Scientific report on the SIMBIOMA-conference:
“SIMBIOMA 2008”
2.4.-5.4.2008 in Konstanz (Germany)
www.uni-konstanz.de/simbioma

In this conference computational scientists have been brought together who are involved in the challenges that are faced in the fundamental modelling of matter on time and spatial scales which are relevant in biosystems and material science at the nanometer length scale. The conference has focused on new techniques as well as on current applications for bridging the gap between ab-initio- and meso- and macroscopic levels.

The conference has been a big success:
The invited speakers in general had a very high international reputation, and the scientific quality of most of the 30 invited and 9 contributed talks has been very good as well as the quality of the majority of the 176 poster contributions. In total we had 262 registrations at the conference. The organization of the conference in plenary talks and few parallel sessions and short oral summaries of the poster contributions as well as well chosen times for breaks allowed vital discussions among the groups participating in the SIMBIOMA ESF programme and others (e.g. invited speakers from the USA). The production of a book with the most important contributions is planned.

A summary of the content of invited talks as well as of the oral and poster contributions is given in the abstract booklet (www.uni-konstanz.de/simbioma/program.htm).

By this conference the SIMBIOMA-community got the chance to exchange novel results and discuss their relevance for future studies such that the cooperations in the SIMBIOMA-programme most probably will result in very valuable scientific results on molecular simulations in biosystems and material science in the future.

The international advisory committee consisted of 47 scientists, the organizing committee was: W. Andreoni, G. Ciccotti, P. Nielaba, B. Smit and R. Vuilleumiere. The conference was organized with 9 plenary sessions with 50-minutes invited talks. Those were selected by the scientific committee to provide large overviews of recent advances in particular fields. The titles and abstracts of those invited talks (as can be seen from the attached excerpt from the book of abstracts) speak by themselves. The first talk by Gross gave the perspectives of the computation of electron dynamics by time-dependent density functional theory. Then Alavi made a presentation of the calculation of electronic correlation energies via path counting, and Landman explained the computational microscopy of materials phenomena in the non-scalable regime. Soft matter aspects have been addressed by Barrat, Dijkstra and Binder. Barrat analyzed the deformation of amorphous materials at low temperature, Dijkstra focussed on colloidal self-assembly, and Binder discussed the phase behavior of fluids, fluid mixtures and polymer solutions. Vanden-Eijnden described the single-sweep methods for free energy calculations, which is a central issue in biophysics. It was a general feeling that those plenary talks were of a very high quality and addressed questions at the heart of the problem faced in molecular simulations in biosystems and material science at the nanometer length scale.

The other talks were grouped into 10 sessions run in two parallel sessions. Each session would start with two 30-minutes invited talks devoted to a presentation of the session subject, followed by one shorter more focused presentation on recent advances. Then at the end of the session, all participants presenting a poster in that session have been given the opportunity to state very briefly (three minutes) what the research reported was about, before the poster session eventually takes place.

The following sessions have been organized:
Proteins and Peptides
Protein Crystallization and Aggregation
Membranes
Quantum Effects in nano-sized Materials
Microfluidics
Soft Matter I
Soft Matter II
Multiscale Methods
Methods
Charge Transfer and Transport in Condensed and Soft Matter

From the point of view of participation, the most successful were the sessions devoted to soft matter and methods. Most of the presentations were dealing with atomistic classical modelling and some tried to connect to macroscopic scales. Abstracts can be found in the conference booklet (see conference web-site, excerpt attached), but a general impression was really that the scientific simulation community starts now to be in a position to model time and space scales which will be comparable with those of some experiments in biosystems and material science at the nanometer length scale. This will certainly be more and more so in the near future. It is also worth to point out that the level of complexity of the fluids under investigation was much higher than just a few years ago. Several sessions revealed the difficulty faced in an atomistic modelling of materials. Simulations have to involve various levels of descriptions: quantum, ab-initio, fully classical, mesoscopic and macroscopic and, of course, multiscale approaches are most of the time necessary to be predictive. Several methodological developments were also presented at the conference.

There was also a part dedicated to the organization of the programme itself. The SIMBIOMA steering committee decided on a large number of workshops to be done during 2008. The SIMBIOMA steering committee strongly supported the idea of convening the community again within a two-years delay on the theme of molecular simulations in biosystems and material science at the nanometer scale. In addition, meetings of the MOLSIMU management committee and of the ESF-forward look initiative for the European simulation community, organized at the conference site in parallel to the conference, attracted scientists from these scientific initiatives to the conference as well and resulted in vital discussions.

SIMBIOMA 2008

University of Konstanz (Germany), April 2 - 5, 2008

Organizing Committee:

W. Andreoni, G. Ciccotti, P. Nielaba, B. Smit, R. Vuilleumier

The Conference

Similar to the SIMU-conference in 2001 (Konstanz), the conference in 2008 will be organized in 9 plenary talks (50 minutes), 10 sessions with three speakers (invited talks with 30 minutes talks and contributing talks with 20 minutes), short poster presentation talks (3 minutes each), and in addition a general poster session.
The topics of the sessions include:

- Proteins and Peptides
- Protein Crystallization and Aggregation
- Membranes
- Quantum Effects in Nano-sized Materials
- Microfluidics
- Soft Matter I
- Soft Matter II
- Methods
- Multiscale Methods
- Charge Transfer and Transport in Condensed and Soft Matter

Time and spatial scales relevant for material science and biosystems are challenges in the fundamental modeling of matter. In this conference we would like to bring together computational scientists facing these challenges and to focus the subject on new techniques as well as on current applications for bridging the gap between ab-initio and meso and macroscopic levels. The conference will aim at developing a real cooperation among the groups participating in the SIMBIOMA ESF program. It is also open to participants, who are not members of this program.

Conference Advisory Committee:

A. Alavi, M. P. Allen, W. Andreoni, M. Athenes, J.-L. Barrat, K. Binder, P. Bolhuis, M.E. Cates, G. Ciccotti, C. Dellago, M. Dijkstra, I. Economou, P. Espanol, R. Everaers, P. Faisca, D. Frenkel, D. Galli, H. Grubmueller, B. Hafskjold, J.P. Hansen, K. Jacobsen, H. Jonsson, K. Kremer, S. Lago-Aranda, E. Leontidis, B. Lesyng, R. Lipowsky, D. Mackernan, D. Marx, V. Mohacek-Grosev, O. G. Mouritsen, R. Netz, P. Nielaba, L. Nilsson, M. Rodger, U. Roethlisberger, J. P. Ryckaert, M. Scheffler, F. Schmid, B. Smit, M. Sprik, S. Succi, J. Ulicny, I. Vattulainen, M. Vendruscolo, R. Vuilleumier, M. Waroquier

Local Organizing Committee:

P. Nielaba, Y. Fischer (Conference Secretary), Members of P. Nielaba's Group

Scientific topics include:

- Proteins and Peptides
- Protein Crystallization and Aggregation
- Membranes
- Quantum Effects in Nano-sized Materials
- Microfluidics
- Soft Matter
- Methods
- Multiscale Methods
- Charge Transfer and Transport in Condensed and Soft Matter

Confirmed speakers:

- A. Alavi (UK)
- S. Baroni (Italy)
- J.-L. Barrat (France)
- J. Bernholc (USA)
- K. Binder (Germany)
- P. Bolhuis (Netherlands)
- I. Burghardt (France)
- M. E. Cates (UK)
- A. Cavallo (France)
- D. Cleaver (UK)
- M. Dijkstra (Netherlands)
- J. Doye (UK)
- D. Frenkel (Netherlands)
- E. K. U. Gross (Germany)
- P. Hünenberger (Switzerland)
- K. Kremer (Germany)
- U. Landman (USA)
- D. E. Manolopoulos (UK)
- N. Marzari (USA)
- R. Netz (Germany)
- B. Roux (USA)
- R. Rudd (USA)
- T. Schilling (Germany)
- F. Schmid (Germany)
- F. Sciortino (Italy)
- S. Succi (Italy)
- M. Tarek (France)
- E. Vanden-Eijnden (USA)
- I. Vattulainen (Finland)
- M. Vendruscolo (UK)

Program SimBioMa 2008

Conference on Molecular Simulations in Biosystems and Material Science

April 2 - 5, 2008
University of Konstanz, Germany

Session	Topics
1	Proteins and Peptides
2	Protein Crystallization and Aggregation
3	Membranes
4	Quantum effects in nano-sized Materials
5	Microfluidics
6	Soft Matter I
7	Soft Matter II
8	Multiscale Methods
9	Methods
10	Charge Transfer and Transport in Condensed and Soft Matter

Time	Thursday, April 03, 2008	
09:00	**Plenary Talk** A. Alavi Audimax (Room: A600)	
09:50	Break	
	Parallel Sessions	
	Session 4 Room: A701	Session 5 Room: A703
10:20	J. Bernholc	S. Succi
10:50	J. Doye	A. Frezzotti
11:20	A. Fortunelli	D.L. Cheung
11:40	Poster Talks	Poster Talks
12:20	Lunch Break	
14:00	**Plenary Talk** U. Landman Audimax (Room: A600)	
14:50	Break	
	Parallel Sessions	
	Session 1 Room: A701	Session 3 Room: A703
15:20	M. Tarek	P. Hünenberger
15:50	R. Netz	F. Schmid
16:20	P.F.N. Faisca	L. Delemotte
16:40	Poster Talks	Poster Talks
19:00	**Banquet** Evening talk: D. Frenkel (Konzil)	

Time	Friday, April 04, 2008	
09:00	**Plenary Talk** J.-L. Barrat Audimax (Room: A600)	
09:50	Break	
	Parallel Sessions	
	Session 2 Room: A701	Session 6 Room: A703
10:20	P. Bolhuis	T. Schilling
10:50	M. Vendruscolo	F. Sciortino
11:20	S. Abeln	S.H.L. Klapp
11:40	Poster Talks	Poster Talks
12:20	Lunch Break	
14:00	**Plenary Talk** M. Dijkstra Audimax (Room: A600)	
14:50	**Plenary Talk** K. Kremer Audimax (Room: A600)	
15:40	Break	
16:10	**Poster Session**	
18:15	**Meetings** (SIMBIOMA/..)	
19:00	**Guided City Tour**	

Time	Saturday, April 05, 2008	
	Parallel Sessions	
	Session 7 Room: A701	Session 9 Room: A703
09:00	M.E. Cates	S. Baroni
09:30	A. Cavallo	Manolopoulos
10:00	D. Cleaver	S. Bonella
10:30	Poster Talks	Poster Talks
11:00	Break	
11:20	**Plenary Talk** E. Vanden-Eijnden Audimax (Room: A600)	
12:10	**Plenary Talk** K. Binder Audimax (Room: A600)	
13:00	**Closing at the University**	
13:15	Lunch Break	
15:00	**Excursion** (Island of Mainau)	

Time	Wednesday, April 02, 2008	
14:00	**Opening / Welcome** Rector / SimBioMa Audimax (Room: A600)	
14:30	**Plenary Talk** E.K.U. Gross Audimax (Room: A600)	
15:20	Break	
	Parallel Sessions	
	Session 8 Room: A701	Session 10 Room: A703
15:50	R. Rudd	I. Burghardt
16:20	I. Vattulainen	N. Marzari
16:50	B. Ensing	J. Blumberger
17:10	C. Simon	S. Meloni
17:30	Poster Talks	Poster Talks
18:00	**Welcome Reception**	

Contents

Plenary Talks

Speakers:

E. K. U. Gross (Berlin, Germany)

A. Alavi (Cambridge, UK)

U. Landman (Atlanta, Georgia, USA)

J.-L. Barrat (Villeurbanne, France)

M. Dijkstra (Amsterdam, Netherlands)

K. Kremer (Mainz, Germany)

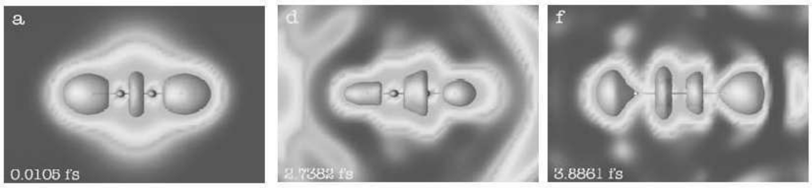
E. Vanden-Eijnden (New York, USA)

K. Binder (Mainz, Germany)

PT-1. Analysis and Optimal Control of Electron Dynamics by Time-Dependent Density Functional Theory

E.K.U. Gross
Freie Universität Berlin

Time-dependent density functional theory (TDDFT) has become the method of choice to describe the dynamics of electrons in real time. Three novel developments in the field of TDDFT will be presented in this lecture: (i) The visualization and analysis of electronic motion by means of the so-called electron localization function (ELF), (ii) the description of electronic (non-equilibrium) transport through molecular junctions, and (iii) optimal control of electronic motion by suitably shaped laser pulses. The ELF provides a way to visualize localization in 2D or 3D real space [1]. It is derived from the conditional probability of finding an electron in the vicinity of a point r if one knows with certainty that there is another electron with the same spin at r. The shape of the ELF (as function of r) allows a topological classification of the different types of chemical bonds. Here we generalize the ELF to the time-dependent case [2]. Two movies of the time-dependent ELF will be presented, one that shows the formation and breaking of chemical bonds in a proton-ethylene scattering process and another one that visualizes a laser-induced π-π* transition in acetylene in a time-resolved fashion (see figure below).



To describe electronic transport through a single molecule sandwiched between semi-infinite leads, the time-dependent Kohn Sham equations are propagated in time upon ramping up a bias between the metallic leads [3]. Applying the algorithm to simple model systems, we observe: (a) After switching-on a dc bias, the current first shows some transient oscillations and then converges to the steady-state value predicted by the Landauer formula if the Hamiltonian does not support bound states. (b) If the long-time limit of the Hamiltonian supports two or more bound states, then **undamped** oscillations of the current occur whose amplitude can be much larger than the steady-state current [4]. This implies, in particular, that the usual Landauer approach is not generally applicable. (c) For a traveling electromagnetic wave, electron pumping is observed, i.e., a net current is produced by the time-dependent field without application of a static bias [5]. Recent experiments have found this phenomenon for a carbon nanotube on a piezoelectric surface when a sound wave is propagated along the surface.

Turning to quantum optimal control theory, we demonstrate how the electronic current can be controlled in a quantum ring [6]. This technique may be relevant in the context of quantum computing. Furthermore, by generalizing the standard formulation [7] of optimal-control theory to the optimization of **time-dependent** control targets [8], we show how to drag an electronic wavepacket along a **given** trajectory through the molecule by a suitably shaped laser pulse.

[1] E. Räsänen, A. Castro, E.K.U. Gross, *Phys. Rev. B* **77**, 115108 (2008).

[2] T. Burnus, M.A.L. Marques, E.K.U. Gross, *Phys. Rev. A* (Rapid Comm.) **71**, 010501 (2005).

[3] S. Kurth, G. Stefanucci, C.O. Almbladh, A. Rubio, E.K.U. Gross, *Phys. Rev. B.* **72**, 035308 (2005).

[4] E. Khosravi, S. Kurth, G. Stefanucci, E.K.U. Gross, arXiv: 0802.2516.

[5] G. Stefanucci, S. Kurth, A. Rubio, and E.K.U. Gross, *Phys. Rev. B* **77**, 075339 (2008).

[6] E. Räsänen, A. Castro, J. Werschnik, A. Rubio, E.K.U. Gross, *Phys. Rev. Lett.* **98**, 157404 (2007).

[7] W. Zhu, J. Botina, H. Rabitz, *J. Chem. Phys.* **108**, 1953 (1998).

[8] I. Serban, J. Werschnik, E.K.U. Gross, *Phys. Rev. A* **71**, 053810 (2005).

PT-2. Calculating electronic correlation energies via path counting

A. Alavi
Department of Chemistry, Lensfield Road, Cambridge CB2 1TQ, UK

In this talk I will present an overview of our efforts of the past few years in developing path-integral based methods for Fermion systems, based on the notion of path-resummations. Instead of sampling closed Fermion paths (ring-polymer analogy), we perform resummations of paths on discrete collections of Slater determinants, to obtain new objects termed ”graphs”, which can either be used directly to estimate the energy, or can be sampled stochastically. Stochastic simpling of graphs turns out not to have the same awful sign-problems that Fermions paths have. We present results for such simulations for some tricky electron correlations problems, such as the dissociation of the N2 molecule, and also for weakly bound rare-gas dimers such as Ne2, and Ar2, and for the H-bonded water dimer. For these systems we are able to match the accuracy of the CCSD method, but at a lower cost, and lower computational scaling. We also discuss a generalisation of our stochastic method to Moller-Plesset perturbation theory, leading to the evaluation of such energies with a lower scaling that full summation over all diagrams.

[1] Electron correlation from path resummations: the double-excitation star, Alex Thom, George Booth, Ali Alavi, *Physical Chemistry Chemical Physics*, in press (2008).

[2] Stochastic perturbation theory, Alex Thom and Ali Alavi , *Phys. Rev. Lett* **99**, 143001 (2007).

[3] A combinatorial approach to the electron correlation problem , Alex Thom and Ali Alavi, *J. Chem. Phys.* **123**, 204106 (2005).

PT-3. Computational Microscopy of Materials Phenomena in the Non-Scalable Regime

Uzi Landman
School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

Investigations of physical systems of small sizes and reduced dimensionalities, exhibiting discrete quantized energy level spectra and specific structures and morphologies, open avenues for systematic explorations of the physical factors and unifying principles that underlie the transition from the atomic and molecular domain to the condensed phase regime. Such behavior, where the properties do not scale with the reduced physical size, but rather where small is different in an essential way that can not be deduced through extrapolation from knowledge of bulk behavior, is emergent in nature. Often, the new and different behavior at the nanoscale can be traced to the circumstance where one (or more) of the physical dimensions of the material aggregate approaches a length-scale characteristic to a physical phenomenon (with different phenomena being characterized by different length-scales).

Gaining insights into the nature of physical and chemical systems of highly reduced sizes, and developing experimental and theoretical methodologies aimed at probing, manipulating and controlling them on the atomic and molecular level, are among the major challenges of current basic interdisciplinary research. Computationally-based theoretical modeling and simulations play an increasingly important role in modern condensed matter physics, chemistry, materials science, and biology. In particular, such studies, that may be called "computational microscopies", allow explorations of complex phenomena with refined resolution in space and time [1].

Emergent physical and chemical phenomena at the nanoscale regime and the use of atomistic simulations as tools of discovery in this area will be discussed and demonstrated through studies of:

(i) Formation mechanisms, mechanical, quantized electric conductance, and chemical properties of metal, semiconductor and superconducting nanowires and their interconnections [2].

(ii) Atomic-scale friction, control of friction through modifications of molecular architecture, and nanotribological processes in lubricated junctions [3].

(iii) Generation, stability and breakup of nanojets [4] and deposited fractal islands [5].

(iv) Nanocatalysis by small gold and palladium clusters, and guidelines for atomic-scale control of catalytic activity [6].

(v) Spontaneous symmetry breaking leading to formation of crystalline patterns (Wigner molecules) in two-dimensional quantum dots and cold atom traps, [7].

(vi) Emergence of magnetism in free and surface-supported small palladium clusters [8].

(vii) Ion-gated charge transport and post-ionization reaction in DNA [9].

Since it is likely that time will not permit coverage of all the topics listed above, a detailed reference list is provided.

[1] U. Landman, perspective article in *Proc. Nat. Acad. Sci. (USA)* **102**, 6671 (2005).

[2] U. Landman et al., *Science* **248**, 454 (1990); R. N. Barnett, U. Landman, *Nature* **387**, 788 (1997); U. Landman et al., *Phys. Rev. Lett.* **85**, 1958 (2000); H. Hakkinen, R. N. Barnett, U. Landman, *J. Phys. Chem. B* **103**, 8814 (1999); A. Marchenkov, Z. Dai, C. Zhang, R. N. Barnett, U. Landman, *Phys. Rev. Lett.* **98**, 046802 (2007); A. Marchenkov, Z. Dai, B. Donehoo, R. N. Barnett, U. Landman, *Nature Nanotech.* **2**, 481 (2007); C. Zhang, R. N. Barnett, U. Landman, *Phys. Rev. Lett.* **100**, 046801 (2008).

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[4] M. Moseler, U. Landman, *Science* **289**, 1165 (2000); W. Kang, U. Landman, *Phys. Rev. Lett.* **98**, 064504 (2007).

[5] C. Brechignac et al., *Phys. Rev. Lett.* **88**, 196103 (2002).

[6] U. Heiz, U. Landman, “Nanocatalysis” (Springer, 2006); A. Sanchez et al., *J. Phys. Chem. A* **103**, 9573 (1999); S. Abbet, U. Heiz, H. Hakkinen, U. Landman, *Phys. Rev. Lett.* **86**, 5950 (2001); M. Moseler, H. Hakkinen, U. Landman, **89**, 033401-1, (2002); H. Hakkinen et al., *Angew. Chem.* (2003); B. Yoon et al., *Science* **307**, 403 (2005); A. Bongiorno, U. Landman, *Phys. Rev. Lett.* **95**, 106102 (2005); D. Ricci, A. Bongiorno, G. Pacchioni, U. Landman, *Phys. Rev. Lett.* **97**, 36106 (2006); C. Zhang, B. Yoon, U. Landman, *J. Am. Chem. Soc.* **129**, 2229 (2007); U. Landman et al., *Topics in Catalysis* **44**, 145 (2007); B. Yoon, U. Landman, *Phys. Rev. Lett.* **100**, 056102 (2008).

[7] C. Yannouleas, U. Landman, *Reports on Progress in Physics* **70**, 2067 (2007); *Phys. Rev. Lett.* **82**, 5325 (1999); ibid. *Phys. Rev. Lett.* **85**, 1726 (2000); *Euor. Phys. J. D* **16**, 373 (2001); C. Yannouleas, U. Landman, *Proc. Nat. Acad. Sci. (USA)* **103**, 10600 (2006); C. Ellenberger et al., *Phys. Rev. Lett.* **96**, 126806 (2006).

[8] M. Moseler, H. Hakkinen, R. N. Barnett, U. Landman, *Phys. Rev. Lett.* **86**, 2545 (2001); **89**, 176103 (2002).

[9] R. N. Barnett et al., *Science* **294**, 567 (2001); R. N. Barnett et al., *J. Am. Chem. Soc.* **128**, 10798 (2006); C. L. Cleveland et al., *JACS* **129**, 8408 (2007).

PT-4. Deformation of amorphous materials at low temperature

J.-L. Barrat
Laboratoire de Physique de la Matière Condensée et Nanostructures,
Université de Lyon et CNRS

I will discuss some aspects deformation and flow in amorphous systems that have been investigated recently using computer simulations. I will start with a description of elastic and plastic [1–3] deformations at zero temperature (”athermal” systems). In this case it is possible to decompose the deformation in terms of elementary plastic events, that eventually interact to create an homogeneous flow.

I will also consider some statistical properties of homogeneous flow in glassy systems at finite temperature using the effective temperature concept [4, 5]. The existence of strain localisation will be addressed, and shown to result from the presence of a nonzero yield stress, larger than the small shear limit of homogeneous flow curves [6, 7]. This in turn implies that the flow curve is effectively nonmonotonic, and allows shear band formation in a restricted domain of shear rates. Finally, I will present some recent results concerning shear induced crystallisation. [8]

[1] ”Plastic Response of a 2D Lennard-Jones amorphous solid: Detailed analysis of the local rearrangements at very slow strain-rate” , A. Tanguy, F. Leonforte, J.-L. Barrat, *European Physical Journal E* **20**, 355 (2006).

[2] ”On the study of local stress rearrangements during quasistatic plastic shear of a model glass: do local stress components contain enough information?” M. Tsamados, A. Tanguy, JL Barrat, *Eur. Phys. Journal E,* in press.

[3] ”Molecular plasticity of polymeric glasses in the elastic regime” GJ. Papakonstantopoulos, R. Riggleman, JL Barrat, JJ. de Pablo, *Phys. Rev E,* in press.

[4] ”Shearing a Glassy Material: Numerical Tests of Nonequilibrium Mode-Coupling Approaches and Experimental Proposals”, L. Berthier, J-L. Barrat, *Phys. Rev. Lett.* **89**, 095702 (2002).

[5] ”Driven activation versus thermal activation”, P. Ilg, **J.-L.Barrat**, *Europhysics Letters* **79**, 26001 (2007).

[6] ”Shear Localization in a Model Glass” F. Varnik, L. Bocquet, J.-L. Barrat, L. Berthier, *Phys. Rev. Lett.* **90** 095702 (2003).

[7] ”A study of the static yield stress in a binary Lennard-Jones glass” F. Varnik, L. Bocquet, J.-L. Barrat *J. Chem. Phys.* **120**, 2758 (2004).

[8] ”Shear induced crystallization of an amorphous system” A. Mokshin, J-L. Barrat, *Phys Rev E* **77**, 021505 (2008).

PT-5. Colloidal Self-assembly: Predicting and designing new structures

M. Dijkstra[1], A.-P. Hynninen[1], C. G. Christova[1], M. E. Leunissen[1], R. van Roij, A. van Blaaderen[1], E. Sanz[1], C. Valeriani[1,3], D. Frenkel[3], A. Fortini[1], A. Cuetos[1], A. Patti[1], S. V. Savenko[1], L. C. Filion[1]
[1] *Soft condensed matter, Debye Institute for NanoMaterials Science, Utrecht University, The Netherlands*
[2] *Institute for theoretical Physics, Utrecht university, The Netherlands*
[3] *FOM-institute for Atomic and Molecular Physics, The Netherlands*

Colloidal suspensions are complex fluids that consist of mesoscopic particles moving around in a solvent. The addition of other components such as salt ions or added polymers enables us to tune the effective interactions between the colloids. In this talk, we show how one can exploit this picture of colloids as extremely tunable ”building blocks” to obtain new phases and new structures which may lead to ”advanced functional materials”, e.g., e-ink displays, photonic bandgap structures, and electrorheological fluids. More specifically, we show that binary hard-sphere mixtures can either give rise to a broad fluid-solid transition or can organize spontaneously into superlattice structures depending on the precise size ratio of the two species. To this end, we develop genetic algorithms to predict the possible binary crystal structures. In addition, mixtures of oppositely charged colloids display a remarkably rich variety of crystal structures as the crystal structure is not dictated by the charge neutrality condition as in the case of ionic crystals. The resulting phase diagram of oppositely charged colloids displays colloidal analogs of simple-salt structures, colloidal counterparts of the doped fullerene structures, but also novel structures with large-small stoichiometries 1:6 and 1:8 that do not have an atomic or molecular analog. In addition, we study the crystal nucleation of oppositely charged colloids. Two different crystal structures compete in the thermodynamic conditions under study. We find that the crystal phase that nucleates is metastable and, more surprisingly, its nucleation free energy barrier is not the lowest one. This implies that, during nucleation, there is insufficient time for pre-critical nuclei to relax to their lowest free-energy structure. We also study nucleation of rodlike particles and the effect of non-adsorbing polymer on the phase behaviour and nucleation process. Finally, we show that many new phases can be manipulated by external fields, e.g., an electric field stabilizes the hexagonal-close-packed, body-centered-orthorhombic, and body-centered-tetragonal phase, while triangular, square, buckling, and prism phases are found in confined hard spheres.

PT-6. Structure based Coarse Graining and Adaptive Resolution Simulations (AdResS) for Soft Matter

K. Kremer
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The relation between atomistic structure, architecture, molecular weight and material properties is a basic concern of modern soft material science. The longstanding aim by now goes far beyond standard properties of bulk materials. A typical additional focus is on surface interface aspects or the relation between structure and function in nanoscopic molecular assemblies. This all implies a thorough understanding on many length and correspondingly time scales ranging from (sub)-atomic to macroscopic. Traditionally computer simulations have been separated in two main groups, namely simplified models to deal with generic or universal aspects, i.e. critical exponents, of polymers and those employing classical force field simulations with (almost) all atomistic detail, i.e. for the diffusion of small additives in small ”sample”. More recently with the development of scale bridging or multi scale simulation techniques, the different particle based approaches have been combined into an emerging rather powerful tool. It is the purpose of this talk to give a few examples of how such an approach, which combines ab initio quantum level calculations, force field simulations as well as coarse grained molecular dynamics simulations in a systematic manner, can be used to understand specific material properties. Questions considered range from surface morphologies of polymer melts close to a metal surface experiencing specific interactions to the classical problem of entanglements.
By using a mapping scheme, which allows for scale bridging in both the coarsening as well as the detailing direction, new classes of problems can be tackled by simulations. To progress further adaptive schemes have to be developed, which allow for a free exchange of particles (atoms, molecules) between the different levels of resolution. We study model systems, which display a spatially variable resolution with a free exchange of particles between the different regimes. The new scheme can be understood within a (limited analogy) to a geometry induced phase transition, where in the transition regime degrees of freedom are switched on or off. Theoretically one can formulate this in terms of fractional degrees of freedom. This methodology has been tested for methane like tetrahedral liquids, polymers in solution and liquid water. In a next step this is also linked to a hydrodynamic continuum.

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PT-7. Single-sweep methods for free energy calculations

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Free energy (or potential of mean force) calculations are a central issue in biophysics. Molecular dynamics (MD) simulations provide a tool for performing such calculations on a computer in a way which is potentially both precise and inexpensive. Since a free energy associated with some collective variables is proportional to the logarithm of the probability density function of these variables, it can in principle be calculated by histogram methods based on the binning of an MD trajectory. This direct approach, however, turns out to be unpractical in general because the time scale required for the trajectory to explore all the relevant regions of configuration space is prohibitively long. The standard way around this difficulty is to use umbrella sampling methods such as the weighted histogram analysis method (WHAM), but this technique is restricted to calculations of free energies in low dimension, i.e. when the number of collective variables is small (typically, 1 or 2). An alternative approach, however, is to calculate the gradient of the free energy (i.e. the mean force) locally, and use these data to reconstruct the free energy globally. In this talk, I will present a new method based on this idea which can be used to map free energy landscapes in multidimensions. The method uses radial-basis functions to represent the free energy and a variational approach to reconstruct the free energy globally from the local data on the mean force. The method will be illustrated on the several examples and compared with existing techniques based on histogram methods such as WHAM or metadynamics.

PT-8. Phase behavior of fluids, fluid mixtures and polymer solutions: Can we predict it by computer simulation?

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The phase behavior of mixtures of simple fluids, polymer solutions, etc. is a difficult problem, since there are several control parameters (temperature, pressure, mole fraction(s)) and complicated phase diagrams result. Even for rather simple fluids, such as carbon dioxide or benzene, "first principle" calculations yield rather unsatisfactory effective potentials. Hence an alternative approach is discussed, where such molecules are represented as Lennard-Jones point particles, plus a quadrupole moment. It is shown that in the parameter range of interest the isotropic averaged quadrupolar interaction is a satisfactory approximation. The quadrupole moment strength is taken from experiment, and the strength and range of the Lennard-Jones potential are taken from the experimental critical point parameters. Finally it is discussed to what extend the corresponding parameters for unlike molecules in a mixture can be simply estimated from the Lorentz-Berthelot rule.

S1-T1. Activation and transport in voltage-gated potassium channels

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Voltage-gated potassium (Kv) channels are complex membrane proteins that control cellular excitability at the molecular level. These channels enable ions to flow through the plasmic cell membrane in response to variations of the local electrostatic potential. The recent high resolution x-ray structure of the mammalian potassium channels Kv1.2 [**?**] allows one to study with greater confidence processes such as activation, gating and ion conduction at the molecular level. In this communication, we present recent results from our investigations of Kv channels using atomistic and coarse grained MD simulations [2], aimed at bringing molecular level insights onto their function in realistic membrane environments.

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S1-T2. Peptide adhesion and friction: Theoretical approaches

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Single-protein behavior combines the fields of non-equilibrium thermodynamics, elasticity theory and hydrodynamics. Theoretical approaches thus rely on molecular simulations, continuum modeling and scaling approaches. This is demonstrated with a few examples:
- Spider silk consists of polypeptides with highly repetitive motives and readily adsorbs on hydrophobic and hydrophilic surfaces. Single molecule AFM studies yield adsorption energies and point to an extremely high mobility on hydrophobic surfaces. The dominant hydrophobic attraction can be quantitatively explained with classical MD simulations including explicit water. Both water structural effects and dispersion interactions contribute to this solvation attraction. [1]
- The friction coefficient of bound peptides is very low on hydrophobic substrates, which is traced back to the presence of a vacuum layer between substrate and water, which forms a lubricating cushion on which a polymer can glide. Conversely, friction forces on hydrophilic substrates are large and make determining the equilibrium binding constant in computer simulations impossible.

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S1-T3. Identifying critical residues in protein folding: Insights from ϕ-value and P_{fold} analysis

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We apply a simulational proxy of the ϕ-value analysis [1] and perform extensive mutagenesis experiments to identify the nucleating residues in the folding 'reactions' of two small lattice G$\bar{o}$ polymers with different native geometries. Our findings show that for the more complex native fold (i.e. the one that is rich in non-local, long-range bonds), mutation of the residues that form the folding nucleus lead to a considerably larger increase in the folding time than the corresponding mutations in the geometry that is predominantly local. These results are compared with data obtained from a rigorous analysis based on the folding probability, P_{fold}, reaction coordinate and on the use of graph theoretical methods (see e.g. [2]). Our study reveals a complex picture of the TS. Indeed, for both protein models, the TS is rather heterogeneous and splits-up into two structurally different populations that have strikingly different statistical weights. For the more complex topology the identified sub-populations are actually structurally disjoint, which indicates two distinct transition states associated with parallel folding pathways. We have further found that folding through the pathway that nucleates the region of the native structure that is exclusively formed by long-range bonds is one order of magnitude faster than if it follows the alternative folding route. For the less complex native geometry we found a broad transition state with microscopic heterogeneity. These findings suggest that the existence of multiple transition states may be linked to the geometric complexity of the native structure. Interestingly, for both native folds, the residues that lead to the highest increase in folding time were found in association with the sub-population that is less statistically relevant. This suggests that ϕ-value analysis can detect minor TS populations. The study of the TS structure reveals, however, that the residues identified as critical through the ϕ-value analysis are not fully native in neither of the ide ntified sub-populations. We have nevertheless found residues with a very high probability (≈ 1) of being native in the TSs of both protein models.

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S2-T1. The molecular (un)folding pathways of proteins revealed by rare event methodology

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All-atom explicit solvent molecular dynamics (MD) simulations of folding and other conformational changes in proteins remain a great challenge in computational biophysics because of the long time scales involved. These long times are due to high free energy barriers between stable states. Recently developed rare event methodology, including Replica Exchange (REMD) and Metadynamics allow the sampling of high barriers, and can obtain the thermodynamics. However, they do not preserve the dynamical pathways needed to gain insight into kinetics and mechanism of conformational change. Transition Path Sampling (TPS) is a technique designed for harvesting an ensemble of dynamical transition paths, and allows computation of the rates and extraction of the reaction coordinates.

In this presentation I will first explain the need for the various rare event methods, and discuss their applicability and limitations. I will illustrate these methods on several processes: the folding of the 20-residue Trp-cage [1], the folding of a 37-residue WW-domain and the conformational changes in the photocycle of the 125-residue bacterial sensor Photoactive Yellow protein (PYP) [2, 3]. For each of these systems we have studied the folding and unfolding pathways, and obtained mechanism, reaction coordinates, folding rates, and/or barriers heights. This work shows that by employing a toolbox of computational techniques we can overcome the timescale gap and gain more insight in protein folding.

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S2-T2. Protein Structure Determination Using NMR Chemical Shifts

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Chemical shifts - the most readily and accurately measurable NMR parameters - reflect with great specificity the conformations of native and non-native states of proteins. I will described a method of using chemical shifts as structural restraints in combination with conventional molecular mechanics force fields to determine the conformations of globular proteins representative of the major structural classes at a resolution of 2 A or better. This strategy should be widely applicable, and will enable quantitative structural analysis to be carried out to address a range of complex biological problems not accessible to current structural techniques.

S2-T3. Steric stabilization of signaling peptides

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Natively unstructured or disordered regions appear to be abundant in Eukaryotic proteins [1]. Many such regions have been found alongside small linear binding motifs [2].

We show that flanking disordered regions may prevent aggregation of such linear motifs. With a coarse grained simulation we show that small hydrophobic peptides without disordered flanks tend to aggregate, whereas peptides embedded in unstructured peptide sequence are at minimum free energy as single molecules or in small clusters. We also show that a previously reported effect of coupled folding and binding that decouples the binding specificity and binding strength [3], holds for such small binding motifs: these small binding motifs also lose configurational entropy on binding. The disordered flanking regions only have a small effect on the folding and binding of the linear motif.

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S3-T1. The influence of polyhydroxylated compounds on phospholipid bilayers

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Molecular dynamics simulations are used to investigate the interaction of the polyhydroxylated cosolutes methanol (MET), ethylene glycol (ETG), glycerol (GLY), glucose (GLU) and trehalose (TRH) with a hydrated phospholipid bilayer in the liquid-crystalline phase at 325 K.

The comparison is performed at constant effective concentration of cosolute hydroxyl groups. The results (along with available experimental data) lead to the formulation of two distinct mechanisms for the interaction of polyhydroxylated compounds with lipid bilayers.

The alcohol-like mechanism (active for MET and ETG) involves preferential affinity of the cosolute for the superficial region of the bilayer interior and is driven by the hydrophobic effect. It results in a lateral expansion of the membrane, a disorder increase within the bilayer, and a partial substitution of water by cosolute molecules at the hydrogen-bonding sites provided by the membrane (predominantly the ester groups).

The sugar-like mechanism (active for GLU and TRH) involves preferential affinity of the cosolute for the bilayer surface (formation of a coating layer) and is driven by entropic effects. It results in the absence of lateral expansion and change in disorder within the bilayer, and a partial substitution of water by cosolute molecules (predominantly at the level of the phosphate groups). It also involves the bridging of lipid molecules via hydrogen-bonded cosolute molecules, a phenomenon that may have implications in the context of membrane stabilization by sugars.

Hydrogen bonding itself is not viewed as a driving force for these two mechanisms, which only involve the (partial) substitution of water-lipid by cosolute-lipid hydrogen bonds (the sum of the two remaining essentially constant, irrespective of the nature and concentration of the cosolute).

S3-T2. Coarse-Graines Simulations of Phase Transitions and Lipid-Protein Interactions in Lipid Membranes

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We study membrane phase transitions and lipid-mediated protein interactions with Monte Carlo simulations of a simple coarse-grained model for self-assembling lipid membranes. The “lipids” are represented by short linear spring-bead chains, which are forced to self-assemble into membranes by a recently introduced, computationally cheap ”phantom” solvent, and the “proteins” by cylinders with diameters corresponding to the diameter of an alpha-helix. The model exhibits the main phases and phase transitions of lipid bilayers: the fluid phase, the gel phase, and various intermediate states. Most notably, it produces different rippled states with properties that are in good agreement with the experimentally observed ripple phases. It is then used to investigate the effective interactions between proteins in a fluid membrane. Different contributions can be identified: Direct contact, lipid layering, and hydrophobic mismatch. The interplay of these factors determines the local structure of protein-protein complexes. The results are analyzed in terms of elasticity theories for lipid-mediated interactions between membrane inclusions.

S3-T3. Modeling transport through ion channels

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Modeling of ion transport through synthetic and biological transmembrane channels has been so far a challenging problem. We introduce here a new method that allows one to study such transport under realistic biological conditions. The method consists of generating a transmembrane potential across a single lipid bilayer by imposing a net charge imbalance between the two electrolytes surrounding it. Beside allowing the firt direct estimates of the membrane capacitance from multiple MD simualtions, we use the approach to investigate the conductive properties of an ion channel formed by a peptide nanotube, embedded in a lipid bilayer. We show that the method is efficient for generating ionic currents (at moderate voltages) and provides estimates of the intrinsic conductance of the channel in agreement with experiments. Further applications to ionic transport in more complex channels such as bacterial potassium channels will be briefly discussed.

S4-T1. Multiscale Simulation and Design of Nanostructures and Biomolecules

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We describe several new developments and applications of real-space multigrid methods in massively parallel electronic structure calculations: (i) Linear-scaling methodology for non-equilibrium quantum transport, which enables calculations for several thousand atoms. As examples, we examine several potential device configurations consisting of organic molecules sandwiched between semiconducting and metallic leads, and establish that the celebrated Negative Differential Resistance (NDR) effects can be expected for a wide range of structures. We also demonstrate how the position and the strength of NDR can be tuned by molecular substitution and doping. In some cases, huge peak-to-valley ratios are obtained, which should result in excellent switching behavior. (ii) In quantum-mechanical simulations of biomolecules in solution, most of the computational effort is spent simulating the solvent molecules. We have developed a hybrid method that allows for explicit quantum-mechanical treatment of the solvent at low computational cost. In this method, Kohn-Sham (KS) DFT is used to describe the biomolecule and its first solvation shells, while the orbital-free (OF) DFT is employed for the rest of the solvent. The OF part is fully O(N) and capable of handling 10^5 solvent molecules on current supercomputers, while taking only $\sim$10% of the total time. The flow of solvent molecules across the KS/OF interface is allowed and the total energy is conserved. As the first large-scale application, the hybrid method has been used to investigate the binding of multiple copper ions to the prion protein (PrP), which is responsible for neurodegenerative diseases, such as the mad cow disease. The results resolve a contradiction found in experiments, in which a stronger binding mode is replaced by a weaker one when concentration of copper ions is increased. Our calculations on full-length PrP suggest a protective role of copper ions in prion diseases. In collaboration with M. Hodak, W. Lu, V. Meunier, F. Ribeiro, S. Wang, and X. Zheng.

S4-T2. Minimal models of self-assembly

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There are many remarkable examples of the biological self-assembly of complex objects. For example, viral capsid proteins are able to reversibly self assemble in vitro into complete viral capsids of given size, structure and symmetry. But what are the physical principles underlying this behaviour? How difficult would it be to create synthetic particles that could similarly self-assemble into monodisperse objects? In this talk I will presents results from an ongoing research programme which is seeking to address these questions, both from the perspective of simple model 'patchy' particles for which a detailed understanding of the kinetic factors affecting their self-assembly can be obtained, and from more realistic models of biological molecules, such as virus capsids and DNA.

S4-T3. Metal adsorption on nanostructured oxide ultrathin films

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The adsorption of Au and Pd atoms on two titania nanostructured phases grown on Pt(111) is investigated via a computational approach. These phases [1, 2] are constituted by TiO_x monolayers which present compact regions (zig-zig-like stripes) intercalated by point defects, i.e., holes exposing the underlying Pt support, and give rise to very regular patterns extending for large lengths. A Pd atom experiences a very flat energy landscape on the zig-zag stripes whereas it is strongly bound to the defects which act as nucleation centers, whence the interest of these substrates as nanotemplates for the growth of metal clusters.

The interaction of Au with the same substrates is peculiarly different: A charge transfer effect from the underlying Pt(111) support makes that Au gets negatively charged and strongly interacts with a Ti atom extracted from the interface in the compact regions, while it penetrates less easily into the defective holes due to its larger size. Comparison with analogous systems shows that these results are paradigmatic for the interaction of metal atoms with polar ultrathin films of oxides grown on metal supports, a novel and promising field in surface science.

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S5-T1. Recent advances in Lattice Boltzmann microfluidics

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Recent advances in Lattice Boltzmann formulations for microfluidic problems will be presented, with special emphasis on very recent applications to capillary filling problems with smooth and chemically/geometrically coated walls.

S5-T2. A Kinetic Model for Fluid-Wall Interaction

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Fluid-wall interaction plays an important role in determining the properties of micro/nanoflows [1]. In regions where the fluid is in contact with a solid boundary, temperature jumps and velocity slip produce deviations from the ordinary hydrodynamic behaviour of the fluid [2]. When dealing with dilute gases [2], the characteristic space and time scales are much larger than molecular sizes and molecular interaction times, respectively. Hence, gas-wall interaction modeling can be based on the assumption that the solid boundary is a smooth, structureless and impenetrable surface whose action on the gas distribution function can be described by a scattering kernel. The determination of the kernel structure from first principles would require solving the complex dynamics of a fluid molecule in interaction with wall molecules, therefore the scattering kernel expressions are more often based on phenomenological models [2]. The need to give physically sound bases to gas-surface interaction model and to relate model parameters to the basic physical properties of molecular interaction has trigger ed a number of studies in which molecular dynamics (MD) techniques have been used to investigate atomic or molecular scattering from solids [3–5]. However, the coupling of MD to Monte Carlo simulations of dilute gases is computationally expensive. The aim of the present work is to formulate and validate a kinetic model of a monatomic fluid interacting with a solid wall. It is assumed that interatomic forces can be derived from a potential which results from the superposition of a repulsive hard sphere contribution and a soft tail.

The adoption of simplifying assumptions about pair correlations leads to a linear Enskog-Vlasov kinetic equation which can be easily solved by the same Monte Carlo scheme used to calculate the fluid motion, thus avoiding hybrid schemes. It is shown that the model predictions are in good agreement with MD simulations [6]. Moreover, the effects of non-local re-emission on drag coefficients of nano-particles are discussed.

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S5-T3. Cylindrical nanoparticles in liquid crystals

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Systems of cylindrical nanoparticles dispersed in nematic and isotropic liquid crystals (LC) are studied using classical density functional theory. Such systems may be regarded as models for carbon nanotubes [1] or nanowires in LCs [2]. Nanoparticles in both bulk LCs and near surfaces have been studied. In the nematic phase the fluid structure around isolated cylinders are highly anisotropic, while in the isotropic phase the structure is rotationally invariant [3]. The anisotropic defect structure around a cylinder leads to interactions between cylinders that depend strongly on direction [4]. For cylinders near solid substrates, the LC-mediated force in the nematic is relatively short-ranged and repulsive, dominated by excluded volume effects and elastic distortions in the LC solvent. In the isotropic phase an attractive interaction, due to capillary condensation between the cylinder and subst rate, occurs [5]. By structuring the substrate an attractive interaction between the cylinder and substrate in the nematic phase may be induced.

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S7-T1. Lattice Boltzmann Studies of Active Nematics

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Active particles violate detailed balance conditions, even at rest, because they are comprised of dissipative elements – such as actin/motor assemblies or bacteria – that can exhibit self-propulsion. When coupled to nematic ordering, this imparts complex and interesting physics to the system, including spontaneously flowing states, which depend strongly on the type of self-propulsion (contractile versus extensile). The basic equations for active nematics have been known for some time [1, 2], with early theoretical studies focussing mainly on linear stability analyses. More recently, simulation via Lattice Boltzmann (LB) methods has allowed their strongly nonlinear physics to be addressed, showing complex flow patterns in two and three dimensions [3]. In this talk I will present recent LB results, mainly in one dimension, that illuminate the peculiar physics of active nematogenic slabs on approach to the isotropic-to-nematic spinodal. This shows a strong sensitivity both to boundary conditions and to the bulk stress/strain-rate curve [4], which shows a positive or negative ‘yield stress’ for contractile or extensile nematic phases. This results in either a viscosity divergence, predicted previously [5], or a spontaneous flow state comprising two nematic bands self-shearing in opposite directions.

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S7-T2. Formation of micelles in homopolymer-copolymer mixtures: field-theoretical calculations vs. particle-based simulations

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Using Monte Carlo (MC) simulations of the bond fluctuation model and self-consistent field (SCF) calculations, we study the formation of micelles in a mixture of B-homopolymers and asymmetric AB-diblock copolymers with composition $f_A = 1/8$. Both types of molecules are fully flexible and have identical length N.

In our particle-based simulations we work in the semi–grandcanonical ensemble, *i.e.*, we fix the monomer density and incompatibility, $\chi N \simeq 100$ (strong segregation limit), and control the composition of the mixture via the exchange chemical potential, $\delta\mu \equiv \mu_{AB} - \mu_B$ between the copolymers and homopolymers. The MC scheme comprises moves that allow B-homopolymers to mutate into AB-diblock copolymers and *vice versa*. These moves are very efficient in equilibrating the configurations. The simulations have been performed using periodic boundary conditions in all directions and also in presence of parallel walls. We accurately locate the critical micelle concentration (CMC), we study the micellar size distribution, and we characterize the shape of the micelles by the tensor of gyration and radial density profiles. An important part of our work focuses on the influence of confinement on all these quantities.

The results of the bulk simulations have been quantitatively compared with predictions of the SCF theory in the grandcanonical ensemble without adjustable parameter. The comparison between MC data and SCF predictions show that only in the limit of very high molecular weight the simulation results approach the mean field behavior. The deviations from ideality often decrease in relative importance like $1/\sqrt{N}$. The SCF calculation have also been extended to study the dependence of the aggregation number and the critical micelle concentration on the incompatibility, χN. For the incompatibility considered in the simulation, $\chi N \approx 100$, the homopolymer solvent penetrates the corona. Upon increasing χN, however, homopolymers are gradually expelled from the corona (dry brush, autophobicity) and, then, the additional free energy cost of the corona-melt interface tends to increase the micelle size. By means of SCF theory we finally investigated the structure and phase behavior of more complex systems, such as mixed micelles.

S7-T3. Molecular Simulation of the Gyroid Phase

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The gyroid is a soft solid phase found on the phase diagrams of many amphiphiles and block-copolymers, usually between the haxagonal and lamellar regions. It comprises two interpenetrating 3d networks separated by a highly curved interface - the result is a structure with 3d periodicity (i.e. a finite shear modulus) but that periodicity is on a supramolecular lengthscale, so that it does not encumber molecular mobility.
Unitil recently, simulations of the gyroid phase have been restricted to continuum descriptions. Here, though, we present ground-breaking work which, for the first time, allows free self-assembly of the gyroid arrangement from conventional MD and MC simulations [1]. From these, we can observe, from a molecular perspective, the mechanisms by which this phase forms - interestingly, the lamellar-to-gyroid transition proves closely related to pore formation in vesicle systems. We shall also discuss issues of phase characterisation and considet the propects for observing the gyroid in more complex simulation systems.

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S8-T1. Atomistic and Multiscale Modeling of the Strength and Failure of Transition Metals

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An important example of multiscale material response is the fracture of ductile solids. [1] In the process of ductile fracture, voids nucleate, grow and coalesce, and it is this linking process that creates the fracture. Ductile fracture has typically been modeled at the continuum level, in a variety of models that may or may not model voids explicitly. Here we extend our previous work [2–4] encompassing an extensive series of simulations of void growth with a study of the coalescence process at three levels of modeling: atomistic, dislocation dynamics and continuum plasticity models. [5, 6] Large-scale atomistic models provide detailed information on void interactions and the plasticity generated as voids coalesce, based solely on the constitutive properties inherent in the interatomic forces. The details of the plasticity are then used to inform dislocation dynamics and continuum plasticity models in order to develop models that scale beyond the nanoscale. We also discuss concurrent multiscale modeling of void growth using Coarse-Grained Molecular Dynamics. [7]

Acknowledgment: Parts of this work were done with J. Q. Broughton, E. Seppala, L. Dupuy and J. Belak. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

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S8-T2. Bridging atom-scale and coarse-grained models for lipid membranes and lipoproteins

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Complex biological systems are fascinating challenges for coarse graining and multiscale modeling. Besides the fact that they are characterized by large length scales, their functions and structural changes take place over long time scales. Nonetheless, their atomistic details are also important, since numerous biologically relevant processes are based on intermolecular processes taking place over atomistic or molecular scales. The challenge to account for both atomistic and larger scales is particularly evident in lipid systems, which range from individual lipids to 10-25 nm sized lipoproteins and further to micron-scale cell membranes. In these systems, the chemistry is definitely important in processes such as recognition events due to the details and stereo-chemistry of glycolipids, among other examples, while coarse grained models are called for in order to understand biological functions over large scales. Here, we discuss ways to bridge these limits through examples for a number of lipid systems, including e.g. domain formation in many-component membrane systems and the structural aspects of lipoproteins known as carriers of cholesterol and cholesterol esters.

S8-T3. Hybrid Atomistic/Coarse Grained Molecular Dynamics

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We have developed a hybrid method to model molecular systems partly in atomistic detail while treating the rest at a lower, coarse-grained, resolution [1]. For the modeling of biomembranes, polymers and proteins, coarse grained molecular dynamics is a particularly successful technique used to simulate large systems for long periods of time. Here, coarse graining basically means lumping atoms together into single interaction sites, in order to drastically reduce the number of particles and pair-interactions. The present hybrid method combines the advantages of maintaining party the atomistic resolution with that of the reduced computational cost of coarse graining in a manner similar to the well-known QM/MM method but at the next larger scale. Special advances are made to allow molecules to travel between the spatial atomistic and coarse-grained regions, changing the number of degrees of freedom on the fly, while recovering the total energy as a conserved quantity.

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S8-T4. Computing Hammet acidity of liquids from *ab initio* molecular dynamics

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The *p*H scale used to measure the acidity of protic solvents, has a limited range of application and is not always easy to define (for example in the case of solvents mixtures). Fortunately, Hammet introduced another acidity scale, H_0 empirically defined using colorimetric indicators [1]. This scale is especially well suited for super-acids, room temperature ionic liquids, mixtures of solvents and concentrated solutions in general.

We will present how to predict H_0 value from *ab initio* molecular dynamcs simulations. The method is directly derived from the experimental procedure [2]: several molecules of different pK$_a$ are simulated in the solvent, for short times (less than 2 ps). The final states (protonated/deprotonated) of the indicator molecules constitute a set of results, which is analysed through maximum likelihood principle [3] and yields an estimate of H_0 and its uncertainty. In spite of the short length of the simulations, it can be demonstrated that even a small set of simulations provides a converged value of H_0 with acceptable uncertainty (compared to experimental errors). We will present the first tests conducted on the experimentally well known water-hydrogen fluoride equimolar mixture [4], and the satisfactory result obtained at relatively low computational cost.

Several computations are currently in progress which results will be possibly presented. By these computations, we intend to address size effects and possible artifacts as well as method sensibility, and the possibility to use the method to follow acidity variations of liquids as their composition varies.

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S9-T1. Density-functional perturbation theory goes time-dependent

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The scope of time-dependent density-functional theory (TDDFT) [1] is limited to the lowest portion of the spectrum of rather small systems (a few tens of atoms at most). In the static regime, density-functional perturbation theory (DFPT) allows to calculate response functions of systems as large as currently dealt with in ground-state simulations [2]. In this talk I will present an effective way of combining DFPT with TDDFT [3, 4]. The dynamical polarizability is first expressed by an off-diagonal matrix element of the resolvent of the Kohn-Sham Liouvillian super-operator. A DFPT representation of response functions permits to avoid the calculation of unoccupied Kohn-Sham orbitals. The resolvent of the Liouvillian is finally conveniently evaluated using a newly developed non-symmetric Lanczos technique, which allows for the calculation of the entire spectrum with a single Lanczos recursion chain. Each step of the chain essentially requires twice as many operations as a single step of the iterative diagonalization of the unperturbed Kohn-Sham Hamiltonian or, for that matter, as a single time step of a Car-Parrinello molecular dynamics run. The method will be illustrated with a few case molecular applications.

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S9-T2. Chemical reaction rates from ring polymer molecular dynamics

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This talk will review the ring polymer molecular dynamics theory of chemical reaction rates [1, 2], and present some new results of the theory for a model of proton transfer between a weak acid (phenol) and a weak base (trimethylamine) in an aprotic polar solvent (methyl chloride).

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S9-T3. Path integral based approximations of symmetrized correlation functions

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This presentation describes a new strategy to approximate quantum time correlation functions. These functions play a crucial role in relating macroscopic observations accessible in experiments to the microscopic dynamics of the constituents of a physical system, but computing them accurately and with reasonable numerical cost is a task at the limit of current simulation capabilities even for comparatively small systems and for all but the simplest interactions. This remains true also in the semiclassical limit, i.e. in situations in which one could hope that corrections to the - computable - classical behaviour would be sufficient to obtain meaningful results. Here we discuss a new method that may offer an interesting alternative to the approaches commonly used in this regime. The symmetrized correlation function in complex time introduced by Schofield in 1960 [1], is expressed as a path integral in a convenient set of variables and its phase Taylor exp anded. Approximations of different order are then derived systematically by truncating the series at successive orders. Alternative, but equivalent, forms for the approximations at the various order are obtained by exploiting the freedom in choosing the integrals that are performed explicitly. In particular, the consequences of truncation at different orders are presented and examined in Hamiltonian and Lagrangian representations for the approximate path integral. In both cases, the first order approximations provide a rigorous derivation of the so called Schofield quantum correction factor. The Hamiltonian form of the second order result is suitable for an intriguing analysis of the advantages and limitations of interpreting semiclassical formulas in terms of paths that can be related to ”guiding” classical trajectories. The Lagrangian-based second order expression, lacks the immediate interpretation in terms of an extended classical phase space of its Hamiltonian equival ent, but it allows studying in more detail the convergence properties of the approximation. This expression also seems to be better suited for numerical purposes and a discussion of a possible Montecarlo algorithm to implement calculations based on it concludes the presentation.

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S10-T1. Ultrafast electronic processes at semiconductor polymer heterojunctions: a molecular-level, quantum-dynamical perspective

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Semiconducting -conjugated polymers are promising low-cost and flexible materials for electronic devices such as organic light-emitting diodes (OLEDs) and solar cells. Many of the unique properties of these materials stem from the combination of the molecular structure of their building blocks and the extended nature of the -system. Thus, excitonic states, i.e., electron-hole quasi-particle states that are delocalized over several or many monomer units, play a central role for the optoelectronic properties. In the present contribution, we focus on the elementary photophysical events at polymer heterojunctions, which provide highly efficient exciton dissociation sites at the interface between different phase-segregated polymers. A molecular-level, quantum-dynamical analysis of phonon-driven exciton dissociation at a TFB:F8BT heterojunction [1] is presented, using a linear vibronic coupling model parameterized for the three most relevant electronic states and 20-30 vibrational modes [2]. Quantum dynamical simulations were carried out using the multiconfiguration time-dependent Hartree (MCTDH) method, in conjunction with a hierarchical electron-phonon model [2]. The generation of a charge separated state on an ultrafast (femtosecond to picosecond) time scale is shown to depend crucially on the presence of intermediate bridge states, and on the dynamical interplay of high-frequency C=C stretch modes and low-frequency ring-torsional modes. The coherent, highly nonequilibrium dynamics is consistent with time-resolved spectroscopic observations.

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S10-T2. Towards first-principles electrochemistry: electron-transfer reactions and electrochemical potentials in fuel cells

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First-principles, quantum-mechanical simulations have become an extremely powerful tool to understand, predict, or even design the properties of complex materials or devices. Quantum simulations of electrochemical systems and processes provide new challenges for this subject, with relevant applications that span the fields of biochemistry, electrochemistry, and materials for energy (e.g. fuel cells and solar cells). In this talk, I will present the approaches we developed to study from first-principles 1) electron-transfer reactions, leading to the determination of the diabatic free energy surfaces for the ferrous-ferric aqua ions self-exchange reaction, and 2) fuel cell electrodes, predicting the Stark tuning shifts for chemisorbed molecules on Pt(111) as a function of the applied electrochemical potential.

S10-T3. Computation of Franck-Condon factors for intra-protein electron transfer: Benchmark calculations on cytochrome c and b_5

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Central to the theoretical description of biological electron transfer (ET) reactions is the electron transfer energy, i.e. the energy required to transfer an electron from an electron donating to an electron accepting cofactor. Computation of the ET energy to a useful degree of accuracy is not straightforward, however, and hampered by the following issues: (i) uncorrected density functional theory calculations are unreliable for computation of charge transfer energies, (ii) the ET energy is not only determined by the redox active cofactors but to a large extent by the protein and surrounding solvent [1, 2], (iii) sampling of the fluctuations of the ET energy over at least several nanoseconds is required to obtain converged averages [1]. To address (i) we exploit the fact that the ET under investigation is long range in nature. The redox active cofactors are separated by 10-25 Angstroms or more; hence the ET energy can be calculated to a good approximation from the ground state energies of donor and acceptor in oxidized and reduced states. To address (ii) and (iii) we present a combined QM/MM [3]//classical MD computational scheme that allows us to calculate the ET energy at the QM/MM level but with the statistical accuracy of classical MD. In this contribution we present results for ET between the heme cofactor of cytochrome c (b5) and a $Ru(bpy)_2(im)$ (bpy=bipyridine, im=imidazole) chromophore docked to a histidine residue at the surface of cyt c (b_5). These are two of the very few systems for which reliable experimental data are available [4] allowing us to benchmark our computational scheme. We set out with a comparison of different density functionals in describing structure and ionization potentials of the redox active cofactors, review the computational strategy and approximations involved, and finally discuss the contributions of the cofactors, single amino acid residues and solvent to the Franck-Condon factor for intra-protein ET in cyt c and b_5.

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S10-T4. Dehydrogenation mechanism in sodium alanates

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Sodium alanates, metal hydrides containing aluminum and sodium, are promising candidates for solid state storage in technological application of hydrogen as an energy carrier. They release hydrogen by means of three reactions:

$$\begin{aligned} 3\mathrm{NaAlH_4} &\Leftrightarrow \mathrm{Na_3AlH_6} + 2\mathrm{Al} + 3\mathrm{H_2} \\ 2\mathrm{Na_3AlH_6} &\Leftrightarrow 6\mathrm{NaH} + 2\mathrm{Al} + 3\mathrm{H_2} \\ 2\mathrm{NaH} &\Leftrightarrow 2\mathrm{Na} + \mathrm{H_2} \end{aligned}$$

While the first two reactions are reversible and compatible with vehicular operational conditions (about room temperature and atmospheric pressure), the third is irreversible and occurs at a too high temperature for practical applications. In spite of the technological relevance of the reaction mechanism leading to hydrogen release, a satisfactory microscopic characterization of the process is still lacking.

Recent experiments have revealed the presence of a highly mobile species during the $\mathrm{AlH_4^-}$ decomposition [1–3]. Palumbo et al [1, 2] identify this species to be hydrogen atoms diffusing locally around $\mathrm{AlH_5^{2-}}$ molecules (defective $\mathrm{AlH_6^{3-}}$ units formed during the first reaction). They have also estimate the activation (free) energy of this process to be 0.126 eV. Voss et al [3], combining quasi-elastic neutron scattering and nudged elastic band calculation on ab-initio models, confirm the existence of mobile species. However, their calculation suggests that the signal corresponds to sodium atom migration within the lattice. The same calculation rejects two possible motions involving hydrogen, the local diffusion in defective Al site invoked by Palumbo and the diffusion of an H from a $\mathrm{AlH_6^{3-}}$ unit to the defect, due to high activations energies (0.4 and 0.3 eV respectively).

In this talk we present our calculations on the first dehydrogenation reaction. We addressed the problem from two different perspectives. First, we tackled the question of the nature of the mobile species by performing accurate free energy calculations. Second, we studied the mechanism of early stage of the first dehydrogenation reaction.

In both cases, we have combined the temperature accelerated molecular dynamics [4] and the single sweep method [5] with an ab-initio description of the system as obtained by the CPMD code [6]. In particular, for the case of mobile species, we monitored an appropriately defined dipole moment of the $\mathrm{AlH_5^{2-}}$ in a sample of an $\mathrm{Na_3AlH_6}$ crystal cell containing one defect. We found that the process of local diffusion is not activated at 380 K. On the contrary, the long range diffusion of H atoms is activated and have a (free) energy barrier compatibles with experimental results.

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