

CPP 15: POSTERS Dynamics and Diffusion

Time: Tuesday 14:00–16:30

Location: P3

CPP 15.1 Tue 14:00 P3

Monte Carlo simulations of chain dynamics in crosslinked polymer networks — SORIN NEDELUCU and ●JENS-UWE SOMMER — Leibniz Institute of Polymer Research Dresden, Germany

We consider the reptation dynamics of freely diffusive long chains in monomodal, crosslinked polymer networks in a dry state, and then in a swollen state. The chain terminal relaxation time shows an increase with the network degree of swelling (Q), with an exponent of about 0.37 ± 0.1 , while the center of mass diffusion coefficient remains almost constant with Q . The monomer friction coefficient decreases with Q vary rapidly, with a coefficient of approximately -1.3 , and this Q -dependence explains why the diffusion coefficient does not change. We also present a dynamical scaling theory to compare with our simulation results, and comparisons with de Gennes predictions for semi-dilute solutions. An important finding is that the number of entanglements that a chain can form seems to vary very little with the network degree of swelling, which is explained by a nonaffine deformation of the network by swelling. The case of unentangled, short chains diffusing in the polymer network, and a comparison with long chain dynamics is briefly reviewed.

CPP 15.2 Tue 14:00 P3

On the diffusion of circular domains on a spherical vesicle — PIETRO TIERNO¹, PRAJNAPARAMITA DHAR², ZIAD KHATTARI³, ●SAEEDAH ALIASKARISOHI⁴, and THOMAS FISCHER⁴ — ¹Universitat de Barcelona — ²University of California Santa Barbara — ³Hashemite University, Zarqa, Jordan — ⁴University of Bayreuth

Tracking the motion of single, two or more lipid domains on a vesicle is a rheological technique allowing to measure surface shear viscosities of vesicular lipid phases. The ratio of surface to bulk viscosity defines a viscous length scale. Hydrodynamic interactions split the motion of the domains into different modes of diffusion. The measurability of surface shear viscosities from any mode of diffusion is limited to viscous length scales between the radius of the domains and the radius of the vesicle. The measurability of the surface shear viscosity results from the sensitivity of the diffusion to surface shear viscosities and from sufficient spatial resolution to resolve the diffusive motion. Switching between the various modes of diffusion is a trade between sensitivity gained and resolution lost by the hydrodynamic interactions leaving the measurability unchanged. Measurability drops with the number of domains making single-domain rheology the best technique to measure surface shear viscosities. Ultimately confinement of the domains to small vesicles renders measurements of surface rheological properties with domain tracking rheology impossible. Our results suggest that recent experiments on the diffusion of domains on liquid ordered vesicles need to be reanalyzed.

CPP 15.3 Tue 14:00 P3

Precise determination of the mutual diffusion and Soret coefficient by a laser beam deflection technique — ●ANDREAS KÖNIGER, BÖRN MEIER, and WERNER KÖHLER — Physikalisches Institut, Universität Bayreuth

We have built a diffusion cell with optical beam deflection readout to measure the mutual diffusion and Soret coefficients in binary liquid mixtures, following a design suggested by Piazza [1]. Utilizing a fiber coupled laser with a very short coherence length, a particularly precise determination of the transport coefficients is possible by comparing the measured beam deflection signal to a numerical solution of the coupled heat and mass transport equations. The onset of convection can be suppressed both for heating from above and from below at least up to temperature differences of 2°C for ethanol-water mixtures.

We performed numerous tests to validate the measurement method and the procedure for data analysis. Measurements of three organic benchmark systems [2] consisting of tetralin, dodecane and isobutylbenzene and the system water-ethanol demonstrate compliance with existing literature values. In the case of ethanol-water, the concentration and temperature range could be expanded in comparison with data available in literature [3].

[1] Piazza R., Phil. Mag. 83, (2003) 2067

[2] Platten J., Bou-Ali M., Costesèque P., Dutrieux J. Köhler W., Leppla C., Wiegand S., Wittko G., Phil. Mag. 83, (2003) 1965

[3] Kolodner P., Williams H., Moe C., J. Chem. Phys. 88, (1988) 6512

CPP 15.4 Tue 14:00 P3

Study of order/disorder transitions in β -hydroquinone clathrates with ^2H -NMR and dielectric spectroscopy — ●ANDRE NOWACZYK, CATALIN GAINARU, SEBASTIAN SCHILDMANN, BURKHARD GEIL, and ROLAND BÖHMER — Experimentelle Physik III, Fakultät für Physik, Technische Universität Dortmund

We are studying the behavior of the guest molecules in partly filled β -hydroquinone clathrates. If the cage occupation x is higher than a critical value x_c , these substances undergo an order/disorder transition at a composition dependent temperature. The advantage of these binary mixtures, when compared for example with plastic crystals, is their stable and well-defined crystal structure into which the guest molecules are embedded. We have grown crystals with acetonitrile or methanol as guest molecules for different occupation factors x . By applying a combination of deuterium nuclear magnetic resonance and dielectric spectroscopy we study the guest-guest interactions in dependence on the occupation factor x . Several ^2H -NMR techniques were applied, comprising relaxation experiments as well as stimulated-echo measurements to gain information on different timescales.

CPP 15.5 Tue 14:00 P3

Water dynamics on the hydrate lattice of a tetra-butyl ammonium bromide semi-clathrate — ●SEBASTIAN SCHILDMANN, ANDRE NOWACZYK, BURKHARD GEIL, CATALIN GAINARU, and ROLAND BÖHMER — Experimentelle Physik III, Fakultät für Physik, Technische Universität Dortmund

Deuteron nuclear magnetic resonance (NMR) and dielectric spectroscopy are utilized to investigate the dynamics of the water molecules in the tetra-*n*-butyl ammonium bromide semi-clathrate (TBAB · 26H₂O). Semi-clathrates are nano-porous structures suitable for the encapsulation of small guest molecules which here are part of the water lattice. Stimulated-echo spectroscopy and dielectric measurements were employed and yielded the same distribution of correlation times corresponding to a mean activation energy of about 5165 K. Solid-echo spectra were acquired over a broad temperature range and compared with random-walk simulations. They exhibit an apparent two-phase character which is discussed in terms of various scenarios. Two-dimensional NMR spectra and four-time stimulated echoes were recorded, but an exchange between slow and fast reorienting molecules could not be detected. Spin-lattice relaxation does not directly reflect the local reorientational motion and its non-exponentiality is interpreted with reference to the translational dynamics of the water molecules. Estimated diffusion coefficients suggest that a translational step takes place after every 10th reorientational step. Replacing the bromide anion by fluoride the semi-clathrate TBAF · 32H₂O is investigated and compared with the former results.

CPP 15.6 Tue 14:00 P3

Para-hydrogen induced nuclear spin polarization at variable magnetic field — ●SERGEY KORCHAK¹, KONSTANTIN IVANOV², ALEXANDRA YURKOVSKAYA^{1,2}, and HANS-MARTIN VIETH¹ — ¹Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — ²International Tomography Center, Institutskaya 3a, Novosibirsk, Russia

A way of boosting the sensitivity of NMR is exploiting hyperpolarization resulting from non-thermal population of the spin energy levels. A very efficient method is enriching the para-spin isomer of H₂ (PHIP) and subsequent transferring the polarization to target spins of choice. This has been applied in magnetic resonance imaging in biological studies. Both the PHIP effect and the polarization transfer vary strongly with an external magnetic field B . We will report a detailed experimental and theoretical study of this magnetic field dependence. As a model system polarized ethylbenzene formed by catalytic attachment of the para-H₂ molecule to styrene was measured at fields ranging from 0.1mT to 7T by use of a fast field-cycling technique. Theoretical simulations of the polarization pattern as a function of B assuming scalar spin-spin coupling to be responsible for the change reproduce the experimental data for this 5-spin system. Polarization transfer across several bonds from the primarily polarized aliphatic protons to the aromatic moiety of ethylbenzene was also observed. The optimal conditions for forming polarization and manipulating its transfer as well as the influence of spin-lattice relaxation will be discussed.

CPP 15.7 Tue 14:00 P3

From Monomers to Polymers: Correlated Segments in Diffusive Transport — ●DOMINIK STADELMAIER and WERNER KÖHLER — Universität Bayreuth, Physikalisches Institut

We have performed measurements on dilute polymer and alkane solutions to investigate the influence of the polymer stiffness on the Soret effect. The Soret effect (thermal diffusion) describes the mass flow in a binary system with a temperature gradient. In the high polymer limit the thermal diffusion coefficient is - contrary to the long-range hydrodynamic coupling in case of isothermal diffusion - independent of the polymer chain length. For polystyrene, thermal diffusion mainly depends on a factor proportional to the correlated segment size and on the solvent viscosity [1]. Measurements with the flexible polymers PDMS and polyethylen-oligomers however show that the solvent viscosity is no longer the only relevant solvent parameter for the Soret effect. Even a sign change is possible if the solvent viscosity is increased. For the measured alkane solutions D_T is always negative thus the alkane molecules are more thermophilic than the solvent. But the crossover from a small molecule to a molecule with polymer properties always takes place at a chain length that is approximately of the size of the Kuhn segment.

[1] Stadelmaier D., Köhler W., *Macromolecules* 41, (2008), 6205

CPP 15.8 Tue 14:00 P3

Brownian Motion of Colloid Particles in Thin Liquid Films — ●INES TRENKMANN, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Chemnitz University of Technology, Institute of Physics, 09107 Chemnitz

The growing field of micro- and nanofluids requires an understanding of the role of solid liquid interactions in hydrodynamics.

It is well-known since some years that thin liquid films form layering structures near smooth surfaces and free interfaces [1]. Thereby it is apparent that the dynamical properties of these films differ from those of bulk liquids. Besides the altered film structure, interfaces enter into the hydrodynamics via the hydrodynamic boundary conditions (HBC). To investigate the alteration of the hydrodynamical features of the liquid films by reduction of the film thickness single-particle tracking is a sensitive method to observe changes in the individual diffusion motion of tracers [2].

We want to show recent measurements of the influence of film thickness on the diffusion behavior of colloid particles as tracers in thin films of a silicon grease. By variation of the tracer size or film thickness the influence of the HBC will be studied down to molecular thin films [3].

[1] G. Evmenenko, et al.: *Langmuir* 17(2001) 4021

[2] J. Schuster, et al.: *Eur. Polymer J.* 40(2004) 993

[3] M. J. Saxton: *Biophys J.* 72 (1997) 1744

CPP 15.9 Tue 14:00 P3

Low Field NMR for Analysis of Heterogeneous Mixtures and Polymers under Stress — ●UTE BÖHME and ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden, Hohe Str. 6, 01069 Dresden

Small and low-cost NMR systems based on permanent magnets provide an interesting alternative for NMR in materials characterization. They are used as fast, non-destructive tools for the routine analysis of food-stuffs, cosmetics and chemicals. They are of particular interest, when shift information is not required, i.e., when there is a priori knowledge about the system. NMR relaxation times provide a wealth of information on molecular mobility, they are influenced by the composition and treatment of the sample. Impacts like stress, heating or cooling change the molecular mobility. Extending the relaxation time measurements to two-dimensions significantly enhances the resolution of the components of the sample despite lack of chemical shift resolution. For our investigations we use an in-house built portable NMR system with Halbach magnets arrangement and a proton Larmor frequency of 32 MHz. Examples shown include the determination of the principal components of water- in- oil- emulsion and stretched polypropylene using T1-T2 correlation experiments at low field. Comparison to results obtained with high-field measurements confirm the results obtained.

CPP 15.10 Tue 14:00 P3

Charge transport and dynamic glass transition in imidazole-based liquids — ●CIPRIAN IACOB¹, JOSHUA RUME SANGORO¹, ANATOLI SERGHEI¹, SERGEJ NAUMOV¹, YASMIN KORTH², JÖRG KÄRGER¹, CHRISTIAN FRIEDRICH², and FRIEDRICH KREMER¹ — ¹Institute of Experimental Physics I, University of Leipzig, Linnéstr. 5, 04103 Leipzig, Germany — ²Freiburger Materialforschungszentrum (FMF)

und Institute für Makromolekulare Chemie der Albert-Ludwigs Universität Freiburg i. Br., Germany

Broadband Dielectric Spectroscopy (BDS), differential scanning calorimetry, rheology and Pulsed Field Gradient - Nuclear Magnetic Resonance (PFG - NMR) are combined to study glassy dynamics and charge transport in a homologous series of imidazole-based liquids with systematic variation of the alkyl chain length. The dielectric spectra are interpreted in terms of dipolar relaxation and conductivity contribution. By applying Einstein, Einstein-Smoluchowski and Stokes-Einstein relations, translational diffusion coefficients - in quantitative agreement with PFG NMR measurements are obtained. With increasing alkyl chain length, it is observed that the viscosity increases whereas the structural α -relaxation rate decreases in accordance with Maxwell's relation. Between the rate of electrical relaxation and the rate of the structural α -relaxation scaling is observed over more than 6 decades with a decoupling index of about 2.

References: C. Iacob et al., : *J. Chem.Phys.*, 2008, In press; J. Sangoro et al., *J. Chem.Phys.* 128, 214509, 2008; J. Sangoro et al., *Phys. Rev. E*, 051202, 2008; F. Kremer et al., *Phys. Rev. E*, 54, 1996

CPP 15.11 Tue 14:00 P3

Diffusion in polymer networks of hydrogels — ●FATEMEH TABATABAEI¹, OLAF LENZ², and CHRISTIAN HOLM¹ — ¹Institute für Computationalphysik, Universität Stuttgart, 70569 Stuttgart, Germany — ²Max-Planck-Institut für Polymerforschung, 55021 Mainz, Germany

In this work we consider the diffusion behavior of a simple spherical tracer particle in polymer networks of hydrogels. There have been hints obtained via Fluorescence Correlation Spectroscopy on FCS tracer particles in a hydrogel. We investigate, by means of MD simulation, the diffusion properties of a tracer particle in a confined geometry of a polymer network. We present single model that shows anomalous diffusion, namely if the tracer particle is confined to follow the coiled polymer contour length. As an extension we investigate the diffusion property of a single tracer particle interacting with the polymer via simple Lennard-Jones potential.

CPP 15.12 Tue 14:00 P3

Fourier-series approach for analytical treatment of diffusion in periodic systems (Floquet method) — ●GÜNTER HEMPEL — Martin-Luther-Universität, Institut für Physik, D-06099 Halle, Germany

The data evaluation of diffusion experiments in periodic systems is often performed (i) at numerical way, (ii) at the basis of an approximately exponential behaviour, or (iii) by means of an analytical solution in terms of rather complicated analytical expressions. Here a simplification is proposed: The diffusion equation is expanded in Fourier series with respect to space coordinates (Floquet method) which results in a system of ordinary differential equations. Solving the latter we obtain the time evolution of the Fourier coefficients of the concentration distribution. They decrease exponentially; the higher the order of the Fourier coefficient is the faster is the decay. At this way the concentration-time dependency can be estimated.

Depending on the experiment, the term concentration might be replaced by temperature, magnetization, spin polarization, or others. Moreover, sometimes not this generalized concentration is of interest but its integral, here denoted as intensity. (In the case of concentration as particle density, the intensity will be the total amount of particles in a certain volume.) This procedure was applied to the data evaluation of a nuclear-spin diffusion experiment in lamellae of a lactide macromonomer. The local magnetization density plays the role of the generalized concentration, and the magnetization of a lamellae that of the intensity.

CPP 15.13 Tue 14:00 P3

Thermal trapping of single molecules in liquids — ●ROMY RADÜNZ¹, FRANK CICHOS¹, and ALOIS WÜRGER² — ¹Molecular Photonics Group, Institute of Experimental Physics I, University Leipzig, Linnéstr. 5, 04103 Leipzig, Germany — ²CPMOH, Université Bordeaux 1, 351 Cours de la Libération, 33405 Talence, France

Brownian motion prevents an extended optical observation of single molecules in solution as it drives molecular species out of the observation volume. To overcome this drawback surface chemistry is applied to immobilize molecular entities for detailed optical studies. But the presence of a surface may change the electrical, optical and conformational properties of molecules considerably. Thus contact-free methods are

needed to confine single molecules or nanoparticles to an observation volume appropriate for optical investigation. Such a trapping in liquids paired with manipulative tools could open a completely new route for single molecule chemistry in solution. Here we propose a thermal trap, which is based on highly localized temperature gradients. Such gradients exert forces on molecules, known as thermophoretic forces. Localized temperature gradients in the fluid are realized by single gold nanoparticles of a diameter of approximately 50 nm, which are immobilized on glass cover slips and selectively excited by a focussed laser beam. Due to the fact that gold nanoparticles exhibit a large absorption cross section near the plasmon resonance they represent very efficient nano heat-sources. In this contribution detailed theoretical considerations on the thermophoretic trap are presented. First experimental results on the trapping of polystyrene beads will be shown.

CPP 15.14 Tue 14:00 P3

Photothermal fluctuation spectroscopy on gold nanoparticle dimers — ●MIRIAM WÄHNERT, NILS NEUBAUER, ROMY RADÜNZ, and FRANK CICHOS — Molecular Nanophotonics Group, University of Leipzig, Linnéstraße 5, 04103 Leipzig

To measure distance changes on the nanoscale, FRET (Fluorescence resonance energy transfer) is a heavily applied technique in biophysical studies. The upper limit of distance fluctuations being measured with this method is about 10 nm. Furthermore it suffers from photochemical degradation mechanisms like blinking and bleaching of the energy transferring dye molecules.

We report on recent experiments using pairs of gold nanoparticles as absorbing markers replacing dye molecules. Gold particles are strongly interacting with light, if they are excited near the plasmon resonance. The resulting dipoles of two closely spaced gold nanoparticles can couple to form a new resonance, which appears in the absorption as a

distinct feature. The strength of this absorption depends on the distance of the two particles and is visible up to a few 10 nm, which clearly exceeds the lengthscale of FRET. The gold nanoparticles are detected by photothermal heterodyne detection, using the release of heat from the absorbing particles to create a local refractive index change around them, which can be probed with a confocal laser scanning setup. Due to the plasmon coupling a fluctuating distance will result in a fluctuating photothermal signal. Numerical analyses of the spectra together with first experimental results will be presented.

CPP 15.15 Tue 14:00 P3

Convection at the isotropic-nematic interface under slow continuous cooling — ●BEATE ULLRICH, DORIS VOLLMER, and GÜNTER K. AUERNHAMMER — Max-Planck-Institut für Polymerforschung, Mainz, Germany

Small amounts of added alkane alter the kinetics of the isotropic-nematic phase transition of cyanobiphenyls such that isotropic and nematic domains coexist within a defined temperature interval. Under continuous cooling, redistribution of alkane between the domains can be limiting and local inhomogeneities may arise. Tracking hydrophobic PMMA tracer colloids close to growing nematic droplets revealed convection-like motion within a range of some 10 μm . This motion pattern seems to require interaction with alkane, as it does not occur in silica colloids. It follows initial colloid attraction towards the interface, and is associated with slow but steady droplet growth at cooling rates below 0.05 K/min. Once developed, it even outlasts coalescence events, but is abolished when the temperature ramp is interrupted and droplet growth ceases. We discuss local alkane concentration gradients as well as alkane effects on the isotropic-nematic interfacial tension as possible driving mechanisms of this small-scale convection.