

## CPP 26 POSTER Dynamics and Diffusion

Time: Thursday 17:00–19:00

Room: P2

CPP 26.1 Thu 17:00 P2

**Influence of isotopic substitution of cyclohexane on transport coefficients of binary liquid mixtures** — ●GERHARD WITTKO and WERNER KÖHLER — Physikalisches Institut, Universität Bayreuth

In a binary system, a temperature gradient does not only lead to a heat flux but also to a mass flux. The latter effect is known as thermal diffusion, or Ludwig-Soret-effect. The Soret coefficient  $S_T$  is a measure for the concentration gradient in the stationary state, where the mass flux due to thermal diffusion is compensated by the mass flux due to Fickian diffusion. Until now there is no microscopic theory on neither thermal diffusion nor diffusion that allows to predict values of  $S_T$  or the diffusion coefficient  $D$  in liquids from molecular properties. We present experimental results on the influence of the isotopic substitution of protonated cyclohexane by perdeuterated cyclohexane in binary liquid mixtures on  $D$ ,  $S_T$  and the thermal diffusion coefficient  $D_T$ . For  $D$  we find almost the same value in both the mixture containing protonated and perdeuterated cyclohexane. In contrast to this,  $S_T$  of the mixture containing the heavier isotope is lower than  $S_T$  of the mixture containing the lighter isotope by about  $\Delta S_T = 1 \times 10^{-3} \text{K}^{-1}$  at all mole fractions.

CPP 26.2 Thu 17:00 P2

**Overlap Concentration of Polymers in a Good Solvent determined by Fluorescence Correlation Spectroscopy (FCS)** — ●UTE LIPPERT<sup>1</sup>, HEIKO ZETTL<sup>1</sup>, ALEXANDER BÖKER<sup>1</sup>, JÖRG ENDERLEIN<sup>2</sup>, and GEORG KRAUSCH<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Universität Bayreuth — <sup>2</sup>Institute for Biological Information Processing IBI 1, Forschungszentrum Jülich

For polymer solutions the dilute and concentrated regime is well investigated by light scattering, rheology, and fluorescence recovery after photo bleaching. The crossover concentration between the dilute and semi-dilute regime and the properties of solutions in the semi-dilute regime are less investigated. This concentration range is difficult to assess with the above mentioned methods. We have prepared monodisperse batches of polystyrenes labeled with a single dye molecule per chain. We use fluorescence correlation spectroscopy (FCS) to determine the diffusion behavior of these chains in solutions containing varying amounts of unlabelled chains. We are able to assign the crossover between dilute and semi-dilute for molecular weights in the range of 4 kg/mol to 1500 kg/mol. We find a scaling law for the dependence of the overlap concentration on molecular weight in agreement with theoretical predictions.

CPP 26.3 Thu 17:00 P2

**N-Alkanes confined in Nanoporous Silicon: An Infrared Spectroscopy and X-ray Diffraction Study** — ●ANKE HENSCHEL, RENÉ BERWANGER, KLAUS NORR, and PATRICK HUBER — Technische Physik, Universität des Saarlandes, 66123 Saarbrücken

The conformation and arrangement of linear hydrocarbons ( $\text{C}_{16}\text{H}_{34}$ - $\text{C}_{21}\text{H}_{44}$ ) confined in tubular pores of porous silicon (mean pore diameter 10nm) is investigated by combined infrared spectroscopy and x-ray diffraction measurements. We find distinct changes in the vibration characteristics, in the structure factor as well as the phase transition temperatures of confined n-alkanes as compared to the bulk phases.

CPP 26.4 Thu 17:00 P2

**Neutron Spectroscopy on Polymers Confined to Nanoporous Glasses** — ●ANDREAS SCHÖNHALS<sup>1</sup>, HARALD GOERING<sup>1</sup>, BERNHARD FRICK<sup>2</sup>, and REINER ZORN<sup>3</sup> — <sup>1</sup>Bundesanstalt für Materialforschung und prüfung, Unter den Eichen 87, D-12205 Berlin — <sup>2</sup>Institut Max von Laue - Paul Langevin (ILL) 6, rue Jules Horowitz, B.P. 156, F-38042 Grenoble Cedex 9 — <sup>3</sup>Forschungszentrum Jülich, Institut für Festkörperforschung, D-52425 Jülich

The behavior polymers confined to geometries of a nanometer scale has become an interesting field. Neutron scattering (NS) is valuable tool to investigate such systems because of the high penetration depth of neutrons. Incoherent NS was carried out on poly(dimethyl siloxane) and poly(methyl phenyl siloxane) confined to Sol/Gel-glasses (7.5, 5.0, 2.5 nm). To cover a broad dynamical range of the scattering function  $S(Q,E)$  time-of-flight and backscattering are combined. For the frequency range of the Boson peak the vibrations at lowest frequencies are depressed by the confinement. Elastic scans were carried out and the mean square

displacement msd was calculated. Above  $T_g$  the characteristic increase of the msd found for the bulk is strongly influenced by the confinement but for both materials in a different manner. The main influence of the confinement on  $S(Q,t)=\text{FT}(S(Q,E))$  is an broadening of  $S(Q,t)$  with increasing confinement. These results are discussed together with dielectric measurements.

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**Semiflexibility accelerates barrier crossing of hinged polymers** — ●WOLFRAM MÖBIUS, RICHARD. A. NEHER, and ULRICH GERLAND — Arnold Sommerfeld Center for Theoretical Physics (ASC) and Center for Nanoscience (CeNS), LMU München

We study the planar rotational diffusion of a semiflexible polymer with one free and one hinged end. The hinged end is subject to a periodic potential that acts on the angle of the attachment. We find that the rate for the crossing of the potential barriers is considerably larger for a semiflexible polymer than for a stiff rod. This enhancement of the rate occurs even at persistence lengths which are much larger than the contour length, so that the average end-to-end distance of the polymer is close to its limiting value. To understand this behavior we consider a system where the polymer is replaced by two elastically jointed segments. This toy model is amenable to analytic treatment and we derive expressions for the diffusion and barrier crossing rates for large bending rigidities. Both models may help to understand the thermally activated wrapping and unwrapping of DNA in nucleosomes.

CPP 26.6 Thu 17:00 P2

**Molecular dynamics in semifluorinated side-chain Polyesters as studied by Broadband Dielectric Spectroscopy** — ●J TSUWI<sup>1</sup>, F KREMER<sup>1</sup>, L HARTMANN<sup>1</sup>, D POSPIECH<sup>2</sup>, L HÄUSSLER<sup>2</sup>, and D JEHNICHEN<sup>2</sup> — <sup>1</sup>Institute for Experimental Physics I, University of Leipzig, Linné Straße 5, 04103 Leipzig, Germany — <sup>2</sup>Leibniz-Institute of Polymer Research Dresden, Hohe Straße 6, 01069 Dresden, Germany

The molecular dynamics in fluorinated side-chain polyesters was studied using Broadband Dielectric Spectroscopy in the frequency range from 0.1Hz to 10MHz and temperatures between 120 K and 500 K. The chemical structure of the main chain was selectively varied in order to elucidate the effect of backbone flexibility on the molecular motion. It is observed that the fluorinated side-chain exhibits two relaxation processes  $\gamma$  and  $\delta$ -like. The  $\gamma$  process is assigned to librational fluctuations at the terminal position of the side chain while the  $\delta$ -like process reflects a cooperative motion of the side chain as a whole. Two more processes ( $\alpha$  and  $\beta$ ) are observed, which are associated with motion of the main chain. With respect to the flexibility of the main chain, an interesting behavior is seen in the dynamics of the backbone when compared to side chain motion. Based on the analysis of the activation plot, it is concluded that a flexible main chain exhibits faster mobility in direct contrast to its side chain motion. The dielectric results are discussed in the context of micro-phase separated layered structures, supported by recent data from DSC and t-SAXS. References [1]Tsuwi, J et.al; Coll.Polym.Sci.2005,283:1321 [2]Tsuwi, J et.al; Macrom.2004,37:6050 [3]Tsuwi et.al; J.Polym.Sci.B:(submitted)

CPP 26.7 Thu 17:00 P2

**Examination of iterative phenomena during the final stages of the pinching processes of polymeric solutions** — ●RAINER SÄTTLER<sup>1</sup>, CHRISTIAN WAGNER<sup>1</sup>, and JENS EGGERS<sup>2</sup> — <sup>1</sup>Universität des Saarlandes, Experimentalphysik — <sup>2</sup>University of Bristol, School of Mathematicsol,

We examine the stretching dynamics of dilute and semidilute solutions of Polyethylene Oxide in both droplet-pinching and capillary-breakup using microscope objectives and high speed video cameras. We investigate the nature and prerequisites for the supposedly iterative formation of beads on the thinning filament, which form as the extension of the polymers saturates. We varied molecular weight, concentration, viscosity of the solvent using different mixtures of glycerol and water and initial diameter, by using different sets of plates and nozzles. Evaluation of the rich behaviour and the present phenomena has yet to prove under which circumstances and for which number of generations the behaviour really shows iterative character and whether or not the size ratios obey deterministic rules. Furthermore the causes for the growth of these in-

stabilities are not yet fully understood and there is not in all cases good agreement between experiments and existing descriptions.

CPP 26.8 Thu 17:00 P2

**The retraction process captured by SANS : segmental fluctuations** — ●EKKEHARD STRAUBE<sup>1</sup>, ARIANE BLANCHARD<sup>2</sup>, WIM PYCKHOUT-HINTZEN<sup>2</sup>, and DIETER RICHTER<sup>2</sup> — <sup>1</sup>Uni Halle-Saale — <sup>2</sup>Forschungszentrum Jülich

The retraction process of linear chains after a fast non-linear stretch was re-investigated in long polyisoprene chains, characterized by approximately 58 entanglements. For the first time, the non-linear process of retraction, along with measurable amounts of constraint-release events could be detected from time-resolved but quenched small angle neutron scattering experiments. This contrasts numerous attempts to proof already decades ago. The results are in fair agreement with a recent curvilinear description, which heavily relied on linear rheology concepts concerning path length fluctuations and constraint release mechanisms. In this work quantitative evaluations of the segmental fluctuation range are now enabled on the basis of a modified single chain approach to which dynamic parameters had been added in a defined way. Also extensive use is made in the experimental carry-through of the parameters of linear rheology. This experimental study covers various strains from linear to non-linear regime and is discussed within the framework of the original Doi-Edwards work. Inadequately described features of the scattering curves in the previous communication, mainly due to the straight comparison of theory with data without optimizing could be relieved. We conclude that segmental fluctuations are anisometric and comparison to rheology is critical.

CPP 26.9 Thu 17:00 P2

**The flow resistance of single DNA-grafted colloids as measured by optical tweezers** — ●C. GUTSCHE<sup>1</sup>, M. SALOMO<sup>2</sup>, Y.W. KIM<sup>3</sup>, R. NETZ<sup>3</sup>, and F. KREMER<sup>1</sup> — <sup>1</sup>Institut für Experimentelle Physik I der Universität Leipzig — <sup>2</sup>Institut für Biochemie der Universität Leipzig — <sup>3</sup>Physik Department TU München

Optical tweezers are microscopic tools with extraordinary precision in the determination of the position ( $\pm 2$  nm) of a colloid (diameter: 2.2  $\mu\text{m}$ ) in 3D-space and in the measurement of small forces acting on it in the range between 0.1 pN - 100 pN ( $\text{pN} = 10^{-12}$  N). In rheological experiments the flow resistance of single blank or DNA-grafted colloids is determined and compared. The length of the double-stranded (ds)-DNA varies between 1000 base pairs (bp), 4000 bp and 6000 bp corresponding to contour lengths between 340 nm and 2040 nm at a grafting density of 0.03  $\pm$  0.01  $\mu\text{m}^2/\text{chain}$ . The degree of swelling of the grafted DNA is adjusted by exchanging the ion concentration of the surrounding medium. For all examined flow velocities ranging between 100  $\mu\text{m}/\text{s}$  to 1200  $\mu\text{m}/\text{s}$  one observes an interesting deviation from Stokes law which can be traced back to a shear-dependent conformational change of the brush layer. The ratio of the effective hydrodynamic radii of DNA-grafted and blank colloids shows a pronounced dependence on the flow velocity, but as well on the length of the grafted DNA and the ionic strength of the solvent. The experimental findings are in qualitative agreement with hydrodynamic simulations based on an elastically-jointed chain model.

CPP 26.10 Thu 17:00 P2

**The interaction between single colloids grafted with DNA of varying molecular weight as measured by optical tweezers** — ●K. KEGLER<sup>1</sup>, C. GUTSCHE<sup>1</sup>, M. SALOMO<sup>2</sup>, J. REIMUTH<sup>1</sup>, V. SKOKOV<sup>1</sup>, and F. KREMER<sup>1</sup> — <sup>1</sup>Institute for Experimental Physics I, University of Leipzig, Linnéstr.5, 04103 Leipzig — <sup>2</sup>ceLectra, Deutscher Platz 5, 04103 Leipzig

Optical tweezers are used to measure the interaction forces between single blank and DNA-grafted colloids (length of DNA: 1000 base-pairs (bp), 2000 bp, 3000 bp, 4000 bp). The forces are measured in two directions, parallel and perpendicular to the axis between the two colloids under study. For blank colloids on approach repulsive forces are observed which depend in their force and range on the ionic strength of the surrounding medium. At a certain separation the colloids jump into contact. This is not the case in deionised water. DNA-grafted colloids behave in principle similarly but with a softer interaction potential. Moving DNA-grafted colloids which are in contact perpendicularly to their central axis results in stick-slip phenomena. Their intensity and dynamics are studied for different molecular weights of the DNA and in media of varying ionic concentration.

CPP 26.11 Thu 17:00 P2

**Spacer effects in branched polymer dynamics** — ●CRISTIAN SATMAREL<sup>1</sup>, CHRISTIAN VON FERBER<sup>1,2</sup>, and ALEXANDER BLUMEN<sup>1</sup> — <sup>1</sup>Theoretische Polymerphysik, Universität Freiburg, Hermann-Herder Str. 3, 79104-Freiburg, Deutschland — <sup>2</sup>Jagellonian University, Reymonta 4, 30-059 Krakow, Poland

We investigate the relation between structure and viscoelastic behavior of branched copolymeric structures, highlighting the important effects of linear spacer segments between branching points [1,2]. In the framework of generalized Gaussian models we succeed in determining the eigenvalue spectra of such networks, by developing an analytical procedure which involves an exact real-space renormalization. This allows us to relate the spectrum of the extended structure (in which the branching points are linked to each other through spacer segments) to that of a simpler, "reduced" structure without spacers. In so doing, we find that the dynamic spectra are related through a global transformation. To exemplify our procedure, we apply the method to typical hyperbranched polymers [1], as well as to randomly linked star polymers [2].

[1] C. Satmarel, C. von Ferber and A. Blumen, in preparation.

[2] C. Satmarel, C. von Ferber and A. Blumen, J. Chem. Phys. 123, 034907, 2005.

CPP 26.12 Thu 17:00 P2

**Dynamic properties of strongly confined dipolar liquids** — ●VLADIMIR FROLTSOV<sup>1</sup> and SABINE KLAPP<sup>2</sup> — <sup>1</sup>Stranski-Laboratorium fuer Physikalische und Theoretische Chemie, Sekr. C7, TU Berlin, Strasse des 17. Juni 135, 10623 Berlin — <sup>2</sup>Institut fuer Theoretische Physik, Sekr. PN 7-1, TU Berlin, Hardenbergstrasse 36, 10623 Berlin

We report molecular dynamics simulation results for a Stockmayer fluid confined to a narrow (5.0 or less particle diameters) slit pore with structureless, non-conducting walls. Translational and rotational dynamics of the dipolar particles are investigated by calculating autocorrelation functions, diffusion coefficients and relaxation times for various pore widths and directions parallel and perpendicular to the walls. The dynamical properties of the confined systems are compared to corresponding bulk properties under the condition of all compared systems having the same chemical potential. We find that the dynamic behavior inside the pore depends on the distance from the walls and can be strongly anisotropic even in globally isotropic system. Relaxation of dipole orientations and angular velocities is slower in directions parallel to the walls, especially close to the walls, and faster in perpendicular direction as compared to the bulk.

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**Length scales and mechanisms of motion in entangled polymer melts** — ●EKKEHARD STRAUBE<sup>1</sup> and RALF EVERAERS<sup>2</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, Fachbereich Physik, Germany — <sup>2</sup>Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, Dresden, Germany

Using a lattice-free dynamical Monte-Carlo method for rod-bead chains up to 512 segments as models of entangled polymer melts the monitoring of the behavior of copies of the system subjected to identical entanglement conditions but different time evolutions created by different sequences of random numbers allows the investigation of the structure of the topological constraints. The investigation of systems with different segment densities supports that the packing length governs the local motion in entangled melts. The analysis of the fluctuation structure of the copies allows the construction of the corresponding tube axis, the tube radius, the step length of the primitive path and the Rouse-like dynamics of the tube axis due to constraint release processes.

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**Structure and IR frequencies of small water clusters on Ni surfaces from DFT calculations** — ●TATIANA MURAKHTINA, LUIGI DELLE SITE, and DANIEL SEBASTIANI — Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

We present adsorption energies, geometries and harmonic frequencies of a series of water oligomers (molecule, dimer, trimer) on nickel surfaces, paying special attention to the effect of a step defect on the adsorption. These frequencies and the change in the electron density distribution upon adsorption are used to characterize the nature of the molecule-surface bonds. We use the "free energy functional" module of Car-Parinello Molecular Dynamics (CPMD) package which allows for fractional occupation numbers of all bands and compare to a standard

Density Functional Theory (DFT) calculation where  $n=2$  is imposed for all electronic states.