

CPP 23: Poster: Polymer Dynamics

Time: Wednesday 11:00–13:00

Location: Poster A

CPP 23.1 Wed 11:00 Poster A

Theoretical Investigations of Semiflexible Dendrimers — ●FLORIAN FÜRSTENBERG, MAXIM DOLGUSHEV, and ALEXANDER BLUMEN — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Deutschland

Dendrimers are branched, highly regular synthetic polymers. Here we investigate the mechanical relaxation of semiflexible dendrimers of arbitrary functionality f and generation g . We focus on the matrix corresponding to their potential energy^[1] and show that the semi-analytical determination of its (highly degenerate) spectrum can be drastically simplified by using a suitable decomposition scheme^[2].

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

[2] F. Fürstenberg, M. Dolgushev, and A. Blumen, to be published.

CPP 23.2 Wed 11:00 Poster A

Simulation of externally stimulated polymer chains — ●KIRSTEN DAMMERTZ, MASOUD AMIRKHANI, and OTHMAR MARTI — Institute of Experimental Physics, Ulm University

In this contribution, we explore by atomistic Molecular Dynamics (MD) simulations the possibility to stimulate and align polymer molecules by electric fields. As model polymers we use various pyridine-containing homopolymers adsorbed on graphite. The primary objective of our study is to investigate conformational changes, dipole reorientations and the trajectory of the molecules. Based on our simulations, we quantify the influence of the chemical composition as well as the strength and orientation of the external field. Polymer-specific conformational characteristics are discussed.

All MD simulations are carried out by means of the LAMMPS software package. To define the potential functions and force field parameters, we apply the polymer consistent force field (pcff).

CPP 23.3 Wed 11:00 Poster A

Controlling adsorption of semiflexible polymers — ●TOBIAS KAMPF and JAN KIERFELD — Technische Universität Dortmund, Deutschland

We investigate the adsorption of single semiflexible polymers on planar and structured substrates. Using Monte-Carlo simulations we determine the critical potential strength for square-well adsorption potentials over a wide range of persistence lengths.

For a planar substrate we find a maximum of the critical potential strength for persistence lengths comparable to the potential range. In the stiff limit, we derive an analytical result, which agrees with the simulation results. We also investigate the influence of an additional surface curvature for adsorption on a sphere and on a "washboard" surface.

CPP 23.4 Wed 11:00 Poster A

The behaviour of a nanoparticle in a polymer melt — ●ANJA KUHNHOLD and WOLFGANG PAUL — Institut für Physik, Martin-Luther-Universität, 06099 Halle

The rheology of polymer melts can be observed by looking at the behaviour of suspended particles (microrheology). For this purpose MD simulations of a bead-spring model including one nanoscopic particle are performed. The dynamic behaviour of the nanoparticle is determined by its mean square displacement (MSD) and velocity autocorrelation function (VCF). Using a generalized Stokes-Einstein equation, we observe the complex shear modulus $G^*(\omega)$ of the melt. Furthermore, the influence of different particle sizes, interaction strengths and polymer chain lengths is studied. The results are in agreement with predictions of the Rouse model in the low frequency regime. Additional structural information of the polymer melt in the vicinity of the nanoparticle are given by radial distribution functions (RDFs).

CPP 23.5 Wed 11:00 Poster A

Ring Rotation Dynamics of Ferrocene and Ferrocene-containing Polymers — ●MARKUS APPEL^{1,2}, BERNHARD FRICK², TINKA SPEHR¹, and BERND STÜHN¹ — ¹TU Darmstadt (Germany) — ²Institut Laue-Langevin, Grenoble (France)

Ferrocene is an organometallic compound consisting of two cyclopentadienyl rings with a reversibly oxidizable iron atom sandwiched in between. Bulk ferrocene shows a structural phase transition at 164 K

(triclinic to monoclinic). Ferrocene-containing polymers are of high interest for applications in nanotechnology as they combine polymeric with metallic properties and can show ferromagnetic susceptibilities.

As an important aspect of the characterization of ferrocene-containing polymers we study the cyclopentadienyl ring rotation dynamics. We aim to compare the ring rotation of bulk ferrocene to ferrocene contained in polymers using inelastic neutron scattering.

Past neutron scattering studies of the ring rotation dynamics in bulk ferrocene mainly focussed on the high temperature phase [1]. We present neutron time-of-flight and backscattering experiments including the new possibility of inelastic fixed window scans (IFWS) on IN16 at the ILL [2] of the low temperature phase of ferrocene. The extracted correlation times and activation energy of the rotation dynamics are found to be considerably higher than for the high temperature phase.

Additionally, we present first measurements on the ferrocene-containing polymer poly(vinylferrocene).

[1] Gardner et al., *Chem. Phys.* 57, 453 (1981)

[2] Frick et al., *Nucl. Inst. and Methods A*, accepted for publication

CPP 23.6 Wed 11:00 Poster A

Experimental and theoretical study of the yellowing of ancient paper — ADRIANO MOSCA CONTE¹, OLIVIA PULCI^{1,2}, ARKADIUSZ KNAPIK³, JACEK BAGNIUK³, JOANNA ŁOJEWSKA³, and ●MAURO MISSORI⁴ — ¹ETSF, Dept. of Physics, Università di Roma Tor Vergata, Rome, Italy — ²Institute of Structure of Matter, National Research Council, Rome, Italy — ³Faculty of Chemistry, Jagiellonian University, Krakow, Poland — ⁴Institute of Complex Systems, National Research Council, Rome, Italy

Paper has been the most widely used writing support since the Middle Ages. The preservation of ancient books and documents must be based on an advanced knowledge of the paper degradation processes. Yellowing causes major damage for the aesthetic appearance of ancient paper and it is due to cellulose oxidation, a complex process with many possible products, some of them chromophores, still to be clarified. In this talk, we will present experimental ultraviolet-visible spectra of ancient papers of the 15th century and, as reference, modern samples artificially aged under different environmental conditions. With the aid of ab-initio Time-Dependent Density Functional Theory calculations, we investigate several possible oxidized forms of cellulose polymers. Through the comparison of measured and calculated optical spectra, we identify those oxidized groups which act as chromophores. Our non-destructive approach could be used as a powerful method to estimate the state of degradation of historical papers and in the research of bleaching and reducing agents to be employed in the restoration practice.

CPP 23.7 Wed 11:00 Poster A

Theoretical aspects of branched semiflexible polymers — ●MAXIM DOLGUSHEV and ALEXANDER BLUMEN — Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Deutschland

In recent years the theory of semiflexible polymers has seen advances in the mathematical-analytical study of branched structures[1]. Nowadays one can model semiflexible treelike polymers, in which the branching points may have arbitrary functionality and stiffness[2,3]. A further step forward concerns the investigation of semiflexible polymers containing loops, i.e. obeying closure conditions. The treatment of such objects is rendered possible through the maximum entropy principle[4], as we have recently shown for rings[5].

[1] M. Dolgushev, G. Berezovska, and A. Blumen, *Macromol. Theory Simul.* 20, 621 (2011)

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

[3] M. Dolgushev and A. Blumen, *J. Chem. Phys.* 132, 124905 (2010).

[4] R. G. Winkler, L. Harnau, and P. Reineker, *J. Chem. Phys.* 101, 8119 (1994).

[5] M. Dolgushev, G. Berezovska, and A. Blumen, *J. Chem. Phys.* 135, 094901 (2011).

CPP 23.8 Wed 11:00 Poster A

Influence of pressure on deviations of chain dynamics from the Rouse model: A molecular dynamics simulation

study of poly(dimethylsiloxane) and polybutadiene melts. — ●PATRICK HENRITZ¹, DMITRY BEDROV², GRANT SMITH², and MICHAEL VOGEL¹ — ¹Intitut für Festkörperphysik, TU Darmstadt, 64289 Darmstadt, Germany — ²Department of Material Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

Molecular dynamics simulations of poly(dimethylsiloxane) (PDMS) and polybutadiene (PBD) melts have been performed as a function of pressure. At atmospheric pressure the single-chain coherent dynamic structure factor of PBD exhibited greater deviation from ideal Rouse behavior than PDMS, in agreement with neutron spin echo (NSE) measurements. Chain dynamics in both PDMS and PBD exhibited increasing deviations from Rouse predictions with increasing pressure. These deviations were found to correlate with the free volume fraction in the melt, implying that inter-chain correlations and not intrinsic rotational barriers are mainly responsible for non-ideal chain dynamics in polymer melts.

CPP 23.9 Wed 11:00 Poster A

Structure and Dynamics of Polyethylene Glycol Polymer Rings — ●SEBASTIAN GOOSSEN¹, ANA RITA BRÁS¹, WIM PYCKHOUT-HINTZEN¹, ANDREAS WISCHNEWSKI¹, JÜRGEN ALLGAIER¹, DIMITRIS VLASSOPOULOS^{2,3}, and DIETER RICHTER¹ — ¹Jülich Centre for Neutron Science JCNS (JCNS-1) & Institute for Complex Systems (ICS), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany — ²FORTH, Institute of Electronic Structure and Laser, Heraklion, Crete, 71110, Greece — ³University of Crete, Department of Materials Science and Technology, Heraklion, 71003, Greece

The structural analysis of highly pure polyethylene glycol (PEG) polymer rings in a theta solvent with SAXS and with SANS in the melt showed a significantly more compact structure for the ring polymers compared to their linear equivalents of same molecular weight. The dynamical behavior of ring polymers and linear chains was studied in the melt by NSE spectroscopy. In comparison the ring polymers showed a significantly faster center of mass diffusion than the linear chains. This turns out to be an explicit violation of the Rouse model. Furthermore blends of ring polymers in a matrix of linear polymer chains were investigated with these techniques. For PEG ring polymers with a molecular weight above the entanglement molecular weight M_e the observed center-of-mass diffusion in the linear matrix is surprisingly low compared to PEG polymer rings below M_e . This leads to the question if, due to the interpenetration of ring polymers and linear polymer chains, collective diffusion occurs in these blends.

CPP 23.10 Wed 11:00 Poster A

Intimate coupling of heterogeneous dynamics and structural relaxation independent of molecular weight, temperature, and pressure. — ●ANDRÉ BORMUTH and MICHAEL VOGEL — Hochschulstraße 6, 64289 Darmstadt

Performing molecular dynamics simulations for an all-atom force field, we study the segmental or, equivalently, α relaxation of poly(propylene oxide) chains consisting of $N = 2 - 100$ monomer units. In particular, we analyze the dependence of the α relaxation time τ_α on molecular weight, temperature, and pressure on the basis of incoherent intermediate scattering functions. Regarding dynamical heterogeneities, we monitor the non-Gaussian parameter and the weight-averaged mean cluster size. Both quantities exhibit a maximum for intermediate times, where the peak height and the peak time τ_p increase upon cooling and pressurizing. Interestingly, we find that data for different chain length, T , and p collapse onto a single Master curve $\tau_p = a * \tau_\alpha^b$, suggesting a close relation between structural relaxation and spatially heterogeneous dynamics. The exponent b turns out to be the same for the non-Gaussian parameter and the weight-averaged mean cluster size, indicating evidence for an underlying basic principle. Using the coupling model from Ngai et al. we discuss a way of tracing back the Parameters a and b to physical quantities.

CPP 23.11 Wed 11:00 Poster A

Weakly Segregated Polymers in Electric Fields — ●CHRISTIAN W. PESTER¹, MARKUS RUPPEL², VOLKER S. URBAN³, and ALEXANDER BÖKER¹ — ¹DWI an der RWTH Aachen and Lehrstuhl für Makromolekulare Materialien und Oberflächen, RWTH Aachen, D-52056 Aachen, Germany — ²Chemical Sciences Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA. — ³Neutron Scattering Science Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, TN 37831, USA.

We elaborate on the effects of electric fields on weakly phase separated

block copolymers in non-selective solvents. In a series of theoretical papers E. Gurovich proposed the reorientation of individual copolymer chain segments due to the external stimulus. The resulting anisotropic distortion of chain conformations results in orientation-dependent alterations of gyration radii with respect to the electric field vector. The resulting anisotropic character of correlation holes is expected to have a profound effect on the small-angle scattering patterns. Indeed, in-situ synchrotron small-angle X-ray scattering (SAXS) at the ESRF in Grenoble allowed us to identify some of the theoretically predicted consequences these elliptical gyration radii would have on the scattering signal, i.e. on domain spacings and order-disorder transitions.

CPP 23.12 Wed 11:00 Poster A

Light-induced deformation of amorphous azo-polymers: structure-property relation — VLADIMIR TOSHCHÉVICOV¹, JAROSLAV ILNYTSKYI², and ●MARINA SAPHIANNIKOVA¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V., Dresden, Germany — ²Institute for Condensed Matter Physics, Lviv, Ukraine

Recently, we have proposed a microscopic theory [1] of light-induced deformations in amorphous side-chain azo-polymers. The theory is able to predict a sign of the sample deformation (contraction/elongation) depending on angular distributions of chromophores in respect to the backbone. For instance, it is shown that an azo-polymer demonstrates a uniaxial elongation along the polarization vector of the light, if azobenzenes are attached to a stiff backbone and have preferable orientation perpendicular to it. This kind of behavior has been indeed observed in molecular dynamics simulations of azo-polymers with short spacers [2]. The present contribution is aimed to relate quantitatively the theoretical and simulation studies by feeding certain structural properties obtained in the simulations into a theory input. Especially, the backbone rigidity and angular distribution of chromophores have been studied at different light intensities and temperatures. This work may open a way for fine tuning of photomechanical properties of azo-polymers by modifying their chemical structure.

This work was supported by the DFG grant GR 3725/2-1.

[1] V.Toshchevnikov, M.Saphiannikova, G.Heinrich. J. Phys. Chem. B 2009, 113, 5032; [2] J. Ilnytskyi, D. Neher, M. Saphiannikova. J. Chem. Phys. 135, 044901 (2011).

CPP 23.13 Wed 11:00 Poster A

Two - point Nanorheology based on single molecule FRET in polymer PMA — ●SUBHASIS ADHIKARI, MARKUS SELMKE, and FRANK CICHOS — Molecular Nano-photonics, Inst. of Expt. Phys I, University of Leipzig

Fluorescence Resonance Energy Transfer (FRET) has been widely used in structural biology, biochemistry and in polymer science to measure the distances in very short range (2nm - 10nm) depending on the donor - acceptor pair. To study the heterogeneous dynamics in polymers near its glass transition temperature (T_g) a new technique, Two-point Nanorheology based on FRET is used in single molecule optical studies. This study will reveal the rheological information of the local environment surrounding the dye molecules at a nanometer length scale by measuring distance fluctuations. Firstly Alexa 488 (donor) and then Alexa 594 (acceptor) are attached to amino - thiol terminated polystyrene polymer by a standard synthesis and characterized by fluorescence methods. The single donor dye labeled polymer aggregates in DMF but not in toluene as detected by Fluorescence Correlation Spectroscopy (FCS) technique. Ensemble FRET and single molecule FRET (smFRET) are measured and compared to each other. The reorientation factor is calculated from fluorescent anisotropy studies.

CPP 23.14 Wed 11:00 Poster A

Filling process in cylindrical nanopores — ●MANUELA LUKAS and BERND STÜHN — Experimentelle Physik kondensierter Materie, TU Darmstadt, Germany

The aim of this work is to investigate the filling flow behavior of polymers in nanopores using time resolved Small-Angle X-ray Scattering (SAXS). The nanoporous samples consist of a polycarbonate foil with thickness 30 μm , irradiated with swift heavy ions (ion tracked polycarbonate: ITPC), treated with UV light and etched in NaOH solution. Varying the etching time the cylinder radii can be controlled. In ITPC nanopores are aligned strictly parallel. For filling experiments polydimethylsiloxane (PDMS) with three different molecular weights, ($M=28,000 \text{ g/mol}$, $M=63,000 \text{ g/mol}$, $M=139,000 \text{ g/mol}$), is used. PDMS was chosen because its electron density with $\rho = 319e/nm^3$ is different to the electron density of the matrix material polycarbonat

with $\rho = 380e/nm^3$ showing a good contrast for SAXS. The filling process is shown by the steady decrease in scattering intensity with time. It turns out that the intensity variation with time follows the Lucas-Washburn equation. The \sqrt{t} -dependency of the filling height is reproduced well throughout the whole filling process. However a quantitative analysis of the full scattering profiles reveals a remarkable deviation from the classical filling behaviour [M. Engel, B. Stühn. *J. Chem. Phys.* 132, 224502, 2010]. Furthermore the data suggest the forming of a precursorfilm.

CPP 23.15 Wed 11:00 Poster A

Specific vs. unspecific interaction and aggregation in bulk supramolecular polymers — •TINGZI YAN¹, KLAUS SCHRÖTER¹, FLORIAN HERBST², WOLFGANG BINDER², and THOMAS THURN-ALBRECHT¹ — ¹Institute of Physics, Martin-Luther University Halle-Wittenberg — ²Institute of Chemistry, Martin-Luther University Halle-Wittenberg

Hydrogen bonded supramolecular polymers have attracted much at-

tention in the past decade due to their special properties. They combine the advantages of polymers and of non-covalently bonded supramolecules with reversible structures. In general, the association behavior in solution is simpler and better understood than in the bulk. We present combined small angle x-ray scattering and rheological experiments, complemented by IR spectroscopy on a series of polyisobutylene chains terminated with hydrogen bonding units of different strengths. While in solution the functional units form specific ordered structures and large aggregates, indicative of additional demixing between the PIB chains and the functional groups. Hydrogen bonds obviously stabilize these aggregates, even at high temperatures as it is shown by IR spectroscopy. The rheological properties which vary strongly between different samples and depend strongly on temperature, result from the combined effect of supramolecular interaction and additional structure formation. The specificity on the hydrogen bonds seems to be lost in the bulk sample.