

CPP 2: Modeling and Simulation of Soft Matter I

Time: Monday 9:30–13:00

Location: H 0107

Invited Talk

CPP 2.1 Mon 9:30 H 0107

Lessons learned from coarse-grained molecular simulations of disordered proteins — ●ARASH NIKOUBASHMAN — Leibniz-Institut für Polymerforschung Dresden, Deutschland — Technische Universität Dresden, Deutschland — Cluster of Excellence Physics of Life, Deutschland

The discovery of intrinsically disordered proteins (IDPs) has heralded a paradigm shift in molecular biology away from the principle of "form follows function". These IDPs can form biomolecular condensates that fulfill numerous functions in living cells, e.g., signal transduction, stress response and controlled reactions. Due to the conceptual similarities between IDPs and classical polymers, physics-based theories and computer simulations can help to understand, predict and engineer the static and dynamic properties of naturally occurring and synthetic IDPs. In this talk, we will present some of the insights we have gained from coarse-grained molecular simulations, and discuss some of the intricacies and limitations of the underlying models. Key findings include that IDPs inherently exhibit heterogeneous interactions that are weak and distributed along the chain contour, and that IDPs collapse at the condensate-water interface and are tangentially oriented.

CPP 2.2 Mon 10:00 H 0107

Phase-Behaviour of Polymer Grafted Colloidal Nano-Crystals with Variable Grafting Density — ●WILLIAM FALL and HENRICUS WENSINK — Laboratoire de Physique des Solides UMR 8502, CNRS, Université Paris-Saclay, 91405, Orsay, France

The effect of short chain grafting on the liquid crystalline ordering of colloidal nano-crystals is investigated using molecular dynamics simulations. Nano-rods with aspect ratios of typical of cellulose nano-crystals (CNCs) are grafted randomly with short oligomers at 5 different grafting densities. Each system is crystallised from the isotropic phase in solution and slowly compressed until the nano-rods spontaneously order. The liquid crystalline behaviour depends strongly on the grafting density as the effective shape and softness of the nano-rods is modified. Ungrafted rods exhibit complex biaxial Nematic and Smectic-C phases at very low volume fractions, which are then preserved upon grafting with at least a 50% occupation of surface sites with oligomers, forming a Nematic and a tilted Smectic-I phase. Heavier grafting results in the disappearance of the Nematic phase and a direct transition to a complex Smectic-B. Interesting behaviour is observed at extremely low grafting densities, around 25%, with the disappearance of Smectic phases and a persistent Nematic phase induced by patchy grafting, which transitions to a Lamellar phase at high concentration. Such systems fall outside of the traditional hard or soft rod descriptions of phase-transitions in rod-like LC systems. Our findings point to as yet undiscovered LC behaviour in grafted and ungrafted rod-like nanocrystals.

CPP 2.3 Mon 10:15 H 0107

Mesoscopic modeling of dynamically helical polymers — KEERTI CHAUHAN¹, MAURICE SCHMITT², PETER VIRNAU², and ●KOSTAS DAOULAS¹ — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Department of Physics, Johannes Gutenberg University, Mainz, Germany

Synthetic helical polymers are interesting for applications including catalysis, chirality recognition, and templating assembly of functional molecules. Some of these polymers, exhibit dynamic helicity: their conformations can randomly switch between left- and right-handed helical senses because of moderate inversion barriers. The helicity of dynamical polymers can be controlled by "doping" their chain with small chiral groups. So far, the influence of biasing groups on helicity has been investigated on the basis of 1D Ising models, which have explained cooperative effects such as majority rules and sergeants-and-soldiers behavior. However 1D Ising models cannot describe the structure of a polymer in three dimensional space. Therefore we develop a mesoscopic molecular model for dynamical helical polymers, combining a worm-like chain representation with special chiral potentials [1]. We investigate conformational properties of helical polymers in dilute solutions with emphasis on topology.

[1] Y. Zhao, J. Rothörl, P. Besenius, P. Virnau, and K. Ch. Daoulas, ACS Macro Lett. 12, 234 (2023)

CPP 2.4 Mon 10:30 H 0107

Knots in polymer melts and films — ●MAURICE SCHMITT¹, SARAH WETTERMANN¹, HENDRIK MEYER², and PETER VIRNAU¹ — ¹Johannes Gutenberg-Universität, Institut für Physik, Mainz, Germany — ²Université de Strasbourg, Institut Charles Sadron, Strasbourg, France

Flory's hypothesis states that chains in polymer melts can be mapped onto corresponding random walks with characteristic Kuhn lengths and monomer numbers. However, when topological properties, namely knotting probabilities and knot spectra, are considered as measures for chain configurations, corresponding random walks only provide a poor description of chains in the melt, particularly for flexible chains. On the other hand, good agreement between chains in a melt and theta-chains, i.e., single chains at the transition point between a self-avoiding and a globular phase, can be observed with respect to topology. Here, we extend our previous analysis and provide a comprehensive comparison between theta-chains and chains in polymer melts as a function of chain stiffness. Furthermore, we investigate knotting in polymer films with varying thickness and compare their topologies with those of confined theta chains. Knotting probabilities of chains in thin films and confined single chains increase near the boundary of the confinement as chains take up flat conformations with overall decreased radii of gyration.

CPP 2.5 Mon 10:45 H 0107

Model-Based Approach to Reinforcement in Filled and Strain-Crystallizing Elastomer Networks — ●LENA TARRACH and REINHARD HENTSCHKE — Bergische Universität Wuppertal, Wuppertal, Deutschland

The objective of this work is the investigation of the interplay and the differences between reinforcement by filler and by strain-induced crystallization (SIC) in elastomer networks such as Natural Rubber. For this purpose, the model for SIC proposed by Plagge & Hentschke [1] is combined with the model for filled rubber developed by Viktorova et al. [2]. The model is extended to investigate the rupture behavior. First, the stress-stretch behavior and crystallinity-stretch curves of non-breaking model networks with variable filler content are analyzed and compared to experimental observations. Secondly, the rupture behavior is examined dependent on the filler content.

[1] Plagge, J. & Hentschke, R. Microphase Separation in Strain-Crystallizing Rubber. *Macromolecules* 54, 5629-5635. <https://doi.org/10.1021/acs.macromol.1c00757> (2021).

[2] Viktorova, M. et al. Mesoscopic Model for the Simulation of Dynamic Mechanical Properties of Filled Elastomers: Model Construction and Parameterization. *ACS Applied Polymer Materials* 2, 5521-5532. <https://doi.org/10.1021/acsapm.0c00868> (2020).

CPP 2.6 Mon 11:00 H 0107

Transferable Local Density-Dependent Friction in tert-Butanol/Water Mixtures — ●MORITZ MATHES, VIKTOR KLIPPENSTEIN, and NICO VAN DER VEGT — TU Darmstadt, Germany

Coarse-grained (CG) models in molecular dynamics (MD) simulations allow to represent the structure of an underlying all-atom (AA) model by deriving an effective interaction potential. However, this leads to a speed-up in dynamics due to the lost friction, which is especially pronounced in CG implicit solvent models. Adding a thermostat based on the Langevin equation (LE) allows to represent the long-time dynamics of CG particles by reintroducing friction to the system. To improve the representability in CG models of heterogenous molecular mixtures and their transferability over the mixture compositions, we parametrise a LE thermostat, where the friction coefficient depends on the local particle density (LD). We simulated *tert*-butanol/water mixtures over a range of compositions, which show distinct clustering behaviour. For these systems we parametrised three different CG models with: 1. no thermostat friction (CG-MD), 2. fixed friction (CG-LE), and 3. local density-dependent friction (CG-LD). The thermostat friction was iteratively optimised with a Markovian variant of the recently introduced *Iterative Optimization of Memory Kernels* (IOMK) method [1]. We find that the CG-LD model reproduces the AA diffusion coefficients well over the full range of mixtures and is therefore transferable. In addition, I will discuss the role of conservative interactions on dynamics and remaining representability challenges beyond diffusion.

[1] J. Chem. Theory Comput. 2023, 19, 1099-1110

15 min. break

CPP 2.7 Mon 11:30 H 0107

Topological phonon boundary modes in polymer chains and supramolecular lattices — ●JOSE D. COJAL GONZALEZ^{2,4}, JAKUB RONDOMASKI^{3,4}, KONRAD POLTHIER^{3,4}, JÜRGEN P. RABE^{2,4}, and CARLOS-ANDRES PALMA^{1,2,4} — ¹Institute of Physics, Chinese Academy of Sciences, 100190 Beijing, P. R. China — ²Department of Physics & IRIS Adlershof, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ³Department of Mathematics and Computer Science, Freie Universität Berlin, 14195 Berlin, Germany — ⁴Matters of Activity - Image Space Material, Humboldt-Universität zu Berlin, 10178 Berlin, Germany

In the domain of topological band theory, phonon boundary modes with non-trivial topology present desirable properties for atomically-precise technologies, including robustness against defects, waveguiding, and one-way transport. Topological phonon properties remain to be studied both theoretically and experimentally in low-dimensional materials at the atomistic level, such as polymer chains and self-assembled supramolecular lattices, especially under thermal fluctuations. Here we show by means of molecular simulations that these materials, following modified Su-Schrieffer-Heeger (SSH) phonon models with heavy boundaries, exhibit robust topological phonon boundary modes under thermal fluctuations. These modes propagate upon the excitation of a single molecule, in contrast to free boundary modes. Our work introduces the study of topological vibrations in supramolecular systems and suggests potential applications in realizing Hall effect phonon analogues at the molecular scale.

CPP 2.8 Mon 11:45 H 0107

Statistical Analysis of the Dimerization of Amyloid- β (1-40) and Amyloid- β (1-42) — ●CHRISTIAN LAUER and WOLFGANG PAUL — Martin-Luther-Universität Halle-Wittenberg, Halle (Saale), Germany

We present a numerical investigation of the dimerization of the Amyloid- β (1-40) and Amyloid- β (1-42) peptides. The study employs the PRIME20 intermediate resolution protein model and a flat-histogram type Monte Carlo simulation approach that gives access to the thermodynamic equilibrium of the system over the complete control parameter range, which here is the temperature. Thermodynamic analysis reveals that for densities comparable to typical in-vitro experimental conditions, the folding and aggregation transitions of the systems occur simultaneously. However, looking at the difference of intra- and inter-molecular energy contributions, an increased aggregation propensity of Amyloid- β (1-42) compared to Amyloid- β (1-40) is revealed. Hydrogen-bond probability maps show segments at the N-terminus of the peptide with intra-chain anti-parallel alignment, corresponding to intra-chain beta-sheet structures, while the C-terminus shows a more diverse cast of possible configurations. We use Ramachandran plots to further investigate the influence of the different chain segments on the structure formation of Amyloid- β .

CPP 2.9 Mon 12:00 H 0107

Charge and shape anisotropy effects on the phase diagram of BSA in a coarse-grained model — ●JENS WEIMAR, FRANK HIRSCHMANN, and MARTIN OETTEL — Eberhard Karls Universität Tübingen, Germany

Bovine Serum Albumin (BSA) is a model globular protein in biophysical research. However, since it consists of more than 500 amino acid residues it is computationally not yet feasible to perform an all-atom simulation of a system containing many BSA molecules. Hence, we employ an existing low resolution 6-bead coarse-grained model with van der Waals and electrostatic interactions between beads and use grand canonical simulations to determine its phase diagram. At the isoelectric point, different charges on the beads define a charge anisotropy of the model which complements the shape anisotropy of the 6-bead model. The critical point noticeably depends on the anisotropy, and its effect is quantified by studying the deviations of the reduced second virial coefficients at the critical point from the Noro-Frenkel law for isotropic systems.

CPP 2.10 Mon 12:15 H 0107

Single Atom Catalysis in aqueous conditions: enhanced interfacial water dissociation on a Fe-porphyrin graphene defect — ●LAURA SCALFI¹, MAXIMILIAN R. BECKER¹, ROLAND R. NETZ¹, and MARIE-LAURE BOCQUET² — ¹Freie Universität Berlin, Berlin, Germany — ²Ecole Normale Supérieure, Paris, France

SAC or Single-Atom-Catalysis is an expanding field of heterogeneous catalysis and is particularly relevant for electrocatalysis in aqueous solutions. In SAC, the catalytically active metallic sites are reduced to single metal ions that are typically supported on a carbon scaffold. It therefore consumes less metallic material, which is an important environmental and economic factor.

Ab initio modelling and experiments mostly propose two types of defects around single metallic sites on graphene scaffolds with pyridine-like or porphyrin-like motives. Most fundamental studies however neglect the solvating water molecules. Here, we investigate how the liquid interfacial water environment interacts with a single Fe ion using extensive spin-polarized density-functional-theory molecular dynamics simulations. We show that both the porphyrin and pyridine Fe SACs spontaneously adsorb two interfacial water molecules from the solvent on opposite sides and unveil a different catalytic reactivity of the two hydrated SAC motives: while the Fe-porphyrin defect eventually dissociates an adsorbed water molecule under a moderate external electric field, the Fe-pyridine defect does not convey water dissociation. This work highlights the major role that solvents can play and the importance of including them explicitly in molecular studies.

CPP 2.11 Mon 12:30 H 0107

Ballistic-Diffusive Heat Transport Crossover in Molecular Junctions — ●PABLO M. MARTINEZ, OSCAR MATEOS, OSCAR GUTIÉRREZ-VARELA, JUAN CARLOS CUEVAS, and GUILHERME VILHENA — Dpto. de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, Spain

Understanding and controlling heat transport at the nanoscale is arguably one of the largest pending challenges of Nanoscience. The field has witnessed a renewed interest with recent spectacular experiments including measuring heat transport through single-atom contacts, then through single-molecule junctions. However, a full understanding of the novel and exotic heat transport phenomena at these scales remains elusive, thus hindering a de-novo design of novel nano-materials.

In this work, we combined advanced all-atom non-equilibrium simulations to achieve detailed insights into heat transport in benchmark alkane single-molecule chains ranging from few atoms up to 4 μm -long chains. Our simulations quantitatively reproduce experimental data, but most importantly they provide a detailed understanding on the breakdown of Fourier's classical law as a new form of coherent heat transport emerges (ballistic). This coherent transport is found to persist even in micron-sized contacts and in the presence of major defects.

Spectral decomposition of heat flux unveils the non-local nature of this phenomenon thus paving the road for chemically engineering heat transport at the nanoscale. Alternatively, we also explore other strategies (force and mass) for controlling the transport regime (ballistic or diffusive) and overall conductance of alkane chains.

CPP 2.12 Mon 12:45 H 0107

Viscosity of flexible and semiflexible ring melts - from molecular origins to flow-induced segregation — ●RANAJAY DATTA, FABIAN BERRESSEM, FRIEDERIKE SCHMID, ARASH NIKOUBASHMAN, and PETER VIRNAU — Institute of Physics, Johannes Gutenberg University, Staudingerweg 9, 55128 Mainz, Germany

We investigate with numerical simulations the molecular origin of viscosity in melts of flexible and semiflexible oligomer rings in comparison to corresponding systems with linear chains. The strong increase of viscosity with ring stiffness is linked to the formation of entangled clusters which dissolve under shear. This, together with an orientation of rings in shear direction lead to pronounced shear-thinning and non-Newtonian behaviour. Viscosity in linear chains on the other hand is associated with entanglements between chains which also dissolve under shear. While mixtures of flexible and semi-flexible rings mix under equilibrium conditions, differences in rheological properties induce separation under flow. This phenomena has potential applications in microfluidic devices and could be used to segregate stiffer semiflexible ring polymers from their fully flexible counterparts of similar mass and chemical composition.