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"Simulation of macromolecules
on different scales"
(Dr. Thomas Gruhn)

Abstracts for Oral Presentations

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Introduction to Monte Carlo Simulation of Polymers

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In this lecture the basic aspects of Monte Carlo simulations are introduced, choosing models of polymers as examples. First the distinction between simple sampling and the Metropolis importance sampling algorithm is discussed, and the main limitations of the latter are discussed: lack of information on the partition function; "dynamical" correlation of "observations" and the resulting interpretation in terms of master equations, which also is the basis for applications to simulate the dynamics of fluctuations, diffusion processes and relaxation processes far from equilibrium; finite size effects, and their analysis in the context of simulations of second-order and first-order phase transitions. Examples discussed will include the dynamics of polymer melts, dynamics of translocation of polymers through membranes, and unmixing of symmetrical binary polymer mixtures, as well as asymmetrical polymer solutions. If time permits, also an introduction to path integral quantum Monte Carlo will be given, mentioning the application to crystalline orthorhombic polyethylene as an example.

Path Sampling

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In this lecture, I will discuss the theory and methodology of transition path sampling. This technique, based on a statistical mechanics of trajectories, can be applied to study rare but important transitions between long-lived stable states. Since transition path sampling does not require a-priori knowledge of the reaction mechanism, it is a natural tool for studying the dynamic of complex processes including the nucleation of first order phase transitions, chemical reactions in solution, and biomolecular conformational changes. The lecture will be structured as follows:

1. Introduction
2. The transition path ensemble

3. Sampling the path ensemble
4. Reaction mechanism: analyzing transition pathways
5. Kinetics

Lattice Boltzmann Simulations of Soft Matter

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Table of Contents:
1. Motivation: Why mesoscopic methods?
   Brownian Dynamics vs. LB/DPD/MPCD (general "philosophy")
2. The importance of momentum conservation: Hydrodynamic interactions,
   long-time tails
3. Lattice Boltzmann: Deterministic version
4. Chapman-Enskog expansion
5. Thermal noise in Lattice Boltzmann simulations
6. Coupling of Brownian particles to LB hydrodynamics
7. Zimm model
8. Application: Hydrodynamic screening in polymer solutions

Classical/Quantum Mechanical Hybrid Methods

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The lecture will start with a summary of the advantages and disadvantages of quantum mechanical and classical, force-field-based methods. Then, the basic principles to combine these two approaches leading to mixed quantum mechanical / molecular mechanical (QM/MM) techniques will be introduced. These will then be applied in their simplest form using the straight-forward implementation of a multi-layer model like the

integrated molecular orbital molecular mechanics (IMOMM) and the *our own N-layered integrated molecular orbital and molecular mechanics* (ONIOM) method.

In the main part of the talk the general form of the QM/MM equation, in which the Hamiltonian is divided into an energy term for the QM and the MM region as well as a QM/MM term describing the interaction between the two regions, is presented. Different theories for the QM part including *semiempirical methods*, *Hartree-Fock* and *post-Hartree-Fock* theory, as well as *density functional theory* will be introduced. Special attention will be paid to the description of transition and excited states. Because molecular mechanics is largely covered by other lectures of the summer school, these methods will only be mentioned briefly. The most complicated part of a QM/MM calculation is the description of the interactions between the QM and the MM part, which should be as accurate as possible. If the border between the two parts only separates complete molecules, as this is the case for the description of chemical reaction in solution, only non-bonding interactions have to be considered. This can be done using different approaches starting from a basic *mechanical* over an *electrostatic* to a *fully polarized embedding*. If the boundary cuts through a molecule, which will be almost always the case in biochemical applications, the broken bonds must be filled especially for the QM calculations. Otherwise these unfilled valences would lead to a large disturbance in the electronic system. Possibilities to circumvent this problem are *capping atoms*, specially parameterized *pseudo-atoms*, *frozen localized orbitals*, or *generalized hybrid orbitals*. In this respect, system specific and general parameterizations will be discussed. Finally, a *Car-Parrinello* QM/MM implementations will be presented. All methodical descriptions will be accompanied by a number of recent, demonstrative applications taken from the literature. This will include enzyme kinetics and proton transfer events in exited states.

Models and Mesoscale Simulations of Membrane Hydrodynamics

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The flow behavior of cells and vesicles 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 the red blood cells. Furthermore, microfluidic devices have been developed recently, which allow the manipulation of small amounts of suspensions of particles or cells. While the membrane of vesicles just consist of a fluid lipid bilayer, red

blood cells have a composite membrane which has in addition an anchored polymer network. This implies that the elastic properties of vesicles and red blood cells are very different. Various models have been developed to describe the properties of such membranes [1,2]. Due to the large length- and time-scale gap between the atomic and the mesoscopic domain in soft matter systems, several mesoscale simulation techniques have been developed in recent years to study their hydrodynamic behavior. We have investigated one of these techniques, multi-particle-collision dynamics [3], in some detail. In particular, it has been shown that the method properly describes hydrodynamic interactions at low Reynolds and high Schmidt numbers, if the parameters are chosen appropriately [4]. This method has then be applied to study the dynamical bevavior of fluid vesicles and model red blood cells both in shear and capillary flows [5-7]. Several types of dynamical behaviors as well as shape transformations occur as a function of shear rate (or flow velocity), membrane viscosity and internal viscosity, which will be discussed in some detail.

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[2] H. Noguchi and G. Gompper, Phys. Rev. E 73, 021903 (2006).
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Lattice simulations of polymer systems

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In this lecture I will first discuss the foundations of the use of lattice models for the simulation of polymer materials and then present three advanced Monte Carlo methods for the simulation of lattice polymer models and discuss some advances in our fundamental understanding of polymer physics that were obtained with these techniques. The use of lattice models for the simulation of polymers rests on the existence of universality in the properties of polymers. I will briefly discuss their occurence in thermodynamics, structure and dynamics to complement the presentation in Prof. Binders

earlier lecture. Then the lecture will move to the discussion of the Wang-Landau Monte Carlo scheme and its application to the phase behavior of a single homopolymer chain. Next we will discuss the use of topology altering Monte Carlo moves and new results on the (non-)ideality of polymer chains in the melt obtained with this simulation technique. Finally we will look at a chain growth algorithm, the Pruned Enriched Rosenbluth Method (PERM), and discuss its application to the thermodynamics and structure of chains of complex architecture.

Car-Parrinello Molecular Dynamics Simulations of Supramolecular Systems

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The determination of intra- and intermolecular conformations of supramolecular assemblies has always been and still is a challenge for modern chemistry. In this lecture, the potential of first-principles calculations will be illustrated for the determination of microscopic structure in a variety of extended systems, ranging from molecular crystals over covalently and hydrogen-bonded nanostructures to liquids and solvated molecules.

A special focus will be put on the combination with the calculation of spectroscopic parameters, which are highly sensitive to the effect of weak interactions, such as hydrogen bonding and the proximity of aromatic moieties. In particular, delocalized electronic states give rise to unique fingerprints in terms of the reaction of the orbitals to external fields. The calculation of the spectroscopic signatures of such packing effects are often more accurate than the direct determination of the corresponding structural features via ab-initio calculations.

In disordered systems like liquids, the experimentally observable properties are computed as ensemble averages over trajectories obtained from sampling Car-Parrinello molecular dynamics simulations. This technique further allows for the direct computational evaluation of the temperature dependence of experimentally accessible spectroscopic properties.

Towards a computational cell: Mesoscopic simulations of membranes, vesicles, and nanoparticles

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Cells maintain strict control over the integrity of their plasma membrane so as to ensure a stable internal environment for their many functions. But material has to be brought in and waste removed in order for the cell to live and grow. The processes of membrane fusion, vesicle budding, endo- and exocytosis, among others, all transport material between the cell's exterior and interior or between various internal compartments.

Although, membrane fusion is controlled by proteins in vivo, simplified model systems of lipid vesicles can also be made to fuse in vitro, and computer simulations have been used recently to explore the various molecular rearrangements that take place during fusion.

An important clinical application of artificial fusion is the controlled delivery of a drug into a cell's cytoplasm. Designing so-called drug delivery vehicles so as to optimize their entry into a cell, and still maintain their stability on the journey to the cell through the circulatory system, is a challenge. The vehicle must remain intact long enough to reach its target, but still be readily degradable on arrival so as to release its drug payload. Various types of vehicle are being investigated, ranging from lipid vesicles and polymer vesicles to layered shells or nanoparticles.

In this lecture, we describe the particle-based mesoscopic simulation technique called Dissipative Particle Dynamics (DPD), and show how it allows us to model fluid lipid bilayer membranes and quasi-rigid nanoparticles that can be made to pass through the membrane in a process that mimics the invagination of the plasma membrane during endocytosis. Although these models are highly simplified, they demonstrate that coarse-grained simulation techniques, such as DPD, can capture the material properties of complex fluids and nanoparticles on the length and time scales needed to explore the behaviour of drug delivery vehicles and, potentially, endocytosis.

Large molecules near metal surfaces: Density-Functional-Based Bridging-Scale Approach

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Topics of the lecture:
(1) Why this kind of systems are truly multiscale ones
(2) Simulation techniques that can be used at each scale (brief introduction)
(2) Their technical (and computational) advantages and disadvantages
(3) How to combine them in a hierarchical consistent way:
    The DFT-based Building Blocks iterative method
(4) Examples of Applications:
(4a) Material science: Polycarbonates on nickel
(4b) Biophysical systems: Polypeptide out of solution on Platinum
(5) The sampling problem and the development of an adaptive technique
(6) Brief introduction to the Adaptive Resolution Scheme AdResS.
(7) Perspectives

Molecular Simulation: From Atomistic to Coarse-Grained Models

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In my presentation I will discuss detailed-atomistic and coarse-grained (CG) force fields for polymer simulations. I will start introducing atomistic force fields for simulations of liquids, solutions and surface interactions. Input from quantum-chemical calculations and experiments will be discussed. In the second part, I discuss methods for polymer coarse-graining; bonded and nonbonded CG interactions will be discussed as well as the dynamic speed-up of the resulting CG polymers force fields. Inverse mapping, or fine-graining, will be discussed as an illustration of how scale-bridging simulations offer challenging opportunities for studying complex, all-atom polymer systems. Depending on the remaining time, I will discuss some of the following applications: self-assembly of coarse-grained dipeptides in water, diffusion of monomer in polystyrene, chemical potentials of phenol in polycarbonate, and oligopeptide interactions with a platinum surface.

Material Properties from Atomistic Simulations

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Outline of the talk:

0) Brief introduction to the simulation of soft matter.
(polymers, liquid crystals, colloids and membranes) Time and length scale considerations for soft matter simulation.

1) Introduction to force fields and atomistic modelling.
Potentials for atomistic simulation.
How force fields are generated for organic compounds.
Force fields from ab initio calculations.
Introduction to molecular dynamics, including equations of motion and how they are solved.
An example finite difference algorithm.
Ensemble considerations.

2) Case study 1 - atomistic simulation of a chromonic liquid crystal.
Including: time correlation functions with examples and analysis of molecular structure.
Link with the quantum scale (atomistic configurations used in quantum calculations).
Methods for obtaining the free energy (application to a chromonic liquid crystal stack).

3) Case study 2 - atomistic simulations of an amphiphilic polymer.
Analysis of molecular structure and link with neutron reflectivity measurements.

4) Case study 3 - atomistic simulations of thermotropic LCs (with an example of a biaxial liquid crystal) Introduction to g1(r), g2(r), radial distribution functions, order parameters and orientational correlation functions.
Calculation of Bulk Properties of Thermotropic LCs .

5) Summary
Including a brief mention of the limits of atomistic simulation in terms of time and length scales; and a link to later talks.

Mesoscale Polymer Simulations

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Hydrodynamic interactions determine the dynamics of polymers and colloids in solution. In order to account for these interactions and to bridge the length- and time-scale gap between the solute and solute degrees of freedom, mesoscale simulation methods are required. As an example for such a method, the multiparticle-collision dynamics (MPC) algorithm will be outlined.

The following points will be stressed:
- Hydrodynamic interactions: Oseen tensor
- MPC method: basic idea, derived quantities, e.g., transport coefficients, relation to Oseen tensor
- Implementation of solute-solvent interaction within MPC
- Combing molecular dynamics simulations with MPC
- Applications of MPC to colloid and polymer solutions at equilibrium and in external fields, e.g., shear flow, microchannel flow, electrophoresis