CECAM/Psi-k Conference on

Multi-scale Modeling from First Principles

Conference Chairs

Michel Mareschal (Zaragoza) and Matthias Scheffler (Berlin)

Conference Sponsors

CECAM

Centre Européen de Calcul Atomique et Moléculaire
EPFL, Lausanne, Switzerland

Psi-k

Ab-initio Calculation of Complex Processes in Materials
Daresbury Science and Innovation campus
Warrington , UK

MM1p

Multiscale Modeling from First Principles
Consortium between the Fritz Haber Institute (Theory Dept) in Berlin, the University of Bremen and the Max Planck Insitute of Halle
Cecam node

ZCAM

Zaragoza Scientific Center for Advanced Modeling
University of Zaragoza
Spanish Cecam node

Welcome

Welcome to the 2013 Cecam-Psik research conference dedicated this year to multi-scale modeling from first principles.

The concept of multi-scale simulations implies that one has to extract sufficient information from a computation extending over microscopic time and space scales to compute properties usually defined at the macroscopic level. In the last twenty years or so, one has witnessed significant methodological progress that allows to obtain properties or reproduce processes on the macroscopic scale based on the information obtained from microscopic models. The new methods are grouped under the name of *multi-scale methods*, and have already led to a considerable development of computational materials sciences and biophysics.

Still, the open questions and uncertainties are severe and we organized the present meeting as a research conference, leaving ample time for discussions and insisting on methodological development rather than applications. As it has been the case for all successes in molecular modeling since the beginning of the field in 50s, methodological progress is based on physical understanding. In this conference, we have gathered experts to confront their techniques developed in order to bridge modeling towards larger scales in time and space.

The conference is sponsored by Cecam and Psi-k. Both organizations have stated at various times the importance of research conferences for the community. A great deal of efforts have been dedicated to have an annual meeting in a timely topic. In this year conference, an effort has been made to mix experts with a quantum and classical background, dealing with solids as well as liquid states. This merging of expertise have proven succesful in the past both for the exchange of ideas and techniques as well as in the community building aspects.

The conference is also the outcome of a collaboration between two Cecam nodes: on one side mm1p, a German node linking the Theory Department of Fritz Haber Institute in Berlin, the Halle Max-Planck Institute and the University of Bremen. On the other side ZCAM, the Zaragoza scientific Center for Adavanced Modeling, which is the Spanish node of Cecam. Let us take the opportunity to thank the technical staff of the two Cecam nodes that made the conference possible : in particular Beatriz Antoli and Birgit La Monaco have made a great work for the preparation and organization of this event.

Michel Mareschal Matthias Scheffler
Conference Co-chairs

General Information

Hotel Address

Hotel Cap Roig
Avenida de Andorra, 18
17251 Playa de Aro
Girona
España

Latitude: 41.827611 - Longueur: 3.083434

Tel : 00 34 972 65 20 00
Fax : 00 34 972 65 08 50

Email : caproig@caproig.com
Web site : www.caproig.com

Meals at hotel

Breakfast time : 7.30 to 9.00
Noon Lunch : 14.00-15.00
Dinner : 20.30

Transfer to and from airports:

Bus from Barcelona airport : Sunday 8th at 13.00 and 18.00
Bus from Girona airport : Sunday at 14.30 and 19.30
Bus to airports : Friday 13th at 11.30 and Saturday 14th at 10.00

Conference excursion :
On Wednesday, after lunch.
2 Buses will leave to Figueres (Dali museum) at 14.30

Conference Dinner on Wednesday evening (21.00 at the hotel)

Presentations : usual laptop and projector made available
Posters : session is on Tuesday afternoon and posters may stay afterwards

Telephone numbers

Michel Mareschal   +34 608 291 261
Matthias Scheffler : +49 170 785 9591

Programme overview

	Monday	Tuesday	Wednesday	Thursday	Friday	
9	Albe	Kapral	Elber	Alavi	Orozco	
10	Hart	Carloni	Hartmann	Artacho	Kremer	Bus
11	coffee break					
11.30	Kratzer	Behler	Ciccotti	Castro	Tildesley	
12.30	Ghiringilli	Dellago	Español	Tildesley	Bus	
14	Lunch					
16.30	Neugebauer	Poster	Excursion and conf dinner	Pagonabarraga	Bus	
17.30	coffee break					
18.00	Reuter	Poster		Warren		
19.00	Draxl			Gompper		
20.30	Dinner			Dinner		

Sunday September 8th, 2013

19.30 Welcome of participants

20.30 Dinner

Monday September 9th

Session 1, Multi-scale Materials
Chair : Claudia Draxl, Humboldt University

9.00 Introduction by the Chair

9.10 Karsten Albe, TU Darmstadt
Plastic Deformation of Nanocrystalline and Glassy Metal Alloys studied by a Hybrid Molecular Dynamics/Monte-Carlo Simulations

10.10 Gus Hart, Brigham Young University
Multiscale Alloy Modeling

11.00 Coffee Break

11.30 Peter Kratzer, Duisburg University
Multiscale Modeling of Au-catalysed GaAs nanowire growth

12.30 Luca Ghiringilli, FHI
Free Metal and Metal-oxide Clusters: beyond the Static, Monostructure Description

14.00 Lunch

16.30
Session 2 : Materials at surfaces
Chair : Matthieu Verstaete, Universite de Liege

Chair Introduction

16.40 Jörg Neugebauer, MPG Düsseldorf
Ab initio based Multiscale Modeling of Structural Materials: From a Predictive Thermodynamic Description to Tailored Mechanical Properties

17.30 Coffee Break

18.00 Karsten Reuter, TU Munich
Towards First-Principles Chemical Engineering

19.00 Claudia Draxl, Humboldt University
Exploring Electron-hole Pairs in Nanomaterials

20.30 Dinner

Tuesday September 10th

Session Biological systems and Neural Network Methods
Chair : Matthias Rupp, Basel University

Chair Introduction

9.10 Ray Kapral, University of Toronto
Molecular Machines and Self-propelled Nano-motors

10.00 Paolo Carloni, Jülich
Membrane Biophysics investigated by Multi-scale Methods

11.00 Coffee Break

11.30 Jörg Behler, Bochum University
Extending the Length and Time Scales of Atomistic Simulations Using Neural Network Potentials

12.30 Christoph Dellago, University of Vienna
Studying Nucleation Processes with Computer Simulations:
Neural Networks for Force Calculation and Structure Recognition

14.00 Lunch

16.00 Poster session with a coffee break at 17.00

Wednesday, September 11th

Session on Stochastic methods and Non-equilibrium states
Chair : Christoph Dellago, University of Vienna

9.00 Chair Introduction

9.10 Ron Elber, UT Austin
From Atomically Detailed Trajectories to Equations for the Density: Coarse graining by Milestoning

10.00 Carsten Hartmann, FU Berlin
Tackling Long Timescales in Molecular Dynamics

11.00 Coffee Break

11.30 Giovanni Ciccotti, La Sapienza University
Time-dependent Non-equilibrium Molecular Dynamics

12.30 Pep Español, UNED Madrid
Statistical Mechanics of Hamiltonian AdResS Adaptive Resolution Simulations

14.00 Lunch

15.00 Excursion

21.00 Conference Dinner (at hotel)

Thursday, September 12th

Session on quantum modeling
Chair : TBA

9.00 Chair Introduction

9.10 Ali Alavi, Cambridge University
Quantum Monte Carlo approach to Quantum Chemical Problems

10.00 Emilio Artacho, Cambridge University and University of the Basque Country
Electronic Effects in Radiation Damage

11.00 Coffee Break

11.30 Alberto Castro, University of Zaragoza

From the Femto- to the Atto-second Time Scale: Analysis and Control of the Electronic Motion with Time-dependent Density Functional Theory.

12.30 Dominic Tildesley, CECAM, EPFL

The Friction between Structured Surfaces

14.00 Lunch

Session on Multi-scale in complex fluids
Session chair : Friederike Schmid, University of Mainz

Chair Introduction

16.10 Ignacio Pagonabarraga, University of Barcelona

Hybrid Kinetic Schemes for Modeling Complex Fluids

17.00 Coffee Break

17.30 Patrick Warren, Unilever, Port Sunlight

Many-body dissipative particle dynamics: application to realistic liquid mixtures

18.30 Gerhard Gompper, Jülich

Mesoscale Modeling of Blood Flow: From Single Cells to Blood Rheology

20.00 Dinner

Friday, September 13th

Session on multi-scale in complex fluids (2)
Session chair : TBA

9.00 Modesto Orozco, Barcelona

The Multi-Scale nature of DNA

10.00 Kurt Kremer, MPG Mainz

Adaptive Resolution Simulations for Soft Matter: Applications and New Developments

11.00 Dominic Tildesley, CECAM
Concluding Remarks

11.30 Coffee Break

List of Invited Talks and Chairs

Alavi	Quantum Monte Carlo approach to quantum chemical problems
Albe	Plastic deformation of nanocrystalline and glassy metal alloys studied by a hybrid molecular dynamics/Monte-Carlo simulations
Artacho	Electronic effects in radiation damage
Behler	Extending the Length and Time Scales of Atomistic Simulations Using Neural Network Potentials
Carloni	Membrane biophysics investigated by multi-scale methods
Castro	From the femto- to the atto-second time scale: analysis and control of the electronic motion with time-dependent density-functional theory
Ciccotti	Time-dependent Non-equilibrium Molecular Dynamics
Dellago	Studying nucleation processes with computer simulations: Neural networks for force calculation and structure recognition
Draxl	Exploring electron-hole pairs in nano-materials
Elber	From atomically detailed trajectories to equations for the density: Coarse graining by Milestoning
Español	Statistical Mechanics of Hamiltonian AdResS Adaptive Resolution Simulations
Ghiringilli	Free metal and metal-oxide clusters: beyond the static, monostructure description
Gompper	Mesoscale Modeling of Blood Flow: From Single Cells to Blood Rheology
Hart	Multiscale Alloy Modeling
Hartmann	Tackling long timescales in molecular dynamics
Kapral	Molecular Machines and Self-Propelled Nanomotors
Kratzer	Multiscale Modeling of Nanowire Growth
Kremer	Adaptive Resolution Simulations for Soft Matter: Applications and New Developments
Neugebauer	Ab initio based multiscale modeling of structural materials: From a predictive thermodynamic description to tailored mechanical properties
Orozco	The multi-scale nature of DNA
Pagonabarraga	Hybrid kinetic schemes for modeling complex fluids
Reuter	Towards a First-Principles Chemical Engineering
Rupp	Session Chair on biomachines and neural networks
Schmid	Session Chair on coarse-graining
Tildesley	The Friction between Structured Surfaces
Verstraete	Session Chair on surfaces
Warren	Many-body dissipative particle dynamics: application to realistic liquid mixtures

Quantum Monte Carlo Approach to Quantum Chemical Problems'

Ali Alavi

Department of Chemistry
University of Cambridge
Lensfield Road, Cambridge CB2 1EW

The ground-state eigenvalue problem posed by the electronic Schrödinger equation can be cast as a stochastic process involving an annihilating population of positive and negative walkers that inhabit Slater determinant space [1]. The population of walkers evolve according to a simple set of rules (akin to a "game of life"), which are derived from the underlying imaginary-time Schrödinger equation, such that the long-time distribution of the walkers matches the exact ground-state eigenvector. We show that this algorithm has a remarkable emergence characteristic, akin to symmetry-breaking phase transitions in classical statistical mechanical systems.

The use of Slater determinants obviates the usual Fermion sign problem of diffusion Monte Carlo (namely the collapse onto bosonic wavefunctions), but instead introduces a different sign problem associated the fact that the off-diagonal Hamiltonian matrix elements are both positive and negative. This sign problem however can be solved through a combination of walker annihilation and a "survival of the fittest" criterion [2] (the latter greatly reducing the dependence of the algorithm on walker annihilation). The method provides a way to compute exact electronic energies within a specified N-electron basis set. We will give examples of the algorithm at work in real systems in sizeable basis sets, ranging from atomic electron affinities, to dissociation energies of diatomic molecules, the uniform electron gas [4], and most recently, to real solids [5].

[1] G.H. Booth, A.J.W. Thom and Ali Alavi, J. Chem. Phys., **131** , 054106, (2009).
[2] Deidre Cleland, G.H. Booth, and Ali Alavi, J. Chem. Phys., **132** , 041103, (2010).
[3] Deidre Cleland, George Booth, and Ali Alavi, J. Chem. Phys., **134** , 024112, (2011)
[4] James Shepherd, George Booth, Andreas Grueneis, Ali Alavi, Phys. Rev B, **85**, 081103, (2012)
[5] George Booth, Andreas Grueneis, Georg Kresse, Ali Alavi, Nature, **453**, 365-370, (2013).

Plastic Deformation of Nanocrystalline and Glassy Metal Alloys studied by a Hybrid Molecular Dynamics/Monte-Carlo Simulations

Karsten Albe, Jonathan Schäfer, Alexander Stukowski, Yvonne Ritter, Daniel Sopu

TU Darmstadt, Fachbereich Material- und Geowissenschaften, FG Materialmodellierung, Petersenstr. 32, D-64287 Darmstadt, Germany

In the past, atomistic computer simulations have contributed significantly to de- velop an understanding of plastic deformation mechanisms in nanocrystalline (nc) metals. In particular, molecular dynamics (MD) simulations revealed that deformation mechanisms change as the grain size is reduced into the nanometer regime. It is nowadays well established that grain rotation and sliding, dislocation emission and absorption in grain boundaries, twinning and faulting as well as diffusional creep and grain boundary migration can contribute to plastic deformation of nc metals depending on grain size and strain rate. In MD simulations the typical deformation strain rates are, however, significantly higher than in conventional experimental setups. The hierarchy between different deformation mechanisms with individual activation enthalpies and activation volumes may therefore change also with the applied strain rate. Thus, care has to be taken when transferring insights from simulations to experimental conditions. Moreover, influence of solutes, commonly present in experimental samples can significantly influence the mechanical response of nc metals, which has hardly been addressed in simulation studies. In this contri- bution, results obtained by a hybrid MD/MC scheme are presented that is sampling the variance-constrained semi-grandcanonical ensemble and thus allows for local chemical and structural relaxation by shortcutting diffusional processes. It is shown that in the nanoregime the grain boundary composition and relaxation state and not the properties of the crystalline grain are controlling the macroscopic deformation behavior. By comparing with results obtained for bulk metallic glasses, analogies in the deformation behavior will be shown, and related experimental results will be discussed.

[1] J. Schäfer, K. Albe, ”*Competing deformation mechanisms in nanocrystalline metals and alloys: Coupled motion versus grain boundary sliding*”, Acta Mat. **60**, 6076, 2012
[2] J. Schäfer, Y. Ashkenazy, Yinon; K. Albe, et al. ”*Effect of solute segregation on thermal creep in dilute nanocyrstalline Cu alloys*” Mat. Sci. Eng. A, **546**, 307, 2012
[3] J. Schäfer, A. Stukowski, K. Albe ”*Plastic deformation of nanocrystalline Pd-Au alloys: On the interplay of grain boundary solute segregation, fault energies and grain size*.” Acta Mater., **59**, 2957, 2011
[4] K. Albe, Y. Ritter, D. Sopu ”*Enhancing the plasticity of metallic glasses: Shear band formation, nanocomposites and nanoglasses investigated by molecular dynam- ics simulations*” DOI: http://dx.doi.org/10.1016/j.mechmat.2013.06.004

Electronic Effects in Radiation Damage

Emilio Artacho

CIC Nanogune and DIPC, Tolosa Hiribidea 76, 20018 San Sebastián, Spain
Basque Foundation for Science, Ikerbasque, 48011 Bilbao, Spain
Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

Simulating the accumulation of damages in a material due to different kinds of radiation (ions, neutrons) is extremely challenging, spanning many scales in both size and time. Multi-scale modeling is the only possible way to face the challenge, and spectacular progress has been made recently, going from atomistic molecular dynamics simulations all the way to finite-element continuum descriptions of damage in polycrystalline materials, including dislocation dynamics and rate equations at intermediate levels. The electronic excitation by swift ions and its equilibrating back into the ion dynamics are important processes in the problem, which have received some attention: there are empirical ways of describing the slowing down of ions by electronic dissipation, as well as for describing the electronic de-excitation into phonons. There is almost nothing done in the simulation of the alteration of the interatomic forces due to the electronic excitation and its effects, and there is very little done in the first-principles description of such electron-ion non-adiabatic processes. We will review our efforts in the first-principles simulation of the electronic stopping power of realistic materials (insulators, semiconductors and different kinds of metals), as well as of the excitation-dependet forces. We will discuss how to connect such simulations with the other scales in the problem.

Extending the Length and Time Scales of Atomistic Simulations Using Neural Network Potentials

Jörg Behler

Lehrstuhl für Theoretische Chemie
Ruhr-Universität Bochum, 44780 Bochum, Germany

The reliability of the results obtained in computer simulations of chemical processes strongly depends on the quality of the employed interatomic potentials. While electronic structure methods like density-functional theory provide an accurate description of many systems, the high computational costs limit the system size to a few hundred atoms at most. The construction of more efficient but equally reliable interatomic potentials applicable to molecules, solids and surfaces is a frustrating challenge because of the very different types of bonding present for instance in molecules, ionic solids and metals. In past decades, many functional forms have been suggested for a variety of systems, but a general-purpose potential suitable for all types of materials is still lacking.

Artificial neural networks (NNs) provide a powerful new approach to fill this gap and to construct potential-energy surfaces with nearly ab initio quality for many systems [1-4]. In most practical applications, however, NN potentials have been restricted to small molecules only. In recent years this limitation could be overcome by the introduction of a high-dimensional NN potential type [5,6], which allows performing molecular dynamics simulations of very larges systems. Like conventional low-dimensional NN potentials, this approach is numerically very accurate and can be combined with any electronic structure method. Its scope and current limitations will be discussed employing a number of illustrative and realistic examples for different systems, from metal surfaces to water clusters.

[1] T. B. Blank, S. D. Brown, A. W. Calhoun, and D. J. Doren, *J. Chem. Phys.* **103**, 4129 (1995).

[2] S. Lorenz, A. Groß, and M. Scheffler, *Chem. Phys. Lett.* **395**, 210 (2004).

[3] C. M. Handley and P. L. A. Popelier, *J. Phys. Chem. A* **114**, 3371 (2010).

[4] J. Behler, *Phys. Chem. Chem. Phys.* **13**, 17930 (2011).

[5] J. Behler and M. Parrinello, *Phys. Rev. Lett.* **98**, 146401 (2007).

[6] J. Behler, *J. Chem. Phys.* **134**, 074106 (2011).

Membrane Biophysics Investigated by Multi-scale Methods

Paolo Carloni

Professor of Computational Biophysics
Institute for Advanced Simulation (IAS)
Forschungszentrum Jülich
D-52425 Jülich, Germany

We will describe recent molecular simulation studies of membranes and membrane proteins. We will start with first principle and coarse grain modeling of ion permeation in these systems. Next, we will describe a recent implementation of a coarse grain/molecular mechanics scheme for membrane proteins. A perspective of the presented simulation tools towards the so-called 'mechanistic systems biology' [1] will finally be given.

[1] *NMR of Biomolecules* , Ivano Bertini, Kathleen S. McGreevy , Giacomo Parigi, Wiley, 2012.

From the Femto- to the Atto-second Time Scale: Analysis and Control of the Electronic Motion with Time-dependent Density-Functional Theory.

Alberto Castro

ARAID Foundation
Instituto de Biocomputación y Física de Sistemas Complejos (BIFI),
Edificio I+D,
Mariano Esquillor Gómez s/n,
50018 Zaragoza, España.

It is now possible to observe and control physical phenomena in the atto-second time scale, thanks to the development of ultra-fast laser technology. This is the time-scale of the electronic motion in atoms and molecules, in contrast to the nuclear velocities, that can be followed in the femto-second regime. These fast developing experimental capabilities renews the interest in the theoretical modeling of non-equilibrium electronic dynamics, which can be studied within the framework of time-dependent density-functional theory. I will review recent advances in this type of modeling, in particular related to the possibility of analyzing attosecond pump-probe experiments, to the application of quantum optimal control theory for steering the electronic motion, and to the electron-ion coupling that is needed to bridge the atto- and femto-second time scale.

Time-dependent Non-equilibrium Molecular Dynamics

Giovanni Ciccotti

Dipartimento di Fisica
Universita' di Roma "La Sapienza"
and
School of Physics
University College of Dublin

We present a way to extend stationary state (equilibrium and nonequilibrium) Molecular Dynamics to time dependent nonequilibrium situations, including the dynamical processes of response and relaxation. The procedure, which we have called Dynamical Non-Equilibrium Molecular Dynamics (D-NEMD), to distinguish it from standard NEMD, only used to simulate stationary nonequilibrium states, is based on a generalization of linear response theory. The idea has been formulated by Onsager in the thirties in metaphysical language; given a solid foundation in the fifties by Green and Kubo (in the linear and nonlinear regime); and adapted to MD simulations by the present author (in collaboration with G. Jacucci and I. R. McDonald) in the seventies. It has been called the nonlinear Kubo-Onsager relation, connecting dynamical nonequilibrium averages or dynamical relaxations to (stationary) initial probability distribution functions suitably sampled. To show the power of the method we apply it to the study of the hydrodynamic relaxation of an interface between two immiscible liquids.

Studying Nucleation Processes with Computer Simulations:

Neural Networks for Force Calculation and Structure Recognition

Christoph Dellago
Faculty of Physics
University of Vienna

Molecular dynamics simulations of nucleation processes in condensed matter systems require the accurate calculation of the forces acting on atoms. While ab initio approaches can be used for this purpose, their high computational cost often precludes their application to large systems. A neural-network-based method recently developed by Behler and colleagues offers an alternative and yields the accuracy of density functional theory calculations at a fraction of the cost. I will present a neural network potential we have developed for copper sulfide and show results obtained for the phase diagram of this material and its superionic properties at high temperature. Motivated by the success of neural network potentials we have also explored the application of this approach for the recognition of atomic arrangements. The ability to distinguish between different local structures is of great importance in the study of many condensed phase processes including freezing, structural phase transitions and the dynamics of defects. Several approaches to determine and classify the environments of individual atoms are currently available, among which local bond order parameters based on spherical harmonics and common neighbor analysis are the most popular ones. For complex substances with rich phase diagrams such as water, however, these methods fail to discriminate between different crystal structures. In this talk, I will show how neural networks can be trained to classify local structures in a simple and accurate way. We demonstrate the validity and practical applicability of the approach using Lennard-Jonesium and water/ice as illustrative examples.

Joint work with Jörg Behler, Andreas Singraber, and Philipp Geiger

Exploring Electron-hole Pairs in Nano-materials

Claudia Draxl

Humboldt-Universität zu Berlin
Physics Department and IRIS Adlershof
Zum Großen Windkanal 6, 12489 Berlin

The solution of the Bethe-Salpeter equation of manybody perturbation theory is the method of choice for describing optical spectra in band-gap materials in order to account for excitonic effects. This method is very demanding what concerns the computational cost, and thus is out of reach for nano-scaled systems. With the final goal to understand optical excitations in organic/inorganic hybrid materials, we are currently exploring a constrained DFT approach. I will discuss in detail what we can expect from this alternative to BSE and which of the spectral features can be more reliably obtained in one or the other scheme.

--

From Atomically Detailed Trajectories to Equations for the Density: Coarse Graining by Milestoning

Ron Elber, PhD

W.A. "Tex" Moncrief Chair in Computational Life Sciences and Biology,
Department of Chemistry and Biochemistry and
Institute for Computational Engineering and Sciences (ICES)
University of Texas at Austin

The algorithm of Milestoning uses short atomically detailed trajectories to build a set of equations for the fluxes in a coarse space. An example is of protein folding in which fully solvated atomistic systems are mapped to dynamics in a reduced peptide-torsion space. We show how the Milestoning flux equation can be transformed into partial and integral equation for the density that in the limit of memory loss is approaching the Master equation. Examples for permeation of small molecules through biological membranes will be discussed. In particular the non-trivial choice of the coarse variables and its impact on the results will be examined.

--

Statistical Mechanics of Hamiltonian AdResS Adaptive Resolution Simulations

Pep Español

Fundamental Physics Department
Faculdad de Ciencias
UNED Madrid

AdResS (Adaptive Resolution Simulations) is a hybrid scheme that allows one to treat a molecular system with different level of resolution depending on the location of the molecules. Molecules change its nature from atomic detail to coarse-grained blob entities as they move in space. This allows to treat the system with chemical detail in certain regions where this is required, and with less (and cheaper) detail where it is not actually needed. The recent construction of a Hamiltonian based on the Adress idea allows to formulate the usual tools of ensembles and statistical mechanics and opens the way to Monte Carlo multiresolution techniques. We present a number of exact and approximate results that provide a statistical mechanics foundation for this simulation method.

Free Metal and Metal-oxide Clusters: beyond the Static, Monostructure Description

Luca Ghiringelli
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6
D-14 195 Berlin-Dahlem / Germany

One of the challenges of present and near future conversion, storage, and transportation of energy is its catalytic transformation into fuels, e.g. in the form of hydrocarbon molecules. Catalysis is also of great importance for pollution control.

The widespread description and modeling of heterogeneous catalysis got stuck in the concepts and methods of the last century. Most (nearly all) catalysis researchers focus on energies and energy barriers, however the dynamics and statistical mechanics are also important. A catalyst is usually not working efficiently from the very moment that the process starts, but a macroscopic "induction period" must rather elapse. In fact, the catalytically active phase may exist only in a narrow range of the external conditions. Not only the surface composition but also surface morphology can change in the course of a catalytic process. Nanostructures of various shapes, point defects, extended defects such as steps, dislocations, and stacking faults, can result from interaction of the surface with the reactive environment. This latter aspect implies that the operating catalyst will never be the pristine material that is initially introduced in the reactor. Furthermore, the difference between "real-life catalysis" and "UHV surface chemical reactions" reflects the so-called "materials" and "pressure gap".

By focusing on gas-phase metal and metal-oxide (sub)nano clusters in a reactive atmosphere, I show how the accurate (and validated) knowledge of the (*ab initio*) potential energy surface cluster + reactant systems can be bridged to simple thermodynamic considerations for modeling the prediction of (meta)stable structures and compositions of the systems at realistic environmental conditions (finite temperature and pressure of the reacting atmosphere).

One of the most delicate assumptions of such model is that the configurational entropy is approximated by the harmonic vibrational entropy. This assumption is not always justified. In fact some (but not all) (sub)nano cluster systems exhibit even at moderate temperatures anharmonic behavior associated with the coexistence of a multiplicity of structures: fluxionality and liquid-like behavior. I will show how massively parallelized (*ab initio*) replica exchange molecular dynamics and efficient reweighting techniques offer a way to describe the relative population of such higly-anharmonic systems, seamlessly bridging the vibrational to the configurational-change time scales.

Mesoscale Modeling of Blood Flow: From Single Cells to Blood Rheology

Dmitry Fedosov and Gerhard Gompper
Theoretical Soft Matter and Biophysics, Institute of Complex Systems and Institute for Advanced Simulation, Forschungszentrum Jülich, D-52425 Jülich, Germany

The flow behavior of vesicles and blood cells is important in many applications in biology and medicine. For example, the flow properties of blood in micro-vessels is determined by the rheological properties of red blood cells (RBCs). Blood flow is therefore strongly affected by diseases such as malaria or diabetes, where RBC deformability is strongly reduced. Furthermore, microfluidic devices have been developed recently, which allow the manipulation of small amounts of suspensions of particles or cells.

Of fundamental interest is the relation between the flow behavior and the elasticity and deformability of the blood cells, their long-range hydrodynamic interactions in microchan- nels, and thermal membrane undulations [1]. We study these mechanisms by combination of particle-based mesoscale simulation techniques [2] for the fluid hydrodynamics with triangulated-surface models [3-5] for the membrane. The essential control parameters are the volume fraction of RBCs, the flow velocity, and the capillary radius.

In narrow channels, single red blood cells in capillary flow show a transition from the biconcave disk shape at low flow velocities to a parachute shape at high flow velocities [4,6]. For somewhat wider channels, other shapes such as slippers intervene between these states [6]. At higher volume fractions, hydrodynamic interactions are responsible for a strong deformation-mediated clustering tendency at low hematocrits, as well as several distinct flow phases at higher hematocrits, such as a zig-zag arrangement of slipper shapes [7]. For large vessels, blood behaves like a continuum fluid. As a function of shear rate, a strong shear-thinning behavior is found, which is predicted from RBC deformability and cell-cell attraction [8].

[1] D. A. Fedosov, H. Noguchi, and G. Gompper, Biomech. Model. Mechanobiol., online (2013); DOI: 10.1007/s10237-013-0497-9.
[2] G. Gompper, T. Ihle, D. M. Kroll, and R. G. Winkler, Adv. Polymer Sci. **221**, 1 (2009).
[3] G. Gompper and D. M. Kroll, in Statistical Mechanics of Membranes and Surfaces, 2nd edition, edited by D. R. Nelson and T. Piran and S. Weinberg (World Scientific, Singapore, 2004).
[4] H. Noguchi and G. Gompper, Proc. Natl. Acad. Sci. USA **102**, 14159 (2005).
[5] D. A. Fedosov, B. Caswell, and G. E. Karniadakis, Biophys. J. **98**, 2215 (2010).
[6] D. A. Fedosov, M. Peltomäki, and G. Gompper, submitted (2013).
[7] J. L. McWhirter, H. Noguchi, and G. Gompper, Proc. Natl. Acad. Sci. USA **106**, 6039 (2009).
[8] D. A. Fedosov, W. Pan, B. Caswell, G. Gompper, and G. E. Karniadakis, Proc. Natl. Acad. Sci. USA **108**, 11772 (2011).

Multiscale Alloy Modeling

Gus Hart

Department of Physics and Astronomy
Brigham Young University
Utah, USA

Lattice-gas models are useful for simulations that take place on a lattice. Some alloy problems can be cast as lattice gas models, and combining the technique of cluster expansion (a lattice-gas model for alloys) and compressive sensing (a model-selection algorithm from the signal processing discipline) provides a direct, simple approach to using DFT data to train fast hamiltonians for solid state simulations of configurational problems. In this talk, you will learn the basics of using the cluster expansion to solve configurational problems and understand the principal ideas of compressing sensing which provides a powerful, new technique for building models from DFT data.

Tackling Long Timescales in Molecular Dynamics

Carsten Hartmann

Institut für Mathematik
Freie Universität Berlin

The simulation of rare events and metastable dynamics is among the most challenging problems in molecular dynamics. Because rare events happen only once in a blue moon, getting reasonable statistics of, e.g., a conformational transition in a molecule requires to generate extremely long trajectories which may cause stability issues in the numerical method used. As was shown by Jarzynski and others, it is in principle possible to speed up rare events sampling by biasing the system's original probability distribution towards a (nonequilibrium) distribution under which the rare event is no longer rare. The distribution of nonequilibrium paths can then be mapped back to the original problem by using a suitable reweighting scheme. Despite its appeal, the nonequilibrium approach suffers from the general problem that almost all naive importance sampling strategies for rare events will increase variance and therefore result in statistical estimators that are much worse than they were before. We present a new method that replaces the path sampling problem by a feasible minimization procedure based on a particular entropy functional; the entropy minimization boils down to finding an optimal nonequilibrium bias for the system that gives a zero-variance estimator for the full rare events statistics. In the talk we will discuss a) the theoretical framework of rare events statistics based on entropy minimization, b) the numerical solution of the resulting optimal control problems and c) the applications to molecular dynamics and single-molecule experiments.

Molecular Machines and Self-Propelled Nanomotors

Raymond Kapral

Chemical Physics Theory Group
Department of Chemistry
University of Toronto

Biological systems make frequent use of molecular motors to perform tasks such as active transport of material in the cell, cell locomotion and biochemical synthesis. Proteins, acting as molecular machines, can undergo cyclic internal conformational motions that are coupled to ligand binding and dissociation events. In contrast to their macroscopic counterparts, these nanomachines operate in highly fluctuating environments and bound to lipid membranes. These environmental factors influence their operation. Recently, a variety of synthetic nanomotors that use chemical reactions to effect self-propulsion have been fabricated. Like their biological counterparts, these nanomotors are subject to strong molecular fluctuations from the environments in which they move. The talk will describe recent work on the mesoscopic multi-scale simulation of the conformational dynamics of protein machines and directed motion chemically-powered nanomotors. The mechanisms by which these nanomotors and machines operate and some of their possible uses will be described.

Multiscale Modeling of Au-catalysed GaAs nanowire growth

S. Sakong, Y. A. Du, V. Pankoke, and P. Kratzer
Faculty of Physics, University Duisburg-Essen, 47048 Duisburg, Germany

Kinetic modeling of epitaxial growth of nanostructures requires scale-bridging simulations that cover macroscopic length and time scales (micro-meters and seconds), while retaining information about the molecular processes at the atomic scale.[1] For the latter ones, e.g. for the energy barriers for surface diffusion, accurate quantum- mechanical calculations are required, using density functional theory (DFT) or even higher-level electronic structure methods.

The statistical aspect of surface diffusion can be modeled as a Wiener process (ran- dom walk), including possible interactions between the surface species by using ki- netic Monte Carlo techniques if required, e.g. for the description of nucleation. For modeling larger scales or processes occurring close to equilibrium, it becomes more efficient to combine these techniques with a description employing locally averaged particle densities, using continuum kinetic equations. On the largest scale, where e.g. the overall shape of the epitaxially grown nanostructures is determined, one is often very close to a mechanical equilibrium to be described as a balance of surface tensions. The latter quantities, too, are accessible to DFT calculations.

In my talk, these concepts will be illustrated by results on the gold-catalysed growth of GaAs nanowires. While the driving force for nanowire growth is the chemical non-equilibrium between the gas phase, the liquid Au-alloy particle and the solid GaAs wire, it is the mechanical equilibrium at the boundary between these three phases that governs the geometrical shape of the nanowire-catalyst interface. We obtain the surface energies of the catalyst particle and the nanowire facets, as well as the energy of the interface between the nanowire tip and the catalyst particle, from DFT calculations. This puts us in position to calculate the contact angle and the thermodynamically determined ’neck’ radius of the nanowire that grows out of a catalyst particle of given volume.[2] DFT calculations also help us to understand the role of the Au catalyst surface for the adsorption and retention of the gas-phase species.[3] Moreover, we employ DFT calculations to determine the potential energy surfaces (PESs) for diffusion of Ga and As adatoms and GaAs molecules adsorbed on the nanowire side facets.[4] As a consequence of the complex interplay of adsorption, diffusion and reaction processes, the ratio of axial to radial growth speed of a GaAs nanowire can be tuned by choosing appropriate conditions, i.e., temperature and V-III ratio in the gas phase.

[1] P. Kratzer and M. Scheffler, Comp. Sci. Eng. **3**, 16 (2001).
[2] S. Sakong, Y. A. Du, and P. Kratzer, submitted to Phys. Rev. B.
[3] P. Kratzer, S. Sakong, and V. Pankoke, Nano Lett. **12**, 943 (2012).
[4] V. Pankoke, S. Sakong, and P. Kratzer Phys. Rev. B **86**, 085425 (2012).

Adaptive Resolution Simulations for Soft Matter: Applications and New Developments

Kurt Kremer

Max Planck Institute for Polymer Research,
Mainz, Germany

The relation between atomistic structure, architecture, molecular weight and material properties is of basic concern of modern soft matter science. A typical additional focus is on surface and interface aspects or the relation between structure and function in nanoscopic molecular solutes or assemblies. Here computer simulations on different levels of resolution play an increasingly important role. To progress further adaptive schemes are being developed, which allow for a free exchange of particles (atoms, molecules) between the different levels of resolution. The lecture will concentrate on these methods and current extensions to open systems MD (grand canonical MD) as well as new Hamiltonian based molecular dynamics and Monte Carlo adaptive resolution methods will be explained. As specific applications the solution properties of triglycene in water urea mixtures and of PNIPAM in water methanol mixtures will be discussed. For the latter the implementation of the quasi grand canonical water methanol exchange allows a rather detailed analysis of the delicate balance of water-methanol-solute interactions leading to the characteristic good-poor-good solvent scheme for PNIPAM in water methanol mixtures as a function of methanol concentration.

A general review on the first part can be found in M. Praprotnik et al. Ann. Rev. Phys. Chem. **59**, 2008
and recent advances in
S. Fritsch et al. Phys. Rev. Lett. **108**, 170602 (2012),
R. Potestio et al Phys. Rev. Lett. **110**, 108301 (2013),
D. Mukherji et al JCTC, **8**, 3536 (2012)

Ab initio based Multiscale Modeling of Structural Materials: From a Predictive Thermodynamic Description to Tailored Mechanical Properties

Jörg Neugebauer, Blazej Grabowski, F. Körmann, and Tilmann Hickel

Max-Planck-Institut für Eisenforschung, Düsseldorf

The combination of accurate first principles calculations with thermodynamic or kinetic concepts opens the door to tackle even advanced engineering problems such as the design of novel high-strength steels with superior mechanical properties. Key to these studies is the highly accurate determination of thermodynamic quantities at finite temperatures. In the first part of the talk it will be shown how novel sampling strategies allow to obtain a highly efficient coarse graining in configuration space resulting in a reduction from 10^7 to a few hundred configurations. This enormous reduction permits to employ highly converged density-functional theory calculations thus providing the basis for accurately determining all relevant temperature dependent free energy contributions such as harmonic and anharmonic vibrations, magnetic excitations or defect creation.

The flexibility and the predictive power of this approach will be discussed in the second part of the talk for a few examples relevant to the design and understanding of a new generation of high-strength steels: Determination of mechanisms that provide an adaptive and self-organized response of the materials microstructure on external forces and which are the basis for superior mechanical properties or unraveling critical failure/embrittlement mechanisms.

The Multi-scale Nature of DNA

Modesto Orozco

IRB-PCB Edifici Clúster
C/Baldiri Reixac 10-12
08028 Barcelona

DNA is a dramatic example of a multi-scale and multi-physics system, where aspects of interest range from the sub-atomic to the entire chromatin levels. Some processes involving DNA happen in the femtosecond time scale, while other occurs in the hours or days scale. This scenario forces the development of new computational methods able to cover this wide scale of problems. I will summarize during my talk recent advances in our group in the development of multi-scale models for DNA, giving emphasis on the possibility to simulate DNA using physical principles at the entire scale range.

Hybrid Kinetic Schemes for Modeling Complex Fluids

Ignacio Pagonabarraga

University of Barcelona

The use of kinetic computational models has opened new strategies to model matter at the mesoscales. The concepts and ideas of kinetic theory provide a solid ground to develop complementary approaches to particle-based computational methods.

In this talk I will discuss briefly the development of kinetic methods applied to the study of complex fluids and how they have evolved to cover the relevant length and time sclaes characetristic of these highly heterogeneous systems. I will describe specifically the lattice Boltzmann technique, because it has proved very efficient and versatile method to describe the hydrodynamics of a large variety of complex materials. I will illustrate the complementary approaches developed in the past with a few relevant examples.

TOWARDS A FIRST-PRINCIPLES CHEMICAL ENGINEERING

Karsten Reuter

Chair for Theoretical Chemistry and Catalysis Research Center
Technical University Munich, Lichtenbergstr. 4, 85747 Garching, Germany

As in many other areas of materials science, modern computational science is becoming a key contributor in the quest to quantitatively understand the molecular-level mechanisms underlying the macroscopic phenomena in chemical processing, which will ultimately enable a rational design of novel catalysts, energy suppliers and improved production strategies. Of particular relevance are hierarchical approaches that link the insights that modelling and simulation can provide across all relevant length and time scales. At the molecular level, first-principles electronic-structure calculations unravel the making and breaking of chemical bonds. At the mesoscopic scale, statistical simulations account for the interplay between all elementary processes involved in the catalytic cycle. At the macroscopic scale continuum theories yield the effect of heat and mass transfer, ultimately scaling up to a plant-wide simulation. A comprehensive control of catalytic and energy processes requires combining all of these facets and thus necessitates novel methodological approaches that integrate the various levels of theory into one multiscale simulation. In my talk I will review our recent activities in this field, focusing in particular on the treatment of the gas or liquid environment in heterogeneous and electro-catalysis [1], respectively, on current challenges in the development of error-controlled first-principles kinetic models of complex reaction networks [2], as well as on the integration of such first-principles microkinetic models into macroscale computational fluid dynamics [3].

[1] M.K. Sabbe, M.-F. Reyniers, and K. Reuter, Catal. Sci. Technol. **2**, 2010 (2012).
[2] M. Maestri and K. Reuter, Angew. Chemie Int. Ed. 123, 1226 (2011); Chem. Eng. Sci. **74**, 296 (2012).
[3] S. Matera and K. Reuter, Catal. Lett. **133**, 156 (2009); Phys. Rev. B **82**, 085446 (2010); J. Catal. **295**, 261 (2012).

The Friction between Structured Surfaces

Catarina Mendonça and Dominic Tildesley,
CECAM, EPFL, Lausanne Switzerland

Multi-scale simulation methods form a set of useful tools for studying friction and lubrication. Working from first principles towards the mesoscale, density functional theory (DFT), molecular dynamics (MD) and dissipative particle dynamics (DPD) can be employed to create models that provide useful insights into the behaviour of lubricants in contact with surfaces.

Molecular interactions at the solid–liquid interface control the performance of lubricant oils, and wear and adhesion at the surface. Atomistic models can help to understand the microscopic origins of static and kinetic friction, the behavior of boundary lubricants, and the link between molecular structure and tribology. These results can provide valuable information in the development and design of new materials (both lubricants and surfaces) and act as an input to the traditional macroscopic measurements of friction, once the surface and the fluid are accurately described. We show models built from first principles, that accurately describe the surface–liquid interactions in an ionic fluid close to a metal and demonstrate how these parameters are used in an MD simulation to study lubrication by imposing shear and load. Properties such as the friction coefficient, friction force and normal force can be extracted along with the microscopic structure at the interface.

The lubrication of surfaces coated with polymers is an also an important technological problem and one that is difficult to solve effectively using non-equilibrium molecular dynamics with atomistic models. The timescale for the relaxation of the polymers are long compared to the simulation lengths. This problem can be addressed in part by switching to a mesoscale model, which still preserves the important elements such as the shape and charge of the adsorbed polymers but allows for a longer time step and a slower shearing velocity.

We describe the development of DPD as an important technique for modelling polymers and surfactants in ionic solvents. The compression-dependence of the friction coefficients of neutral and charged polymer brushes at the same surface coverage is studied using dissipative particle dynamics (DPD) at two different shear rates. The chemical potential of the solvent particles is kept constant along the compression curve in order to mimic the experiment. We conclude that the kinetic friction coefficient between charged brushes is higher than that of neutral brushes at low compressions and smaller at high compressions. These differences are small. We also show that it is possible to simulate ultra-low friction coefficients comparable with experiments using the smallest shear rate accessible in a mesoscale simulation. The unexpected behavior of the shear deformation-induced structural heterogeneities in charged polymer brushes calls for further experiments to elucidate this local reorganization of the ions in adsorbed charged polymers.

Many-body Dissipative Particle Dynamics: Application to Realistic Liquid Mixtures

Dr Patrick B Warren,

Unilever R&D Port Sunlight,
Quarry Road East, Bebington,
Wirral, CH63 3JW, UK.

Many-body dissipative particle dynamics (MDPD) for two component mixtures is constructed, together with a new thermodynamic mapping scheme based on trial particle identity swap moves. This extends the standard strong segregation approach [Groot and Warren, J. Chem. Phys. **107**, 4423 (1997)] to weakly-interacting systems and allows MDPD to be applied to miscible systems with a composition dependent chi-parameter, such as polyethylene glycol solutions below the lower critical solution temperature. Further, the methodology allows coexistence compositions to be decoupled in immiscible systems, so that for example the solubility of water in oil can be adjusted separately to the solubility of oil in water. These developments bring MDPD conceptually close to the embedded atom methods widely used in electronic structure calculations.

List of Contributed Posters

Mr Francisco Alarcon	Lattice-Boltzmann method applied to micro-swimmer suspensions
*Ms Marta Dudek	Interplay between amikacin and its ribosomal binding site studied by molecular dynamics, spectroscopic, and calorimetric techniques
Mr David Gao	Multiscale Modeling of NC-AFM Experiments
Dr. Vihar Georgiev	Molecular Metal-Oxide nanoelectronics
Mr Henry Heitzer	First-Principles Calculation of Dielectric Response in Molecule-Based Materials
Mr Thomas Heinemann	Multiscale modeling approach towards understanding coronene self-assembly
*Ms Nicola Kleppmann	Simulation of C60 non-equilibrium surface growth
Dr. Martin Lisal	DPD Simulations with Chemical Reactions: Application to Thermal Decomposition of RDX
Mr Gaëtan Maurel	Toward the understanding of the polymer-filler interaction by using a multi-scale modeling
Prof. David Mebane	A Bayesian Framework for Uncertainty Quantification in Multi-Scale Models of Chemical Process Systems
Dr. Carlo Motta	Multi-scale method for charge transport in organic semiconductors
Mr Karol Palczynski	Exploring molecular-scale crystal structure formation of para-Sexiphenyl by all-atom Molecular Dynamics computer simulations
Mr Peter Palenčár	Thermal stability and self-assembly of long Î±-helices in the gas phase
*Dr. Sumathy Raman	ReaxFF, Parallel Replica Dynamics
Mr Juliusz Stasiewicz	Fragment-Orbital Modeling of Charge Transport in RNA
Dr. Ralf Tonner	Adsorption on the semiconductor surfaces Si(001) and TiO2(110): prototypical cases for dispersion-corrected DFT methods
*Dr. Ekaterina Voronina	Multiscale Simulation of Atomic Oxygen Impact on Nanostructures
*Ms Tongyu Wang	Multi-scale Modeling

Lattice-Boltzmann method applied to micro-swimmer suspensions study.

Francisco Alarcón
Departament de Física Fonamental, Universitat de Barcelona, C. Martí i Franqués, 1, 08028 Barcelona, Spain

Ignacio Pagonabarraga
Departament de Física Fonamental, Universitat de Barcelona, C. Martí i Franqués, 1, 08028 Barcelona, Spain

Collective motion is one of the most common and spectacular manifestation of coordinatedbehavior [1] . In particular, micro-swimmer suspensions at low Reynolds number, such as bacterial colonies [2], exhibit fascinating collective behaviour, including the possibility of non-equilibrium phase transitions between disordered and ordered states, novel long-range correlations, and pattern formation on mesoscopic scales [3]. Making use of the squirmer model [4] we have observed that hydrodynamic signature of swimmers (squirmers in our case) is a relevant parameter to have macroscopic ordered states or states where squirmers are agglomerated forming clusters [5], with the advantage that hydrodynamics is taken in count explicitly under the Lattice Boltzmann method scheme.

Here, we show a systematic study of the different phases we found in suspensions where swimmers interact not only hydrodynamically but by a Lennard-Jones (LJ) potential.

This competition between the LJ interactions and the activity of the squirmers give rise to a new regime of large density fluctuations. We have fully characterized the clusters and the collective coherent orientation of the swimmers movement which emerge for some cases.

We analyze the transition of the spontaneously formed structures as a function of the relative strength of the LJ interactions and by the active stresses generated by the squirmers.

[1] T. Vicsek and A. Zafeiris, Physics Reports, **517**, 17 (2012).
[2] C. Dombrowski, L. Cisneros, L. Chatkaew, R. Goldstein, J. Kessler, Phys. Rev. Lett. **93**, 098103 (2004).
[3] A. Baskaran and M.C. Marchetti, Proc. Natl Acad. Sci. **106**, 37 (2009).
[4] J.R. Blake, Journal of Fluid Mechanics, **46**, 01 (1971).
[5] F. Alarcón, I. Pagonabarraga, Journal of Molecular Liquids (2013), http://dx.doi.org/10.1016/j.molliq.2012.12.009

Interplay between amikacin and its ribosomal binding site studied by molecular dynamics, spectroscopic, and calorimetric techniques

Marta Dudek[1,2], Julia Romanowska[3,4], Tomasz Witula[1], Joanna Trylska[1]

[1] *Centre of New Technologies, University of Warsaw, Zwirki~i~Wigury 93, 02-089 Warsaw, Poland*
[2] *Institute of Biochemistry and Biophysics Polish Academy of Sciences, Pawínskiego 5a, 02-106 Warsaw, Poland*
[3] *Interdisciplinary Centre for Mathematical and Computational Modelling, University of Warsaw, Pawínskiego 5a, 02-106 Warsaw, Poland*
[4] *Heidelberg Institute for Theoretical Studies, Schloss-Wolfsbrunnenweg 35, D-69118 Heidelberg, Germany*

Amikacin is an antibiotic of the aminoglycoside family, administered in cases of sepsis, endocarditis and various hospital infections. Its primary mechanism of action leads via inhibition of the bacterial translation. Amikacin binds to the decoding region of the small ribosomal subunit, called the A-site. Understanding the microscopic mechanism of its action may help us design novel drugs with similar activity but less side effects.

Here, we focus on understanding the thermodynamics of interactions of amikacin with the ribosomal A-site. We use both computational and experimental techniques. To examine the thermodynamics of amikacin binding we performed isothermal titration calorimetry, differential scanning calorimetry, and UV-monitored thermal denaturation studies. As we observed, the reaction between amikacin and the A-site oligonucleotide exhibited positive entropy change. In this aspect amikacin differs from other aminoglycosides that were tested in similar conditions. To investigate the reasons for positive entropy change, we performed molecular dynamics simulations of free amikacin and bound to ribosomal RNA fragment mimicking the A-site.The results from the computational studies suggested that amikacin, particularly its \textsc{l}-HABA group became more flexible after binding to the A-site, which can lead to increase in entropy.

Multiscale Modeling of NC-AFM Experiments

David Z. Gao[1], M. B. Watkins[1], A. L. Shluger[1,2]
[1]*Department of Physics and Astronomy, University College London, Gower Street, London WCIE 6BT, United Kingdom*
[2]*WPI-AIMR, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

Studying the geometric parameters and the mechanisms of adsorption, diffusion, and growth of organic molecules at insulating surfaces is critical in the fields of catalysis, molecular electronics, molecular sensors, and molecular magnets. Individual molecules at surfaces have been studied successfully on conducting surfaces using scanning tunneling microscopy (STM) [1]. The conductivity of bulk wide gap oxides, however, is too low for STM measurements. These materials must be examined using noncontact atomic force microscopy (NC-AFM) [2]. Interpretation of these experimental results can be difficult due to the multiscale nature of these systems. The timescale at which molecules are able to bind, diffuse, and form films can be orders of magnitude faster than the speed at which the AFM tip can scan the surface. Additionally, the instrument is primarily sensitive to forces and the macroscopic tip-surface van der Waals forces present are orders of magnitude stronger than the short range interactions that are critical for producing image contrast.

A combined theory and experimental effort using metal coated tips has been used to unambiguously determine the adsorption, bonding, and translational pathways of a metal-organic complex on bulk insulators [3, 4]. We demonstrate that the methods employed provide information about the properties of organic molecules on bulk insulators while taking the greatly varying timescales involved and force contributions into consideration. These techniques are used to examine interactions starting at the atomic level and predict binding sites, orientations, and the tip induced motion of individual atoms and molecules. The knowledge gained through *ab initio* studies was then used to study a range of mechanisms from film formation to the imaging mechanisms of the AFM instrument itself at the macroscale.

[1] S. W. Hla and K. H. Rieder, *Annu. Rev. Phys. Chem.* **2003**, *54*, 307-330.

[2] C. Barth, A. Foster, C. Henry, and A. Shluger, *Adv. Mater.* **2001**, *23*, 477-501.

[3] K. Lämmle, T. Trevethan, A. Schwarz, M. Watkins, A. Shluger, and R. Wiesendanger, *Nanolett.* **2010**, *10*, 2965-2971.

[4] A. Schwarz, D. Z. Gao, K. Lämmle, J. Grenz, M. B. Watkins, A. L. Shluger, and R. Wiesendanger, *J. Phys. Chem. C* **2013**, *117*, 1105-1112.

Molecular-Metal-Oxide-nanoelectronicS (MMOS): Achieving the Molecular Limit

Vihar P. Georgiev, Stanislav Markov and Asen Asenov
Device Modelling Group, School of Engineering, University of Glasgow,
G12 8LT Glasgow, UK
Laia Vilà-Nadal, Christoph Busche and Leroy Cronin
WestCHEM, School of Chemistry, University of Glasgow,
G12 8QQ Glasgow, UK

Nowadays interest in electronic, magnetic and optical materials based on inorganic, organic, hybrid and nano-materials is increasing significantly. The EPSRC funded M-MOS Programme Grant provides an exciting opportunity for research in the field of molecular electronics based on hybrid nano-materials. Its main aim is to establish a link between the variability, scalability and reliability of a non-volatile flash-memory cell, in which the charge-storing components constitute of a layer of polyoxometalates molecular clusters (POMs). POMs are metal-oxide inorganic molecules formed by early transition metal ions and oxo ligands. Importantly, they can undergo multiple times reversible reduction/oxidation, which makes them attractive candidates for multi-bit storage for flash memory cells. The use of redox-active molecules to form the floating gate (FG) could offer several very important advantages over the conventional polysilicon FG[1].

However, the latter concept has not been proven so far and the on-going effort in modelling and simulations of flash-cell transistors with a POM-based floating gate plays a pivotal role for the sustainability of any farther experiment effort in this direction. In this work we use a plethora of modelling techniques embodied in a custom-built Simulation Domain Bridge, connecting the quantum chemical and mesoscopic device modelling, that illustrates the proposed advantages of POMs in the non-volatile molecular memories. Our ultimate goal is to provide informed guidance for both chemical synthesis and device design and fabrication, with the knowledge derived from device modelling and simulation and computational chemistry calculations.

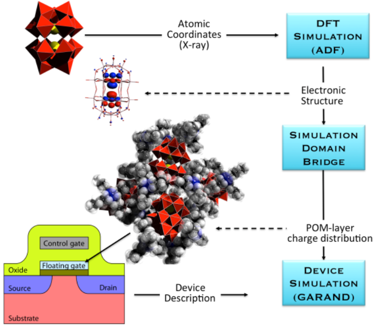


Figure 1. Simplified block diagram of the simulation methodology, linking DFT and flash-cell modelling.

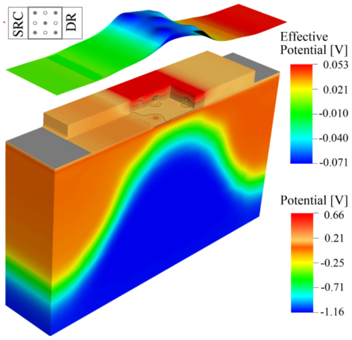


Figure 2. Potential barrier profile along the channel and distribution of electrostatic potential of the flash cell.

[1] J. Lee, S. H. Hur, J.-D. Choi, *IEEE Electron Device Letters*, 2002, 23/5, 264-266.

First-Principles Calculation of Dielectric Response in Molecule-Based Materials

Henry M. Heitzer, Tobin J. Marks, and Mark A. Ratner
Department of Chemistry and the Materials Research Center, Northwestern University,
2145 Sheridan Road, Evanston IL 60208

The dielectric properties of materials are of fundamental significance to many chemical processes and the functioning of numerous solid state device technologies. While experimental methods for measuring bulk dielectric constants are well-established, far less is known, either experimentally or theoretically, about the origin of dielectric response at the molecular/multi-molecular scale. We use response techniques developed for inorganic materials and apply them to molecular materials to determine their dielectric responses. We assess the accuracy of the method by reproducing the experimental dielectric constants of several bulk π-electron materials, and demonstrating the ability of the method to capture dielectric properties as a function of frequency and molecular orientation in representative arrays of substituted aromatic derivatives.[1] The role of molecular alignment and packing density on dielectric response is also examined, showing that the local dielectric behavior of molecular assemblies can diverge significantly from that of the bulk material. Lastly, we examine self assembled monolayers (SAMs) to determine what material properties, such as packing density and molecular alignment, achieve the largest dielectric response in both conjugated and non-conjugated organics.[2] It is determined that high surface coverage and proper alignment (parallel to the applied field) of SAMs can increase the dielectric response of a material. These results give important design rules that can help develop the next generation of high capacitance organic dielectrics.

[1] H.M. Heitzer, T.J. Marks and M.A. Ratner, Submitted to J. Am. Chem. Soc.

[2] H.M. Heitzer, T.J. Marks and M.A. Ratner, to be published.

Multiscale modeling approach towards understanding coronene self-assembly

Thomas Heinemann[1], Karol Palczynski[2], Joachim Dzubiella[2], Sabine H. L. Klapp[1]

[1]Institut für theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36,
10623 Berlin
[2]Institut für Physik - Komplexe Systeme, Humboldt Universität Berlin, Newtonstr. 15,
12489 Berlin

Understanding the interactions between organic molecules on atomistic and coarse-grained levels is an important prerequisite for selecting suitable molecules for optoelectronic applications. Here we explore coarse-graining strategies for coronene.

We first determine the main physical interactions that govern self-assembly of coronene by using all-atom Molecular Dynamics simulations and free energy calculation techniques like the weighted histogram analysis method.

We then transfer these angular-dependent interactions into a coarse-grained Gay-Berne-like model potential [1] with an additional quadrupole moment to take electrostatics into account.

So far there only exists a complicated, temperature-independent coarse-grained model for coronene, which has been used for static calculations [2]. Within our modeling approach, it is possible to account for atomistic vibrations at different temperatures.

We perform a quantitative comparison of the two model systems composed of atomistic and coarse-grained coronene, respectively. This is done by analyzing the stability of crystalline coronene and by investigating the columnar structure of uncharged coronene.

[1] V. N. Kabadi, Ber. Bunsenges. *Phys. Chem*. **90** (1986) 327.
[2] O. I. Obolensky et al., *Int. J. Quantum Chem.* **107** (2007) 1335.

Simulation of C60 non-equilibrium surface growth

Nicola Kleppmann*
Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Sebastian Bommel
Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, 22607 Hamburg, Germany and Institut für Physik, Humboldt- Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Stefan Kowarik
Institut für Physik, Humboldt- Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Sabine H. L. Klapp
Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, 10623 Berlin, Germany

Kinetic Monte Carlo simulation methods allow the simulation of non-equilibrium epitaxial surface growth over experimentally realized time spans of minutes and growth of multiple layers of particles [1]. Through variation of simulated temperature and adsorption rate the structures formed can be manipulated and predictions for experimental methods such as molecular beam epitaxy can be made. We apply the method to simulate multilayer growth of C60. The material parameters are obtained through comparison with grazing-incidence X-ray spectroscopy measurements [2]. The simulations allow for a time-resolved analysis of the real and reciprocal surface, geometric and statistical analysis as well as an understanding of microscopic processes obtained from particle trajectories.
We use C60 as a model system with both atomic and colloidal aspects and correlate local dynamics with the overall surface morphology on micrometer length scales and time scales of minutes.

[1] A. F. Voter, in *Radiation Effects in Solids*, Springer-Verlag New York Inc. (2007), ISBN:978-1-4020-5294-1
[2] S. Kowarik, A. Gerlach, S. Sellner, F. Schreiber, L. Cavalcanti and O. Konovalov, *Phys. Rev. Lett.* **96**, 125504 (2006)

Dissipative Particle Dynamics Simulations with Chemical Reactions: Application to Thermal Decomposition of RDX

Martin Lísal[1,2], John K. Brennan[3], Joshua D. Moore[3], and Sergey Izvekov[3]

[1]*E. Hála Laboratory of Thermodynamics, Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Czech Republic*

[2]*Department of Physics, Faculty of Science, J. E. Purkinje University, Ústí nad Labem, Czech Republic*

[3]*Weapons and Materials Research Directorate, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, USA*

Many applications of solid composite materials involve chemical energy release. For example, energetic materials, composites of high-energy, high-density crystallites and polymer binder, are used as explosives, propellants and detonators. Likewise, microstructured metallic systems are of interest in many different areas, including soldering in electronic-parts assembly and thermites for biocidal applications [1]. Energy exchange mechanisms for these materials occur over many length and time scales, where the energy release rate is intimately controlled by the nano- and microstructure of the composite, such as the crystallite size distribution, porosity, defects, and passivation layer.

For such systems, modeling and simulation is a useful tool, since it is not hampered by the experimental challenges caused by the steep thermal and chemical gradients. Rather, limitations are due to the approximations made in the models, computational resources, and the available methodologies. For example, continuum scale modeling can depict macro-scale events; however, it lacks the modeling fidelity to properly include material microstructure that influences the overall behavior. While atomistic-level simulations can provide more detailed descriptions, these simulations cannot access the length and times scales necessary to adequately model a microstructurally-heterogeneous material. These well-recognized limitations at either scale have motivated us to develop particle-based simulation models and methods to bridge these spatial and temporal modeling regimes while ensuring multiscale consistency. The approach must be capable of capturing the known thermo-mechanical responses for these systems, including phase transitions, structural rearrangements, and chemical reactions.

We find the constant-energy and constant-enthalpy Dissipative Particle Dynamics (DPD) methods [2-4] coupled with accurate coarse-grain models [5, 6] to be viable tools for simulating condensed-phase reactive events. We are developing a method within the DPD framework that can capture chemical reactivity. The approach, termed DPD-RX, was inspired by the work of Maillet and co-workers [7] and it treats the coarse-grain particle as a *microreactor* as opposed to a methodology that requires a reactive-type interaction potential. An additional progress variable is assigned to each particle that monitors the "extent-of-reaction" associated with reactions occurring within each particle. The evolution of the progress variable is governed by the kinetics of the reactions. Demonstration of the DPD-RX method is based upon thermal decomposition of a molecular crystal into gaseous species, specifically thermally-initiated cyclotrimethylene trinitramine (RDX) decomposition.

References

1. National Academy of Sciences Report, *Advanced Energetic Materials*, National Research Council*,* National Academy Press, 2004.
2. J. Bonet Avalos, A. D. Mackie, *Europhys. Lett.* **40**, 141, 1997.
3. P. Español, *Europhys. Lett.* **40**, 631, 1997.
4. M. Lísal, J. K. Brennan, J. Bonet Avalos, *J. Chem. Phys*. **135**, 204105, 2011.
5. S. Izvekov, P. W. Chung, B. M. Rice, *J. Chem. Phys.* **133**, 064109, 2010.
6. S. Izvekov, P. W. Chung, B. M. Rice, *J. Chem. Phys*. **135**, 044112, 2011.
7. J. B. Maillet, L. Soulard, G. Stoltz, *Europhys. Lett*. **78**, 68001, 2007.

TOWARD THE UNDERSTANDING OF THE POLYMER-FILLER INTERACTION BY USING A MULTI-SCALE MODELING

G. Maurel[a,b], B. Schnell[a], F. Goujon[b], M. Couty[a] and P. Malfreyt[b]

[a] *Manufacture Française des Pneumatiques MICHELIN, Centre de Technologies Ladoux, 63000 Clermont-Ferrand, France*
[b] *Institut de Chimie de Clermont-Ferrand, ICCF UMR CNRS 6296, Université Blaise Pascal, 63177 Aubière, France*

Filled elastomers systems are extensively used in the rubber industry, not only for the reinforcement of the polymer matrix but also to reduce the cost of the final product. Nowadays, both organic and inorganic (with or without a coupling agent) fillers be used to improve the properties of rubber materials. In spite of visible change in properties at a macroscopic level, as for example an increase in the shear modulus, an accurate description of mechanisms that are associated to this reinforcement is still missing. Nevertheless, it is known that the spatial distribution of the fillers is of high importance for the reinforcement of the rubber materials [1]. Analytical calculations show that this spatial distribution is governed by the effective polymer-mediated filler-filler interaction [2]. The latter effective potential is highly dependent of the polymer-filler interaction, which is difficult to describe quantitatively.

A way of considering the polymer-filler interaction is to use current simulation tools to study the motions of such a system. However, polymeric systems have various kinds of motions and a multiscale approach is required to sample the largest length and time scales. Microscopic simulations using atomistic models are used to perform the calculation of potentials of mean force. These potentials can be used to describe polymer-filler interaction at a mesoscopic scale using the Dissipative Particle Dynamics (DPD). DPD has been used at the beginning with generic potentials that were not designed for modelling polymer of a specific chemistry. The way of developing the potentials (i.e. at constant pressure using the iterative Boltzmann inversion) allows to conserve the chemical nature and the thermodynamic conditions of the system. Initially, the study was performed on a polybutadiene bulk matrix in order to validate this method [3]. It is then extended to others systems (isoprene rubber, polydimethylsiloxane, butyl rubber) in order to show that this method allows to distinguish several kinds of polymer microstructures. It is also extended for quantitative predictions to a composite model that consists of two planar fillers of silica confining several chains of polymer, grafted or not.

[1] Akcora P, Kumar SK, Moll J, Lewis S, Schadler LS, Li Y, Benicewicz BC, Sandy A, Narayanan S, Ilavsky J *et al*, *Macromolecules* **2009**, *43* (2), 1003-1010

[2] Jayaraman A. and Schweizer K.S., *Macromolecules* **2008**, *41* (23), 9430-9438

[3] Maurel G, Schnell B, Goujon F, Couty M. and Malfreyt P, *J. Chem. Theory Comput.* **2012**, *8*, 4570-4579

A Bayesian Framework for Uncertainty Quantification in Multi-Scale Models of Chemical Process Systems

David S. Mebane
Department of Mechanical and Aerospace Engineering,
West Virginia University, Morgantown, WV, USA.

Uncertainty quantification and minimization provides a framework for multi-scale modeling in chemical process systems. From a starting point of the Kennedy-O'Hagan methodology for Bayesian calibration, a framework suitable for chemical process modeling was established. First-principles calculations are used to establish prior probability distributions for physical parameters. Techniques in non-parametric data regression -- including a novel method called ``dynamic discrepancy'' -- are employed to find a candidate set of chemical kinetic models. These models have a mixed first-principles and empirical character, and are computationally tractable for use at the scale of chemical process modeling. Combination of the {\em prior} (which in this sense refers to both the priors for the physical parameters and the space of candidate kinetic models) with the experimental data according to Bayes' Theorem leads to a {\em posterior} probability distribution defined on a space of kinetic functions. The posterior ranks the candidate functions (in a sense of probability) according to their consistency with all available theoretical and experimental information. The uncertainty represented in this posterior can then be propagated to the process scale, which typically involves an extrapolation in the space of time-varying input functions (temperatures, gas compositions, etc.). A resulting {\em predictive} distribution can be defined on any output at the process scale, including the space of input functions. A set of input functions can then be sampled from this predictive distribution, closing the loop on an iterative process of data production, calibration, upscaling and repeated data production that can effectively prevent extrapolation in upscaling.

The framework is demonstrated on hypothetical and real-world examples.

Multi-scale method for charge transport in organic semiconductors

Carlo Motta
School of Physics, Trinity College, University of Dublin, Ireland

Efficient charge transport in organic semiconductors is the key ingredient for their application in organic electronics. In order to model realistic devices, an essential step is to predict the charge carrier transport of pure organic crystals at different temperatures. Despite various approaches have been proposed to this purpose, we want to establish a robust methodology which is material-specific, which correctly accounts for the van der Waals interactions of this long-range interacting systems, and which includes all the vibrational contributions to the overall mobility. Such an approach can be elegantly obtained in an *ab initio* framework via the Wannier functions of the system, which constitute a way to parametrize its tight-binding Hamiltonian. We intend to apply this methodology to the case of durene, a small π-conjugated molecule which forms a herringbone stacked crystal, expected to show high mobilities. Furthermore, we aim to estimate the spin transport properties of this material, by including spin-orbit and hyperfine interactions in the Hamiltonian.

Exploring molecular-scale crystal structure formation of para-Sexiphenyl by all-atom Molecular Dynamics computer simulations

Karol Palczynski, Joachim Dzubiella
Institut für Physik, Humboldt Universität Berlin, Newtonstr. 15, 12489 Berlin

Theoretical crystal structure prediction of organic molecules will increase the efficiency for the selection of suitable molecules for applications in optoelectronic devices in the future.

In this study we first determine the main physical interactions that govern self-assembly of para-Sexiphenyl (6P) by employing classical all-atom Molecular Dynamics computer simulations. The temperature dependent crystal structure of 6P is analyzed by means of orientational and conformational order parameters. The sensitivity of the obtained structures to the selection of atomic partial charges is studied and the calculated results are being compared with experimental x-ray data.

The room temperature crystal structure of 6P can be reproduced quite accurately[1]. Subsequently, using the force-field parameters from the 6P simulations, we can now try to predict crystal structures of 6P derivatives.

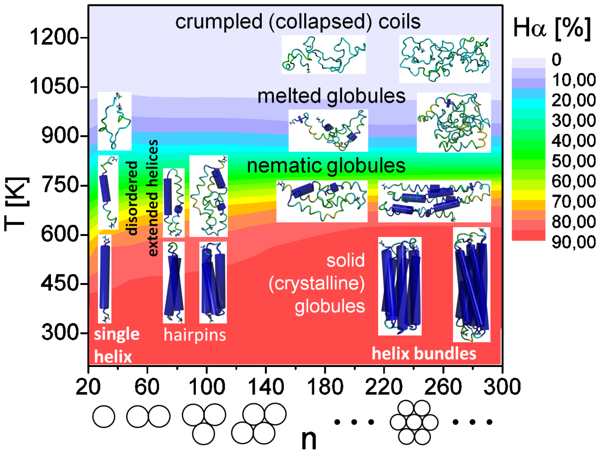
[1] K. Palczynski, J. Dzubiella, to be published.

Thermal stability and self-assembly of long α-helices in the gas phase

Peter Palenčár and Tomáš Bleha
Polymer Institute, Slovak Academy of Sciences, 845 41, Bratislava, Slovakia

Recent progress in experimental techniques such as ion mobility spectrometry coupled to mass spectrometry allows studying the conformation of flexible molecules including large biomacromolecules and synthetic polymers in the gas phase [1,2]. The adjustable temperature in experiment typically from 80 to 800 K allows the observation of thermal motion of floppy molecules or unfolding process of folded structures without dissociation of their covalent bonds. To interpret the indirect structure information from the gas phase experiments various computational techniques are applied [3]. The high temperature structure of typical nonpolar polymer is described as random coil. However, polymers such as polypeptides with highly developed hydrogen bonds network can sustain their secondary structure even at elevated temperatures.

Thermal stability of a single α-helix in the gas phase was studied by molecular dynamic simulations at atomistic details. The range of polymer chain length, *n* and temperature, *T* studied and the corresponding α-helical content, H_α is shown in the conformational state diagram below. We observed highly ordered helical structures of Ala_n molecules at room temperature [4,5] and disordered and compacted non-random structures at *T* above 800 K. The conformational and secondary structure analysis was performed. Surprisingly, high amounts of helices, turns and bends were found in chains at $T > 800$ K, due to strong hydrogen bonding and of inter-residual attraction. The scaling exponents calculated for the radius of gyration, R_g *vs* chain length, *n* showed that the structure of Ala_n is contracted compared to a random coil - “crumpled” coil and condensed globule are observed. At room temperature, the self-assembly of an α-helix (H_α ~90 %) was observed. The straight α-helix is fragmented into antiparallel helices joined by short coils. The number of helices is dictated by *n*. The hairpin structures and helix bundles are found. The energy analysis reveals increased stability of the hexagonal (6+1) structure over the other.



Acknowledgement. This work was supported by APVV under the contract No. APVV-0451-11 and by the Grant Agency VEGA, grants No. 2/0079/12 and 2/0093/12.

[1] K. Breuker and F. W. McLafferty, *Proc.Natl.Acad.Sci.U. S. A.*, 2008, **105**, 18145-52
[2] T. Wyttenbach and M. T. Bowers, *Top. Curr. Chem.* 2003, **225**, 207-232
[3] T. Mayer, V. Gabelica, H. Grubmuller and M. Orezco, *DOI: 10.1002/wcms.1130*
[4] P. Palenčár and T. Bleha, *Macromol. Theor. Simul.* 2010, **19**, 488-495
[5] P. Palenčár and T. Bleha, *Comp. Theor. Chem.* 2013, **1006**, 62-69

A Reactive Molecular Dynamics Study of Thermal Cracking of Hydrocarbons

Sumathy Raman, Chenyu Zou[a], Adri van Duin[b]

ExxonMobil Research and Engineering, 1545 Route 22 East, Annandale, New Jersey
[a]Summer Intern from Pennsylvania State University
[b]Department of Mechanical and Nuclear Engineering, University Park, PA 16802

Modeling of complex reaction systems is necessary in the design, analysis and optimization of many technologically important processes such as thermal maturation of kerogens, pyrolysis, steam cracking, coking, partial oxidation and combustion. The complexity in kinetic modeling of all these processes is introduced by the feed which is often a hydrocarbon mixture. Recent advances[1] in automated mechanism generation tools allow for the generation of complex reaction networks and leave the assignment of rate parameters for all the reactions in the network or devising appropriate estimation rules for all reaction classes in the network generation to be the remaining challenge. Improved numerical methods and increased computational capabilities in the last decade or two has enabled us to address this challenge using the state-of-the-art ab initio methods together with reaction rate theories. However, ab initio calculations are limited to systems with less than a hundred atoms. Consequently, network generation for a complicated carbonaceous matter like coal or heavy hydrocarbons begins with identification of substructures, construction of reaction network and kinetic model for each of the substructures and unification of substructure kinetic models viz., Chemical Structure-Compositional Yield Model[2,3] (CS-CYM). Alternatively, the last decade also has witnessed the development of reactive force fields (ReaxFF[4]) from quantum calculations and this provides a new paradigm for the extension of length scales of first principles based reactive atomistic simulations. REAXFF uses a general relationship between bond distance and bond order on one hand and between bond order and bond energy on the other hand that leads to proper dissociation of bonds to separated atoms. In addition, it has Coulomb and Morse (van der Waals) potentials to describe non-bonded interactions between all atoms. The caveat in reactive MD is to accelerate the reaction timescale by artificially raising the reaction temperature and pressure in order to study the process within a simulation time of couple of nanoseconds. This talk will highlight our strategy for the estimation of kinetic parameter and lumped kinetic models for thermal cracking and address the challenges involved in predicting the product selectivity. The presentation will also cover some of our recent efforts to couple ReaxFF with many of the accelerated dynamic algorithms[5] based on infrequent event assumption as introduced by Art Voter.

1. S. Raman, H.-H. Carstensen, *Int. J. Chem. Kin.*, **44** (2012) 327
2. H. Freund, C. C. Walters, S. R. Kelemen, M. Siskin, M. L. Gorbaty, D. J. Curry and A. E. Bence, *Org. Geochemistry*, **38** (2007) 288.
3. C.C. Walters, H. Freund, S. R. Kelemen, P. Peczak, D. J. Curry, *Org. Geochemistry*, **38** (2007) 306.
4. A. C. T. van Duin, S. Dasgupta, F. Lorant, W. A. Goddard III, *J. Phys. Chem. A*, **105** (2001) 9396.

Fragment-Orbital Modeling of Charge Transport in RNA

Juliusz Stasiewicz
Laboratory of Bioinformatics and Protein Engineering,International Institute of Molecular and Cell Biology in Warsaw,
Ks. Trojdena 4, 02-109 Warsaw, Poland

Janusz M. Bujnicki
Laboratory of Bioinformatics and Protein Engineering, International Institute of Molecular and Cell Biology in Warsaw,
Ks. Trojdena 4, 02-109 Warsaw, Poland
Laboratory of Bioinformatics, Institute of Molecular Biology and Biotechnology, Faculty of Biology, Adam Mickiewicz University
ul. Umultowska 89, 61-614 Poznàn, Poland

The ability of DNA strands to transport electric charge captured lots of attention over the recent years [1]. It is widely believed that conductivity of DNA may be involved in repair of oxidatively damaged genetic code, i.e. by allowing migration of radicals to non-coding regions. It has also been suggested that positive charge from DNA base stack can oxidize aromatic amino acids in DNA-binding proteins. Although indications do exist that the same issues may arise in RNA [2], the topic of RNA conductivity remains largely overlooked.
According to current state of the art, positive charges are localized mainly on bases, preferably guanine. Guanine posesses the least ionization potential (ca. 0.4 V less than adenine and 1 V less than cytosine and uracil) [3], being the most prone to electron detachment. The hole (unocuppied HOMO) is believed to be the charge carrier, which can do multistep hopping or tunneling between neighbor bases.
In this work we propose a computational scheme for evaluation of hole conductivity in RNA strands. In the scheme we treat all selected fragments (bases, nucleotides or base pairs) on the Density Functional Theory level. The dynamics of system is reproduced by Molecular Dynamics, in the QM/MM spirit. Interactions of the quantum and newtonian parts are accounted for by the means of partial atomic charges. We evaluate the tight binding Hamiltonian as the model for charge movements.

We also present custom C++ codes that perform multiscale modeling with the efficient technique of template metaprogramming.

[1] B. Giese *Annu. Rev. Biochem.* **71**:51 (2002)
[2] D. T. Odom, J. K. Barton *Biochemistry* **40**:8727 (2001)
[3] T. Kubar *et al. J. Phys. Chem. B* **112**:7937 (2008)

Adsorption on the semiconductor surfaces Si(001) and TiO_2(110): prototypical cases for dispersion-corrected DFT methods

R. Tonner
Fachbereich Chemie and Materials Sciences Center, Philipps-Universität Marburg Hans-Meerwein-Straße, 35032 Marburg

Semiconductor surfaces are widely investigated e.g. due to their importance in the microelectronics industry (silicon) or their photocatalytic activity (titanium dioxide). Before investigations about surface reactivity on these prominent surfaces can take place, appropriate methods have to be identified to enable the derivation of reliable computational data. In recent years, it was shown by several groups that the workhorse of surface and materials science – density functional theory – can be problematic here.[1] Namely the at least incomplete description of dispersion forces with many widely used density functionals was identified. In the meantime, many approaches have been put forward and thoroughly tested for molecular systems as well as metal surfaces. As it was deemed to be less important for these systems, only in recent years investigations were carried out for semiconductor solids and surfaces[2] and the question about the importance of dispersion interactions here is still under discussion. We carried out investigations of systems where reliable experimental data is available and conclude that for weakly bound adsorbates, dispersion forces should not be neglected on semiconductor surfaces.

[1] a) S. Grimme *WIREs Comput. Mol. Sci.* **2011**, *1*, 211; b) A. Tkatchenko, L. Romaner, O. T. Hofmann, E. Zojer, C. Ambrosch-Draxl, M. Scheffler *MRS Bull.* **2010**, *35*, 435; c) J. Grafenstein, D. Cremer *J. Chem. Phys.* **2009**, *130*, 124105; d) E. R. Johnson, I. D. Mackie, G. A. DiLabio *J. Phys. Org. Chem.* **2009**, *22*, 1127; e) T. Sato, H. Nakai *J. Chem. Phys.* **2009**, *131*, 224104.

[2] a) J. Moellmann, S. Ehrlich, R. Tonner, S. Grimme *J. Phys. Condens. Matter* **2012**, *24*, 424206; b) H. J. Kim, A. Tkatchenko, J. H. Cho, M. Scheffler *Phys. Rev. B* **2012**, *85*, 041403.

Multiscale Simulation of Atomic Oxygen Impact on Nanostructures

Voronina E.N., Novikov L.S.
Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University,
Leninskie gory 1-2, 119991, Moscow, Russia,
E-mail: voroninaen@nsrd.sinp.msu.ru

Nanostructures of various geometry and composition are considered currently as very promising materials for space applications. However, the critical issue is the durability of these novel materials to the space environment influence. In low-Earth orbits, one of the main factors that cause the damage of spacecraft surface materials is atomic oxygen (AO) of the Earth's upper atmosphere. Due to the high reactivity of O atoms which is enhanced by their high (~5 eV) kinetic energy because of the spacecraft orbital velocity, AO impact leads to the erosion and mass losses of materials. Moreover, the oxidation is one of the most widely used methods for the purification of carbon nanostructures and tailoring their properties [1], so the investigation of AO influence on nanostructures is very important.

This paper focuses on studying the destruction of carbon and boron nitride nanotubes (CNTs and BNNTs, respectively) under the influence of AO flow. For this task it is necessary to investigate elementary physical and chemical processes that occur in nanostructures under the impact of hyperthermal O atoms, and to find out how these processes influence the nanotube structure. The computer modelling may become an efficient mean for such researches, and the multiscale simulation methods are needed.

The density functional theory (DFT) method was applied to study changes in CNT and BNNT structures induced by the O atom adsorption, including nanotube unzipping. The calculated dependences of the adsorption energy on diameter of CNTs and BNNTs demonstrated that the interaction of O atoms with nanotubes weakens as their diameter increases. The study of unzipping processes revealed that BNNTs are more durable to unzipping under AO impact than CNTs due to chemical bond formation between adsorbed O atoms [2].

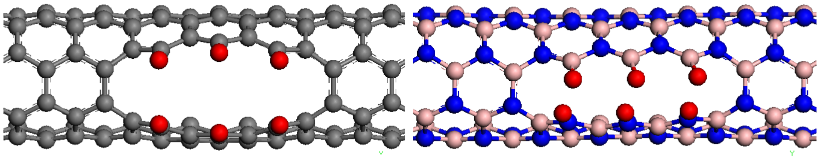

a b

Figure 1: The unzipping process in the (4,4) CNT (a) and BNNT (b) as a result of sequential attacks of three O pairs.

The impact of thermal and hyperthermal O atoms on CNTs and BNNTs of small diameter was simulated with SCC DFTB dynamics. The formation of O-containing groups on the surface of nanotubes is in good agreement with the results of DFT calculations. The obtained regularities are used to develop kinetic Monte–Carlo model for describing the interaction of AO flow of high fluences with nanostructures.

[1] P. M. Ajayan and B. I. Yakobson, *Nature* 2006, **441**, 818.
[2] E.N. Voronina, L.S. Novikov, V.N. Chernik, et al., *Inorg. Mat.: Appl. Res.* 2012, **3**, 95.

Exploring Morphology-Activity Relationships: Ab Initio Wulff Construction for RuO_2 Nanoparticles under Oxidizing Conditions

Tongyu Wang[a], Jelena Jelic[a], Dirk Rosenthal[b], and Karsten Reuter*[a]

[a] Chair for Theoretical Chemistry and Catalysis Research Center, Technical University Munich, Lichtenbergstr. 4, D-85747, Germany
[b] Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195, Berlin, Germany

We present a density-functional theory based Wulff construction of the equilibrium shape of RuO_2 particles in an oxygen environment. The obtained intricate variations of the crystal habit with the oxygen chemical potential allow for a detailed discussion of the dependence on the oxidizing pretreatment observed in recent powder catalyst studies [1-3]. The analysis specifically indicates an incomplete particle shape equilibration in previously employed low temperature calcination [1]. Equilibrated particles could be active CO oxidation catalysts with long-term stability in oxidizing feed and then represent an interesting alternative to the previously suggested core-shell concept.

[1] V. Narkhede, J. Aβmann, M. Muhler, *Z. Phys. Chem*. **2005**, *219*, 979-995.
[2] D. Rosenthal, F. Girgsdies, O. Timpe, R. Blume, G. Weinberg, D. Teschner, R. Schlögl, *Z. Phys. Chem*. **2009**, *223*, 183-207.
[3] D. Rosenthal, F. Girgsdies, O. Timpe, G. Weinberg, R. Schlögl, *Z. Phys. Chem*. **2011**, *225*, 57–68.

List of Participants

Mr Francisco Alarcon	
Prof. Ali Alavi	
Prof. Karsten Albe	
Prof. Emilio Artacho	
Prof. Jôrg Behler	
Prof. Paolo Carloni	
Dr. Alberto Castro	
Prof. Giovanni Ciccotti	
Prof. Christoph Dellago	
Prof. Claudia Draxl	
Ms Marta Dudek	
Prof. Ron Elber	
Prof. Pep Español	
Mr David Gao	
Dr. Vihar Georgiev	
Dr. Luca Ghiringilli	
Dr. Gerhard Gompper	
Prof. Gary Hart	
Dr. Karsten Hartmann	
Mr Thomas Heinemann	
Mr Henry Heitzer	
Prof. Ray Kapral	
Ms Nicola Kleppmann	
Dr. Kurt Kremer	
Mr Alexander Kolokol	
Prof. Peter Kratzer	
Dr. Martin Lisal	
Dr. Jean-Bernard Maillet	
Prof. Patrice Malfreyt	
Prof. Michel Mareschal	
Mr Gaëtan Maurel	
Prof. David S. Mebane	
Dr. Ana C. F. Mendonça	
Dr. Carlo Motta	
Prof. Jôrg Neugebauer	
Dr. Modesto Orozco	
Dr. Roar A. Olsen	
Prof. Ignacio Pagonabarraga	
Mr Karol Palczynski	
Mr Peter Palenčár	
Dr. Sumathy Raman	
Dr. Javier Ramos	
Prof. Karsten Reuter	
Mr Robin Richardson	

Dr Inga Ringdalen	
Dr Matthias Rupp	
Prof.. Matthias Scheffler	
Prof. Friederike Schmid	
Prof. Andrzej L. Sobolewski	
Mr Juliusz Stasiewicz	
Dr Domiic Tildesley	
Dr. Ralf Tonner	
Dr Matthieu Verstraete	
Dr. Ekaterina Voronina	
Ms Tongyu Wang	
Dr. Patrick Warren	

Index

Mr Francisco Alarcon 38
Prof. Ali Alavi 9, 13
Prof. Karsten Albe 7, 14
Prof. Emilio Artacho 9, 15
Prof. Jôrg Behler 8, 16
Prof. Paolo Carloni 8, 17
Dr. Alberto Castro 10, 18
Prof. Giovanni Ciccotti 9, 19
Prof. Christoph Dellago 8, 9, 20
Prof. Claudia Draxl 7, 8, 21
Ms Marta Dudek 39
Prof. Ron Elber 9, 22
Prof. Pep Español 9, 23
Mr David Gao 40
Dr. Vihar Georgiev 41
Dr. Luca Ghiringilli 7, 24
Dr. Gerhard Gompper 10, 25
Prof. Gary Hart 7, 26
Dr. Karsten Hartmann 9, 27
Mr Thomas Heinemann 43
Mr Henry Heitzer 42
Prof. Ray Kapral 8, 28
Ms Nicola Kleppmann 44
Dr. Kurt Kremer 10, 30
Mr Alexander Kolokol
Prof. Peter Kratzer 7, 29
Dr. Martin Lisal 58
Dr. Jean-Bernard Maillet 58
Prof. Patrice Malfreyt 47
Prof. Michel Mareschal 3, 58
Mr Gaëtan Maurel 47
Prof. David S. Mebane
Dr. Ana C. F. Mendonça 35
Dr. Carlo Motta 49
Prof. Jôrg Neugebauer 7, 31
Dr. Modesto Orozco 10, 32
Dr. Roar A. Olsen 58
Prof. Ignacio Pagonabarraga 10, 33
Mr Karol Palczynski 43, 50
Mr Peter Palenčár 51
Dr. Sumathy Raman 53
Dr. Javier Ramos 58
Prof. Karsten Reuter 8, 34
Mr Robin Richardson 58
Dr Inga Ringdalen 58
Prof. Matthias Scheffler 3, 58

Prof. Andrzej L. Sobolewski 58
Mr Juliusz Stasiewicz 54
Dr Dominic Tildesleysley 10, 11, 35
Dr. Ralf Tonner 55
Dr. Ekaterina Voronina 56
Ms Tongyu Wang 57
Dr. Patrick Warren 10, 36