

CPP 38: Computational Physics of Soft Matter I

Time: Wednesday 9:30–13:00

Location: C 264

Invited Talk

CPP 38.1 Wed 9:30 C 264

Challenges for the development of coarse-grained simulation models for complex soft matter systems — ●CHRISTINE PETER — University of Konstanz, Germany

Inherent to the concept of coarse graining is a loss of transferability, i.e. a decreasing ability to correctly describe a system at several thermodynamic state points. Intimately linked to this is a loss of the ability to correctly represent all structural, thermodynamic and dynamic properties of the system. Examples for these limitations are easily found in all coarse-grained (CG) simulations of multicomponent or multiphase soft matter systems. Here, one needs to solve the question how to represent phase transitions, phase coexistence, conformational transitions that are coupled to environmental changes, surface effects, etc. This is not only connected to finding an appropriate method of generating CG potentials but also to understanding one's choice of reference state point. On top of these thermodynamic challenges, one needs to be aware of the problem of dynamics in CG models: coarse graining leads to accelerated dynamics due to smoother (free) energy landscapes compared to higher-resolution descriptions. Approaches to rigorously map dynamics of models on different scales are limited to simple model systems, while in soft matter systems different dynamic processes may experience different speedups – a challenge for a correct representation of pathways and intermediates. I will use a liquid crystalline as well as biomolecular systems as examples to illustrate the above aspects of CG simulation models.

CPP 38.2 Wed 10:00 C 264

Thermodynamic and microscopic aspects of cosolvent-specific effects in coil-to-globule transition — ●JAN HEYDA¹ and JOACHIM DZUBIELLA^{2,3} — ¹Department of Physical Chemistry, Institute of Chemical Technology, Prague, Czech Republic — ²Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Germany — ³Department of Physics, Humboldt-University Berlin, Germany

An implicit-solvent, explicit-cosolvent Langevin dynamics of generic homopolymer provides three distinct regimes of cosolvent effects on coil-to-globule transition; namely cosolvent exclusion, weak binding, and strong binding, i.e., bridging (10.1021/ma302320y). We have introduced thermodynamic model interpreting observed regimes of cosolvent effects on the cloud-point temperatures of thermoresponsive polymers (10.1021/jp5041635). The microscopic details (excess adsorptions) from solution theory are approachable by simulation methods.

Original study was thus extended for an effect of cosolvent concentration. Results are in accord with our thermodynamic model and provide a consistent framework for cosolvent effects on cloud-point temperature. Among others, transition entropy was found to be independent of, or weakly, and strongly decreasing with cosolvent concentration in three regimes. All, in accord with recent calorimetry data.

Interpretation of protein denaturation/stability data is a next application of our model, which moreover accounts for and interpret reentrant transition (coil-globule-coil), grabbing recently experimental and theoretical attention (dx.doi.org/10.1038/ncomms5882).

CPP 38.3 Wed 10:15 C 264

Relative resolution: A hybrid strategy for molecular modeling — ●AVIEL CHAIMOVICH¹, KURT KREMER¹, and CHRISTINE PETER² — ¹Max-Planck-Institut für Polymerforschung, Mainz — ²University of Konstanz, Konstanz

Over the past decade, hybrid strategies, which switch from a full-atomistic (FA) to a coarse-grained (CG) description in terms of a spatial coordinate, have become numerous [1-4]. Concurrently, parametrization procedures, which aim at generating an optimal CG model given a reference FA model, have also become common [5]. In this work, we develop a hybrid strategy which naturally attains a very efficient parametrization scheme. Our approach appears to be especially powerful for modeling multi-component mixtures.

[1] M. Praprotnik, L. Delle Site, and K. Kremer. The Journal of Chemical Physics, 123(22):224106, 2005.

[2] C. F. Abrams. The Journal of Chemical Physics, 123(23):234101, 2005.

[3] B. Ensing et al. Journal of Chemical Theory and Computation, 3(3):1100-1105, 2007.

[4] R. Potestio et al. Physical Review Letters, 110(10):108301, 2013.

[5] W. G. Noid. The Journal of Chemical Physics, 139(9):090901, 2013.

CPP 38.4 Wed 10:30 C 264

The role of stiffness in polymer aggregation: Leading from amorphous aggregates to polymer bundles — ●JOHANNES ZIERENBERG and WOLFHARD JANKE — Institut für Theoretische Physik, Universität Leipzig, Germany

We use parallel multicanonical simulations of a few homopolymers in order to map out generic temperature-stiffness structural phase diagrams, from flexible to stiff polymers. The systematic overview highlights the key role of stiffness on structural phases in polymer aggregation for an entire class of semiflexible polymers covering both the limit of flexible theta polymers and the worm-like chain limit. The structural motifs range from amorphous aggregates to twisted polymer bundles, for rather flexible and rather stiff polymers respectively. For the first-order aggregation transition of several polymers, we provide strong evidence that the free-energy barrier increases with stiffness. Thus, this general study of an entire class of semiflexible polymers supports recent claims that the free-energy barrier for the transition into bundles is larger than for the transition into amorphous aggregates.

CPP 38.5 Wed 10:45 C 264

Aggregation of flexible polymers under spherical constraints — JOHANNES ZIERENBERG, ●MARCO MUELLER, PHILIPP SCHIERZ, MARTIN MARENZ, and WOLFHARD JANKE — Institut für Theoretische Physik, Universität Leipzig, Germany

Applying parallel multicanonical simulations, we study the aggregation transition of finite flexible polymers in dependence on the density, where we keep the polymer length fixed as a chemical property. A spherical confinement is imposed to control the translational entropy. We show that the competition between single-polymer collapse and many-polymer aggregation yields a lower temperature bound for the isolated chain approximation. For dilute polymers, we present entropic and energetic arguments that allow to relate the inverse aggregation to the density of the monodisperse systems.

15 min. break.

CPP 38.6 Wed 11:15 C 264

Conformations of a Long Polymer in a Melt of Shorter Chains: Generalizations of the Flory Theorem — ●MICHAEL LANG¹, MICHAEL RUBINSTEIN², and JENS-UWE SOMMER^{1,3} — ¹Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany. — ²Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, United States. — ³Institute of Theoretical Physics, Technische Universität Dresden, Zellescher Weg 17, 01062 Dresden, Germany.

Large scale simulations of the swelling of a long N -mer in a melt of chemically identical P -mers are used to investigate a discrepancy between theory and experiments. Classical theory predicts an increase of probe chain size $R \sim P^{-0.18}$ with decreasing degree of polymerization P of melt chains in the range of $1 < P < N^{1/2}$. But both experiment and simulation data are more consistent with an apparently slower swelling $R \sim P^{-0.1}$ over a wider range of melt degrees of polymerization. This anomaly is explained by taking into account the recently discovered long range bond correlations in polymer melts and corrections to excluded volume. We generalize the Flory theorem and demonstrate that it is in excellent agreement with experiments and simulations.

CPP 38.7 Wed 11:30 C 264

Lattice Monte Carlo simulations of polymer melts — ●HSIAO-PING HSU — Max-Planck-Institut für Polymerforschung, Mainz, Germany

We use Monte Carlo simulations to study polymer melts consisting of fully flexible and moderately stiff chains in the bond fluctuation model at a volume fraction 0.5. In order to reduce the local density fluctuations, we test a pre-packing process for the preparation of the initial configurations of the polymer melts, before the excluded volume interaction is switched on completely. This process leads to a significantly

faster decrease of the number of overlapping monomers on the lattice. It is useful for studying the statistical properties of the model with a marginally incomplete elimination of excluded volume violations. We find that the internal mean square end-to-end distance for moderately stiff chains in a melt can be very well described by a freely rotating chain model with a precise estimate of the bond-bond orientational correlation between two successive bond vectors in equilibrium. The plot of the probability distributions of the reduced end-to-end distance of chains of different stiffness also shows that the data collapse is excellent and described very well by the Gaussian distribution for ideal chains. However, while our results confirm the systematic deviations between Gaussian statistics for the chain structure factor for fully flexible chains in a melt, we show that for the available chain length these deviations are no longer visible, when the chain stiffness is included. The mean square bond length and the compressibility estimated from collective structure factors

Invited Talk CPP 38.8 Wed 11:45 C 264

Answering old questions with new simulation methods: what is the behavior of fluctuation spectra and Frank constants in polymer nematics? — ●KOSTAS DAOULAS and PATRICK GEMÜNDEN — Max-Planck-Institut für Polymerforschung, Mainz, Germany

Long wavelength behavior of dense polymer nematics has attracted considerable attention from the physics community due to intriguing features. In contrast to liquid crystals (LC) with small molecules, linking mesogenes into polymer chains leads to long-range coupling of density and director fluctuations. Thus related correlation functions exhibit unusual behavior, the "bowtie shape" of the density structure factor being a characteristic example. Several analytical theories have been developed, describing fluctuation spectra and related elastic constants (e.g. Frank constants). Interestingly, some of the theoretical results are very controversial. The growth of the splay constant with chain length is a well-known example, where linear (Meyer, 1982) and quadratic (de Gennes, 1982) dependencies were predicted.

In this study we validate early analytical theories employing efficient Monte Carlo simulations of polymer nematics described by a worm-like chain model combined with soft anisotropic non-bonded interactions. We demonstrate that the analytical theories indeed can capture several features of the fluctuation spectra calculated from simulation data. Based on these spectra, elastic constants are extracted and compared with theoretical predictions. Our results are found to support strongly the theories proposing a linear dependence of splay constant on chain length.

CPP 38.9 Wed 12:15 C 264

Molecular Dynamics Simulations of Hyperbranched PAMAM Vicsek Fractals — ●FLORIAN FÜRSTENBERG¹, ANDREY A. GURTOVENKO², MAXIM DOLGUSHEV¹, and ALEXANDER BLUMEN¹ — ¹Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg, Deutschland — ²Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi pr. V.O. 31, St. Petersburg, 199004 Russia

In the last few years hyperbranched macromolecular structures have become an important field of investigation. Within this broad class, highly symmetrical polymers (such as dendrimers) are of special theoretical interest. While dendrimers were extensively synthesized, Vicsek fractals (VF) constitute another interesting class of symmetrical, deterministic structures. Here we introduce the new class of polyamidoamine Vicsek fractals (PVF). Although a VF architecture is not being synthesized so far, we study PVF *in silico* and employ extensive molecular dynamics simulations along with the coarse-grained MARTINI force-field^[1] to unravel their structural and dynamic character-

istics in dilute solution. Following the method developed for PAMAM dendrimers (PD) in Ref. [2], allows us to discuss the differences in the investigated quantities for PD and PVF brought about by their different molecular architectures^[3].

[1] S.J. Marrink et al., J. Phys. Chem. B 27, 7812 (2007).

[2] H. Lee and R.G. Larson, Macromolecules 44, 2291 (2011).

[3] F. Fürstenberg et al., Macromol. Theory Simul. (2014). DOI: 10.1002/mats.201400063

CPP 38.10 Wed 12:30 C 264

Collective Motion of Spherical Microswimmers in a Quasi-2D Geometry — ●MAURICE MAURER, ANDREAS ZÖTTL, and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, D-10623 Berlin

The collective motion of microorganisms and artificial microswimmers exhibits interesting dynamic structure formation on length scales much larger than the size of an individual particle.

Experiments with self-propelled colloids in a quasi-2D geometry show dynamic clustering behavior and phase separation due to hydrodynamic interactions. Motivated by these experiments, we numerically investigate the collective behavior of spherical model swimmers [1]. Using domain decomposition and the message passing interface (MPI), we developed a highly scalable parallel version of multi-particle collision dynamics - a particle-based solver of the Navier-Stokes equations.

Here we study squirmers, which mimic the propulsion mechanism of active emulsion droplets and ciliated microorganisms like volvox algae by a surface velocity field. Furthermore, we simulate active Janus particles, the surfaces of which are only partly active. For low densities the colloids show gas-like behavior while at high densities crystalline structures emerge. Only for neutral squirmers and Janus particles almost fully covered by the active region, we observe that structural order increases steeply at a critical density, indicating a non-equilibrium phase transition. Finally, we also show how system size and reducing the colloidal degrees of freedom influence our findings.

[1] A. Zöttl and H. Stark, Phys. Rev. Lett. 112, 118101 (2014).

CPP 38.11 Wed 12:45 C 264

Interactions at the solid-liquid interface from a molecular simulation perspective — ●PETER SPIJKER¹, BERNHARD REISCHL², and ADAM FOSTER¹ — ¹COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland — ²Nanochemistry Research Institute, Curtin University, Perth, Australia

Solid-liquid interfaces are ubiquitous and have an important, if not fundamental, role in many phenomena from different fields. But despite the importance of these interfaces, deep understanding of the physical properties of them remains scarce. Atomic force microscopy (AFM) has the advantage of probing the solid-liquid system locally and it allows sub-nanometer studying of the interface. Combined with large-scale molecular dynamics (MD) simulations we are able to start to elucidate the physical origins of the solid-liquid interfaces. Over the last few years considerable experimental and theoretical progress has been made in understanding the water hydration structure on different atomically flat surfaces. In the current work we show how MD simulations and theoretical analysis can be used to understand much more complex hydration structures on non-trivial solid-liquid interfaces (molecular crystals, clay surfaces, etc.) and to allow for as direct comparison as possible between theory and experiment. In the case of the calcite-water interface we modeled the AFM tip and are capable to extract force curves similar to experimental data. Our joined theoretical and experimental approach demonstrates our ability understanding details of these heterogeneous molecular solid-liquid interfaces.