

## CPP 15: Diffusion and Transport Processes

Time: Tuesday 14:30–16:45

Location: H47

CPP 15.1 Tue 14:30 H47

**Effect of coarse-graining on the dynamics of fluid mixtures: how important is the structure?** — ●JÖRG SILBERMANN, SABINE KLAPP, and MARTIN SCHOEN — Stranski-Laboratorium für Physikalische und Theoretische Chemie, Sekretariat C7, Technische Universität Berlin, Straße des 17. Juni 115, D-10623 Berlin, Germany

We consider a colloidal model suspension consisting of large solute ( $A$ ) particles immersed in a bath of smaller ( $B$ ) particles with all interactions being of the Lennard–Jones type. This (reference) system is systematically simplified (coarse-grained) by replacing the original  $B$  particles by a reduced number of larger and heavier ones such that the mass and volume fraction of  $B$  particles is kept constant. Using Boltzmann inversion we adjust the (effective) intermolecular interactions between  $A$  particles in the coarse-grained system such that the static  $A$ – $A$  structure of the reference system is preserved. By means of this procedure a whole set of systems is generated all exhibiting the same static  $A$ – $A$  structure regardless of the degree of coarse-graining. We take the mass ratio of  $A$  and  $B$  particles to vary between 64 (reference system) and 1. Based on molecular dynamics (MD) computer simulations we identify the effects that coarse-graining of the solvent imposes on typical microscopic time correlation functions characterizing the single-particle and collective dynamics of the solute. Our results [1] indicate that coarse-graining may have a pronounced effect on the dynamics of the solute depending on the total packing fraction of the binary mixture.

[1] J. R. Silbermann et al., *Mol. Phys.*, (2006) submitted.

CPP 15.2 Tue 14:45 H47

**Temperature Dependence of Positron Lifetime in a Polymer of Intrinsic Microporosity** — ●KLAUS RÄTZKE<sup>1</sup>, RODRIGO LIMA DE MIRANDA<sup>1</sup>, JAN KRUSE<sup>1</sup>, FRANZ FAUPEL<sup>1</sup>, DETLEV FRITSCH<sup>2</sup>, VOLKER ABETZ<sup>2</sup>, PETER BUDD<sup>3</sup>, JAMES SELBIE<sup>3</sup>, NEIL MCKEOWN<sup>4</sup>, and BADER GHANEM<sup>4</sup> — <sup>1</sup>Univ. Kiel, Materialverbunde, Kaiserstr. 2, 24143 Kiel — <sup>2</sup>Institut für Polymerforschung, GKSS, Max-Planck-Strasse 1, 21502 Geesthacht — <sup>3</sup>School of Chemistry, The University of Manchester, Manchester M13 9PL, UK. — <sup>4</sup>School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK.

The performance of polymeric membranes for gas separation is mainly determined by the free volume. Polymers of intrinsic microporosity are interesting candidates for state of the art gas separation membranes due to the high abundance of accessible free volume. Positron annihilation lifetime spectroscopy is a generally accepted technique for investigation of free volume in polymers where the orthopositronium lifetime is directly connected to the mean free volume size. We performed measurements of the temperature dependence of the positron lifetime in a polymer of intrinsic microporosity (PIM-7) in the range from 143 to 523 K. The mean value of the free volume calculated from the ortho-positronium life time ( $\sim 5$  ns) is in the range of typical values for high free volume membrane polymers ( $V = 0,47 \text{ nm}^3$ ). However, the temperature dependence of the positronium-lifetime is non-monotonous. Comparison with thermal expansion measurements will be made and a possible explanation of this unexpected behavior given.

CPP 15.3 Tue 15:00 H47

**Beitrag abgesagt** — ●XXX XXX —

CPP 15.4 Tue 15:15 H47

**Microscopic Protein Diffusion at High Concentration** — ●SEBASTIAN BUSCH<sup>1</sup>, WOLFGANG DOSTER<sup>1</sup>, STÉPHANE LONGEVILLE<sup>2</sup>, VICTORIA GARCÍA SAKAI<sup>3,4</sup>, and TOBIAS UNRUH<sup>5</sup> — <sup>1</sup>Physics-Department E13, Technische Universität München, James Franck Straße 1, D-85747 Garching, Germany — <sup>2</sup>Laboratoire Léon Brillouin, CEA-CNRS, DSM-DRECAM, CEA Saclay, 91191 Gif-sur-Yvette, France — <sup>3</sup>NIST Center for Neutron Research, National Institute of Standards & Technology, Gaithersburg, MD 20899, U.S.A. — <sup>4</sup>Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, U.S.A. — <sup>5</sup>Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), TU München, Lichtenbergstr. 1, D-85747 Garching, Germany

A characteristic of the interior of cells is the high total concentration of macromolecules, occupying up to 20-30% of the total volume.

This affects protein diffusion and protein association equilibria (highly nonideal solutions). The goal of our project is to understand the effect of protein-protein interactions on molecular diffusion at high concentration. The self-diffusion of myoglobin in concentrated solutions was investigated by neutron back-scattering spectroscopy. The quasi-elastic spectrum can be decomposed into two Lorentz curves: one with a linewidth increasing with  $Q$ , which is assigned to translational diffusion, the other broad  $Q$ -independent, reflecting protein-internal motions. The apparent diffusion coefficient decreases with increasing concentration and wave-vector, suggesting that protein diffusion deviates at high  $Q$  ( $1.75 \text{ \AA}^{-1}$ ) from its long-time Brownian limit.

15 min. break

CPP 15.5 Tue 15:45 H47

**Modelling polyelectrolyte dynamics: The importance of hydrodynamic interactions** — ●KAI GRASS<sup>1</sup> and CHRISTIAN HOLM<sup>1,2</sup> — <sup>1</sup>Frankfurt Institut für Advanced Studies, Max-von-Laue-Strasse 1, D-60438 Frankfurt am Main, Germany — <sup>2</sup>Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

In this contribution, we investigate the dynamical properties of short strongly charged polyelectrolytes by means of coarse-grained molecular dynamics simulations. By comparing a purely implicit treatment of the solvent with a Lattice Boltzmann modelled fluid, we show that hydrodynamic interactions have to be included to model the experimentally observed behaviour.

We compare the obtained results to recent experimental studies and illustrate the decisive features, such as the non-monotonic behaviour of the electrophoretic mobility on short length scales and the well-known transition to the free-draining regime. Additionally, we use the obtained diffusion and mobility coefficients to calculate estimates for the effective charge and hereby check the validity of the available theories for charge condensation.

All transport coefficients were obtained at zero and low-field conditions, respectively, in order to not perturb the counter ion cloud, and thus match experimental conditions closely.

CPP 15.6 Tue 16:00 H47

**Diffusion and local dynamics in polysiloxane-based polymer electrolytes** — MIRIAM KUNZE<sup>1</sup>, YUNUS KARATAS<sup>2</sup>, HANS-DIETER WIEMHÖFER<sup>2</sup>, HELLMUT ECKERT<sup>1</sup>, and ●MONIKA SCHÖNHOF<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie und SFB 458, WWU Münster, Germany — <sup>2</sup>Institut für Anorganische und Analytische Chemie und SFB 458, WWU Münster, Germany

A new improved Li ion conducting salt-in-polymer electrolyte system consisting of a polysiloxane backbone with oligoether side chains and added  $\text{LiF}_3\text{SO}_3$  (Li triflate = LiTf) is studied concerning the mechanisms governing ion dynamics. Conductivity values at 30 C reach up to  $7.8 \times 10^{-5} \text{ S cm}^{-1}$  after crosslinking, which is employed to enhance mechanical stability. We characterize this system by a combination of pulsed field gradient (PFG)-NMR diffusion and spin relaxation ( $R_1$  and  $R_2$ ) of  $^7\text{Li}$ ,  $^{19}\text{F}$  and  $^1\text{H}$  in dependence on T and salt content. Comparing diffusion coefficients of Li and Tf with conductivity data by the Nernst-Einstein-equation reveals that transport is dominated by diffusion of neutral ion pairs and clusters, while only a low fraction of free ions exists. Evaluating activation energies from diffusion coefficients and relaxation rates, respectively, shows that the underlying activation processes governing ionic mobility can be discussed by their relevant length scale rather than by the ion involved: Activation energies of diffusion, a long range process, are much larger than those of  $R_2$ , which describe local mobility. An important conclusion is that the relatively high ionic conductivity could even be increased, if salt dissociation can be enhanced further.

CPP 15.7 Tue 16:15 H47

**Single molecule fluorescence correlation spectroscopy study of polymer-surfactant interactions** — ●STANISLAUS JOHN BOSCO<sup>1</sup>, HEIKO ZETTL<sup>1</sup>, JÉRÔME CRASSOUS<sup>2</sup>, MATTHIAS BALLAUFF<sup>2</sup>, and GEORG KRAUSCH<sup>2</sup> — <sup>1</sup>Physikalische Chemie II, Universität Bayreuth, 95440, Bayreuth, Germany — <sup>2</sup>Physikalische Chemie I, Universität Bayreuth, 95440, Bayreuth, Germany

The association between water soluble polymers and surfactants has drawn much attention to understand the fundamental properties in intermolecular interactions and hydrophobic aggregation phenomena. In order to understand the polymer/surfactant interactions in a single molecule level, we have used fluorescence correlation spectroscopy (FCS). As a model system we investigated complex formation between a hydrophobically modified nonionic polymer, methyl cellulose and the anionic surfactant sodium dodecyl sulfate (SDS) in water. FCS can follow the motion of individual SDS micelles and single MC/SDS aggregates via measurement of the diffusion time of single dye molecules attached to MC/SDS complexes [1]. Two possible aggregations (large and small) can be distinguished above the critical aggregation concentration (CAC). Rheology was used to follow the macroscopic properties of the polymer/surfactant systems. The dynamic behavior of the large aggregates found in FCS resembles the macroscopic properties. Moreover the influence of temperature on the aggregation behavior has also been studied.

[1] S. John Bosco, H. Zettl, J.J Crassous, M. Ballauff, G. Krausch, *Macromolecules*, 39, 8793-8798 (2006)

CPP 15.8 Tue 16:30 H47

**PhoCS - Photothermal Correlation Spectroscopy** — ●ROMY RADÜNZ and FRANK CICHOS — Molecular Nanophotonics, Universität Leipzig, Linnéstraße 5, 04103 Leipzig

Fluorescence correlation spectroscopy (FCS) is a versatile tool to explore molecular dynamics with single molecule sensitivity. It is widely used in exploring biophysical processes even in living cells. However, it is based on fluorescence and therefore suffers from photophysical weaknesses of the chromophores, such as photoblinking, photobleaching or weak signal to background contrast due to autofluorescence. We present results of a new experimental technique called photothermal correlation spectroscopy (PhoCS). PhoCS employs a photothermal contrast mechanism to detect non-fluorescent nanoparticles of only a few nanometers in size. Light, which is absorbed by the particle is released as heat and induces a local refractive index change around the nanoparticle, which is optically detected. This contrast mechanism is used to generate timetraces of nanoparticle diffusion in an equivalent way as it is done in FCS. Thus PhoCS opens new ways of local dynamic measurements with nanometer sized photostable tracers.