CPP 57: Polymer Dynamics and Rheology (joint session CPP/DY, organized by CPP)

Time: Thursday 15:00–18:30 Location: H40

CPP 57.1 Thu 15:00 H40

Iso-flux tension propagation theory of driven polymer translocation through a nano-pore — •Jalal Sarabadani[1], Tapio Ala-Nissila[2], and Timo Ikonen[3] — [1]Department of Applied Physics, Aalto University, Espoo, Finland — [2]Department of Applied Physics, Aalto University, Espoo, Finland — [3]VTT Technical Research Centre of Finland Ltd., Espoo, Finland

We investigate the dynamics of pore-driven polymer translocation mainly by using analytical model and also by molecular dynamics (MD) simulations [1]. By using the tension propagation theory within the constant flux approximation an explicit equation of motion for the tension front is derived. This equation leads us to a scaling relation for the average translocation time, τ, which captures the asymptotic result $\tau \sim N_0^{1+\nu}$. Here, N_0 is the chain length and ν is the Flory exponent. Moreover, we derive the leading correction-to-scaling term to τ which is a finite chain length correction term ($\sim N_0$) due to the effective pore friction. Then by incorporating the fluctuations in the initial configuration of the polymer into the model in addition to thermal noise, the model not only reproduces previously known results but also considerably improves the estimates of the monomer waiting time distribution and the time evolution of the translocation coordinate $s(t)$, showing excellent agreement with MD simulations. We also discuss the effect of a flickering pore and an oscillating external driving force on the translocation time using the new model [2]. [1] J. Sarabadani, T. Ikonen and T. Ala-Nissila, J. Chem. Phys. (141), 214907 (2014). [2] J. Sarabadani, T. Ikonen and T. Ala-Nissila, J. Chem. Phys. (143), 074905 (2015).

CPP 57.2 Thu 15:15 H40

Polymer translocation through nanopores: An unbiased perspective on free energy landscapes and essential dynamics — Evangelos Tzaras, Florian Weik, Christian Holm, and •Jens Smiatek — Institut für Computerphysik, Universität Stuttgart, D-70569 Stuttgart, Germany

We studied the translocation of uncharged polymers through thin nanopores by coarse-grained Molecular Dynamics simulations in combination with a forward flux sampling approach. Our results for short and intermediate chain lengths reveal that the translocation behavior is mostly governed by the transition probabilities of single monomers. Specific configurational changes of the polymer or chain tension effects are minor important. We propose an analytic approach for the free energy landscapes which is in good agreement with the simulation results. The outcomes of an essential dynamics analysis verify that only a small number of eigenvectors is substantial for a reliable description of the polymer motion. A comparison with polymers in dilute bulk solution indicates the presence of quasi-equilibrium states which are important for the validity of the underlying free energy landscapes.

CPP 57.3 Thu 15:30 H40

The Origin of Strong Slip Of Polymer Melts on Structured Surfaces: A Molecular Approach. — •Mischa Klos[1], Laurent Joly[2], Sebastian Backes[1], and Karin Jacobs[1] — [1]Saarland University, Dept. of Experimental Physics, D-66041 Saarbruecken — [2]Univ Lyon 1, Inst Lumiere Mat, 43 Blvd 11 Novembre 1918, F-69622 Villeurbanne

Flow dynamics at the solid/liquid interface gain more importance when it comes to small scales. In special systems, a liquid can reach a finite velocity at the boundary to the solid. Our experiments probe this phenomenon via the dewetting of thin polymer films on hydrophobic substrates [1]. As hydrophobic coatings we use thin amorphous polymers films or different types of ordered self-assembled silane monolayers on silicon substrates. On silane surfaces, polystyrene (PS) of low molecular weight exhibit slip lengths up to micrometers [2]. On AF1600, no significant slip is observed. Scattering studies indicate an interfacial layer at the interface depending on the structure of the substrate [3]. Simulations where able to refine the molecular idea of the used SAMs [4]. However, strong slip is reduced if PMMA or polyvinylpyridine (PVP) are used instead of PS. MD-Simulations of our systems allow detailed insights into the dynamics of the polymer melt. [1] O. Bäumchen, et.al., J. Phys. Condens. Matter 24 325102 (2012) [2] R. Fetzer, et. Al., Europhys Lett. 75 638 (2006) [3] P. Gutfreund, et. al., Phys. Rev. E 87 012306 (2013) [4] J.M. Castillo Sanchez, et.al., Langmuir 31, 2630 (2015)

CPP 57.4 Thu 15:45 H40

Contact Kinetics in Fractal Macromolecules — •Maxim Dolgushev[1], Thomas Guérin[2], Alexander Blumen[1], Olivier Bénichou[3], and Raphaël Voituriez[3] — [1]Physikalisches Institut, Universität Freiburg, Hermann-Herder-Strasse 3, 79104 Freiburg, Germany — [2]Université de Bordeaux and CNRS, Laboratoire Ondes et Matière d'Aquitaine (LOMA), UMR 5798, 33400 Talence, France — [3]Laboratoire de Physique Théorique de la Matière Condensée, CNRS/UPMC, 4 Place Jussieu, 75005 Paris, France

We investigate the effect of the complex connectivity of macromolecules on the contact kinetics by focusing on the case of fractal macromolecules [1]. In our theoretical description, the non-Markovian feature of monomer motion, arising from the interactions with the other monomers, is captured by accounting for the non-equilibrium conformations of the macromolecule at the very instant of first contact. This analysis reveals a scaling relation for the Mean First Contact Time as a function of the equilibrium distance between the reactive monomers and of the spectral dimension of the macromolecule, which is independent on the microscopic details of the macromolecules. We show that the non-Markovian effects increase for the structures with higher degree of hyperbranching, for which the conformations at first contact are getting much more different from equilibrium looping conformations. Our theoretical predictions are in excellent agreement with numerical stochastic simulations.

[1] M. Dolgushev, T. Guérin, A. Blumen, O. Bénichou, and R. Voituriez, Phys. Rev. Lett. 115, 208301 (2015).

CPP 57.5 Thu 16:00 H40

Branch Point Motion in Asymmetric Star Polymers Investigated by Molecular Dynamics Simulations — •Stefan Holler[1,2], Angel Moreno[2], Michaela Zamponi[1], and Dieter Richter[1] — [1]Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — [2]Centro de Fisica de Materiales, 20018 San Sebastian, Spain

Large-scale molecular dynamics simulations of three-arm asymmetric star polymers have been performed to study the motion of the branch point and the so-called hopping parameter p^2 that characterizes the effective friction associated to the short side arm. The simulated star polymer systems consist of a large backbone (10 or 16 entanglements) and a central short unentangled side arm.

This work expands the investigation by Bacova et al. [1] in similar stars with entangled side arms. Surprisingly, the frictional contribution of the unentangled side arms on the motion of the linear backbone is much larger than assumed by theory. The value of p^2 can be calculated from the simulation data using general assumptions that hold true for all versions of hierarchical relaxation models. The most consistent description of the simulation results suggests that p^2 is not a constant but depends on architecture and molecular weight, and that hopping occurs in the bare, undilated tube.

[1] Bacova et al., Macromolecules 47 (2014) 3362

CPP 57.6 Thu 16:15 H40

Disentanglement of Two Overlapping Polymer Chains: Contacts vs. Knots — •Diddo Diddens, Nam-Kyung Lee, Sergei Obukhov, Jörg Baschnagel, and Albert Johner — Institut Charles Sadron, Université de Strasbourg, CNRS UPR22, 23 Rue du Loess, 67034 Strasbourg Cedex 2, France

The role of topological constraints is one of the remaining challenges in polymer physics. While it is evident that the non-crossability heavily affects the motion of long polymer chains in dense solutions and melts, these constraints are usually neglected in theoretical descriptions of the polymer dynamics in dilute solutions. However, the situation becomes less clear in the limit of long chains and/or rather dense polymer coils (e. g. close to the Θ-point), since even for a single chain, distinct segments are more likely to be intertwined or knotted.

To address this issue, we present a comprehensive study comprising MC and MD simulations as well as analytical calculations, and investigate the relevance of non-crossing constraints for two polymer chains brought into initial overlap. In particular, we join two long polymers by a labile bond, and focus on their separation directly after the cleavage of this bond. We demonstrate that the average time

for this process strongly correlates with the number of monomeric contacts between the two strands. Moreover, in case of highly entangled or knotted starting configurations, the segregation time is several orders of magnitude larger than expected for a purely diffusive process, thus clearly highlighting the importance of topological constraints. Finally, we also give a brief account on the role of hydrodynamics.

15 min. break

CPP 57.7 Thu 16:45 H40

Static and dynamic properties of polymer melts: equilibrium and non-equilibrium molecular dynamics studies — •Hsiao-Ping Hsu and Kurt Kremer — Max Planck Institute for Polymer Research

We present a detailed study of the static and dynamic behavior of semiflexible polymer chains in a melt starting from the previously obtained fully equilibrated high molecular weight polymer melts by a hierarchical strategy. For semiflexible chains in a melt, we see that results of the mean square internal distance, the probability distributions of the end-to-end distance, and the chain structure factor are all described very well by the theoretical predictions for ideal chains to some extent. We examine the motion of monomers in polymer melts by molecular dynamic (MD) simulations using the ESPResSo++ package. The scaling predictions of the mean square displacement of monomers based on the Rouse model, and the reptation theory are verified, and the related characteristic relaxation time scales are determined. We also check the topological structures of polymer chains through the primitive path analysis (PPA), and give the evidence that the entanglement length determined through PPA in the standard expression of the plateau modules is consistent with the value obtained from stresses using the Green-Kubo relation. Finally, the non-linear viscoelastic properties of deformed polymer melts after a step uniaxial elongation and the conformational changes of chains during the relaxation process are investigated through a non-equilibrium MD study. We acknowledge the cooperation of G. Zhang, T. Stuehn, and K. Ch. Daoulas.

CPP 57.8 Thu 17:00 H40

Knots as Topological Order Parameter for Semiflexible Polymers — •Martin Marenz and Wolfhad Janke — Institut für theoretische Physik, Leipzig, Germany

We used a combination of the multicanonical Monte Carlo algorithm and the replica-exchange method to investigate the phase diagram of a semiflexible polymer in dependence of the polymer stiffness. We found a novel phase in the phase diagram which is best described by the knot type of the polymer conformation. Almost all conformations in these phases have the same knot type after applying a procedure which connects the termini of the polymer. Therefore, they are thermodynamically stable and considerable different from the knots found in the swollen and globular phase of flexible polymers. We also showed that a derivative of the Alexander polynomial is a well suited order parameter to distinguish the *knotted* phases. Moreover, the transitions into the knotted conformations exhibit a phase coexistence, but happen at an almost constant mean total energy, hence we observed no latent heat.

CPP 57.9 Thu 17:15 H40

Packing Length Dependence of Chain Dynamics in Polymer Melts near the Unentangled-Entangled Crossover — •Herwin Jerome Unidad[1], Michaela Zamponi[1], Oxana Ivanova[1], Lutz Willner[2], Wim Pyckhout-Hintzen[2], Andreas Wischnewski[2], Dieter Richter[2], and Lewis J Fetters[3] — [1]JCNS, Outstation at MLZ, Forschungszentrum Juelich, Garching, Germany — [2]JCNS-1/ICS-1, Forschungszentrum Juelich, Juelich, Germany — [3]Department of Chemical and Biological Engineering, Cornell University, Ithaca, New York

Recently, we showed that the ratio between the critical molecular weight (Mc) and the entanglement molecular weight (Me) does not have the universal value of 2 for all polymer melts but rather shows a subtle dependence on the so-called packing length (p). All three parameters are important in describing the rheology and chain dynamics of polymer melts. With this, the packing length seems to be an important length scale for describing the non-universality of chain dynamics. To clarify this role, we performed neutron spin echo experiments on two polymer series with various molecular weights and different packing lengths. We obtained a good description of the measured intermediate scattering function using the Rouse model by suppressing long-wavelength internal modes. We then examine how this mode suppression could proceed as a function of both the chain length and the packing length. These findings are explained in the framework of earlier ideas on entanglement formation.

CPP 57.10 Thu 17:30 H40

Disentanglement of polymers under shear — Maciej Kawecki[1], Philipp Gutfreund[2], Franz Adlmann[1], Stephane Longeville[3], Alain Lapp[3], Piotr Zolnieczuk[4], Peter Falus[2], and •Max Wolff[1] — [1]Department for Physics and Astronomy, Uppsala University, Sweden — [2]Institut Laue-Langevin, Grenoble, France — [3]Institut Leon Brillouin, Scala, France — [4]Oak Ridge National Laboratory, Oak Ridge, USA

Neutron Spin Echo spectroscopy provides unique insight into molecular and sub-molecular dynamics in soft matter. In polymer physics a stress plateau is observed for increasing shear rate, which might be explained by an entanglement-disentanglement transition and change the dynamics of the chains drastically. Neutron Spin Echo provides information about entanglement length and degree by probing the local dynamics of the polymer chains. Combining shear experiments and neutron spin echo is challenging since, first the beam polarisation has to be preserved during scattering and second, Doppler scattered neutrons may cause inelastic scattering. We demonstrate that a high beam polarisation can be preserved and present SANS data revealing shear-induced conformational changes in highly entangled polymers as well as Spin Echo measurements indicating an disentanglement transition under shear.

CPP 57.11 Thu 17:45 H40

Extensional and shear rheology as a powerful tool for characterisation of physical networks in polymer nanocomposites — •Milan Kracalik — Johannes Kepler University Linz, Institute of Polymer Science, Altenberger Str. 69, 4040 Linz, Austria

Polymer nanocomposites are an interesting class of materials, in particular in the field of light weight construction. With increasing knowledge about proper processing protocol and resulting nanocomposite structure and property profile, respectively, it is possible to utilize polymer nanocomposites in many applications like automotive or aerospace industry. During material development procedure, rheological investigation possesses crucial information about material structure/performance already in the processing stage. Therefore, right compilation and interpretation of rheological measurements can significantly speed up the developing procedure. In this contribution, selected polymer nanocomposites have been characterized by both extensional as well as shear rheology. Using novel evaluation of oscillatory shear flow data, it was possible to correlate data of shear rheometry with those of elongational rheometry and, consequently, to obtain complex rheological information about different physical networks of nanopartikel in polymer matrix.

CPP 57.12 Thu 18:00 H40

Co-non-solvency of smart polymers: Physical concepts and computer simulations — •Debashish Mukherji and Kurt Kremer — Max-Planck-Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Smart polymers are a modern class of soft materials that show drastic changes in their physical properties by a slight change in external stimuli. One such phenomenon is known as co-non-solvency. Co-non-solvency occurs when a polymer is added to a mixture of two (perfectly) miscible and competing good solvents. As a result, the same polymer collapses into a globule within intermediate mixing ratios. More interestingly, polymer collapses when the solvent quality remains good or even gets increasingly better by the addition of the better cosolvent [1]. This puzzling phenomenon, where the solvent quality is completely decoupled from the polymer conformation, is driven by strong local preferential adsorption of better cosolvent with the polymer [1,2]. Because a polymer collapses in good solvent, the depletion forces, that are responsible for poor solvent collapse, do not play any role in describing co-non-solvency [3]. Furthermore, it will be presented that this phenomenon can be understood within a universal (generic) concept. Therefore, a broad range of polymers is expected to exhibit co-non-solvency and the specific chemical details do not play any role in understanding these complex conformational behaviors [4].

[1] D. Mukherji and K. Kremer, Macromolecules (2013). [2] D. Mukherji, et al. Nat. Commun. (2014). [3] T. E. de Oliviera, et al., Soft Matter (2015). [4] D. Mukherji, et al, JCP (2015).

CPP 57.13 Thu 18:15 H40

PNIPAM dynamics in water-methanol mixtures — •Konstantinos N. Raftopoulos[1], Konstantinos Kyriakos[1], Olaf Holderer[2], Oxana Ivanova[2], Michael Ohl[3], Peter Müller-Buschbaum[1], and Christine Papadakis[1] — [1]Physik-Department, Technische Universität München, Garching, Germany — [2]JCNS at Outstation MLZ, Garching, Germany — [3]JCNS at Outstation Oak Ridge, Tennessee, USA

In aqueous solutions, at low temperatures, the hydrophilic groups of Poly(N-isopropylacrylamide) form H-bonds with the water molecules and the polymer dissolves. Above the cloud point, the chain dehydrates and phase-separates. Although the polymer dissolves well in methanol too, the cloud point in water-methanol mixtures decreases considerably with respect to that in aqueous solutions. The phenomenon is termed cononsolvency. The physical mechanisms behind the process are still not clear and even less is known about the dynamics. Aiming to shed some light in this question, we followed the segmental dynamics of the polymer in water-methanol mixtures by neutron spin echo spectroscopy. The experiments were performed 2 and 5 K below the cloud points, in a temperature region where the solution is in θ-conditions. Methanol slows down the segmental dynamics of the polymer, but there is no evidence for a change of the mobility mechanism. The deceleration is more pronounced at higher polymer concentrations.