method to solve the Boltzmann kinetic gas equation

Achievements of the model beyond experiments
The modelling of the plasma flow dynamics and particle trajectories permitted to define the process at different scales and to predict the influences of the main process parameters (e.g. effects on nanopowder production yield when changing the reactor geometry and operating conditions).
The model enabled the design of an optimum reactor chamber with increased flow of particles for collection thus avoiding an expensive try-and-fail approach, and saving time and effort in optimising the lab scale process and in transferring main results to an industrial ICP installation.

Application
Production of anode material (nano-silicon based) for Li-Ion battery and photovoltaic applications

Relevant review articles
Colombo V et alii, Journal of Physics D: Applied Physics 42 (5), 2009
Colombo V et alii, Plasma Sources Sci. Technol. 19 (2010) 065024
Colombo V et alii, J. Phys. D: Appl. Phys. 43, 105202 - 105214 (2010).
Colombo V et alii, IEEE Trans. Plasma Sci, 6th Triennial Special Issue on Images in Plasma Science, 2011.
Colombo V et alii, Plasma Sources Sci. Technol. 21, 025001 (2012)

Summary of the project

The project SIMBA addresses the upscaling of synthesis of metallic nanoparticles with the Inductively Coupled Plasma (ICP) technique. This project developed an industrial production line including on-line monitoring systems for silicon and silicon-based alloyed nanoparticles, which can be applied as anode material in battery applications. It included an on-line functionalisation technique and an industrial powder injection system to ensure a continuous production.

Summary of the modelling

An advanced CFD model FLUENT (including electromagnetics, non-LongTermEvolution effects, chemical non equilibrium, turbulence models, discrete-phase model with plasma-particle interaction, plasma thermodynamic and transport properties) was used in SIMBA. This code uses parallel computing, and is capable of capturing the fine geometric details. The existing model can predict temperature and flow fields of different plasma mixtures of a variety of gases together with injected particle temperature and trajectory prediction. This model for plasma fluid-dynamics has been extended to simulate non-equilibrium plasma (low pressure operating conditions and the strong temperature gradients due to the quenching system) and for the nanopowder nucleation out of the gas phase (aerosol model to track the particle size-distribution and particle population in the reactor region and to calculate process yield). This model for the precursor particle thermal history and trajectory prediction is using a Lagrangian approach for continuum CFD methods.

The first order perturbation solution of the Boltzmann kinetic equation, i.e. the Chapman Enskog method, has been used for the calculation of the transport properties of SIMBA gas mixtures.

The model is applied to the actual lab-scale Empa reactor (plasma torch and reaction chamber) and has been proven to calculate temperature, velocity, viscosity profiles of plasma flow in the whole system. The model has been validated through comparison with enthalpy probe measurements of temperature under different operating conditions and calorimetric measurements for energy balance of the plasma system. The computational effort of this calculations is reduced by a) limiting the computational domain to the most important regions of the reaction chamber (e.g.: the quenching zone); b) decoupling the plasma torch with the reaction chamber domain, using the calculated plasma torch outflow fields (temperature, velocity, concentration, ...) as boundary condition for the reaction chamber.

The model has allowed a design-oriented modelling approach to optimize the lab scale process and then to transfer main results to an industrial ICP installation.

www.simba-project.eu

Modelling in SimPhoNy 604005

Subject of the modelling
Integrated multiscale modelling environment applied to nano- and micro-fluidic applications

Physics/Chemistry models used
Electronic: Density Functional Theory ([DFT](#))
Atomistic: [Molecular Dynamics](#) (MD)
Mesoscopic: [Coarse-Grained Molecular Dynamics (CGMD)](#), [Dissipative Particle Dynamics (DPD)](#), [Lattice Boltzmann (LB)](#)
Continuum: CFD

Simulation software and type of numeric used
Electronic: Quantum-Espresso and VASP (DFT)
Atomistic: LAMMPS (MD)
Mesoscopic: LAMMPS (CGMD and DPD), JYU-LBM and Palabos (Lattice Boltzmann Methods)
Continuum: OpenFOAM (FVM), NUMEROLA (FEM), Kratos (FEM, DEM), SimPARTIX (DEM, SPH), LIGGGHTS (DEM) solvers of the FVM and FEM type, Smoothed Particle Hydrodynamics (SPH) and Particle Dynamics methods (DEM)

Achievements of the model beyond experiments
The applications developed in the SimPhoNy project will enable scientists and engineers to obtain information that current experimental technology is unable to reveal easily, such as molecular structure and thermodynamics properties in the liquid near walls or in confined regions and self-organization of nanoparticles and fibers as a function of local fluid properties.

Application
- Nanotubes as single molecule-mass detectors or NEMS (Nano-Electro-Mechanical Systems)
- Optimization and design of novel nano-printing processes
- New foam-forming process for biodegradable materials
- Enhanced nano- and microfluidics

Relevant review articles covering the topic (not necessarily their own):
1. E. Weinan, B. Engquist, X. Li3, W. Ren, E. V. Eijnden. Heterogeneous Multiscale Methods: A Review. Commun. Comput. Phys., 2, 367 (2007).
2. J. Larson, R. Jacob, E. Ong. The Model Coupling Toolkit: A New Fortran90 Toolkit for Building Multiphysics Parallel Coupled Models. Int. J. High Perf. Comp. App., 19, 277 (2005).
3. S. Portegies Zwart, S. McMillan, at al. A Multiphysics and Multiscale Software Environment for Modeling Astrophysical Systems, New Astronomy, 14, 369 (2009).
4. J. Hegewald, M. Krafczyk, at al.. An agent-based coupling platform for complex automata. ICCS, volume 5102 of Lecture Notes in Computer Science, Springer, 227, (2008).
5. M.J. Buehler, J. Dodson, J., Meulbroek, P., Duin, A. & Goddard, W. A. The Computational Materials Design Facility (CMDF): A powerful framework for multiparadigm multi-scale simulations. Mat. Res. Soc. Proceedings, 894, LL3.8 (2006).

Summary of project
SimPhoNy will develop data interoperability interfaces that allow seamless linking and coupling of models each describing material phenomena on a specific scale. These models will be the building blocks for multiscale simulations. One of the main focuses of the SimPhoNy project is to develop a user friendly, extendable and open platform for the integration of various existing open source and commercial simulation and pre- and post-processing software packages. From the application side, SimPhoNy focuses on a cluster of related nano- and microfluidic applications that requires solving of problems not addressable by individual codes alone.

Standard interfaces and data structures
The SimPhoNy Application Programming Interface (API) provides a common interface to all simulation software tools, while the data compatibility layers, using the Common Universal/Unified Data Structure (CUDS), take care of data conversion between the different computational and pre- and post-processing tools and the SimPhoNy environment. Together with 5 other NMP projects on multi-scale modelling (DEEPEN, ICMEg, MMP, MODENA, and NANOSIM) communication standards (metadata keywords and an overall data structure for file based information exchange) will be elaborated. These will be used in the SimPhoNy platform. ICMEg will organise workshops to reach European endorsement. The CUDS are a set of knowledge-based keywords and values with metadata that transcend scales and methods. It allows defining common language and terminology enabling seamless communications between different applications. The main issue here is the mapping of application specific settings and keywords to a standard and default set, namely the CUDS, so that an application agnostic approach to the development of multiscale science can be facilitated. Regardless of the specific applications integrated, the same set of API and CUDS keywords can be used. In this way, users may focus on the science instead of on the specific technical details of the applications. The CUDS enable the development of inter-process and inter-scale communications in a standard and open manner. The interfaces will be developed in compliance with the GNU LGPL license, or a more permissive license, to allow their interaction with open-source as well as with commercial packages. This will ensure sustainability over time through an open development process. In addition, three new and improved pre- and post-processing and scientific visualization tools will be further developed and integrated within the environment. These are AViz for publication-quality rendering of atomistic and electronic modelling data, Open nCAD-fluid for CAD-like pre-processing capabilities targeted at nano- and microfluidic applications and Mayavi2 for processing for complex visualization.

Integration of codes
In the first step, wrapping of computational tools will be designed based on indirect operations through file input and output (File-IO) without requiring any alteration to the native code of the respective integrated applications. The File-IO is not expected to be efficient for all production run scenarios due to its high IO overhead. It nevertheless offers an excellent platform for rapid development and debugging of new methodologies for concurrent modelling, and provides an efficient means for sequential multi-scale models, where moderate and infrequent data exchange is required. In the second step, the internal interfaces of the respective computational tools will be modified to allow the wrapper a direct access via a library interface to the internal state of the simulation tools. The internal interface library will allow the models to communicate through the defined common API and CUDS on a level that allows seamless integration and development of efficient inter-process and inter-model communications in particular for concurrent coupling of simulations.

Linking and coupling of models
One of the fundamental and challenging issues that will be tackled in SimPhoNy pertains to the question of consistency and reversibility between models applied to all scales, especially when the multi-scale modelling approach is connecting two methods having only a small subset of the degrees of freedom in common (e.g., atomistic and continuum). The work will therefore focus on investigating the loss of information, its impact on the accuracy, and how it may be remedied by enhanced coupling schemes. The SimPhoNy platform will provide a rapid development environment where intricate schemes for data reduction, extraction and transfer between models and methods can be easily and rapidly developed, and consequently tested and validated. Linking and coupling of models will cover problems requiring both direct transfer of properties from one model and computational method to another and more complex concurrent scenarios requiring extraction, averaging and filtering of data between two or more models. Simple examples include transfer of atomic positions from MD to DFT, or global rheological properties from one system to another. Besides model development and integration, SimPhoNy also includes elements of validation by comparing simulation data against a set of experimental test cases that will be performed within the project by manufacturing end user partners.

Modelling

in SIMUGLASS 233524

Subject of the modelling
Precision glass moulding

Models used
Continuum:
CFD for
Laminar flow of ideal gas (protection gas):
Navier–Stokes equations (continuum equation, momentum equation and thermal equation),
for conduction, convection, radiation
Mechanics models:
Elastic model (for mould) and visco-elastic models (for glass)
Thermo-rheologically model for viscoelastic material based on Kelvin equation, Burgers equation, Newton's fluid, WLF shift function, Narayanaswamy equation

Simulation software and type of numerics used
ABAQUS, ANSYS (Finite Element codes)
        Transient solving, implicit method

Achievements of the model beyond experiments
Shape of moulds can be now predicted with the help of modelling of the glass shrinkages, which had to be done previously by expensive try-out experiments.
Index drop inside glass lens can be now predicted with the help of modelling of the structure relaxation behaviour of glass material, which was unknown only by pure experiments.
Material flow and temperature during forming process can be predicted, which can not be observed and measured in the real moulding process.

Application
Optics for lighting and photovoltaic
Optics for imaging
Optics for laser apparatus

Relevant review articles

O. Dambon, F. Wang, Y. Chen, A. Y. Yi, F. Klocke, G. Pongs, "Efficient Mould Manufacturing for Precision Glass Moulding," J. Vac. Sci Technol. B, 27 (3), 1445-1449 (2009).
A. Jain, A. Y. Yi, X. Xie, R. Sooryakumar, "Finite Element Modeling of Stress Relaxation in Glass Lens Moulding Using Measured, Temperature-Dependent Elastic Modulus and Viscosity Data of Glass," Model Simul Mater SC, 14 (3), 465-477, Mar (2006).

Summary of the project

This project has developed a FEM-tool for material modelling, process simulation and optimization of optical glass moulding. The relevant thermal, mechanical, rheological and optical glass material properties and their dependence on the moulding parameters (forming velocity, temperature, force, etc.) were investigated.

Summary of the modelling

The simulation of hot glass deformation is a complex thermo-mechanical problem comprising interactions between radiative/conductive thermal transport phenomena, incompressible, viscous fluid dynamics of softened glass and the large strain/large displacement visco-elastic/visco-plastic deformation of glass due to pressing in the mould.
Some of the important issues to be addressed by modelling are (a) large free surface deformations (b) complex contact phenomenon (c) high deformation rate (d) time and temperature dependent boundary conditions and (e) high degree of material non-linearity

The project has developed a generalized simulation tool covering the whole cycle of glass moulding for the whole relevant temperature range incl. newly developed glass material models.

The micromechanics code is based on the commercial packages MARC, DEFORM 3D, FIDAP, POLYFLOW, SYSTUS, ANSYS, ABAQUS, and LS-DYNA. The project developed a CFD model for the behaviour of the laminar flow of the protection gas, which is usually nitrogen gas. Such protection gas is used only not to prevent the heated glass material from being oxidised, but also to help the heat flow convect more efficiently inside the machine chamber. This is used to determine the thermal boundary conditions for the FEM model of the glass forming process. New glass material model for the thermo-rheologically viscoelastic material behaviour, which occurs in the moulding process, is developed based on existing models like Hooks, Maxwell, Kelvin, Burgers fluid, Newton's viscosity materials model, in which the strain rate and time dependency is considered.

The result is a complete process simulation including structural and thermal analysis, which covers all the important procedures during the moulding process: heating, soaking, moulding, holding and cooling.

www.simuglass.com

Modelling

in SMASH 228999

Subject of the modelling

GaN nanocolumn LEDs

Models used

Electronic:
  [Quantum mechanical models](#) for eigenstates of confined particles in nanostructures in continuous medium ([EFA](#) [k·p](#)) and [empirical tight-binding](#) level
  Statistical mechanics based [electron and hole transport models](#)
Continuum: [EM models](#) for optical properties

Simulation software and type of numerics used

TiberCAD for strain/electronic modeling
QUATRA/CELS for luminescence modelling
OptiWave for electromagnetic properties
Numerical libraries, such as portable extensible toolkit for scientific computation and scalable library for eigenvalue problem computations (PETSc, SLEPc)

Achievements of the model beyond experiments

The modelling and simulation of GaN-based LEDs is able to guide the device design, by optimizing strain, polarization and quantum effects in order to improve the performance of the devices. Atomistic simulations can shed light on the effect of clustering in the alloy active regions.

Application

LEDs

Relevant review articles

Auf der Mau, M et al; IEEE TRANSACTIONS ON ELECTRON DEVICES, Vol. 58, No. 5, May2011, overview on the multi-scale approach is given, and on what is essential to simulate the growth and the electro-optic properties of nanowires.

Summary of the project

The project SMASH has developed LEDs of high efficiency and low cost. An epitaxial growth technique based on nano-rod coalescence on ultra-low defect density templates has been realised. Also growth of directly emitting Gallium Nitride based nano-rod structures has been developed. High efficiency devices covering the entire visible spectrum and phosphor-free white LEDs have been manufactured.

Summary of the modelling

The multiscale simulation tool TiberCAD includes all the relevant physical models, at electronic, atomistic and continuous level, for the investigation of strain, transport and optoelectronic properties of GaN nanocolumn structures.

The calculation of strain in lattice mismatched heterostructures is based on linear elasticity theory of solids, assuming pseudomorphic interfaces between different materials.

Transport of electrons and holes is treated in a semi-classical picture based on the drift-diffusion model. The particle fluxes are written in terms of the electrochemical potentials. The carrier statistics are given by Boltzmann or Fermi-Dirac statistics, assuming as usual local equilibrium. The conduction and valence band edges and effective masses are obtained from bulk k·p calculations, which include the local corrections due to strain. Quantum mechanical models used for the calculation of eigenstates of confined particles in nanostructures, are based on the envelope function approximation (EFA) and on the empirical tight binding (ETB) model. In the first case, the Hamiltonian of the system is constructed in the framework of single-band and multiband k·p theory. The ETB method is an atomistic approach where electron and hole states of the QD states are written as a linear combination of atomic orbitals (LCAO). Self consistent band profiles have been calculated by concurrently solving the Poisson/drift-diffusion and the quantum mechanical models. Carrier capture and escape in and out of the well is described with a combination of a drift-diffusion model in the contact region and more sophisticated quantum description in the region close to the quantum well is used. The atomistic structure, which is needed for ETB calculations, is generated internally in TiberCAD according to the macroscopic device description and crystallographic orientation.

Strain maps and the effects of strain, piezo and spontaneous polarizations, as well as surface states, on band profiles have been studied in GaN nanocolumn p-i-n diode structures with different active regions, such as Quantum Disk (QD) and Core Shell.

Electroluminescence spectra are obtained with a custom developed quantum kinetic model (CELS/QUATRA). Optical properties of nanorods, in particular the extraction efficiency, emission directionality and polarization, are calculated with the electromagnetic simulation tool OptiWave. Optical emission spectra and the dependence of transition energies on geometrical and material parameters have been found.The microscopic complex refractive index is taken as input, as well as the different absorption by metals and semiconductors. The wave guiding properties of a single nanorod, as well as the electromagnetic coupling of the rod arrays forming a collective photonic crystal emitter or bottom distributed reflector are investigated, and an optimum design is developed.

Coupled electro-optical properties in a LED device are studied by applying a combination of the described above. Exciton and carrier distributions, polarization states of emitted photons, radiation characteristics are calculated also by finite element tools FDmax and CELS/QUATRA. Finally, key device specifications such as the internal and external efficiency of nanorods in LED geometries are simulated and structure parameters for an optimized LED performance are determined. In particular, the design for phosphor-free white light emitting devices is optimized, which is crucial to meet specific colour coordinates. The model results have been used as input to adjust epitaxial growth conditions and stamp design.

Modelling

in SOLARDESIGN 310220

Subject of the modelling
Solar cells (flexible thin film Cu(In,Ga)(S,Se)$_2$)

Models used
Electronic: [quantum mechanics](#), [electronic transport](#)
Atomistic: [Monte Carlo simulation](#)
Continuum: [electrical](#), [thermal](#) and [mechanical modelling](#) of the device
Continuum: [fabrication process modelling](#)

Simulation software and type of numerics used

Electronic and atomistic: TCAD for charge generation and transport
Modelling of manufacturing processes and computing mechanical stress with TCAD SENTAURUS PROCESS
Electrical, thermal and optical modelling with TCAD SENTAURUS DEVICE for the device behavior
Different optical solvers will be used to handle light propagation and absorption (e.g. transfer matrix method, ray tracing, beam propagation method, but also solution of the Maxwell's wave equation using with the Finite-Difference Time-Domain method (FDTD).

Achievements of the model beyond experiments

The methodological toolbox provides design rules for the best Cu(In,Ga)(S,Se)$_2$ solar cell super-structure and module design layout for a given application reducing significantly the number of experimental trials and reducing costs. Models are used to correlate the impact of process variation to parametric yield, thereby lowering production costs, as well as the geometrical design of the solar module in order to meet the custom product requirements.

Application
Custom designed thin film Cu(In,Ga)(S,Se)$_2$ solar cells for energy harvesting in buildings, products and textiles.

Relevant review articles
- U. Malm, M. Edoff, 2D device modelling and finite element simulations for thin-film solar cells, Solar Energy Materials & Solar Cells 93 (2009) 1066–1069
  Joar Johansson, Modelling and Optimization of CIGS Solar Cell Modules, Master's Thesis, Lunds universitet, 2008
- M. Lee, D. Pramanik, H. Liang, E. Korczynski, J. van Duren, Optimization of Graded CIGS Solar Cells Using TCAD Simulations, MRS Proceedings, Volume 1447 / 2012,
  DOI: http://dx.doi.org/10.1557/opl.2012.1167
- J.Malmström, On Generation and Recombination in Cu(In, Ga)Se2 Thin-Film SolarCells, PhD Thesis, ppsalaUniversity,2005
  URL: http:// www.diva-portal.org/diva/getDocument?urn_nbn_se_uu_diva-5721-1__fulltext. pdf
- J. Lähnemann, Spectrally Resolved Current Losses in Cu(In,Ga)Se2 Thin-film Solar Cells, Diploma Thesis at the Freie Universit¨at Berlin carried out at the Institut des Materiaux Jean Rouxel /Universit´e de Nantes, France, 2008

Summary of project

SolarDesign has the goal to deliver innovative and cost-effective custom designed solar cell prototypes suitable for the integration into building skins, roof tiles or electric devices. The aim is to obtain new custom designed systems for decentralized solar power generation ranging from low- to high power applications.

For these applications the solar cells need to be flexible and obey certain electrical constraints. This project is developing interconnection of thin- film solar cells created with a simplified production process of thin-film modules that allows adjustment the specifications of a PV module "on-the-fly" without excessive set-up times.

Summary of the modelling

Simulations will provide a detailed physical description of the new solar cells operation, allowing researchers, designers and architects to explore new cell/module concepts and meet specific requirements as well as to optimize current fabrication technologies.

SolarDesign will use an advanced multiscale device (TCAD) simulator capable of simulating electrical, thermal, and optical characteristics of CIGS solar cells/modules, for development and optimization of their performance.

TCAD 1D QM electronic simulations for small geometries in SolarDesign will provide insights into the physical mechanisms affecting charge transport within the solar cell such as optical generation, surface and bulk recombination processes, grain boundary effects, contact design, and interconnect losses, texturing. These quantum effects will be included in continuum models.

Process simulation TCAD SENTAURUS PROCESS will deal with modelling (2D- or 3D-) of the fabrication steps of solar cells/modules, like e.g. different types of depositions, etching, oxidation, diffusion, and implementation of models for custom solar cell processes. The mechanical models (particularly doping and material growth) are either based on basic diffusion equations or an analytic Gaussian solution is assumed. Process conditions like the ambient chemical composition, pressure, temperature etc. during individual fabrication steps can be implemented in the model. The simulation tool will allow the researcher to select parameters to be investigated and visualize the influence of each parameter, as well as to compute the influence of mechanical stresses in PV cells.

The continuum electrical models are based on Poisson and continuity equation together with the material relations and a carrier transport model (either electronic drift-diffusion, atomistic Monte Carlo or continuum hydrodynamics). The material properties are given by the carrier mobilities, the susceptibility and eventually the band structure from the electronic modeling. The project will explore solar cell/module design alternatives in order to meet the performance goals. The model will simulate dark and light I-V curves, internal and external quantum efficiency, fill factor and other key cell performance attributes using monochromatic, and standard solar spectra (e.g. AM1.5g) as well as other illumination spectra (indoor applications).

The project will use the electrical device design code TCAD SENTAURUS DEVICE in a customized approach. The simulation tool will support mixed-mode simulations, combining numerical simulations and lumped circuit elements to analyze, for example, resistive losses in the metallisation and will allow exploring different device designs.

Modelling

in Solarogenix 310333

Subject of the modelling
Electronic properties of semiconducting oxides for water splitting applications

Physics/Chemistry models used
Electronic: quantum chemical methods centered around density functional theory ([DFT])

Simulation software and type of numerics used
Electronic: VASP, a plane wave basis code and GPAW: real space basis code

Achievements of the model
Ab-initio simulations allow to evaluate the effect of specific material modifications such as doping etc. In experiments the effect of specific modifications is often hard to quantify, due to the interference with other effects such as morphology changes etc.

The same holds true for stability calculations of specific intermediates of the photocatalytic reaction chain. Experimentally single reaction steps are difficult to access. Computationally the properties of single reaction intermediates can be studied in dependence of various dopants or other material modifications. In general *ab-initio* simulations are used as important tool to gain deeper insights and a more comprehensive understanding of fundamental processes in water splitting applications.

Additionally, *ab-initio* simulations are used to screen material modifications with respect to their usefulness in enhancing photocatalytic efficiencies. For instance the band alignment in heterostructures plays a decisive role in the efficient separation of photoexcited charge carriers. Here computational material screening can already predict (with some limitations in the accuracy) which material combinations are promising candidates for application in photoelectrodes.

Application
Photoelectrochemical water splitting processes

Relevant review articles covering the topic (not necessarily their own):
"Enabling practical electrocatalyst-assisted photoelectron-chemical water splitting with earth abundant materials", X. Yang, R. Liu, Y. He, J. Thorne, Z. Zheng, D. W. Wang, *Nano Res.* **2015,** 8(1), 56-81 , DOI: 10.1007/s12274-014-0645-2
"Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting", T. Hisatomi, J. Kubota, K. Domen, *Chem. Soc. Rev.* **2014,** *43(22),* 7520-7535. DOI: 10.1039/c3cs60378d
"Thermally-driven processes on rutile TiO2(110)-(1 x 1): A direct view at the atomic scale", Z. Dohnalek, I. Lyubinetsky, Rousseau, Roger **,** *Prog. Surf. Sci.* **2010,** 85 (5-8), 161-205 DOI: 10.1016/j.progsurf.2010.03.001

Summary of project
The SOLAROGENIX project investigates the application of earth abundant metal oxide semiconductors (TiO2, Fe2O3 and WO3) as water oxidation catalysts (WOC) in a photoelectrochemical (PEC) water splitting configuration in order to provide an alternative and sustainable source for hydrogen. Starting from fundamental theoretical investigations, over materials synthesis, modification and up-scaling, in-depth characterization of materials properties and efficiency is carried out, in order to end up with an industrial prototype demonstrating the feasibility of this technology compared to existing electrolysers. Modelling is therefore in integral part of the project structure enabling a detailed insight into reaction pathways and screening potential materials combinations. Nonetheless, due to the complexity of a PEC cell with solid/solid, solid/electrolyte, as well as solid/gas and electrolyte/gas interfaces complete modelling of the on-going reactions lies beyond the capability of today's models.

Summary of the modelling
Electronic density functional theory including the correction of the self-interaction error for highly localized electrons by the DFT+U method and hybrid functional methods are used. As input the atomistic geometries of the structures which determine the external potential seen by the electrons is required. As output electronic properties such as the density of states, band structure, electron density, single particle energies are obtained in addition to structural properties such as the stress tensor or forces acting on single atoms.
In order to take into account correlation effects for the localized d-electrons in transition metal oxides, DFT+U and hybrid functionals such as HSE06 are employed.
The influence of material modifications such as doping and hydrogen treatment on the electronic structure and stability of intermediate steps in the catalytic water oxidation is investigated and the behaviour of heterojunctions with respect to the formation of potential profiles within photoelectrodes is simulated. With this model the fundamental reaction pathways could be understood.

Modelling

in SSEEC 214864

Subject of the modelling
Magnetic materials, micromagnetism, magnetic cooling engines

Models used
Electronic: Ab initio DFT models of non-collinear magnetic material groundstates (electronic quantum mechanical models using 10s of atoms)
Mesoscopic: Micromagnetic (mesocale) models, including exchange-coupled nanocomposites (1-10 nm)
Continuum: modelling of materials including conductive and convective heat flow equations, Maxwell equations and fluid dynamics equations and magnetic cooling engine modelling

Simulation software and type of numerics used
Ab initio DFT models: OpenMX (http://www.openmx-square.org/) and VASP (http://www.vasp.at/). Site-based magnetic moments were calculated using the Voskown analysis within the general gradient approximation scheme.
Preisach model of hysteresis: original C++ code written and solved in-house.
Micromagnetics: Free energy of a magnetic solid, solved using in-house C++ code.
Magnetic cooling engine prototypes: COMSOL Multiphysics, Matlab, Mathematica. Finite element and analytical treatments were used. The entropy generation method was developed for efficiency analysis.

Achievements of the model beyond experiments
The materials modelling gave us invaluable feedback on experimental development, reducing the time that would otherwise be required to make multiple measurements or a full phase space of physical samples.
Regarding the cooling engines, the 2D model of an active magnetic regenerator (AMR) enabled accurate optimisation of geometry (packing density, absolute length scales), system operating parameters (frequency, flow rate) and identification of optimal (or ideal) refrigerant material properties (magnetocaloric effect and heat capacity) against overall efficiency and power requirements.

Application
Magnetic materials, manufacturing industry, magnetic cooling engines

Relevant review articles
The papers containing the DFT work are:
Barcza, Gercsi, Knight and Sandeman, Phys. Rev. Lett. **104** 247202 (2010)
Gercsi and Sandeman, Phys. Rev. B. **81**, 224426 (2010)
Gercsi, Hono and Sandeman, Phys. Rev. B. **83**, 174403 (2011)
Micromagnetics: Basso, J. Phys. Condens. Matt. **23** 226004 (2011).
Reviews: "Gas-free refrigeration" K.G. Sandeman, Magnetics Technology International, **1** 30 (2011); "Magnetocaloric materials: the search for new systems" K.G. Sandeman, Scripta Materalia **67** 566-571 (2012)

Summary of the project
The ultimate goal of this project was to lower the economic barrier to entry of magnetic cooling as a high efficiency cooling technology free from greenhouse gas refrigerants. SSEEC's efforts in this direction centred around the development of a low power heat pump based on a highly efficient magnetic refrigeration cycle. The device features a magnetic refrigerant that is magnetised and demagnetised by movement relative to a permanent magnet. The core materials research concerned the identification, synthesis, modelling and production of low cost, environmentally friendly magnetic refrigerant materials based on new (nano)-architectures.

Summary of the modelling
SSEEC aimed to develop an integrated approach to magnetic cooling for an end-user application. This entailed characterisation of materials, integration of those into prototype cooling engines, and integration of those engines into an end-user (heat pump) system. The modelling work examined magnetic refrigerants (novel physical mechanisms of magnetic cooling) and magnetic cooling engines (an integrated view of the impact of design on cost and performance).

Magnetic refrigerants: DFT models were used to calculate site-based magnetic moments using the Voskown analysis within the general gradient approximation scheme. Giant magneto-elastic coupling in CoMnSi (a metamagnetic refrigerant material) and thereby the dependence of magnetism on Mn-Mn interatomic distance in Mn-based materials of the same structure (*Pnma* space group) was modelled as it can be used to understand and control magnetic phase transitions. This modelling led to predictive synthesis of new metamagnets. The exchange coupling between the phases in the composite material was calculated (note this is at nano-scale).
The phenomelogical Preisach model of hysteresis (irreversibility) was applied for phase transformations at the mesoscale. It was found that the entropic, or cooling effect of a nano-scale spin reorientation-based refrigerant is diluted by any amount of second, exchange-coupled phase, and that, for the oxide systems synthesised, retention of a single phase is more desirable. However, for other systems a second phase could be of use in broadening the temperature range of use of a candidate refrigerant.

Micromagnetics models used exchange couplings, dependent on composite geometry, as an input. First the effect of mixing a spin reorientation material with a ferromagnet in a nano-composite in which the constituent phases were exchange coupled was modelled. It was demonstrated that the total entropy change of the composite was reduced, but spread over a wider temperature range. Secondly a nano-scale magnetic heterostructure comprised of two different hard magnetic materials with orthogonal axes of unaxial anisotropy was designed and proved to function as a theoretical anisotropy switch, the optimal dimensions of which were determined by the composition of each layer.

Magnetic cooling engines: different cooling cycles were modelled using "real" magnetic materials that have magnetic phase transitions (required for magnetic cooling) which exhibit magnetic hysteresis (a source of loss). Experimental data were used to generate a detailed picture of the magnetic cooling effect of La-Fe-Si when deployed in a relevant, "regenerative" cooling cycle. Cooling engine modelling underpinned a comprehensive design approach for the development of magnetic cooling engine prototypes as well as optimising the design of individual components. The model couples the different aspects at work within a magnetic cooling engine: heat transfer, fluid flow, magnetic fields and loss processes, and uses the material properties calculated with DFT as input. Over 100 magnet designs were examined and tuned, valves were optimised for flow, pressure drops and flow rates, and magnetic forces inside the cooling engine (both regenerators and magnetic valves) were optimised. Accurate optimisation of an overall system design that can meet the power, weight, span, volume and cost targets needed for a commercial system was achieved.

http://www.sseec.eu

Modelling

in SUPER-IRON 283204

Subject of the modelling

Physical properties of iron-pnictides superconductors (spin susceptibility and effective electron-electron interaction) in superlattices, thin-films, interfaces, grain or twin boundaries

Models

Electronic: Various [Density Functional](#) implementation and [effective tight binding model](#)
Bogoliubov-de Gennes model for the superconducting and magnetic phases

Simulation software and type of numerics used

All-electron codes (Fleur, Elk and FLAPW)
Plane-waves implementations (VASP, Quantum-Espresso)
Local basis, linear scaling DFT codes (Siesta, OpenMX)
The DFT implementations are all stable, optimized, parallelized and highly maintained codes. They are mainly based on complex matrix manipulations and Fast Fourier Transform operations.
Specific developed software will be based on iterative matrix diagonalization and many-body multiband Hamiltonian solution.

Achievements of the modelling beyond experiments

Prediction of high-pressure phase transitions in $Ba(Ca)Fe_2As_2$ and of non-hydrostatic effect, confirmed by high-pressure XRD measurements
Prediction of the peculiar structural and electronic modification upon doping with rare-earth metals in $CaFe_2As_2$
Understanding of disorder, surface and interface effects
Model calculations, joined with DFT calculations, were able to predict a tri-critical point in the phase diagram of iron-pnictides, now a hot subject for experimental confirmation

Application

Non-conventional iron-based superconductors systems

Relevant review articles

M.Putti, et al., "New Fe-based superconductors: properties relevant for applications" Supercond. Sci. Technol. **23** (2010) 034003
K. Tanabe and H. Hosono "Frontiers of Research on Iron-Based Superconductors toward Their Application" Japanese Journal of Applied Physics **51** (2012) 010005
G. R. Stewart "Superconductivity in iron compounds" Reviews of Modern Physics, **83** (2011) 1589

Summary of project

The topic is to investigate Fe-based superconductors characterized by FeAs (or FeSe) planes separated by different layers. Among these compounds there are the so called 1111 phase (represented by the LaFeAsO), the 122 ($BaFe_2As_2$), the 111 (LiFeAs) and the 11 (FeSe) phases as well as the new pnictide oxide superconductors intercalated by oxides blocking layers. Superconducting properties will be investigated also under high magnetic field and/or pressure and visualization of local electric field and current will be carried out with a number of techniques. SUPERIRON will then depict the roadmap for exploring and exploiting the potentialities of Fe-based superconductors (FeSC).

Summary of the modelling

SUPER-IRON will use models to predict structural, electronic and superconducting properties of interfaces in FeSCs. In particular, they will study: single crystal properties (superlattices), the interface between two layers of the same material but with differently oriented crystalline axes and properties of interfaces between two different materials (blocking layers, superconductor/metal interface).

Bulk samples of single crystals will be simulated with parameter free first-principles simulations (Density Functional Theory, DFT). The effect of substitutions, various kinds of defects and applied pressure on the structural, electronic, magnetic and superconducting properties of FeAs superconductors will be investigated. This will provide input parameters for multiband analyses of superconducting and normal state properties.

Interface properties will be simulated by first-principles structural models. The study will address layers with misoriented crystalline axes, the stability and energetics of thin film geometry and superlattices formed by different layers of various FeAs superconductors. Lattice mismatch, uni-axial pressure effects, interface and surface states will be investigated.

Also the possibility of incorporating perovskite and metal blocking layers intercalated with FeAs planes will be studied. The structural stability of the terminations, defect formations and their effect on the electronic, magnetic and superconducting properties will be predicted.

The interplay of temperature and pressure, structural and magnetic transition will be studied by Landau theory developed from ab-initio calculations fully taking into account the effect of the crystalline structure.

Effective tight-binding Hamiltonians will be constructed starting from first-principles to describe the electronic properties of defects, superlattices and grain boundaries and simulate the superconducting properties (Jc, Hc, Tc) by means of Bogoliubov-De Gennes equations. This will give information on the superconducting properties: order parameters in real space across the boundary, superconducting current flow at the boundary and critical currents (Jc° and how the superconducting properties of FeSCs are affected by the mis-orientation angle will be predicted.

First-principles models of effective interactions between electrons, including spin fluctuations, will be elaborated to provide fundamental information on the superconducting transition, and its dependance on the critical temperature. The calculation of superconducting properties will be done extending the ab-initio SuperConducting Density Functional Theory with electronic pairing interactions.

A different crystallographic orientation of the grains and different properties of the grain boundaries result in a strongly inhomogeneous current flow. A model, based on an approach for percolation in MgB_2, will be developed, which predicts loss-free macroscopic currents.

Modelling

in SUPERLION 214832

Subject of the modelling

Nano-architectured battery materials and 3D microbattery components

Models used

Atomistic: [Molecular Dynamics (MD)](#) for electrochemical phenomena for material/battery/production process optimisation
Mesoscopic: [Lattice Gas Model](#) for charge and mass transport
Continuum: [Fluid dynamics](#) and [electrochemical modelling](#)

Simulation software and type of numerics used

COMSOL multiphysics for the flow and electrochemical phenomena
DL_POLY for MD
MCGEN for nanoscale battery architecture

Achievements of the model beyond experiments

The model allowed shortened and better-informed selection of the most efficient cell architectures and geometries, and the optimal cell materials. Modelling can avoid excessive and often futile efforts to create more impressive micro-architectured electrodes, since these will often not result in improved battery performance.

Application

On board microbatteries for electronic and medical devices

Relevant review articles

Kasemägi et al., Solid State Ionics, 168 (2004) 249
Brandell et al., J. Mater. Chem., 15 (2005) 4338
Thomas et al., ECS Meeting Abstracts, Los Angeles, Oct. 2005
Thomas et al., Modelling studies of 3D-Microbatteries, IMLB-13, Biarritz, May 2006
Liivat et al., Polymer, doi: 10.1016/j.polymer.2007.08.05
Liivat et al., J. Mater. Chem., doi:10.1039/b706938c

Summary of the project

The project SUPERLION has contributed to improved materials synthesis, and the design and fabrication of novel 3D nano-architectured microbattery components.

Summary of the modelling

Molecular Dynamics (MD) modelling of branched PE/PEO as a host matrix for Li-ion battery electrolytes, and electrochemical and transport modelling with Finite Element (FE) modelling is made of the individual materials considered for relevant battery architectures and geometries.

Electrochemical system modelling (with the code Comsol) has provided new and invaluable insights into the optimal device configurations, given the technological and materials limitations. A first approach exploiting Newmann theory has simulated the porous electrodes in prospective micro-scale Li-ion batteries and has given current-voltage relationships for the complete 3D-MB device. This work has provided valuable input for material/battery/production process optimisation.

This approach has been accompanied by simulation of charge and mass transfer in the 3D-MB structures. The description of equilibrium potential of the electrode material has been based on the Lattice Gas Model with COMSOL. Diffusion of Li ions inside the electrode material is simulated by numerically solving the relevant diffusion equations for appropriate geometries. Simulation of electrolyte phenomena has been made by applying the Nernst-Planck approximation.

Simulations of complete 3D-MB geometries are done at both an atomic- and continuum-level to better understand the underlying reasons for critical current distributions within micro-/nano-micro-battery systems. Work at both levels is needed in understanding the basic functionality/design relationships in 3D micro- and nanoscale battery architectures. DL_POLY is the software codes used for atomic-scale polymer Molecular Dynamics and MCGEN and COMSOL are used for FEA modelling of 3D-microbattery architectures.

SUPERLION investigated a link between MD and a continuum mechanical model but the statistics in the MD did not contain enough ion jumps to be able to extract meaningful classical ion diffusion constants (D). The runs were exceptionally long - up to 6 months (shared time) on a "supercomputer" and the models contained up to 50 000 atoms - but nevertheless "MD box-sizes" and run-times were still too small/short to accumulate enough "ion-jump events".

Modelling

in SURFUNCELL 214653

Subject of the modelling
Adsorption phenomena at the interface of cellulose surfaces

Models used
Electronic: DFT for hydrogen bonding and dispersion interaction between cellobiose and glucose
Coupled-Cluster electronic calculations
Atomistic: Molecular Mechanics for cellulose/water interface with molecular mechanics using the GLYCAM06 force field
Mesoscopic: Coarse grained grid-based model of the interaction of nanoparticles among each other and with cellulose substrate

Simulation software and type of numerics used
Molecular mechanics (MM) using the GLYCAM06 force field(supercell approach with periodic boundary condition). Programs: ChemShell, DL_POLY DFT and DFT-D functionals used: BP86, B3LYP, M06
TURBOMOLE, TERACHEM
In-house code for CGMD

Achievements of the model beyond experiments
Modeling reproduced and predicted the strength and structured buildup of hydrogen bonds of water to the cellulose surface and inside the water layer as a function of the water layer thickness. This led to suggestions for the design of the surface structure and charge distribution at cellulose surfaces.

Application
Interfacial chemistry

Summary of the project

The aim of the project is the creation of functional surface modifications using polysaccharides and nano-particles leading to four different demonstrators in the fields of pulp and paper, cellulosic yarns, cellulose films and filter membranes.

Summary of the modelling

Adsorption of water or small or large carbohydrates on cellulose surfaces is frequently attributed to the formation of highly stable hydrogen bonds. Adsorption phenomena at the interface of cellulose surfaces require modeling of a system that is composed of two subsystems: the cellulose bulk and the adsorbate. The modelling of the interaction between cellulose and water using force fields is very delicate: water-water interaction in bulk water can be described with water models, which are not part of the force fields used for cellulose. Therefore the modelling of the interaction at the interface has to be considered as crucial and this can only be done by comparing results at different level of theory ((electronic) quantum mechanical and (atomistic) molecular mechanics model).

Within the Surfuncell project, a study was started with classical molecular dynamics using CHEMSHELL and DL-POLY on the strength of different H-bonds in cellulose, separating the intrinsic H-bond dissociation energy (H-bond strength) from the atom-pair van der Waals interactions. The interaction of cellulose surface of different morphologies and any kind of adsorbates as a function of the water layer thickness using molecular dynamics simulations was also studied to get a feeling for the number of water molecules that are necessary for the adsorption of solvated molecules at the cellulose surface.

Coarse grained modelling with in-house codes was used to simulate the formation of layers of nanoparticles on cellulose surfaces. For this purpose, a grid-based, discrete model operating at the scale of the nanoparticles has been developed. The model assumes a simplified geometry of the particles, a limited discrete set of particle locations and orientations and a simplified, short ranged interaction between particles and the surface. In return, this coarse-grained approach allows the simulation of layer formation involving millions of particles and a subsequent analysis of the layers' statistical properties.

www.surfuncell.eu

Modelling

in SYNAPSE 310339

Subject of the modelling
Electro-thermal behavior of chalcogenide nanowires (NWs) in simple structures, including core-shell

Models used
Electronic: DFT
Atomistic: classical molecular dynamics (MD) simulations, based on an interatomic potential generated by means of a neural network (NN) scheme.
Continuum: coupled models for electrical and thermal behavior based on Poisson's equation for electrical conductivity and the Fourier's heat law

Simulation software and type of numerics used

CP2k open source code for ab-initio molecular dynamics simulations based on Density Functional Theory and a Car-Parrinello-like scheme
Proprietary RuNNer code for molecular dynamics simulations with the NN interatomic potentials (several thousand atoms and several tens of ns)
The electrical and thermal models will be solved numerically by employing both MATLAB and COMSOL software suites

Achievements of the model beyond experiments

DFT simulations allowed uncovering the atomistic structure of the amorphous phase of several phase change compounds, the microscopic origin of the resistivity and optical contrast between the crystalline and amorphous phases and the vibrational signature of different local atomic configurations in the amorphous network.
Large scale molecular dynamics simulations based on the NN potential have provided insights on the origin of thermal conductivity in the bulk and on the origin of the fast phase change.
Thermo-electrical models have helped to understand, or predict, several effects occurring in nanoscaled devices and they thus provide crucial insight for the actual implementation of memory devices.

Application
multi-level phase change memory devices.

Relevant review articles
S. Caravati, M. Bernasconi, T.D. Kuehne, M. Krack, and M. Parrinello, Appl. Phys. Lett., 91 (2007) 171906; S. Caravati, et al., J. Phys. Cond. Matt. 21 (2010) 255501; ibidem 22 (2010) 315801; B. Huang and J. Robertson, Phys. Rev. B 81 (2010) 081204; Mazzarello et al., Phys. Rev. Lett., 104 (2010) 085503
T. D. Kuehne, M. Krack, F. R. Mohamed, and M. Parrinello, Phys. Rev. Lett. 98 (2007) 66401
G.C. Sosso, et al., Phys. Rev. B, 85 (2012) 174103; G.C. Sosso et al, Phys. Stat. Solidi, 249 (2012) 1880; J. Behler and M. Parrinello, Phys. Rev. Lett. 98 (2007) 146401
D. Yu, S. Brittman, J. S. Lee, A. L. Falk, H. Park, Nano Lett., 8 (2008) 3429
J. P. Reifenberg, D. L. Kencke, K. E. Goodson, IEEE Electron Device Lett.
J. Liu, B. Yu, M. P. Anantram, IEEE Electron Device Letters, 32, 1340
F. Leonard, Applied Physics Letters 98 (2011) 103101

Summary of project

The SYNAPSE project will study metal-organic chemical vapor phase deposition (MOCVD) and study chalcogenide single material (core) and double material (core-shell) nanowires (NWs), to be used for multi-level phase change memories (PCM).

The project aims to downscale PCM cells by employing chalcogenide Ge-based and In-based NWs, deposited by MOCVD on different substrates and using bottom-up approaches like the vapor-liquid-solid deposition technology(VLS) and selective area growth technique (SAG). Different material combinations (Ge-Sb-Te/In-Sb-Te/In-GeTe) will be explored to expand the memory level operational features of PCM devices. The NW synthesis will be supported by the development and test of precursors for MOCVD. A detailed study of the NW phase switching behaviour (reversible amorphous-crystalline transitions) will be carried out with special attention to electrical and thermal properties of the NWs, their phase formation/crystallization dynamics, size-dependent effects and structural/chemical composition.

Summary of the modelling

SYNAPSE will do theoretical modelling and simulation of both crystallisation dynamics and electro-thermal behavior. Car-Parrinello-like molecular dynamics simulations based on density functional theory will be performed to uncover the atomistic structure of the amorphous and crystalline phases of the involved chalcogenide alloys. A comparison between theory and the experimental data will be used to aid the interpretation of the experiments. Secondly, large scale classical molecular dynamics simulations will be carried out to study the crystallization dynamics and thermal properties of the amorphous phase in the bulk and in NWs, by using suitably devised interatomic potentials. An interatomic potential (with accuracy close to that resulting from a full DFT calculation) has been already generated for bulk GeTe by fitting a huge DFT database by means of Neural Network (NN) techniques. The NN potential was able to successfully reproduce structural, dynamical and thermo-dynamical properties (including melting and crystallization) of liquid, crystalline and amorphous GeTe. We aim at extending the NN potential to GeTe NWs and to other phase change materials.

Existing electro-thermal models based on Poisson's equation for electrical conductivity and Fourier's heat law, can be tailored to fit different materials (In-Sb/In-Te, In-Sb-Te) and architectures (confined cell PCM, free-standing NWs, confined NWs) will be considered and solved with COMSOL and MATLAB. The model takes into account the thermal boundary resistance and the crystallization rate of the phase-change materials. At the same time, in-house custom models will be possibly developed, if needed to cope with novel phenomena (such as scaling, core-shell interaction, etc…). Material properties, source terms and boundary conditions of known materials will be used, or extracted from experimental data available in literature, if needed. Moreover, all boundary conditions (electrical and thermal) will be set so as to match those of the actual device. The modeling will be performed both at steady-state conditions and in transient.

Modelling

in ULTRAMAGNETRON 214469

Subject of the modelling

Optical control of nanomagnets (rare earth transition metals, diluted magnetic semiconductors) including reversal and (thermal) relaxation

Models used

Electronic: ab-initio QM for ultrafast laser-induced magnetization reversal based on the use of the Heisenberg formalism for the exchange interaction between atomic spins

Atomistic: Atomistic spin model of a ferrimagnetic material with magnetic compensation points

Landau-Lifshitz-Bloch (LLB) equation

Simulation software and type of numerics used

Parallel version of the codes

Achievements of the model beyond experiments

Materials with a compensation point are shown to be very promising media for magnetic recording.

The magnetization reversal by a single circularly polarized laser pulse has been successfully simulated.

A phase diagram for opto-magnetic reversal was obtained, demonstrating a window of peak electron temperature and effective magnetic field pulse duration for opto-magnetic switching

A new mechanism of linear magnetization reversal was discovered

Experimentally the two sublattices of a ferrimagnetic alloy (GdFeCo) were found to demagnetise at different rates which was then confirmed by the model

The model predicted that the ferrimagnet transitioned into a transient ferromagnetic phase stable for only around 300femtoseconds which was found experimentally (Nature 2011)

The theoretical model predicted that the magnetisation of the ferrimagnet reversed spontaneously on application of a heat pulse, which was then experimentally verified (Nature Comm.2012)

Application

THz magnetic recording and information processing devices
(opto-magnetic read-head and the required picosecond laser and write heads)

Relevant review articles

Nature, 472, 205 (2011); Nature Communications 3, #666 (2012)

Summary of the project

The objective of the EU-India project was to develop "opto-nano-magnetism" that is, the manipulation of the magnetic properties of nanomagnetic materials with light using (magneto-) optical effects, as a novel approach for future magnetic recording and information processing technology. This topic is situated at the junction of coherent nonlinear optics, nanophotonics and magnetism. In particular, we investigated the effects of light on magnetic order at the nanoscale, optimized materials and conditions for highly efficient and ultrafast (10-12 seconds and faster) optical control of nanomagnets and in this way tried to initiate a development of novel technology for unprecedented fast (THz) magnetic recording and information processing.

Summary of the modelling

Models have been developed for the physical understanding of the opto-magnetic process. The models have given an understanding of the thermal processes involved in the opto-magnetic reversal process. The electronic ab-initio QM model is based on the use of the Heisenberg formalism for the exchange interaction between atomic spins. It is demonstrated that ultrafast reversal can occur on heating close to the Curie temperature in the presence of a large applied field

After establishing the basic physics of the reversal detailed calculations were carried out using an atomistic spin model based on the Landau-Lifshitz-Bloch (LLB) equation. The LLB equation has the property that the magnetisation is not conserved which means that it can be used in calculations at elevated temperatures up to and even beyond the Curie temperature. In a single spin approximation, the LLB equation is computationally efficient and the influence of a magnetic field on the recovery phase following a rapid heat-pulse was investigated. This field originates in the laser-pulse due to the inverse Faraday effect.

The micromagnetic modelling is applied to ferrimagnetic material such as GdFeCo. Ferrimagnets have a magnetic compensation point which may contribute to the ultrafast reversal. It is important to study the dynamics of ferrimagnetic materials in order to understand their ultrafast dynamic magnetisation properties. For the modelling of laser-induced magnetization reversal at the nano level opto-magnetic switching processes of a single macro-spin in the framework of the Landau-Lifshitz-Bloch (LLB) equation recently derived by D. Garanin [Phys. Rev. B 55, 3050 (1997)] was investigated. It was found that the maximal electron temperature, as well as the field pulse duration, influences the reversal of the magnetic system. These findings coincide with observations found experimentally. Furthermore, it has been shown numerically as well as experimentally that the occurring reversal is not precessional in nature, but has instead a linear character, proceeding via a strongly-nonequilibrium state. The so-called linear reversal mode previously investigated analytically for a single LLB macro-spin leads to reversal processes on an ultra-short time scale. The next step went beyond this single-macro spin approach and extended the approach to a LLB based multi-macro spin simulation. The exchange coupling as well as the dipolar interaction is taken into account. Here, the long-range dipole-dipole interaction is calculated with the aid of the well-established fast-Fourier transformation (FFT). Furthermore, the code was paralellised in order to simulate extended systems of realistic size up to 107 macro-spins on our computer cluster at Konstanz.

With these new programs, systems were simulated with up to 4*106 macro-spins. A Gaussian electron temperature profile was assumed in order to model a realistic laser spot as used in the experiments. The magnetization evolution corresponds to those found in the experiment.

http://www.ultramagnetron.org

Modelling

in VINAT 295322

Subject of the modelling
Deformation and damage of ultrafine grained (UFG) metals and nanostructured biocompatible materials

Models used
Atomistic: MD for dislocation dynamics , determination of elastic properties of nTi
Continuum: Micromechanical models complemented with crystal plasticity constitutive equations, dislocation density based constitutive equations for deformation behaviour of nanomaterials

Simulation software and type of numerics used
Atomistic: MBN Explorer (full-atom molecular dynamics simulations of nanoindentation and diffusion processes occurring in crystalline and nanostructured materials), Open source code Lammps
Continuum: FE Code ABAQUS; newly developed ABAQUS subroutines UMAT, VUMAT

Achievements of the model beyond experiments
It is impossible to separate all effects influencing deformation and strength behavior of materials that are due to – non-equilibrium grain boundaries of nanomaterials, foreign atoms, small size of grains, specific properties of grain boundary phases (like content of vacancies)… in real experiments. Fortunately multi-scale model and inverse modelling can explain the individual effects

Application
Strength, reliability and biocompatibility of implants from UFG metals and their coatings
Development of new medical implants, with improved performances

Relevant review articles covering the topic
L. Mishnaevsky Jr. R. Valiev, E. Gutmanas et al. Nanostructured titanium based materials for medical implants: Modeling and development, *Materials Science & Engineering R: Reports*.Vol. 81, 2014, pp. 1–19
L. Mishnaevsky Jr, E. Levashov, *Computational Materials Science,* Special Issue of Journal devoted to the ViNaT Project, 2013, Vol. 76
E.A. Levashov, et al., Nanostructured titanium alloys and multicomponent bioactive films: Mechanical behavior at indentation, *Materials Science & Engineering A* 570 (2013) 51–62
H.S. Liu, L. Mishnaevsky Jr., Gradient ultrafine-grained titanium: computational study of mechanical and damage behavior, *Acta materialia,* Vol. 71, 2014, pp. 220-233

Summary of project

The project aimed to develop multiscale theoretical models of biocompatible metallic nanomaterials and apply them for the analysis, design and optimization of implant materials. Two groups of nanomaterials were considered, namely pure titanium and TiNi alloys.

Summary of the modelling

Virtual investigation of reserves of improving of mechanical properties of nanomaterials: the deformation and strength behaviour of ultrafine grained (UFG) titanium is controlled by the interaction of atomistic defects (e.g., vacancies, dislocations), properties of grains and (supposedly, amorphous) grain boundary phases and boundary conditions. These effects determine the reliability of new biocompatible and strong dental implants.

Using a phenomenological approach to describe dislocation kinetics, we obtained constitutive equations for grains (which included their sizes) and grain boundaries as function of vacancy density and other physical values, like Burgers vector of dislocations, diffusion coefficient, stacking fault energy, shear modulus, atomic radius, atomic volume, Poisson's ratio. The values of the elastic constants for nanocrystalline titanium appearing in this CE were obtained using atomistic MD simulations. The constitutive equations were implemented in the commercial finite element code ABAQUS VUMAT subroutine. Using this approach, a number of various structures were tested virtually. The effects of grain size, non-equilibrium of the GB phase (characterized by the initial dislocation density and diffusion coefficient) and the gradient of grain sizes on the mechanical behaviour and damage initiation of the UFG titanium were studied with this model.Using computational experiments, we established several effects that can positively influence the mechanical response and strength of UFG titanium (homogeneity of grain sizes, dispersoids/precipitates in GB and initial dislocation density in GB).

A complex of computational models for the analysis of the deformation, diffusion and strength of ultrafine metals for medical implants has been developed. The software tool includes the molecular dynamics (MD) model to calculate elastic properties of nTi solved by movable automata and continuum (finite element) models of structure evolution under severe plastic deformation. The developed computational model complex allows analysis of the structure evolution and formation, mechanical behaviour, strength and biocompatibility of ultrafine grained and nanocrystalline metallic materials as well as shape memory allows. The model complex provides the necessary tools and numerical environment for the virtual testing and computational design and development of new advanced materials for medical implants. Results can be found on the project website.

Modelling

in YBRIDIO 309560

Subject of the modeling

The induction heating of composite laminates and metal composite hybrids via electromagnetic induction and laser radiation to facilitate the joining of two dissimilar materials

Models used

Continuum:
macro mechanics of materials and heat transfer in solids
electromagnetism modeling (Maxwell equations in the eddy current (induction-diffusion) approximation)

Simulation software and type of numerics used

Finite Element Analysis (FEA) codes COMSOL AB's COMSOL Multiphysics and LSTC's LS-DYNA 980 solver for electromagnetism, solid mechanics and heat transfer.
Boundary element (BEM) and finite element (FEM) methods

Achievements of the model beyond experiments

Models help understand the effects of the many processing parameters and gives information of material (e.g. temperature and pressure at the bond line or at the connection interface of the two parts being joined) which is extremely difficult to measure to the necessary level.

Application

Automotive, aerospace industry, consumer goods, electronics

Relevant review articles

- P. L'Eplattenier, G. Cook, C. Ashcraft, M. Burger, A. Shapiro, G. Daehn, M. Seith, "Introduction of an Electromagnetism Module in LS-DYNA for Coupled Mechanical-Thermal-Electromagnetic Simulations", 9th International LS-DYNA Users conference", Dearborn, Michigan, June 2005.
- Duhovic M, Moser L, Mitschang P, Maier M, Caldichoury I, L'Eplattenier P: Simulating the Joining of Composite Materials by Electromagnetic Induction. In Proceedings of the 12th International LS-DYNA® Users Conference, Detroit, 2012, Electromagnetic (2)
- L. Huiping, Z. Guoqun, N. Shating and H. Chuanzhen, "FEM simulation of quenching process and experimental verification of simulation results", in Materials Science and Engineering A, April 2007, pp. 705-714
- Martínez, S., Ukar, E., Lamikiz, A., Liébana, F. "Laser hardening prediction tool based on a solid state transformation numerical model". Proceedings of AMPT 2010 ISBN: 978-0-7354-0871-5 Advances in materials and processing, 2010. Paris.

Summary of project

Within the YBRIDIO project the necessary know-how and equipment will be created to join thermoplastics and thermoplastic based composites with dissimilar materials, especially metals. The goal is to replace common methods (adhesive bonding, mechanical joining, ultrasonic welding, injection moulding, etc.) by a more efficient process. As a consequence, productivity can be increased while energy and raw material consumption are decreased. In addition, new knowledge-based materials, such as enhanced composites and metals with improved surfaces, will be created. Moreover new process control systems for laser and induction joining will be developed.

Summary of the modelling

Computational models are used to simulate the joining process.

The simulation of material processing using electromagnetic induction is a multiphysics problem involving the theories of [electromagnetism](#) and [heat transfer](#). If the thermal and [mechanical stresses](#) are also to be taken into account then a three-way Electro-Thermal-Mechanical (ETM) simulation coupling is required. Joule heating of composite laminates via electromagnetic induction will be modeled using general multiphysics Finite Element Analysis (FEA) codes which use a "continuum modelling approach" of the mechanics of materials in particular applying the physics of electromagnetism, solid mechanics and heat transfer using either a finite element or boundary element formulation.

Two Finite Element Analysis (FEA) software codes capable of such simulations are COMSOL AB's COMSOL Multiphysics and LSTC's LS-DYNA 980 solver. The electromagnetic behaviour is calculated by solving Maxwell's equations in the eddy current (induction-diffusion) approximation using boundary elements (rather than FE) coupled to the outer surfaces of the parts meshed using solid 3D finite elements which take care of the model's thermal and mechanical behaviour. There are advantages and disadvantages with both methods. The former, for example, provides a more efficient formulation for large (component scale) static induction heating simulations while the latter is more suited for smaller dynamic simulations where a moving coil or workpiece is required.

Given a 2D or 3D geometry, mechanical properties of the composite laminate, its thermal conductivity, specific heat capacity, thermal expansion, electrical conductivity, induction skin effect depth, heat transfer conductance, heat convection coefficient and properties of the tooling and induction equipment (mechanical properties and thermal conductivity, applied pressure, induction frequency, current amplitude, electrical conductivity, heat convection coefficient), the outputs available from the modelling are an optimized induction coil and flux concentrator, shape design, velocity, distance from work piece; induction generator: voltage, current, power; material: temperature and pressure at the bond line (or connection interface of the two parts being joined). The modelling will predict also the Joule heating temperatures, cooling behaviour, pressure requirements for consolidation, magnetic fields, electric fields, Lorentz forces, thermal expansion/deflection.

All physics equations are solved in a coupled model within each completely independent FEA code. There is no need for data transfer between the two codes. The characterization experiments necessary for gathering the verification data for such simulations is captured for both the heating and cooling cycles and is then used to verify simulation models of the same experiment before more complex joining scenarios through simulation are considered.

Modelling

in Z-ultra 309916

Subject of the modelling
Thermodynamics and kinetics of particle precipitation in heat resistant steels

Physics/Chemistry models used

Electronic: Density Functional Theory (DFT), Tight Binding (TB), Bond Order Potentials (BOP)
Atomistic: Classical Molecular Dynamics (MD),
Mesoscopic: Kinetics of particle precipitation based on thermodynamic extremum principle,
    discrete dislocation dynamics (DDD), constitutive equations based on dislocation
    densities and interactions with evolving particle microstructure
Continuum: Solid mechanics and thermodynamics

Simulation software and type of numerics used

Electronic: Mixed-Basis Pseudopotential Program (MBPP, IWM own code); SIESTA; PWscf
Atomistic: own MD code; GULP; LAMPPS
Mesoscopic: MatCalc, Thermocalc, own models for Z-phase nucleation, own DDD program
Continuum: ABAQUS; Paton Institute own FE code for welding

Achievements of the model beyond experiments
Tracer diffusion experiments are possible but expensive, and require laboratories which can
handle radioactive substances. The nucleation mechanism of the Z phase can hardly be
understood from experiments alone. Before an alloy is physically available (which requires
several months), modelling can predict its properties and helps to define the best alloy
composition and heat treatment. Residual stresses in the interior of large components are
nearly impossible to measure, but can be taken from simulations.

Application
Z-phase strengthened, heat-resistant steel
heat treatment, welding

Relevant review articles covering the topic (not necessarily their own):
M. Mantina, Y. Wang, R. Arroyave, L.Q. Chen, and Z.K. Liu, and C. Wolverton, *First-principles
calculation of self-diffusion coefficients*, Phys. Rev. Lett. 100, 215901 (2008)
E.R. Margine, A.N. Kolmogorov, M. Reese, M. Mrovec, C. Elsasser, B. Meyer, R. Drautz, and D.
G. Pettifor, *Development of orthogonal tight-binding models for Ti-C and Ti-N systems,*
Phys. Rev B 84, 155120 (2011)
M. Mrovec, D. Nguyen-Manh, C. Elsasser, and P. Gumbsch, *Magnetic Bond-Order Potential for
Iron,* Phys. Rev. Lett. 106, 246402 (2011)
J. Svoboda, F.D.Fischer, P. Fratzl, E. Kozeschnik, *Modelling of Kinetics in Multi-Component
Multi-Phase Multi-Particle Systems I. – Theory*, Mat. Sci. Engng. A, 385, 166-174 (2004)
E. Kozeschnik, J. Svoboda, P. Fratzl, F.D. Fischer, *Modelling of Kinetics in Multi-Component
Multi-Phase Multi-Particle Systems II. – Numerical Solution and Application*, Mat. Sci.
Engng. A, 385, 157-165 (2004)

Summary of project

The aim is to develop a heat resistant steel which allows increasing the thermal efficiency of fossil power plants in order to reduce the CO2 emissions.

Summary of the modelling
The experimental material development is supported by multiscale modelling activities ranging from quantum-mechanical DFT models over thermodynamic/kinetic models to macroscale models describing different processing steps and the material and component behavior under service conditions. The project applied the following models

DFT:
Input: parameter-free; lattice symmetry prescribed; symmetry of defect configuration
Output: model finds the energetically favourable lattice symmetry, formation energy, elastic moduli; formation energies of vacancies, interstitials and substitutional defects; migration energies of defects → diffusion coefficients
Limitation: Up to a few hundred atoms can be modelled

TB and BOP:
Input: Hamilton matrix elements from DFT
Output: Same as DFT, less reliable, but for larger numbers of atoms; large number is needed for dilute defects to minimize unrealistic interactions

MD:
Input: Atomic interaction forces from DFT and BOP
Output: Same as TB and BOP, less reliable, but for much larger numbers of atoms

DDD:
Input: Initial dislocation configuration, particle distribution
Output: Evolution of dislocations, influence of the particles

Thermodynamic/kinetic models:
Input: Chemical composition of alloy; thermodynamic data base; kinetic data base
Output: Equilibrium phase composition; evolution of phase composition

Constitutive equations:
Input: Model parameters from a set of experiments on the considered material
Output: Mechanical material behaviour under arbitrary stress-temperature-time histories

Annex III
List of software codes used in NMP projects

SOFTWARE	where they are used by the NMP projects	website
ABAQUS	Continuum solid mechanics (micro and macro); fluid dynamics; process	www.3ds.com/fr/products/simulia/portfolio/abaqus/overview
ABINIT	Electronic: quantum mechanical	www.abinit.org
ACEFEM	Continuum solid mechanics (micro and macro)	www.wolfram.com/products/applications/acefem
ADF	Electronic: quantum mechanical and and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.scm.com/Products/ADF
AMBER	Atomistic: ab-initio molecular dynamics and Quantum Mechanics/Molecular Dynamics	www.ambermd.org
AMPAC	Electronic: quantum mechanical and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.semichem.com
ANSYS (FLUENT)	Continuum solid mechanics (micro and macro); fluid dynamics	www.ansys.com
ANSYS HFSS	Continuum: Electomagnetism	www.ansys.com
BOLTZTRAP	Electronic: many-body and semi-empirical or parametrised electronic models	www.icams.de/content/departments/ams/madsen/boltztrap
CANTERA		code.google.com/p/cantera
CASTEP	Electronic: quantum mechanical and Atomistic: ab-initio molecular dynamics and Quantum Mechanics/Molecular Dynamics	www.castep.org
CHEMKIN	Continuum: chemistry	www.reactiondesign.com/products/open/chemkin
CHEMSHELL	Continuum: chemistry	chemcell.sandia.gov
CFX ANSYS	Continuum: fluid mechanics	www.ansys.com/Products/Simulation+Technology/.../ANSYS+CFX
CODICE_DEG	Continuum: solid mechanics (micro)	www.codice-project.eu/codes and demos
CODICE_MEC	Continuum: solid mechanics (micro)	www.codice-project.eu/codes and demos
COMSOL	Mesoscopic: statistical methods, Continuum solid mechanics (micro) ; continuum thermodynamics; electrochemistry; continuum EM	www.comsol.com

CP2K	Electronic: quantum mechanical and Atomistic: ab-initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.cp2k.org
CRYSTAL MAKER	Electronic: quantum mechanical	www.crystalmaker.com
CTQMC	Electronic: many-body and semi-empirical or parametrised electronic models	inhouse (GOFAST)
CTS studio suite	continuum EM	www.cst.com/2010
DALTON	Electronic: quantum mechanical	www.dirac.chem.sdu.dk/daltonprogram.org/
DEFORM3D	Continuum mechanics (macro)	www.deform.com/products/deform-3d/
DEMON2K	Electronic: quantum mechanical	www.demon-software.com
DESSIS	Continuum: Device modelling	www.iue.tuwien.ac.at/phd/klima/node8
DETCHEM	Continuum: Chemistry	www.detchem.com
DIFFRACMOD	Continuum EM	www.foservice.com/SOFTWARE/diffractmod
DGCA	Mesoscopic: micromagnetics, file compression	inhouse (DYNAMAG)
DL_POLY	Electronic: quantum mechanical and device level	http://www.stfc.ac.uk/cse/25526.aspx
DMM	Mesoscopic: micromagnetics This is a frequency domain technique rather a simulation code	In-house [DYNAMAG and MAGNONICS]
ELK	Electronic: quantum mechanical	www.elk.sourceforge.net
Elmer	Continuum: flow	http://www.csc.fi/english/pages/elmer) http://www.simpartix.com/
FDMAX	Continum: Electomagnetics	
FEAP	Continuum solid mechanics (micro) and process	www.ce.berkeley.edu/feap
FEMAP	Commercial continuum solid: pre-processor	www.plm.automation.siemens.com
FEMME	Mesoscopic: micromagnetics	www.suessco.com/simulations/solutions/femme-software
FIREBALL	Electronic: quantum mechanical	http://onlinelibrary.wiley.com/doi/10.1002/pssb.201147259/abstract;jsessionid=7E7A482F6EFD483AEB9979289EDEE0EE.d03t04)
FLAPW-FLEUR	Electronic: quantum mechanical, DFT	www.flapw.de
GARAND	Atomistic: statistical methods; drift diffusion	www.goldstandardsimulations.com/services/service-simulations/statistical-variability/atomistic-simulator
GAUSSIAN	Electronic: quantum mechanical and many-body and semi-empirical or parametrised electronic models and Atomistci Quantum Mechanics/Molecular Dynamics and Atomistic: statistical methods	www.gaussian.com
GPAW	Electronic: quantum mechanical	www.csc.fi/english/research/software/gpaw

GROMACS	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods, molecular dynamics	www.gromacs.org/About_Gromacs
GROMOS	Mesoscopic: molecular dynamics	www.gromos.net
HYPERCHEM	Electronic: semi-empirical and ab-initio molecular orbital methods, as well as density functional theory Atomistic: molecular mechanics, molecular dynamics	www.hyper.com
INFOLYTICA	Continuum: behaviour of magnets	www.infolytica.com/en/products/magnet
KMC-MD	Atomistic: statistical methods (Molecular Dynamics - kinetic Monte Carlo)	www.kintechlab.com/products/md-kmc
LAMMPS	Atomistic: statistical methods (molecular dynamics)	www.lammps.sandia.gov
LLG	Mesoscopic: Micromagnetics	http://llgmicro.home.mindspring.com
Madrid/Konstanz code	Mesoscopic: micromagnetics	Inhouse (FEMTOSPIN)
MAGPAR	Mesoscopic: micromagnetics	www.magpar.net
MARC	Continuum mechancis (macro)	www.mscsoftware.com/Products/CAE-Tools/Marc.aspx
MATERIALS STUDIO	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods and Mesoscopic: statistical methods	www.accelrys.com/products/materials-studio
MCGEN	Continuum: device modelling	Inhouse (SUPERLION)
MicroMagus	Mesoscopic: micromagnetics	http://www.micromagus.de/
MSC.MARC/MENTAT	Continuum solid mechanics (micro and macro); fluid dynamics; process	www.mscsoftware.com
MSINDO	Electronic: many-body and semi-empirical or parametrised electronic models	www.thch.uni-bonn.de
MUMAX	Mesoscope: micromagnetics	code.google.com/p/mumax
NAMD	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.ks.uiuc.edu/Research/namd
NMAG	Mesoscopic: micromagnetics	www.nmag.soton.ac.uk
NMTO	Electronic: many-body and semi-empirical or parametrised electronic models	www2.fkf.mpg.de/andersen
NXNastran	Continuum solid mechanics	http://www.plm.automation.siemens.com
OCTOPUS	Electronic: quantum mechanical in response of time dependent fields	www.tddft.org
OOMMF	Mesoscopic: micromagnetics	www.ngs.ac.uk/use/applications/engineering/oommf

OpenKIM	Atomistic: interatomic potentials and simulations	www.openkim.org
OPENMX	Electronic: quantum mechanical	www.openmx-square.org
OPTILAYER	Continuum: EM	www.optilayer.com
OPTIWAVE	Continuum: EM	www.optiwave.com
PICMC (DSMC)	Atomistic: statistical methods	Inhouse (ORAMA)
POM-POM TUBE	Continuum: fluid dynamics: polymer melt rheology This is a constitutive equation not a simulation package!	Inhouse (MODIFY)
PWM	Mesoscopic: micromagnetics	inhouse (DYNAMAG)
PWSIC	Electronic: quantum mechanical	Inhouse (ATHENA)
QUATRA/CELS	Atomistic: semi-classical drift-diffusion method and quantum kinetic model	inhouse (SMASH)
QLDFT	Electronic: quantum mechanical	physics.joacobs.university.de/theine/re search/qldft/
QUANTUM ESPRESSO	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics	www.quantum-espresso.org
QUIP	Electronic: quantum mechanical and Atomistic: ab- initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.libatoms.org
RANDOMSPICE	Continuum: Device modelling: statistical circuit simulator	www.goldstandardsimulations.com/pro ducts/randomspice
RETICOLO	Continuum: Electromagnetism	Inhouse (NIM-NIL)
RIG-VM	Atomitsic: Boltzmann transport equation solver, Direct Simulation Monte-Carlo and Particle in Cell plasma modelling for coating processes, optical modelling	http://www.ist.fraunhofer.de/en/servic es/simulation.html
RSPt	Electronic: many-body and semi-empirical or parametrised electronic models	www.fplmto-rspt.org
SE-MARGL	Mesoscopic: micromagnetics This software for post-processing the data from micromagnetic simulations	www.magnonics.org/semargl/
SIESTA	Electronic: quantum mechanical and and many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.nanotec.es/products/siesta.php
SIMPARTIX	Continuum: flow	www.simpartix.com
SPINPM	Mesoscopic: micromagnetics	www.apl.aip.org/resource/1/applab/v9 6/i2/p022504_s1?view=refs
TIBERCAD	Electronic: many-body and semi-empirical or parametrised electronic models, Atomistic: continuum mechanics (micro)	www.tibercad.org/
TINKER	Electronic: many-body and semi-empirical or parametrised electronic models and Atomistic: statistical methods	www.dasher.wustl.edu/ffe/
TURBOMOLE	Electronic: quantum mechanical and quantum mechanical in response of time dependent fields	www.turbomole.com/

UppASD	Atomistic: statistical methods and Mesoscopic: micromagnetics	Inhouse (MONAMI)
Uppsala code	Electronic: quantum mechanical in response of time dependent fields	Inhouse (FEMTOSPIN)
VASP	Electronic: quantum mechanical and Atomistic: ab-initio molecular dynamics and Quantum Mechanics/Molecular Mechanics	www.vasp.at
WANT	Electronic: quantum mechanical	Inhouse (ATHENA)
WIEN2K	Electronic: quantum mechanical	www.wien2k.at
WISETEX	Continuum: solid and fluid mechanics	www.mtm.kuleuven.be/Onderzoek/Composites/software/wisetex
YORK code	Atomistic: statistical methods	Inhouse (FEMTOSPIN)

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The future of the European industry is associated with a strong modelling capacity. An efficient modelling approach is needed to shorten the development process of materials-enabled products.

This Review of Materials Modelling describes modelling of materials, their properties and use in industrial applications illustrated by FP7 Industrial Technologies NMP Materials projects. It does not require prior knowledge of the subject. It is written for anybody interested. It contains no equations. The Review is to provide insight into the work of the modellers and help the reader to see the models as more than mere "black boxes".

This Review of Materials Modelling shows that industry is a very active player both in modelling for production and in modelling research areas. Industry identifies the specifications for material properties and the modelling then finds which material composition can meet the specs and how production can be done. This "Materials by Design" approach has been supported during the last decade in the EU Framework Programmes.

Application areas of modelling span all industrial sectors. The bulk of the projects are applying existing models to new materials, which shows that the current state of the art of modelling can be characterised as "mature".