

CPP 37: Fluids and Glasses I

Time: Wednesday 10:15–13:00

Location: ZEU 255

CPP 37.1 Wed 10:15 ZEU 255

Effects of the molecular polarity on the structural and dynamical properties of liquid silica — ●ELVIRA PAFONG and BARBARA DROSSEL — Institut für Festkörperphysik, Technische Universität Darmstadt

Silica is a network-forming liquid that shares many properties with water. Both liquids are polar, which leads to directional bonds and complex structural and dynamical features. In particular, liquid silica undergoes a transition from a strong to a fragile glass former, comparable to the transition from a high-density liquid (HDL) to a low-density liquid (LDL) reported in water. Here, we investigate the effect of the molecular polarity on the structure and dynamics of liquid silica using molecular dynamics simulations. We modify polarity by changing the partial charges assigned to each atom. We find that the glass forming ability of liquid silica is enhanced by an increase of the partial charges of up to +20%. The temperature corresponding to the maximum or the minimum in density, the average tetrahedral order parameter as well as the correlation times increase also. Interestingly, when the partial charges are increased further to +30%, a fifth atom enters the first neighbouring shell for temperatures above 4000 K, resulting in a structure that is locally less ordered and therefore in less pronounced anomalies.

CPP 37.2 Wed 10:30 ZEU 255

Metabasin Lifetimes of Sheared Supercooled Liquids — ●MARKUS BLANK-BURIAN and ANDREAS HEUER — Institut für Physikalische Chemie, WWU Münster, Deutschland

In the limit of small shear rates and temperatures around the glass transition temperature T_g , a sheared supercooled liquid can be described by hopping processes between so called metabasins [1]. However, in the limit of small temperatures and high shear rates the dynamics can be described by vanishing energy barriers in the PEL [2].

We analysed this crossover region with molecular dynamics simulations at various temperatures ($0.01 \leq T \leq 1.0$) and shear rates ($10^{-6} \leq \dot{\gamma} \leq 10^{-1}$). A very small system size ($N = 130$) was used, which is not affected by major finite size effects. A plastic event in this system size typically spans the whole box, so that the system does not show shear banding.

We can show, that two simple models, describing the metabasin lifetimes under constant shear rate and finite temperature, are in good agreement with our numerical data. The first model assumes that the metabasin energy dependent activation barriers are continuously reduced by shearing the system. The second, more simplistic model, assumes a superposition of transition rates, reflecting the limit of low temperature and the limit of low shear rates, respectively, to characterize the transition region between temperature- and shear-dominated dynamics.

[1] A. Heuer, J. Phys.: Condens. Matter 20, 37 (2008)

[2] D. J. Lacks, Phys. Rev. E 66, 5 (2002)

CPP 37.3 Wed 10:45 ZEU 255

Dielectric Spectroscopy Below the Glass Temperature — ●KORBINIAN GEIRHOS, PETER LUNKENHEIMER, and ALOIS LOIDL — Experimental Physics V, University of Augsburg, Germany

The dynamics of glassy matter above the glass temperature (T_g) is already extensively studied by dielectric spectroscopy in a broad frequency and temperature range. Dielectric data of glasses below T_g , however, are rather scarce. The dielectric spectra of glass formers above T_g are dominated by relaxation processes. These contributions may hide additional processes, which are proposed by different models, like the "Nearly Constant Loss" of the Coupling Model [1] or the fast β -Process of the Extended Mode Coupling Theory [2]. Below T_g , however, the main relaxation features are shifted out of the experimental frequency window. As a consequence, possible additional processes can be observed and studied. For this purpose, we provide temperature- and frequency-dependent dielectric data of different glass formers down to temperatures of 4 K.

[1] K. L. Ngai, J. Phys.: Condens. Matter 15, 1107 (2003). [2] W. Götze *et al.*, Rep. Prog. Phys. 55, 241 (1992).

CPP 37.4 Wed 11:00 ZEU 255

Dynamic glass transition in the supercooled liquid and plastic

crystal of ethanol — ●YEONG ZEN CHUA¹, AMANDA R. YOUNG-GONZALES², RANKO RICHERT², and CHRISTOPH SCHICK¹ — ¹Institut für Physik, Universität Rostock, Rostock, Germany — ²School of Molecular Sciences, Arizona State University, Tempe, Arizona, USA

Ethanol has been widely investigated and is well-known to exhibit a very interesting polymorphism of different solid phases: a fully-ordered (monoclinic) crystal, a (bcc) plastic crystal, a glassy plastic crystal and an ordinary amorphous glass. Physical vapor deposition (PVD) has been used to prepare amorphous glasses of ethanol, which upon heating to higher temperature transforms into the plastic crystal of ethanol. The dynamic glass transition of supercooled liquid of ethanol is successfully measured by AC nanocalorimetry. Preliminary results for the plastic crystal are also presented. With that, the frequency dependency of the dynamic glass transition of the supercooled liquid of ethanol is measured and compared with published dielectric data. Comparison of dielectric data of supercooled liquid of ethanol with AC nanocalorimetric data shows that ethanol exhibits Debye peak, which cannot be observed in AC nanocalorimetry. In previous published dielectric data, the prominent Debye peaks have been mistaken as structural α relaxation. The dielectric data have been re-evaluated and the high frequency wing in the dielectric spectra is identified as the structural α relaxation.

Invited Talk

CPP 37.5 Wed 11:15 ZEU 255

Nonlinear dielectric spectroscopy in supercooled liquids

— PETER LUNKENHEIMER¹, MARION MICHL¹, THOMAS BAUER¹, FRANCOIS LADIEU², SAMUEL ALBERT², and ●ALOIS LOIDL¹ — ¹Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, Germany — ²SPEC, CEA, CNRS, University Paris-Saclay, France

We summarize the recent experimental status in non-linear dielectric spectroscopy on supercooled liquids. Nonlinearity can be measured by comparing the complex dielectric constants of high- and low-field permittivities [1] or by the determination of the higher harmonics of the permittivity [2]. Performing high-precision nonlinear dielectric experiments on glycerol and propylene carbonate, we find experimental evidence for growing cooperativity, implying clusters containing correlated molecules on approaching the glass transition. We were able to demonstrate that the number of dynamically correlated particles increases in much the same way as the effective energy barrier, [1] as predicted fifty years ago by Adam and Gibbs. By comparing third and fifth order susceptibilities, we again document the increase of amorphous order on decreasing temperatures. Moreover, we were able to determine the fractal dimension of these growing clusters. We find that they are compact and thus the glass transition can be regarded as a critical phenomenon, different from canonical phase transitions [3].

[1] Th. Bauer *et al.*, Phys. Rev. Lett. 110, 107602 (2013).

[2] Th. Bauer *et al.*, Phys. Rev. Lett. 111, 225702 (2013).

[3] S. Albert *et al.*, Science 352, 1308 (2016).

15 min break

CPP 37.6 Wed 12:00 ZEU 255

Dynamics of Ethanol/Water mixtures studied by Dielectric spectroscopy

— ●ALEXANDER MATT, LAURA VIETZE, and BERND STÜHN — Institut für Festkörperphysik, Technische Universität Darmstadt, D-64289, Germany

Water and alcohol mixtures have been an important part in studying the hydrogen bond network in water and the influence of guest molecules on the network. Since Ethanol is soluble in water at all concentrations it is well suited to act as a disturbance to the water network. In this work we use Ethanol, because of it is structural similarity to Poly(ethylene glycol), the only polyether soluble in water.

Ethanol and water mixtures form an eutectic system [1]. We use Differential Scanning Calorimetry in order to observe melting processes as well as glass transition temperatures. This method allows us to determine the eutectic phase diagram. In order to study the dynamics above, below and at phase transition temperatures Broadband Dielectric Spectroscopy is used. Measuring in the high frequency range between 200 MHz and 50 GHz both pure water and pure alcohol dynamics can be investigated [2] as well as their interplay. Results show, that adding small amounts of alcohol to water slows down the water

dynamics and that the interaction between the Ethanol molecules has an influence as well. The results of both measurement techniques are compared and used to understand the influence of temperature and Ethanol concentration on the mixture. [1] K. Takaizumi et. al., *J. Solution Chem.* 26, 927(1997) [2] R. Böhmer et. al., *Physics Report* 545, 125(2014)

CPP 37.7 Wed 12:15 ZEU 255

^1H NMR at Larmor frequencies down to 3 Hz by means of Field-Cycling techniques — •BENJAMIN KRESSE¹, MANUEL BECHER¹, ALEXEI F. PRIVALOV¹, MARIUS HOFMANN², ERNST A. RÖSSLER², MICHAEL VOGEL¹, and FRANZ FUJARA¹ — ¹Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany — ²Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

Field-Cycling (FC) NMR traces spectral densities of molecular or ionic motions by measuring the spin-lattice relaxation dispersion in a broad range of Larmor frequencies. By rapidly switching the magnetic field from a high polarization field down to a small evolution field the relaxation process can be tracked in ultra low magnetic fields by switching up to a high detection field for signal acquisition. This contribution briefly deals with the technical part of our home built FC relaxometer and focuses on experiments at ultra low Larmor frequencies down to about 3 Hz demonstrating the performance of FC NMR. Several low field experiments are presented: Larmor precession about tilted evolution fields, simultaneous measurements of the Larmor frequency and the spin-lattice relaxation [B. Kresse, A. F. Privalov, A. Herrmann, M. Hofmann, E. A. RöSSLer, F. Fujara; *Solid State NMR* 59-60 (2014) 45-47.] as well as the irradiation of oscillating transversal magnetic field pulses as a novel method for field calibration in low field FC NMR. The potential of low field FC is exemplified by the ^1H relaxation dispersion of water at low frequencies stemming from the slow proton exchange process.

CPP 37.8 Wed 12:30 ZEU 255

Incipient Ferroelectricity of Nano-Confined Water Molecules — BORIS GORSHUNOV^{1,2}, ELENA ZHUKOVA^{1,2}, MIKHAIL BELYANCHIKOV², VICTOR THOMAS³, PAVEL TOMAS⁴, MAXIM SAVINOV⁵, CHRISTELLE KADLEC⁵, and •MARTIN DRESSEL¹ — ¹Phys. Inst., Univ. Stuttgart, Germany — ²MIPT, Dolgoprudny, Russia — ³Inst. Geol. Mineral., Novosibirsk, Russia — ⁴Indep. Univ. Moscow, Russia — ⁵Czech Acad. Sci., Praha, Czech Republic

Although H_2O molecules exhibit an extremely large electrical dipole

moment, neither liquid water nor ice are ferroelectric since short-range hydrogen bonds screen the long-range intermolecular dipole-dipole coupling. The situation changes drastically when water is confined on the nanoscale. Though theoretically predicted and simulated, the H_2O ferroelectric ordering has never been clearly observed experimentally.

We have placed H_2O in the matrix of a beryl crystal lattice where the single water molecules are separated far enough from each other to avoid hydrogen bonds, but close enough to retain the dipole-dipole interaction. Using broad-band dielectric spectroscopy we demonstrate incipient ferroelectricity within the ensemble of interacting water molecules: on cooling, the static permittivity increases according to the Curie-Weiss law as a ferroelectric soft mode develops in the THz frequency range. At low temperatures quantum fluctuations eventually suppress the ferroelectric phase transition and lead to a saturation of the soft mode parameters and of the static permittivity. We model the results with the approach of a ferroelectric orientational phase transition.

CPP 37.9 Wed 12:45 ZEU 255

Dielectric response in organic solvents: polarizable force field models for dichloroethane — •JAKOB TIMMERMANN, ZHU LIU, CHRISTOPH SCHEURER, and KARSTEN REUTER — Theoretische Chemie, TU München, Lichtenbergstr. 4, 85748 Garching bei München, Germany

Liquid/liquid interfaces between two immiscible fluids, e.g. between an aqueous phase and an organic solvent, have been considered as promising environments to embed catalytically active nano-particles into [1]. For most predictive-quality first-principles electronic structure calculations investigating catalytic processes in such systems, it is crucial to efficiently, yet accurately, model the interfacial region. One common approach is to explicitly simulate the solvent region via molecular dynamics (MD), approximating the Coulomb interaction among solvent molecules, as well as the electrostatic QM embedding via static, atom-centred partial charges. While these models are reported to yield sufficiently accurate results for isotropic bulk fluids, the approach is most likely insufficient to fully describe the anisotropic character of and electronic polarization at the interface. Based on the Drude oscillator model [2, 3] we developed a polarizable model of 1,2-dichloroethane (DCE) and analysed its performance for several macroscopic properties including the dielectric permittivity in comparison to our recently reparametrized non-polarizable 1,2-DCE model.

[1] Ge et al., *PNAS* 109 (2012), 11558.

[2] Lamoureux and Roux, *J. Chem. Phys.* 119 (2003), 3025.

[3] Dequidt et al., *J. Chem. Inf. Model.* 56 (2016), 260.