

CPP 15 Dynamics and Diffusion

Time: Wednesday 14:00–15:00

Room: ZEU 114

CPP 15.1 Wed 14:00 ZEU 114

Anomalous diffusion in short chain polymer melts — ●M. ZAMPONI¹, A. WISCHNEWSKI¹, M. MONKENBUSCH¹, L. WILLNER¹, B. FARAGO², and D. RICHTER¹ — ¹Forschungszentrum Juelich, 52425 Juelich, Germany — ²Institut Laue-Langevin, 38042 Grenoble, France

The dynamics of linear polymer chains in the melt depends strongly on the chain length: Short unentangled chains perform free Rouse motion, long chains are confined by mutual entanglements. In the reptation model these topological constraints are described by a virtual tube which follows the primitive path of the observed test chain. However, this definition means that a test chain with a length in the order of one entanglement distance can not be captured in a tube, even if the matrix chains are much longer than the test chain.

We report on a systematic neutron spin echo study of different binary polyethylene blends. The measured dynamic structure factor of short test chains of various lengths (below or about the entanglement length) in a long chain matrix shows significant deviations from the expected Rouse behavior pointing to the fact that the short labelled chains are subject to topological constraints. Also anomalous behavior in the time dependence of the center of mass mean squared displacement was found showing a clear subdiffusive regime. Blends of short unentangled chains in a matrix of the same length still show discrepancies: Although the segmental diffusion shows Rouse behavior, again anomalous behaviour of the c.o.m. diffusion is found. These deviations may be explained by taking intermolecular interactions as discussed by Guenza [M.Guenza, *Macromolecules* 35, 2714 (2002)] into account.

CPP 15.2 Wed 14:15 ZEU 114

Diffusion processes in binary fluid mixtures in confined geometries. — ●JOCHEN SOMMERFELD and MARTIN SCHOEN — Stranski-Laboratorium für Physikalische und Theoretische Chemie, Sekretariat C 7, Technische Universität Berlin, Strasse des 17. Juni 135, 10623 Berlin

By means of molecular dynamics (MD) simulations we study the dynamical properties of binary fluid mixtures confined by planar substrates. Molecules of fluid mixtures interact through Lennard-Jones(12,6) potentials. Interactions between fluid particles and the wall substrates are described by Lennard-Jones(10,4) potentials. Thus we can explore both symmetric and asymmetric mixtures by choosing the depth of potentials $\{\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}\}$ and energetic preference of one kind of fluids by substrates (i.e., the selectivity of the substrates). We calculate transport coefficients using the Green-Kubo relations (i.e., integrating of time correlation functions). We focus on the calculation of diffusion coefficients, both self-diffusion coefficients D_{AA} and D_{BB} and interdiffusion coefficient D_{AB} , and the self-part of the intermediate scattering function $F_s(k, t)$ depending on the distance between substrates, selectivity of the walls, and the Lennard-Jones parameters of the two kinds of particles. The effect of phase separation on calculated quantities will be analyzed.

CPP 15.3 Wed 14:30 ZEU 114

Diffusion of dye molecules through nanoporous TiO₂ networks — ●M. DÜRR, M. OBERMAIER, A. SCHMID, A. YASUDA, and G. NELLES — Materials Science Laboratory, Sony Deutschland GmbH, D-70327 Stuttgart

Nanosize-structured materials with their unique physical and chemical properties are recently attracting a growing interest. For many applications, diffusion of molecules in solution through such nanoporous materials can be of great importance, e.g. for the sensitization of nanoporous TiO₂ when used in dye-sensitized solar cells. To quantify the influence of the nanoporous TiO₂ network on the diffusion of both Ru-complexed bipyridine dye molecules as well as porphyrin molecules, we investigated the diffusion limitations to the adsorption of dye molecules on the surface of the TiO₂ nanoparticles. A simple model is shown to be capable of reproducing the uptake curves obtained by means of optical absorption spectrometry for materials with different porosity and average size of the nanoparticles. The effective diffusion constants are found to be reduced by up to 3 orders of magnitude in the porous layers when compared to diffusion in the pure solvent. Depending on the strength of the interaction between the dye molecules, two different modes of diffusion limitation can be distinguished. In the case of porphyrin molecules, the $\pi - \pi$ - interaction energy was determined.

CPP 15.4 Wed 14:45 ZEU 114

Molecular view of a colloidal gelation — ●SYLVIE ROKE — Max-Planck Institute for Metals Research, Heisenbergstr. 3, Stuttgart, Germany

Many colloidal particles are coated physically or chemically by adsorption with a thin outer layer. Often this layer serves different purposes, such as shielding van der Waals interactions, providing so-called steric stabilization and/or to passivate surface states. If molecular transitions take place in the layer, as a function of temperature, pressure or solvent composition, dramatic changes in collective particle behaviour may result.

So far, particle properties have only been studied experimentally by techniques that lack molecular interface specificity. As a result, the molecular surface properties of the colloids that can affect the particle interaction have never been investigated directly.

We have used the recently developed technique vibrational sum frequency scattering to obtain molecular information about octadecyl-coated silica particles dispersed in n-hexadecane that undergo a gelation. The interface molecules are completely disordered in fluid suspension at high temperatures and become ordered prior to gel formation at lower temperatures. The appearance of interfacial order is accompanied by the liberation of heat and densification, and results in increased van der Waals forces between the particles leading to gelation. On a timescale of days the interface becomes completely ordered, which can affect aging in such gels.