CPP 40: Modeling and Simulation of Soft Matter I (joint session CPP/DY)

Time: Wednesday 15:00–17:00   Location: H18

CPP 40.1 Wed 15:00 H18

Thermodyanmics of Supramolecular Polymers with Hydrogen Bonding Ends — •Eunsang Lee and Wolfgang Paul — Institut für Physik, Marin-Luther-Universität Halle-Wittenberg, 06108 Halle, Germany

Rheological properties of supramolecular polymers (SMPs) depend on their equilibrium structure including the size, the number, and the topology of aggregates. In this work we investigate the thermodynamics of SMPs with H-bonding ends in a wide range of densities. Replica exchange stochastic approximation Monte Carlo simulations with coarse-grained models for polyethylene and polybuthylene glycols are used. Our heterocomplementary SMP system includes the same concentration of two different molecules, each of which is functionalized by different H-bonding stickers at both ends. Due to the chemical structure of sticker association, the functionality of the sticker varies depending on temperature, which is described by our H-bond potential and optimized parameters. Our simulation shows that SMPs have three transition lines with increasing temperature, a micelle (or gel)-ring transition, a ring-linear transition, and a linear-free chain transition. Because of the temperature-dependent functionality of the sticker, we can see the micelle (or gel)-ring transition at very low temperature which has not been observed in other associating polymers with fixed functionality. Below this transition line, the polymers in dilute concentration form flower-like micelles but polymers in semi-dilute concentration form a gel.

CPP 40.2 Wed 15:15 H18

Simulation of a large polymer with untruncated interaction near the collapse — •Stefan Schnabel and Wolfhard Janke — Universität, Leipzig

Off-lattice polymer models usually incorporate monomer-monomer interactions that act – at least in principle – at any distance. In consequence, calculating the energy and in particular the change in energy during a Monte Carlo move is typically an operation of computational complexity $\mathcal{O}(N^2)$, where N is the number of monomers. Since this complexity is inherited by the individual Monte Carlo move, only small polymers can be simulated without truncating the interaction potentials. We show how this can be avoided at temperatures near or above the collapse transition by using a Metropolis algorithm that tolerates inaccurate estimates of ΔE and present results for a polymer with Lennard-Jones interactions and $N \leq 65536$.

CPP 40.3 Wed 15:30 H18

Is there a universal equation of state for flexible polymers beyond the semi-dilute regime? — •Jaroslaw Paturej[1,2], Jens-Uwe Sommer[1], and Torsten Kreer[1] — [1]Leibniz Institute of Polymer Research, Dresden, Germany — [2]University of Szczecin, Szczecin, Poland

We reconsider the isothermal equation of state (EoS) for linear homopolymers in good solvents, $p = p(c,T)$, which relates the osmotic pressure, p, of polymers with the bulk concentration, c, and the temperature, T. The classical scaling theory predicts the EoS in dilute and semi-dilute regimes. We suggest a generalized EoS which extends the universal behavior of polymer solutions up to the highly concentrated state and confirmed it by molecular dynamics simulations and using available experimental data. Our conjecture implies that properties of polymer chains dominate the EoS in the presence of many-body interactions. Our theoretical approach is based on a viral expansion in terms of concentration blobs leading to a superposition of two power laws in the regime of concentrated solutions.

CPP 40.4 Wed 15:45 H18

Comparison of strain-induced transitions from liquid to solid of poly(ethylene oxide) and polyamide chains in water — •Sergii Donets[1], Olga Guskova[1], Gary Dunderdale[3], Oleksandr Mykhaylyk[3], and Jens-Uwe Sommer[1,2] — [1]Institute Theory of Polymers, Leibniz-Institute of Polymer Research, D-01069 Dresden, Germany — [2]Technische Universität Dresden, Institute for Theoretical Physics, D-01069 Dresden, Germany — [3]Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, UK

Aqueous solutions of poly(ethylene oxide) (PEO) and polyamide oligomers are capable of undergoing a phase transition as a result of loss of the hydrated structure. Our simulations using an atomistic model clearly indicate that an elongating force dipole acting on both chain ends of oligomer chains initiates interchain aggregation with the formation of highly oriented fibrillar nanostructures [1]. The strain-induced demixing transition from liquid to solid occurs primarily due to the favorable hydrophobic interactions in case of PEO chains and, in addition, due to the intermolecular hydrogen boding in case of polyamide chains. A tensile stress introduced into the aqueous solution changes the solvent quality from good to poor as a function of conformational state of the chains and, if there are other oligomer chains present in the simulation box, leads to a phase separation from water. The strain-induced demixing of the extended chains provides the possibility to obtain polymer fibers with low energy costs.
[1] J. Phys. Chem. B, 2018, 122 (1), 392-397

CPP 40.5 Wed 16:00 H18

Soft deformable colloids: self-assembly and structure through computer simulations — •Mihir Khadilkar and Arash Nikoubashman — Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany

Colloids represent a rich class of soft materials that are important not only as model systems to study physical processes at nanoscale, but also as versatile building blocks towards a variety of technological applications. While hard-core models of colloids (with solely excluded volume interaction) have had great success in studying ordering, structure and dynamics in the past, most experimental systems exhibit varying degrees of softness that could potentially drastically alter their static and dynamic properties. Using molecular dynamics (MD) simulations of mesh models, we study the self-assembly of soft spherical and spheroidal colloids as a function of their elasticity and packing density. We quantify their arrangement and deformation using various order parameters. Further, we asses the dependence of eventual thermodynamic properties on the asphericity and softness of the colloids. For instance, we find that soft prolate ellipsoidal colloids (with aspect ratio 2) undergo a convex-to-concave transition at high pressures. The crystal structure also gets distorted, accompanied by an asymmetric deformation of principal directors. Addressing the structure-property relationship between softness arising from microstructure and the macroscopic properties could provide new routes towards designing and fabricating novel materials with tailored structural properties.

CPP 40.6 Wed 16:15 H18

Self-assembly of triblock terpolymers system using dissipative particle dynamic simulations — •Deepika Deepika and Arash Nikoubashman — Institute of Physics, Johannes Gutenberg University, Staudingerweg 7, 55128 Mainz, Germany

Self-assembly of triblock polymers into ordered structures has emerged as a promising technique for generating morphologies with nanometer range periodicity. The self-assembled structures dictated by the volume fraction of each block and interactions between them. In this work we are interested in the self-assembly behavior of polystyrene-polybutadiene-polymethyl-methacrylate (SBM) triblock copolymers in melt and in solution. The ternary phase diagram of SBM melt includes complex morphologies like spheres in lamellae cylinders in lamellae, cylinders in cylinder and many other. Equally intriguing is the solution phase behavior of SBM; recent experiments conducted by Groeschel et al. suggested ellipsoid aggregates of SBM in which layers of SBM are stacked in an ABCBA pattern. We conducted extensive DPD simulations to elucidate the effect of the process parameters, such as the volume fraction of each block and the Flory-Huggins interaction parameters, on the self-assembled structures. Our simulations give microscopic insights into the self-assembly behavior and provide useful design guidelines for fabricating structured nanoparticles in experiments.

CPP 40.7 Wed 16:30 H18

Construction of core-double-shell nanostructures via adsorption of mixed star polymers — •Qiyun Tang and Marcus Mueller — Institut für Theoretische Physik, Universität Göttingen

The adsorption of two kinds of star polymers with strongly adsorbing arm ends but distinct arm lengths onto one big gold nanoparticle re-

sults in the formation of a core-double-shell nanostructure. This radial-organized nanostructure finds potential applications in plasmonic and biomedical disciplines. Here we use theory and simulation to systematically study the formation process of this advanced nanostructure. Theoretical calculations predict that this structure does not reach equilibrium, but strongly depends on the formation kinetics. Simulation results show that the adsorption of short star polymers are chiefly dictated by diffusion whereas the adsorption of the end of a long star polymer implicates a high free-energy barrier generated by other chains, resulting in a protracted adsorption. The fabrication of the core-double-shell nanostructure is a combination of the diffusion-limited and the reaction-limited processes of short and long polymers, respectively, which is confirmed by experimental findings.

CPP 40.8   Wed 16:45   H18

Mixtures of Dendrimers and Linear Polymers — •Martin Wengenmayr[1,2], Ron Dockhorn[1], and Jens-Uwe Sommer[1,2] — [1]Leibniz Institute of Polymer Research, Dresden, Germany — [2]TU Dresden, Germany

One of the largely unsolved problems in polymer science is the effect of polymer architecture on the thermodynamics and functional properties of a polymer system. In particular, there is no commonly accepted explanation for the conformation properties of branched polymers immersed in a melt of chemically identical linear polymers. Based on Monte Carlo simulations of dendrimers with various generations and spacer lengths immersed in a solution of polymer chains of different degree of polymerization and concentrations we show that flexible dendrimers do not collapse into a compact globule as the concentration of linear chains is increased. Instead, we observe a crowded state distinct from athermal or theta solvent state. Beside the nontrivial conformational changes of the dendrimer the mixing of polymers of the same chemical composition but different branching induces secondary interactions between the species. Our work addresses the question of the strength of the secondary interactions in terms of intermolecular interactions and depletion attraction.