

## CPP 6: Poster Session II

Complex Fluids and Colloids, Micelles and Vesicles (1-6); Crystallization, Nucleation and Self-Assembly (7-9); Modeling and Simulation of Soft Matter (10-19); Polymer and Molecular Dynamics, Friction and Rheology (20-23); Polymer Networks and Elastomers (24-26).

Time: Tuesday 17:30–19:30

Location: P

CPP 6.1 Tue 17:30 P  
**Self-assembled micelles in aqueous diblock copolymer solution** — ●YANAN LI<sup>1</sup>, CHIA-HSIN KO<sup>1</sup>, VARVARA CHRYSOSTOMOU<sup>2</sup>, DMITRY MOLODENSKIY<sup>3</sup>, STERGIOS PISPAS<sup>2</sup>, and CHRISTINE M. PAPADAKIS<sup>1</sup> — <sup>1</sup>Physics Department, Technical University of Munich, Garching, Germany — <sup>2</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece — <sup>3</sup>EMBL at DESY, Hamburg, Germany

Micelles with stimuli-responsive behavior have attracted great interest as nanocarriers, especially for drug delivery. Here, we investigate the diblock copolymer poly(2-(dimethylamino) ethyl methacrylate)-*b*-poly(lauryl methacrylate) (PDMAEMA-*b*-PLMA), having both pH and thermoresponsive properties in aqueous solution [1]. The self-assembled micelles can be applied in gene transfer and drug delivery applications. We investigate both the pH-dependent micellar structures depending on concentration and the designable micellar shapes from two preparation methods by dynamic light scattering and synchrotron small-angle x-ray scattering. Depending on the preparation method, cylindrical or ellipsoidal micelles are formed. In addition, as the solution is brought from the basic to the acidic state, the micellar size increases, which we attribute to the expansion of the charged PDMAEMA blocks.

[1] V. Chrysostomou, S. Pispas, *J. Polym. Sci. A: Polym. Chem.* **2018**, *56*, 598.

CPP 6.2 Tue 17:30 P  
**Direct Measurement of the Forces Acting Between Colloidal Silica Particles** — ●THOMAS TILGER, MICHAEL LUDWIG, and REGINE VON KLITZING — Department of Physics, Technische Universität Darmstadt, Darmstadt, 64289, Germany

Natural colloidal dispersions have accompanied mankind in the form of blood or milk ever since. Besides this, artificial systems have gained a significant importance for our daily life during the last decades. From the production of many cosmetics or the water purification and sewage water treatment to the medical field, colloidal systems are widely used nowadays.

For all these applications, it is of special interest to gain an understanding of which interparticle forces govern the stability of colloidal dispersions and how this stability can be tailored. In electrolyte solutions, the classical DLVO theory describes these interactions as a superposition of van der Waals and electrostatic double layer forces. Complex fluids such as micellar dispersions show additional oscillatory contributions caused by a structuring of the micelles.

For a detailed examination of these two regimes, we directly measure the forces between two colloidal silica particles in aqueous solutions by the colloidal probe AFM (atomic force microscopy) technique. Varying the concentration of sodium chloride solutions allows us to compare the transition from the double layer to the van der Waals dominated regime with the predictions of the DLVO theory. Similar measurements for the anionic surfactant sodium dodecyl sulfate (SDS) reveal a structuring of the SDS micelles under confinement.

CPP 6.3 Tue 17:30 P  
**Aggregation of Gold Nanoparticles: Effects of Ion Type, Salt Concentration, and Aging** — ●PHILIPP RITZERT and REGINE V. KLITZING — TU Darmstadt, Institute for Condensed Matter Physics, Soft Matter at Interfaces, Hochschulstr. 8, 64283, Darmstadt

The combination of inorganic nanoparticles (NPs) with (responsive) organic polymer matrices advances numerous scientific and technical applications, *e.g.* catalysis, nanoactuation, and medical engineering. Despite considerable progress of embedding NPs into a matrix, the process is often not well-controlled and the composite manufacturing relies on trial-and-error to augment the product quality. Better control over the product manufacturing (*i.e.* NP incorporation) enhances the applicability through more complex NP assemblies.

The project aims at the control of gold NP structuring in a polymer brush matrix. Gold NPs present a versatile model system as they are easily synthesized and stabilized. Furthermore, they exhibit a strong

localized surface plasmon resonance in the visible range. Addition of salt triggers the re-ordering, thus, providing multiple adjusting parameters: salt concentration, ion type, and exposure time.

Preceding composite manufacturing, characterizing the response of gold NPs is essential. The present contribution studies the time evolution of the optical absorption spectra of citrate-capped gold NP suspensions (diameter approx. 13 nm) containing different concentrations of various monovalent sodium salts along the Hofmeister series. In addition, the project exemplifies the influence of basic gold NP properties, namely size and capping molecule.

CPP 6.4 Tue 17:30 P  
**Mesoscale computer simulations of diffusion and sedimentation of colloidal suspensions** — ●YASHRAJ WANI<sup>1</sup>, PENELOPE GRACE KOVAKAS<sup>2</sup>, ARASH NIKOUBASHMAN<sup>1</sup>, and MICHAEL HOWARD<sup>2</sup> — <sup>1</sup>Institute of Physics, Johannes Gutenberg University Mainz, Staudingerweg 7, 55128 Mainz, Germany — <sup>2</sup>Department of Chemical Engineering, Auburn University, Auburn, AL 36849, USA

The diffusive motion in colloidal suspensions is a central process in soft matter, and it also plays an essential role for a wide range of applications. Through simulations, we investigated the self- and collective diffusion in suspensions of spherical colloids at various solute concentrations. To this end, we tested several methods with and without hydrodynamic interactions (HI). We found reasonable agreement for the long-time self-diffusion coefficients between all methods, which is in agreement with previous theoretical considerations. There were, however, fundamental differences in the collective diffusivity (quantified via the sedimentation coefficients) between the various methods: When HI were neglected, the collective diffusivity was identical to the short-time self-diffusion, whereas in the simulations with HI, the sedimentation coefficients decreased with increasing solute concentration. Finally, we applied our methodology to study the equilibrium dynamics of cubic colloids.

CPP 6.5 Tue 17:30 P  
**Effects of polymer block length asymmetry and temperature on the nanoscale morphology of thermoresponsive double hydrophilic block copolymers in aqueous solutions** — ●APOSTOLOS VAGIAS<sup>1</sup>, ARIS PAPAGIANNPOULOS<sup>2</sup>, LUCAS P. KREUZER<sup>1</sup>, DESPOINA GIAOUZI<sup>2</sup>, SEBASTIAN BUSCH<sup>3</sup>, STERGIOS PISPAS<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1,4</sup> — <sup>1</sup>Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, 85748 Garching, Germany — <sup>2</sup>Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 11635 Athens, Greece — <sup>3</sup>German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ), Helmholtz-Zentrum Hereon, 85748 Garching, Germany — <sup>4</sup>Technische Universität München, Physik-Department, Lehrstuhl für Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching, Germany

We combine Fourier transform infrared (FTIR) spectroscopy and small angle neutron scattering (SANS) to identify block length asymmetry and temperature effects on the nanoscale assemblies of novel thermoresponsive double hydrophilic poly(*N*-isopropylacrylamide)-*b*-poly(oligo ethylene glycol methyl ether acrylate) (PNIPAM-*b*-POEGA) diblock copolymers. Morphological transformations from hierarchical assemblies to more well-defined spherical morphologies were identified upon heating. Alteration in the PNIPAM block length induces differences in the strength and/or amount of hydrogen bonding and hydrophobic interactions and molecular solvation.

CPP 6.6 Tue 17:30 P  
**Rotating spherical particle in a continuous viscoelastic medium — a microrheological example situation** — ●SONJA K. RICHTER, CLAUDIUS D. DETERS, and ANDREAS M. MENZEL — Otto-von-Guericke-Universität Magdeburg, Magdeburg, Germany

We consider rigid spherical particles in a continuous one-component viscoelastic environment that are subject to an external dynamic torque. A dynamic relaxation parameter quantifies the deformational

memory of the embedding material. Consequently we can interpolate between damped reversible deformation dynamics and net terminal flow of the viscoelastic surroundings using the same formalism [1]. On this basis, we determine the dynamic linear response function for particle rotations that are driven by the external torque under no-slip conditions on the particle surface [2]. Specifically, we derive explicit expressions for the induced deformation and flow fields in the surrounding viscoelastic medium. To link to magnetic microrheology, we address magnetically anisotropic particles that are driven by a dynamic external magnetic field. Corresponding magnetic susceptibility functions are evaluated [2]. Overall, we expect that our results will be important in the context of microrheological measurements on soft and biological viscoelastic matter.

- [1] M. Puljiz, A. M. Menzel, *Phys. Rev. E* **99**, 012601 (2019).  
 [2] S. K. Richter, C. D. Deters, A. M. Menzel, *EPL (Europhys. Lett.)*, accepted.

CPP 6.7 Tue 17:30 P

**STM and DFT study of BF<sub>4</sub> anion migration on a triaza-triangulenium SAM on Au(111)** — ●SERGIH SNEGIR<sup>1</sup>, YANNICK DAPPE<sup>2</sup>, DMYTRO SYSOIEV<sup>3</sup>, OLIVIER PLUCHERY<sup>4</sup>, THOMAS HUH<sup>1</sup>, and ELKE SCHEER<sup>1</sup> — <sup>1</sup>University of Konstanz, Konstanz, Germany — <sup>2</sup>SPEC, University Paris-Saclay, France — <sup>3</sup>I. Org. Chem. & Biochem., Prague — <sup>4</sup>INSP, Sorbonne University, France

Chemical coupling of functional molecules with so-called platforms allows the formation of functional Self-Assembled Monolayer (SAM). An example is triaza-triangulenium (TATA), with an extended aromatic core, allowing the formation of good electronic contact with the metal surface. Here we present studies on SAMs of TATA-BF<sub>4</sub> molecules on Au(111) by means of Scanning Tunneling Microscopy (STM) and Density Functional Theory (DFT). In solution, these molecules exist as ion pairs of TATA<sup>+</sup> and BF<sub>4</sub><sup>-</sup>. However, under electrochemical deposition on Au(111), on the TATA<sup>+</sup> cations formed SAMs the BF<sub>4</sub><sup>-</sup> anions seemingly disappear. Our STM experiments reveal dissociation of the TATA-BF<sub>4</sub> complex. The TATA<sup>+</sup> remains stable within the SAM while the BF<sub>4</sub><sup>-</sup> spontaneously migrates through the TATA SAM on the surface. DFT calculations show a reduction of the TATA-BF<sub>4</sub> binding energy after deposition. I.S.Snegir, Y. J.Dappe, D.Sysoiev, O.Pluchery, T.Huhn, E.Scheer, PCCP 2021, 23, 9930 - 9937.

CPP 6.8 Tue 17:30 P

**Ordering of small polymer systems through the prism of partition function zeros.** — ●TIMUR SHAKIROV and WOLFGANG PAUL — Institute of Physics, University of Halle, Halle, Germany

Typical low temperature conformations of small alkane systems (single chains and few chain aggregates) differ frequently from the melt ones: even relatively short chains are folded in non-trivial structures at low temperatures [1]. The ordering of a system is related to change of thermodynamic and conformational characteristics of chains. In the case of big systems, the changes occur at one the same transition temperature, whereas for small systems the typical temperatures of the changes can be shifted relative to each other. The sensitivity of thermodynamic functions to the shift differs and can be hidden because of a widening of the transition region of the small system. We present here the results of an analysis of the partition function zeros, which helps to identify a two stage conformational reorganization of small alkane systems. Our calculations are based on Wang-Landau-type Monte Carlo simulations [2,3] of a chemically realistic united atom model [4].

- [1] T. Shakirov, and W. Paul, *J. Chem. Phys.* 2019, 150, 084903.  
 [2] F. Liang, C. Liu, R. J Carroll, *J. Am. Stat. Assoc.* 2007, 102, 305-320.  
 [3] T. Shakirov, *Comp. Phys. Commun.* 228 (2018): 38-43.  
 [4] W. Paul, D. Y. Yoon, and G. D. Smith, *J. Chem. Phys.* 103 (1995) 1702-1709.

CPP 6.9 Tue 17:30 P

**Alteration of self-assembly monolayers and their interactions with zinc oxide surfaces: A DFT study** — ●AZADE YAZDAN YAR<sup>1</sup>, PETIA ATANASOVA<sup>2</sup>, and MARIA FYTA<sup>1</sup> — <sup>1</sup>Institute for Computational Physics, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany — <sup>2</sup>Institute for Materials Science, Bioinspired Materials, Heisenbergstr. 3, 70569 Stuttgart, Germany

Self-assembled monolayers (SAMs) have gained profound interest due to their broad range of applicability such as in molecular electronics, bio-sensing and heterogeneous catalysis. One of the advantages of SAMs is the feasibility they provide in altering and controlling the properties of the substrate. Here, we use Density Functional Theory

(DFT) to study the influence of various variations on the SAM-zinc oxide surface interactions. Specifically, we study the effect of several head groups (thiol, silane, phosphonate) and various crystallographic planes. We limit our work to SAMs of three methylene groups (CH<sub>2</sub>) in the chain with an azide functional group. The energetics of the system will be determined and compared in order to understand the strength of the SAM-surface interaction, which we expect to be greatly impacted by the type of the head group of the SAMs. We will also provide details on the specific interaction sites of the head group with the surface and the electronic structure. We discuss the relevance of these materials as functionalized templates for novel applications in catalysis and sensing.

CPP 6.10 Tue 17:30 P

**Dissipative Self-Organization of Interfaces and Membranes** — ●GREGOR IBBEKEN and MARCUS MÜLLER — Frierich-Hund-Platz 1, 37075 Göttingen

Coupling a self-assembling system to a reaction cycle, we go beyond equilibrium self-assembly toward systems that dissipate energy and thus exhibit new, unique features of dynamic self-organization. We consider the general case of a precursor reacting with a fuel to a product, which itself can decay back to the precursor. To do so, a continuum model is utilized that treats concentrations as order parameters. Within the model, the free energy is given as a functional of the concentrations and the dynamics are computed via the chemical potentials. We show that under the assumption that the fuel diffuses faster than the reacting polymers, reactions introduce an effective connectivity between precursor and product. This way the systems show entirely different features than their respective equilibrium counterpart. For instance, a homopolymer melt can form lamellae, cylinders, spheres, as well as networks, similar to a diblock copolymer melt, and a solution with two reacting homopolymers can form bilayers. The length scale of emergent structures depends on the reaction rates. This way, one can control the size of micelles and vesicles in solution, by coupling an amphiphilic diblock copolymer to a hydrophilic precursor, giving rise to an interplay between the architecture- and the reaction-rate-determined length scales.

CPP 6.11 Tue 17:30 P

**Measuring the line tension of a hemifusion diaphragm** — ●YU-JUNG SU, YULIYA SMIRNOVA, and MARCUS MÜLLER — Institut für Theoretische Physik, Georg-August-Universität, 37077 Göttingen, Deutschland

Changes of membrane topology are essential to cellular transport processes, such as e.g., synaptic release. The molecular pathways, however, are only incompletely understood. The hemifusion diaphragm (HD) is a putative intermediate, where two apposing membranes are locally fused into a single-membrane patch. The line tension of the three-bilayer junction at the rim of the HD controls the size and stability of the HD, and it is an important parameter for phenomenological free-energy models of fusion and fission processes. In the canonical ensemble, where the number of lipids is fixed, the line tension,  $\lambda$ , of the HD, which tends to decrease the area of the HD, is balanced by the membrane tension,  $\pi$ , resulting in a two-dimensional analog of the Laplace equation between  $\lambda$ ,  $\pi$ , and the radius,  $R$ , of the HD. Using molecular dynamics simulation of the coarse-grained MARTINI model, we study this free-energy balance and calculate the line tension as a function of the membrane tension or the distance between the flat membranes in apposition. The results are compared to alternate estimates, e.g., obtained from the shape fluctuations of the rim of the HD.

CPP 6.12 Tue 17:30 P

**Stability of the hemifusion diaphragm and the rim pore** — ●YULIYA SMIRNOVA and MARCUS MÜLLER — Institute for Theoretical Physics, Georg-August University, Göttingen, Germany

Synaptic transmission is a fundamental biophysical process that involves the exocytosis (neurotransmitter release) and endocytosis (vesicle recovery) of small synaptic vesicles at the presynaptic plasma membrane. Whereas the molecular mechanisms of these topology-altering membrane processes are only incompletely understood, it is hypothesized that a hemifusion diaphragm (HD), i.e., an extended single-membrane-thick, lipidic connection between the two apposing membranes, is an important intermediate state. We develop a phenomenological model to investigate the free-energy landscape of a HD with a (rim) pore (RP) that is formed inside the HD and borders the three-bilayer junction at the HD's rim. In the limit that the RP attains the

size of the HD, a complete fusion pore is formed. In the absence of the RP, HDs of different sizes are (meta)stable in the canonical ensemble. It appears, however, to be difficult to stabilize a HD+RP complex in the canonical ensemble. Membrane tension, intermembrane distance, and the line tensions of a membrane pore, a HD, and a fusion pore, as well as external control of the HD's size are important parameters that dictate the (meta)stability of the HD+RP complex and, thereby, the pathway of synaptic transmission.

CPP 6.13 Tue 17:30 P

**Analytical and computational study of advection-diffusion-reaction processes in catalytic fibrous membranes** — ●GABRIEL SITARU and STEPHAN GEKLE — Biofluid Simulation and Modeling, Theoretische Physik VI, Universität Bayreuth

We investigate the efficiency of multi-step catalytic systems where a reactant species is flown through a set of fibrous catalytic membranes. The complexity of such systems arises from the interplay of three different time scales: advection, diffusion and reaction. A theory based on infinitely long cylindrical catalytic sites is developed for the steady-state of an advection-diffusion limited reaction. Additionally, the time-dependent concentration profiles are computed using a Lattice-Boltzmann solver for both the advection-diffusion-reaction and the Navier-Stokes equations. The comparison shows a good agreement between the theory and the numerical results in the intermediate and high Péclet regimes. Both methods can be easily used to predict the efficiency of a multi-step catalysis in fibrous membranes with various geometries.

CPP 6.14 Tue 17:30 P

**Boltzmann: Predicting effective pair potentials and equations of state using neural networks** — ●FABIAN BERRESSEM and ARASH NIKOUBASHMAN — Johannes Gutenberg University, Mainz

Neural networks (NNs) are employed to predict equations of state from a given isotropic pair potential using the virial expansion of the pressure. The NNs are trained with data from molecular dynamics simulations of monoatomic gases and liquids, sampled in the NVT ensemble at various densities. We find that the NNs provide much more accurate results compared to the analytic low-density limit estimate of the second virial coefficient and the Carnahan-Starling equation of state for hard sphere liquids. Furthermore, we design and train NNs for computing (effective) pair potentials from radial pair distribution functions,  $g(r)$ , a task that is often performed for inverse design and coarse-graining. Providing the NNs with additional information on the forces greatly improves the accuracy of the predictions since more correlations are taken into account; the predicted potentials become smoother, are significantly closer to the target potentials, and are more transferable as a result.

CPP 6.15 Tue 17:30 P

**Establishment of a workflow and comparison of scattering data driven molecular dynamics simulations for two water models** — ●VERONIKA REICH<sup>1</sup>, SEBASTIAN BUSCH<sup>1</sup>, and MARTIN MÜLLER<sup>2</sup> — <sup>1</sup>German Engineering Materials Science Centre (GEMS) at Heinz Maier-Leibnitz Zentrum (MLZ), Helmholtz-Zentrum Hereon, Lichtenbergstr. 1, 85748 Garching bei München, Germany — <sup>2</sup>Institute of Materials Physics, Helmholtz-Zentrum Hereon, German Engineering Materials Science Centre (GEMS) and Heinz Maier-Leibnitz Zentrum (MLZ)

Molecular dynamics simulations are increasingly used to evaluate scattering data. For many systems, reliable force fields are available that yield simulations which are compatible with the measured data. For many other systems, however, the agreement between simulation and experiment is not satisfactory yet. In this work, we aim to couple measured and simulated data on the example of different liquid water models in order to optimize force fields.

Two water models, TIP3P and TIP4P/2005, were first simulated by molecular dynamics simulations with the program LAMMPS and further the program SASSENA was used to calculate the corresponding scattering signals. The outcomes were compared to already existing experimental data and changes in the underlying force fields were evaluated in terms of their impact on the behaviour of the simulation.

CPP 6.16 Tue 17:30 P

**Ground- and excited-state properties of tetraphenyl compounds from first-principles calculations** — ●KEVIN EBERHEIM, CHRISTOF DUES, and SIMONE SANNA — Institut für Theoretische Physik and Center for Materials Research, Justus-Liebig-Universität

Gießen, 35392 Gießen, Germany

Tetraphenyl compounds with formula  $X(C_6H_5)_4$  (X being a tetravalent atom of the 14<sup>th</sup> group such as C, Si, Ge, Sn, Pb), crystallize either in a tetragonal crystalline structure or in an amorphous phase [1]. Depending on their habitus, the compounds are characterized by very different optical properties. The molecular crystals are known for their second harmonic generation (SHG) properties, while the amorphous phase is a white light emitter. Tetraphenyl molecules feature indeed the delocalized  $\pi$ -orbitals, which have been proposed as a prerequisite for the white-light generation [2]. In an attempt to understand the mechanisms related to the white light emission, we model the structural, electronic and vibrational properties of different  $X(C_6H_5)_4$  structures within density functional theory. The calculated structural parameters closely reproduce the measured values, however vdW corrections are crucial for a correct description of the structural properties. This confirms that dispersion forces are responsible for the intermolecular bonds in the compound. Different implementations of the vdW forces lead to very similar results. Calculated vibrational properties are in agreement with measured Raman spectra. [1] A Kitaigorodsky, Molecular crystals and Molecules, Acad. Press (1973). [2] Nils W. Rosemann et al., J. Am. Chem. Soc. 138, 16224 (2016), Science 352, 1301 (2016).

CPP 6.17 Tue 17:30 P

**Polymer Architectures by Chain Walking Catalysis - Topological Transition From Linear Chains to Dendrimers** — ●RON DOCKHORN<sup>1</sup>, LAURA PLÜSCHKE<sup>1</sup>, ALBENA LEDERER<sup>1</sup>, JAN MERNA<sup>3</sup>, and JENS-UWE SOMMER<sup>1,2</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany — <sup>2</sup>Technische Universität Dresden, Institute for Theoretical Physics, D-01069 Dresden, Germany — <sup>3</sup>University of Chemistry and Technology Prague, CZ-16628 Praha, Czech Republic

Chain walking (CW) catalysis is a unique approach to synthesize dendritic polyethylenes by a "walking" Pd- $\alpha$ -diimine catalyst into a variety of complex branch-on-branch architectures. Coarse-grained Monte Carlo simulations utilizing the bond fluctuation model of the CW process are performed to investigate the influence of the walking mechanism on the polymer topology. Two distinct regimes can be identified: For low walking rates the structure growths with linear chain extension and low amounts of side chains, whereas high walking rates promote random and isotropic dendritic growth of the molecule. The transition regime is characterized by large amount of branched side chains reflecting a cross-over regime with characteristics of disordered dendronized bottle-brushes controllable by the walking rate of the catalyst. SANS experiments of the CW-polymerized ethylenes are compared to simulation data verifying the observed macro-conformational transitions. The CW one-pot preparation setup tunable by external parameters provides a powerful synthesis route to create dendrigrafts / dendronized polymers.

CPP 6.18 Tue 17:30 P

**Aggregation of several flexible-semiflexible block-copolymer chains: flat histogram Monte Carlo simulation** — ●VIKTOR IVANOV<sup>1,2</sup>, EKATERINA KRUGLOVA<sup>2</sup>, JULIA MARTEMYANOVA<sup>2</sup>, TIMUR SHAKIROV<sup>1</sup>, and WOLFGANG PAUL<sup>1</sup> — <sup>1</sup>Martin-Luther-University Halle-Wittenberg, Institute of Physics, 06099, Halle, Germany — <sup>2</sup>Lomonosov Moscow State University, Faculty of Physics, 119992 Moscow, Russia

We study conformational properties of a single multi-block copolymer chain consisting of flexible (F) and semi-flexible (S) blocks with equal composition of F- and S-units and with different affinity to a solvent, as well as the aggregation of several such chains. We perform flat histogram Monte Carlo simulations based on the stochastic approximation Monte Carlo (SAMC) algorithm. We use the two-dimensional density of states, which depends on the energy of intramolecular stiffness and on the energy of non-valence interactions. We present data on different non-trivial globular morphologies, including several structures with high orientational ordering of bonds. Pseudo-phase diagrams in variables temperature vs. stiffness parameter are presented for different values of the block length. We also present our recent results on the aggregation behaviour of several FS-block-copolymer chains and discuss the possibility of shape-persistent aggregation of globules. We acknowledge the financial support from RFBR (grant 19-53-12006-NNIO-a) and DFG (project PA 473/18-1) and thank Moscow State University Supercomputer Center for providing the computational resources.

CPP 6.19 Tue 17:30 P

**Crystallization of oligomers in melts between two hard walls: flat histogram Monte Carlo simulation** — ●EVGENIIA FILIMONOVA, TIMUR SHAKIROV, and VIKTOR IVANOV — Martin-Luther-University Halle-Wittenberg, Institute of Physics, 06099, Halle, Germany

We study conformational properties of short polymer chains in melts between two hard walls. Our final goal is to reveal physical factors which are responsible for a particular scenario of surface-induced polymer crystallization (e.g., the nucleation and growth or the 1st order prefreezing). We use a coarse-grained model and perform flat histogram Monte Carlo (MC) simulations based on the stochastic approximation Monte Carlo (SAMC) algorithm. We analyse different order parameters: nematic orientational order parameter, bond orientation order parameters (Steinhardt parameters), hexagonal order parameter (which shows a quasi-two-dimensional stacking of chain cross sections in a plane perpendicular to the director). We see the nematic transition (formation of rotator phase) upon cooling, followed by a crystallization transition. We are able to observe a coexistence of an isotopic structure in the center of the film with ordered structures at the walls at intermediate values of energies (in microcanonical analysis). We are able to localise the transition points between different pseudo-phases quite precisely. Financial support of the International Graduate School AGRIPOLY supported by the European Social Fund (ESF) and the Federal State Saxony-Anhalt is acknowledged.

CPP 6.20 Tue 17:30 P

**Pressure and temperature-dependent changes in the microstructure of linear mono-ols** — ●JENNIFER BOLLE<sup>1</sup>, ALEXANDER FAULSTICH<sup>1</sup>, MARTINA POŽAR<sup>2</sup>, AURÉLIEN PERERA<sup>3</sup>, MICHAEL PAULUS<sup>1</sup>, METIN TOLAN<sup>1</sup>, and CHRISTIAN STERNEMANN<sup>1</sup> — <sup>1</sup>Fakultät für Physik/DELTA, Technische Universität Dortmund, 44227 Dortmund, Germany — <sup>2</sup>University of Split, Faculty of Science, Rudera Boškovića 33, 21000, Split, Croatia — <sup>3</sup>Sorbonne Université, Laboratoire de Physique Théorique de la Matière Condensée, 4 Place Jussieu, F75252, Paris. cedex 05, France

Hydrogen bonds are essential for understanding the microscopic structure of water, aqueous solutions and associated fluids in general. They stabilize the structure of peptides and proteins and are the driving force for association in molecular fluids. In this study, the evolution of the microstructure of a series of linear monohydroxy alcohols (mono-ols) with temperature and pressure was investigated by X-ray diffraction at beamlines BL2 and BL9 of the synchrotron radiation source DELTA (TU-Dortmund, Germany). Comparing the behavior of the so-called pre-peak in the diffraction patterns of the mono-ols with increasing chain length, the influence of steric hindrance on the charge order of these liquids was systematically studied. The results are compared with calculated diffraction intensities based on molecular dynamics simulations and interpreted on the basis of changes in their microstructure. We observe that the charge order for all the studied alcohols is significantly affected by pressure and temperature and strongly depends on chain length.

CPP 6.21 Tue 17:30 P

**Systematic derivation of hydrodynamic equations for viscoelastic phase separation** — ●BURKHARD DUENWEG<sup>1</sup>, DOMINIC SPILLER<sup>1</sup>, MARIA LUKACOVA<sup>2</sup>, AARON BRUNK<sup>2</sup>, HERBERT EGGER<sup>3</sup>, and OLIVER HABRICH<sup>3</sup> — <sup>1</sup>MPI for Polymer Research Mainz — <sup>2</sup>Mathematics, JGU Mainz — <sup>3</sup>Mathematics, TU Darmstadt

We present a simple hydrodynamic two-fluid model aiming at the description of the phase separation of polymer solutions with viscoelastic effects. It is directly based upon the coarse-graining of a molecular model (such that all degrees of freedom have a clear molecular interpretation), and a free-energy functional. The dynamics is split into a conservative and a dissipative part, following the GENERIC formalism. In a first step, we derive an extended model where inertial dynamics of the macromolecules and of the relative motion of the two fluids is taken into account. In the second step, we eliminate these inertial contributions and, as a replacement, introduce phenomenological dissipative terms. The final simplified model is similar, though not identical, to models that have been discussed previously. In contrast to the traditional two-scale description that is used to derive rheological equations of motion, we here treat the hydrodynamic and the macromolecular degrees of freedom on the same basis. Notably, we find a rheological constitutive equation that differs from the standard Oldroyd-B model. This difference may be traced back to a different underlying statistical-mechanical ensemble that is used for averaging the stress.

CPP 6.22 Tue 17:30 P

**Controlling the dynamics of soft, coarse-grained polymer fluids at surfaces** — ●PRITAM KUMAR JANA<sup>1</sup>, PETRA BACOVA<sup>2</sup>, LUDWIG SCHNEIDER<sup>1</sup>, VANGELIS HARMANDARIS<sup>2</sup>, PATRYCJA POLINSKA<sup>3</sup>, CRAIG BURKHARD<sup>4</sup>, and MARCUS MÜLLER<sup>1</sup> — <sup>1</sup>Institute for Theoretical Physics, University of Goettingen — <sup>2</sup>Institute of Applied and Computational Mathematics, Foundation for Research and Technology-Hellas, Heraklion, Greece — <sup>3</sup>Goodyear S.A., Colmar-Berg L-7750, Luxembourg — <sup>4</sup>The Goodyear Tire and Rubber Company, Akron, Ohio 44305, United States

The rheological properties of composites derived from fillers in a polymer matrix depend on particle size, filler loading, and dispersion, as well as the interfacial interaction between the fillers and polymer matrix. For the coarse-grained modeling of such systems, it is crucial to pay attention to the fluid flow past the solid filler surface because the classical no-slip hydrodynamic boundary condition does not hold on the micro- and nanoscopic length scale. Instead, the flow is characterized by a microscopically small but finite slip length. To explore the dynamics and slippage, we perform both atomistic and highly coarse-grained (hCG) simulations. In the atomistic simulations, we study the dynamics of polybutadiene close to a silica surface. In the hCG scale, since the solid surface appears smooth, special simulation techniques are required to generate friction at the solid-fluid contact and control slippage. We devise a simulation strategy that can reproduce the dynamics of the polymers close to the wall as seen in the atomistic simulations. The parametrized hCG model, which is devised by comparison with the atomistic simulations, allows the exploration of the dynamics and slippage of polymers with a wide range of molecular weights.

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**Molecular origins of shear-thinning in polymer melts** — ●RANAJAY DATTA, FRIEDERIKE SCHMID, and PETER VIRNAU — Institute of Physics, Johannes Gutenberg University, Staudingerweg 9, 55128 Mainz, Germany

We investigate the molecular origin of shear-thinning in melts of flexible, semiflexible and rigid oligomers with coarse-grained simulations of a sheared melt [1]. Emergence of entanglements and nematic phases in equilibrium, alignment, stretching and tumbling modes or suppression of the latter all contribute to understanding how macroscopic flow properties emerge from the molecular level. By performing simulations of single chains in shear flow, we identify which of these phenomena are of collective nature and arise through interchain interactions and which are already present in dilute systems.

Reference:

[1] <https://arxiv.org/abs/2101.03645v2>

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**Phase behavior of randomly crosslinked diblock copolymers** — ●GAOYUAN WANG, ANNETTE ZIPPELIUS, and MARCUS MÜLLER — Institut für Theoretische Physik, Georg-August-Universität Göttingen, Deutschland

We have investigated the structure and the phase behavior of randomly crosslinked polymer networks formed by connecting symmetric diblock copolymers via covalent bonds. Particle-base Monte-Carlo simulation is applied to study the order-disorder transition, controlled by the Flory-Huggins parameter  $\chi$ . We provide an accurate phase diagram, in which the  $\chi_c N$  of the ODT is shown as a function of the crosslink density  $p$  and Flory-Huggins parameter of the preparation state  $\chi_p N$ . Depending on  $\chi_p N$ , the random crosslinks support the disordered or periodically ordered state over a larger range of incompatibilities ( $\chi N$ ), because the irreversible bonds impart a memory of the structure that existed at their formation. Knowing the amount of crosslinking required to retain a microphase-separated or disordered structure at a  $\chi N$  that considerably differs from the preparation state is helpful for generating desired states, which may only be metastable without crosslinks.

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**Understanding the structure of reversible networks made of star polymers** — ●KIRAN SURESH KUMAR<sup>1,2</sup>, TONI MÜLLER<sup>1,2</sup>, JENS-UWE SOMMER<sup>1,2</sup>, and MICHAEL LANG<sup>1</sup> — <sup>1</sup>Leibniz-Institut für Polymerforschung Dresden, Institut Theorie der Polymere, Hohe Strasse 6, 01069 Dresden, Germany — <sup>2</sup>Institute für Theoretische Physik, Technische Universität Dresden, Zellescher Weg 17, 01069 Dresden, Germany

Bonds in reversible networks break and form continuously allowing the material to flow and self-heal on long time scales while being a solid on short times. Recent work utilized a regular star branched architecture in combination with a controlled pairwise association of reversible groups to reveal the impact of network defects on the material properties [1-4]. We develop a model for network structure by combining previous work on network defects in irreversible networks [5] with the method of balance equations [6] for reversible systems. The model predictions for the frequency of different star types are tested by Monte Carlo simulations of network structure.

[1] Rossow, T.; Habicht, A.; Seiffert, S. *Macromolecules* 2014, 47, 6473-6482. [2] Tang, S.; Wang, M.; Olsen, B. D. *J. Am. Chem. Soc.* 2015, 137, 3946-3957. [3] Tang, S.; Habicht, A.; Li, S.; Seiffert, S.; Olsen, B. D. *Macromolecules* 2016, 49, 5599-5608. [4] Ramirez, J.; Dursch, T. J.; Olsen, B. D. *Macromolecules* 2018, 51, 2517-2525. [5] Lang, M.; Schwenke, K.; Sommer, J.-U. *Macromolecules* 2012, 45, 4886-4895. [6] Lang, M.; Kumar, K. S. *Macromolecules* 2021, 10.1021/acs.macromol.1c00718.

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**Thermal transport of epoxy networks: Bond engineering and network microstructures** — •MANJESH KUMAR SINGH<sup>1</sup> and DEBASHISH MUKHERJI<sup>2</sup> — <sup>1</sup>Department of Mechanical Engineering, In-

dian Institute of Technology Kanpur, Kanpur: 208016, Uttar Pradesh, India — <sup>2</sup>Quantum Matter Institute, University of British Columbia, Vancouver BC V6T 1Z4, Canada

Thermal transport coefficient ( $k$ ) is a central property of condensed matter systems, where establishing the molecular level understanding is extremely important to tailor the materials properties for their possible uses under extreme environmental and practical conditions. Here polymers are an important class of materials because they provide different pathways for the energy transfer. For example, the heat flow between the two covalently bonded monomers is over 100 times faster than between the two non-bonded monomers [1]. Therefore, the delicate balance between these two contributions often provides a guiding tool for the design of tailor made polymeric materials with extraordinary thermal properties. Traditionally most studies have investigated  $k$  in the linear polymeric materials, the recent interests have also been directed towards the epoxy network. Using molecular dynamics simulations, we investigate the factors effecting  $k$  of epoxy networks. We emphasize on the importance of the bond types and their influence on the network microstructures, with a goal to provide a guiding principle for the tunability in  $k$  [2].

[1] Bhardwaj et al., *ACS Nano* 15, 1826 (2021). [2] Mukherji et al., *Physical Review Materials* 5, 025602 (2021).