

CPP 20: Polymer and Molecular Dynamics, Friction and Rheology

Time: Tuesday 9:30–12:30

Location: ZEU 255

Invited Talk

CPP 20.1 Tue 9:30 ZEU 255

Granular Matter Rheology – fluid-/solid-like behavior and state-transitions — ●STEFAN LUDING — University of Twente, NL

The dynamic and static behavior of particulate and granular matter (like sand, powder, suspended particles, often with a wide distribution of particle sizes) is of considerable interest in a wide range of industries and research disciplines. Special is that they can behave both solid-like and fluid-like, which is a challenge for both academia and industry. The related mechanisms/processes in particle systems are active at multiple scales (from nano-meters to meters), and explaining their multiple states, and transitions, will lead to a better understanding of natural disasters like avalanches or industrial problems like silo-failure.

To understand the fundamental micro-mechanics and -physics, one can use particle simulation methods. However, large-scale applications (due to their enormous particle numbers) have to be addressed by coarse-grained models or by continuum theory. For this, to derive constitutive rheology relations, so-called micro-macro transition methods are necessary, which translate particle positions, velocities and forces into density-, stress-, and strain-fields, which must be compatible with the balance equations for mass, momentum, and energy of continuum theory. Additional non-classical fields describe the micro-structure (fabric, force-chains) or the statistical fluctuations, before an universal granular rheology can be defined, involving state-transitions between the states, the so-called jamming/un-jamming transitions.

CPP 20.2 Tue 10:00 ZEU 255

Phase-Sensitive, Active Microrheology via Probe-Free Application of Thermoviscous Flows — ●ILIYA STOEVIĆ, ELENA ERBEN, VENKAT KRISHNASWAMY, ANTONIO MINOPOLI, SUSAN WAGNER, BENJAMIN SEELBINDER, NICOLA MAGHELLI, and MORITZ KREYSING — Max Planck Institute of Molecular Cell Biology and Genetics, Pfotenhauerstraße 108, 01307, Dresden, Germany

We recently found how thermoviscous expansion phenomena give rise to a new, contactless particle trap that is characterised by a linear force-extension relationship and can therefore be employed in non-invasively measuring femtoNewton forces with thermally limited sensitivity. Our new force-measurement method is based on optically generated flows, thereby lifting prerequisites related to the probe material and resulting in only moderate heating at the position of the micromanipulated object. This methodology offers an appealing alternative to the use of optical tweezers in highly delicate samples and living systems. Next, we asked the question if our thermoviscous flows can be used to obtain more quantitative data and possibly demonstrate the equivalence between flow-driven and force-driven rheology in their ability to extract phase angles as a measure of relative mechanics. With our new flow-based and phase-sensitive microrheology, we provide access to the mechanics of highly viscous media, tenuous gels and even cellular cytoplasm. Further refinements of the method aim at multiplexing and removing the need for using fluorescent tags.

CPP 20.3 Tue 10:15 ZEU 255

Nanoscale Friction on Monolayer MoS_2 in Presence of Water Investigated with Molecular Dynamics — ●MILJAN DAŠIĆ and IGOR STANKOVIĆ — Scientific Computing Laboratory, Center for the Study of Complex Systems, Institute of Physics Belgrade, University of Belgrade, Pregrevica 118, 11080 Belgrade, Serbia

We have implemented and applied a molecular dynamics (MD) simulation setup in order to study the nanoscale friction on monolayer MoS_2 plate in the presence of different quantities of water. Our setup mimics a standard AFM experiment, including an amorphous SiO_2 probe, a monolayer crystalline MoS_2 plate, and water molecules in-between. Presence of water molecules matches experimental conditions of air humidity. We studied two different quantities of water: (1) *full water layer* - SiO_2 probe is fully immersed in water and surrounded by water molecules, and (2) *capillary water* - water forms a capillary around the SiO_2 probe, with lateral vacuum gaps. We conducted two modes of simulations: vertical approach of SiO_2 probe towards MoS_2 plate and lateral sliding of SiO_2 probe. There are always *trapped* water molecules in the gap between the probe and the plate; their number drops with the increase of temperature. We have obtained well-pronounced *stick-slip* friction loops; we found that an increase of the applied normal load leads to the more pronounced stick-slip be-

haviour, as seen in AFM experiments. The amount of water present in the studied nanoscale tribosystem has a pronounced impact on the stick-slip frictional behaviour.

CPP 20.4 Tue 10:30 ZEU 255

Polymers of Intrinsic Microporosity - Molecular Mobility and Physical Aging Revisited by Dielectric Spectroscopy and X-Ray Scattering — ●FARNAZ EMAMVERDI, GLEN JACOB SMALES, MARTIN BÖHNING, and ANDREAS SCHÖNHALS — Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

The applications of polymers of intrinsic microporosity (PIMs) membranes are restrained by their strong tendency to physical aging. Aging phenomenon involves a significant loss of their good performance in gas separation technology. The initial microporous structure approach a denser state via local rearrangements, leading to a reduction of the permeability. In this work, the dielectric behavior of PIM-1 films and their behavior upon hating (aging) were revisited by isothermal frequency scans during different heating/cooling cycles over a broad temperature range between 133 K and 523 K. In addition, the obtained results were compared with data of samples that were annealed at ambient temperatures over different time scales. Multiple dielectric processes were observed: several relaxation processes due to local fluctuations and a Maxwell-Wagner-Sillars polarization effect related to microporosity. The temperature dependence of the rates of all processes follows the Arrhenius law where the estimated activation energy depends on the nature of the process. SAXS/WAXS patterns were measured as a function of temperature during heating/cooling in a temperature range corresponding to that covered by dielectric spectroscopy. The influence of the aging on the processes is discussed in detail.

CPP 20.5 Tue 10:45 ZEU 255

Viscoplastic Modeling of Surface Relief Grating Growth on Isotropic and Pre-oriented Azopolymer Films — TVERDOKHLEB NINA¹, LOEBNER SARAH², SANTER SVETLANA², and ●MARINA SAPHIANNIKOVA¹ — ¹Institute Theory of Polymers, Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany — ²Institute of Physics and Astronomy, University of Potsdam, 14476 Potsdam, Germany

We report on solving two intriguing issues concerning the inscription of surface relief gratings within azopolymer thin films under irradiation with SS, PP and RL interference patterns. For this, we utilize the orientation approach and viscoplastic modeling in combination with experimental results, where the change in surface topography is acquired in-situ during irradiation with modulated light. First, the initial orientation state of polymer backbones is proved to be responsible for the contradictory experimental reports about the efficiency of the SS interference pattern. Different orientation states can influence not only the phase of SS grating but also its height, which is confirmed experimentally using special pre-treatments. Second, faster growth of gratings inscribed by the RL interference pattern is shown to be promoted by a weak photo-softening effect. Overall, the modeled results are in good agreement with the order of relative growth efficiency: RL-PP-SS.

CPP 20.6 Tue 11:00 ZEU 255

Equilibration of free-standing films of highly entangled polymer melts — ●HSIAO-PING HSU and KURT KREMER — Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128, Mainz, Germany

Equilibrating confined and free-standing films of highly entangled polymer melts is a challenge for computer simulations. We approach this problem by first studying polymer melts based on a soft-sphere coarse-grained model confined between two walls. The distance of the walls is compatible with the simulation box of bulk melts in equilibrium, while periodic boundary conditions in the directions parallel to the walls are kept. Then we successively insert more fine grained polymer representations until the underlying microscopic details of the bead-spring model are reached. Tuning the wall potential, the monomer density of confined polymer melts in equilibrium is kept at bulk melt density even near the walls. Switching to another recently developed variant of the bead-spring model we can study melts at zero pressure [1] and study free-standing polymer films [2]. Furthermore, this also allows us

to study free-standing films under strain and analyze the influence of entanglements on the local film morphology.

[1] H.-P. Hsu, K. Kremer, *J. Chem. Phys.* 150, 091101 (2019); 150, 159902 (2019).

[2] H.-P. Hsu, K. Kremer, *J. Chem. Phys.* 153, 144902 (2020); 156, 019901 (2022).

15 min. break

CPP 20.7 Tue 11:30 ZEU 255

A nanofluidic system based on cylindrical polymer brushes: molecular dynamics simulation and scaling theory — ●CHENG-WU LI — Leibniz-Institut für Polymerforschung Dresden, Germany

Using molecular dynamics simulations and scaling theory, we present a systematic study of the function of cylindrical nanopores which are decorated with polymer brushes. Our focus is on the regimes in which these systems are able to function as controllable (switchable) gates for bulky nanoparticles. In a slightly poorer solvent, closed cylindrical brushes facilitate the self-organised formation of droplets from a continuous flow of incoming nanoparticles. We analyze droplet formation and propagation by means of simple scaling arguments which are tested in the simulations. Polymer brushes in marginally poor solvents serve as a pressure feedback system, exhibit a collapse transition under the moderate pressure of the incident flow, without the need for additional external stimuli, and finally close spontaneously after droplet passage. Our results qualitatively demonstrate the control of polymer brushes over continuous fluids and droplet formation, and its effectiveness as a means of fluid control can be used to design nanofluidic rectification devices that operate reliably under moderate pressure.

CPP 20.8 Tue 11:45 ZEU 255

Polymer chain dynamics under shear studied by rheological NMR — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany

The NMR spin-lattice relaxation time T_2 is particularly sensitive to slow chain-segment motion in polymers, at least two components in the signal decay are observed, a faster relaxing component from chain segments of motion restricted by crosslinks or entanglements and a slower component associated with parts moving more freely. Ordering of the polymer chains under shear would result in restrictions for the segment motion and thus a shortening of T_2 , a loss of entanglements due to the shear results in a prolongation of T_2 . Rheological NMR combined external shear with NMR experiments. In a polymer melt of poly(dimethylsiloxane) under shear longer relaxation times are observed. Together with a reduction of the fraction of shorter T_2 this indicates the loss of entanglements is the dominating process for high molecular weight. In a new experimental setup both the amplitude and the frequency of the deformation are varied. It demonstrates that a minimum strain rate above 1000/s is required to observe the loss

of entanglements. Combining pulsed-field-gradient (PFG) NMR with NMR imaging permits to measure flow pattern. After the turning point in oscillatory shear counterflow is observed when a fraction of the liquid at the static wall still is in initial flow direction while liquid in contact with the moving bob started in the new direction. At this time the velocity gradient drastically exceeds the velocity gradient at the point of maximum velocity representing a high shear rate.

CPP 20.9 Tue 12:00 ZEU 255

On the Relaxation Behavior of Linear Chains under Oscillatory Forces — ●RON DOCKHORN¹ and JENS-UWE SOMMER^{1,2} — ¹Leibniz-Institut für Polymerforschung Dresden e.V., D-01069 Dresden, Germany — ²Technische Universität Dresden, Institut für Theoretische Physik, D-01069 Dresden, Germany

We are studying the relaxation spectra and the force-extension behavior of linear chains under externally driven oscillatory periodic forces f in means of theory and simulations. An oscillatory force $f = f_0 + f_a \cdot \sin(\omega t)$ is applied on the chain ends and the response of the end-to-end-distance R as well as the relaxation time τ_R on the oscillatory frequency ω is investigated. An analytical expression for the end-to-end-distance $R(f)$ is derived by using the Rouse model and compared to simulations. The dissipated energy is calculated by the hysteresis loop $A = |\oint df R(f)|$, which shows a characteristic maximum at $\omega\tau_R \simeq 1$ for ideal chains independent of the applied force. Contrary, excluded volume chains show a force dependence on the relaxation time $\tau_R \sim f^{-0.3}$ as well as a shift on the hysteresis in the Pincus regime. Extensive computer simulations are performed to investigate the scaling properties utilizing the Bond-Fluctuation-Model. Furthermore, the relaxation behavior of different polymer architectures (ring polymer, 3₁-trefoil knot, two concatenate rings) are compared to the linear chain behavior. The theory and simulations suggests implications for dynamic experiments of biopolymer subject to external forces.

CPP 20.10 Tue 12:15 ZEU 255

Orientation Polarization Spectroscopy — ●FRIEDRICH KREMER, WYCLIFFE KIPNUSU, and MARKUS ANTON — Leipzig University, Peter Debye Institute for Soft Matter Physics, Linnéstr.5,04103Leipzig,Germany

The theory of orientation polarization and dielectric relaxation was developed by P. Debye more than 100 years ago. It is based on approximating a molecule by a sphere having one or more dipole moments. By that the detailed intra- and inter-molecular interactions are explicitly not taken into consideration. In this contribution the principal limitations of the Debye approximation are discussed and novel experiments based on Quantum Cascade IR-Lasers are presented [1] which enable to determine the orientation polarization of selected molecular moieties for the example of the glass forming liquid glycerol. [1] Kremer, F. et al. *Int. J. Mol. Sci.* 23, 8254 (2022)