

CPP 21: Polymer dynamics

Time: Tuesday 9:30–13:00

Location: C 264

CPP 21.1 Tue 9:30 C 264

Self-Entanglement of a Long Polymer Chain — ●DIDDO DID-
DENS, ALBERT JOHNER, and JÖRG BASCHNAGEL — Institut Charles
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We study the effective interaction between the two halves of a long polymer chain under Θ -conditions by both Monte Carlo and Molecular Dynamics simulations. It is well known that in good (poor) solvents, different chain segments repulse (attract) each other, whereas these two opposing effects roughly cancel in the vicinity of the Θ -point. However, the *topological* self-interaction of long polymer chains under these conditions is less clear, which motivated our present analysis.

In a first step, we analyze structural properties such as the number of monomeric contacts between the two halves of the chain as well as characteristic topological quantities. Subsequently, we focus on the dynamical processes leading to the disengagement of the two halves after cutting the chain in the middle. This question is relevant for stimuli-responsive materials, in which e. g. the central bond of a long polymer chain is cleaved photochemically. Another motivation stems from biological issues such as the enzymatic cutting of long DNA/RNA strands in a crowded medium, which also involves the disengagement of distinct parts of long polymer chains. Finally, we will give a brief account on other architectures such as polymer stars.

CPP 21.2 Tue 9:45 C 264

Numerical rate theory approach to polymer escape — ●HARRI
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The polymer escape problem in an external double well potential is studied. The polymer is known to cross the energy barrier in a coiled form below critical length N_C and in a stretched form above N_C , corresponding to so called "kink" solution in instanton theory [1,2]. We perform Brownian dynamics simulations to obtain the crossing rate \mathcal{R}_{MD} as a function of the chain length N and the spring constant K . We numerically find the minimum energy path of the transition and by using the harmonic approximation of transition state theory recover the crossing rate \mathcal{R}_{HTST} agreeing with the simulations up to N_C . Above N_C the energy barrier of the transition becomes flat so the crossing rate by harmonic approximation fails to give the quantitatively correct rate. We study the diffusive mechanism on top of the flat barrier to obtain dynamical corrections $f(N)$ for the harmonic approximation of the crossing rate $\mathcal{R}' = f(N)\mathcal{R}_{HTST}$.

[1] S. K. Lee and W. Sung, *Phys. Rev. E* **63**, 021115 (2001).

[2] H. Mökkönen, T. Ikonen, H. Jonsson, T. Ala-Nissila, *J. Chem. Phys.* **140**, 054907 (2014).

CPP 21.3 Tue 10:00 C 264

Dynamics of Living Polymers — ●ALI MALEK. and REINER KREE
— Georg August Universität Göttingen

Living polymers constitute an important class of active soft matter. They refer to a large class of polymers whose lengths are ever changing. These changes in length, in many cases, is due to addition (polymerization) or subtraction (depolymerization) of monomer units at their active ends. We construct an analytically tractable model for a flexible chain (Rouse Model), which grows in length by a power law $l(t) = \gamma t^\alpha$. We find asymptotically exact solutions in the long-time regime, which allow to calculate the dynamical structure and the rheological properties both for free and forced chains. Our analytical results agree with simulations for times larger than a crossover time t_c . As a result we give new scaling laws for end-to-end distance correlation, the viscosity and the force against a wall.

CPP 21.4 Tue 10:15 C 264

Studying linear and nonlinear viscoelasticity of highly entangled polymer melts with computer simulations — ●GUOJIE
ZHANG, TORSTEN STUEHN, KOSTAS DAOULAS, and KURT KREMER —
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Mainz, Germany

Viscoelasticity of entangled polymeric liquids is important for both basic science and industrial applications, e.g. polymer processing. Partic-

ularly important is the regime of nonlinear viscoelastic behavior, which however is still not well understood. Using computer simulations, we focus on obtaining a molecular understanding of chain retraction process in entangled polymers under a large step-strain. Benefiting from a simulation scheme recently developed, equilibrated configurations of high molecular weight polymer melts (number of entanglements per chain $Z > 100$) described with microscopic details are generated. Regimes of linear and nonlinear viscoelasticity of entangled polymers are addressed by imposing a stepwise strain on these samples. In those highly entangled melts, a clear plateau modulus is observed in the linear regime (e.g. small step strain). A quantitative agreement between value of entanglement length estimated from the plateau modulus and that measured from primitive path analysis is found. To study chain retraction process in nonlinear regime, we monitor the evolution of entanglement densities and single-chain structure factor in a largely strained sample.

CPP 21.5 Tue 10:30 C 264

Relaxation of Semiflexible Polymers with Branching, Loops, and Dihedral Interactions — ●MAXIM DOLGUSHEV — Theoretical
Polymer Physics, University of Freiburg, Germany

This talk concentrates on recent advances in the mathematical-analytical theory of semiflexible polymers[1-3]. Based on the framework of semiflexible treelike polymers[4] as well as on its further extensions, the following results of new investigations will be presented:

(1) The study of the orientational relaxation of the single segments in semiflexible dendrimers [1]. Here, focusing on the NMR relaxation functions, it has been shown that including bending rigidity allows one to distinguish between segments for different dendrimer's shells, whereas the fully flexible model does not show such a feature.

(2) The basic model of Ref. [4] involves only angular restrictions. A next step forward is devoted to the investigation of the role of dihedral constraints. Remarkably, also in this, more complex situation one can obtain analytic results, as we show for linear chains [2].

(3) The semiflexibility constraints are introduced in a mean-field way [2,4], i.e. they do not reduce the number of degrees of freedom. However, for polymers with loops the closure conditions represent strict holonomic constraints. These can be taken into account based on the penalty function method [3].

[1] D.A. Markelov et al., *J. Chem. Phys.* **140**, 244904 (2014).

[2] M. Dolgushev, A. Blumen, *J. Chem. Phys.* **138**, 204902 (2013).

[3] M. Dolgushev et al., *J. Chem. Phys.* **141**, 014901 (2014).

[4] M. Dolgushev, A. Blumen, *J. Chem. Phys.* **131**, 044905 (2009).

CPP 21.6 Tue 10:45 C 264

Entropic segregation of ring polymers confined to a cylinder
— ●ELENA MININA and AXEL ARNOLD — Institute for Computational
Physics, University of Stuttgart, Allmandring 3, 70569, Stuttgart, Ger-
many

Newly replicated circular chromosomes segregate inevitably during cell division in elongated primitive bacteria such as E.coli. Although many proteins surrounding the chromosomes are possibly involved in this process, the chromosomes would also move apart without these. The reason is, that overlapping chromosomes lose conformational entropy, and the only chance to gain this entropy is to segregate. In the present study we investigate entropic segregation of ring polymers confined to a cylinder. Using MD simulations and renormalized Flory theory, we estimate how fast overlapping rings segregate and show that the obtained results can be explained by previous results on linear polymers and a simple rescaling argument. This rescaling is based on an argument that a ring can be treated as two independent chains trapped in smaller subcylinders. Our results indicate that this argument can be extended to arbitrary amounts of overlapping chains occupying different amounts of space. The polymers however start segregation only after the initial symmetry of full overlap has been broken. This induction happens by rearranging the polymer ends. We previously showed for linear chains, that this induction time grows exponentially with the polymer length, making segregation a rather slow process. The ring topology however facilitates the segregation process reducing the induction time significantly compared to linear polymers.

CPP 21.7 Tue 11:00 C 264

Chain Dynamics near the Unentangled-Entangled Transi-

tion — ●HERWIN JEROME UNIDAD¹, MICHAELA ZAMPONI¹, OXANA IVANOVA¹, LUTZ WILLNER², WIM PYCKHOUT-HINTZEN², ANDREAS WISCHNEWSKI², DIETER RICHTER^{1,2}, and LEWIS FETTERS³ — ¹JCNS, Outstation at MLZ, Forschungszentrum Juelich, Garching, Germany — ²JCNS-1/ICS-1, Forschungszentrum Juelich, Juelich, Germany — ³Department of Chemical and Biological Engineering, Cornell University, Ithaca, New York

It is well-known that the transition between unentangled to entangled dynamics occurs at a critical molecular weight (M_c), typically assumed to be twice the entanglement molecular weight (M_e). Recently, we have reiterated a previous finding that the ratio between M_c and M_e doesn't assume a universal value of 2 for all polymer melts but in fact shows a dependence on the packing length (p). Notwithstanding, the physical picture behind the independent existence of M_e and M_c remains unclear.

Here, we reinvestigate the problem by probing the microscopic dynamics of polybutadiene melts near the transition by neutron spin echo spectroscopy. We analyze the dynamic structure factor within the framework of the Rouse model with modified mode spectrum. We find that suppression of long-wavelength modes in the spectra already occurs for melts with molecular weight above M_e , even if they are still below M_c . We rationalize these results based on earlier ideas on entanglement formation. We also apply this framework in confronting our viscosity data for various polymers.

15 min. break.

CPP 21.8 Tue 11:30 C 264

Model-free information on polymer dynamics from neutron backscattering — ●FELIX ROOSEN-RUNGE and TILO SEYDEL — Institut Laue-Langevin, Grenoble, France

Quasi-elastic and inelastic neutron backscattering is well-suited to study dynamics at time scales of several pico- to nanoseconds and nanometer length scales. Dynamical transitions in polymers versus temperature or time can be monitored via the mean-squared displacement obtained in a model-free way from scans of the elastic scattering at zero neutron energy transfer. Recent instrument updates at the spectrometer IN16B (Institut Laue-Langevin, Grenoble) allow for so-called inelastic fixed window scans (IFWS) at fixed non-zero neutron energy transfer [1]. In combination with the achieved high flux, IFWS allow to monitor dynamics in more detail, e.g. focusing on tunnel spectra. A generalized mean-squared displacement from IFWS can be used as a model-free indicator of confined and anomalous diffusion [2]. We outline the power of the IFWS using analytical results for the measured quantities. Our results allow a direct evaluation of the effect of instrumental resolution on the measured mean-squared displacement. We discuss further application of IFWS such as monitoring dynamical heterogeneities in the sample.

[1] B. Frick et al., Nucl. Instrum. Meth. A 669, 7 (2012)

[2] F. Roosen-Runge, T. Seydel, EPJ Web of Conferences, in press

CPP 21.9 Tue 11:45 C 264

Shear-induced ordering or disentanglement? — ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

Rheo NMR permits the investigation of molecular dynamics in a wide range of correlation times of polymer melts or solutions under shear in a Couette cell. transverse relaxation T_2 is strongly affected by the slow dynamics of polymer chain segments. One would expect a strong shortening of T_2 as a result of shear-induced ordering of the polymer chains in a Couette cell. However the opposite is observed T_2 becomes longer in melts of poly(propylene) and solutions of poly(styrene sulfonate), which can be explained by a loss of entanglements as a result of the shear.

CPP 21.10 Tue 12:00 C 264

Bottlebrush melts — ●JAROSLAW PATUREJ^{1,2}, SERGEI SHEIKO³, and MICHAEL RUBINSTEIN³ — ¹Leibniz-Institut of Polymer Research, Dresden, Germany — ²Institute of Physics, University of Szczecin, Szczecin, Poland — ³Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA

A bottlebrush polymer is a branched macromolecule composed of a linear chain (backbone) with sidechains densely tethered to it. High grafting density of side chains gives rise to various unique structural properties, such as highly extended conformations of their backbones and tunable character of their stiffness and rheological properties with degree of polymerization of the side chains. We conducted coarse-

grained molecular dynamics simulations to determine how the number of Kuhn segments in a bottlebrush backbone L and in the sidechains N affect size, stiffness, and structure of these molecules. We found that the size (mean-squared radius of gyration and end-to-end distance) and persistence length of bottlebrushes in a melt state scales as $N^{1/2}$.

CPP 21.11 Tue 12:15 C 264

Thermophoresis of linear polymers: is it Rouse or Zimm? —

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Polymer thermophoresis, the migration of dissolved polymer chains along a temperature gradient, is independent of molar mass for sufficiently long chains. Systematic experiments in our group have shown that the relevant units are not the monomers but rather correlated entities of the size of the Kuhn segment. The molar mass independent thermophoretic mobility has been interpreted in the literature in terms of a Rouse-type dynamics based on a draining coil model. Recent results reported for linear chains, crosslinked microgels, and core-shell particles of the thermoresponsive polymer PNIPAM together with older data for copolymers suggest, however, a non-draining coil with hydrodynamic coupling (Zimm). We show that the relevant thermophoretic interactions decay $\propto r^{-2}$ and, thus, much slower than the short-ranged ($\propto r^{-6}$) van der Waals interactions. In consequence, thermophoresis results from volume rather than surface forces. The hydrodynamic flow penetrates only into a boundary layer of the coil and causes tangential stress on the coil as a whole, and not on the scale of the individual segments. The experimentally observed molar mass independence of the thermophoretic mobility naturally follows from the model.

CPP 21.12 Tue 12:30 C 264

Water enhanced dynamics of cellulose paper — ●BJÖRN KUTTICH, ANN-KATHRIN GREFE, and BERND STÜHN — Experimental Condensed Matter Physics, TU Darmstadt, Germany

With over 50 weight percent cellulose represents the main part of plant cells. In terms of soft matter physics it is a rather complex and important biopolymer. Corresponding to its biological application cellulose is insoluble in water, but due to the monomers hydroxy groups it has a hygroscopic tendency. In industrial applications cellulose is the major component of paper, where water uptake can become important during manufacturing or processing.

While hydration effects on crystalline cellulose are already investigated the dynamics in cellulose papers, where highly oriented cellulose fibres are used, are less understood. In this work we therefore focus on a systematic variation of the hydration level of cellulose paper with different porosities. By using a hydration chamber for the humidification process, in which the relative air humidity can precisely be tuned, a water content in the sample between a few weight percent of water up to almost 20 percent can be realised. While our investigations by dielectric spectroscopy show only minor influences of the papers porosity, accelerated dynamics due to the presence of water become apparent. In contrast to the acceleration also the suppression of a local relaxation mode, which is not observed for crystalline cellulose, is found. To monitor water uptake of the sample and its characteristic time scale, all measurements are accompanied by time resolved weighing experiments, which reveal an uniform hydration process.

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Glassy dynamics of Poly(2-Vinyl-Pyridine) brushes with varying grafting density — ●NILS NEUBAUER¹, RENÉ WINKLER²,

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The molecular dynamics of poly(2-vinyl-pyridine)(P2VP) brushes is measured by Broadband Dielectric Spectroscopy (BDS) in a wide temperature (250 K–440 K) and broad spectral (0.1 Hz–1 MHz) range. This is realized using nanostructured highly conductive silicon electrodes being separated by silica spacers as small as 35 nm. A “grafting-to”-method is applied to prepare the P2VP-brushes with five different grafting densities (0.03 nm⁻²–0.12 nm⁻²), covering the “true-brush” regime with highly stretched coils and the mushroom-to-brush transi-

tion regime. The film thickness ranges between 1.8 to 7.1 (± 0.2) nm. Two relaxations are observed, an Arrhenius-like process being attributed to fluctuations in the poly(glycidyl methacrylate) (PGMA) linker used for the grafting reaction and the segmental dynamics (dy-

amic glass transition) of the P2VP brushes. The latter is characterized by a Vogel-Fulcher-Tammann dependence similar to bulk P2VP. The results can be comprehended considering the length scale on which the dynamic glass transition (≤ 1 nm) takes place.