

CPP 66: Glasses and Glass Transition (joint session DY/CPP/DF, organized by DY)

Time: Friday 10:00–12:30

Location: ZEU 118

CPP 66.1 Fri 10:00 ZEU 118

Molecular Dynamics Simulations of Aqueous Mixtures in Bulk and Nano-Confinement — •NIELS MÜLLER, REBECCA SCHMITZ, and MICHAEL VOGEL — Institut für Festkörperphysik, Technische Universität Darmstadt

Binary mixtures of glass forming liquids have complex dynamical properties, leading to shifted time scales of the dynamics or changed temperature dependence compared to the respective behavior of the pure liquids. We performed MD simulations of ethylene-glycol water mixtures in silica-pores, which show unmixing near the pore wall and a change from non-Arrhenius to Arrhenius like temperature dependence. To single out the origin of these unusual behaviors we use binary mixtures composed of two water-like molecules with different polarity as a model system. These systems avoid steric effects from molecules of different size and have the characteristic tetrahedral order of water, but form hydrogen bonds of different strength. Through simulations in a wide temperature range we probe unmixing transitions of these systems. In addition, we confine these model mixtures by walls formed by fixed molecules of one of the water-like species. In this way, we systematically study the effect of the polarity of the confinement on mixtures of hydrogen-bonded liquids. Performing spatially resolved analyses or selecting a subset of the system we can gather detailed insights into the effects of confinement on the dynamics of these systems.

CPP 66.2 Fri 10:15 ZEU 118

The glass transition as a mixture of random organization and athermal jamming — MOUMITA MAITI and •MICHAEL SCHMIEDEBERG — Institut für Theoretische Physik 1, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany

We explore the properties of the glass transition by employing a model system for a mixture of athermal jamming and random organization. We start with random configurations of soft repulsive spheres. While athermal jamming is realized by heading for the local minimum of the overlap energy without crossing energy barriers, random organization is obtained if we displace overlapping particles randomly in each step [1]. When mixing these protocols, we obtain a transition which is in the universality class of a directed percolation transition in time. Furthermore, we reveal that the limit of a small but nonzero probability of random steps differs from the case without random steps. This limit corresponds to the glass transition at small but non-zero temperatures. As a consequence the glass transition is a directed percolation transition and is fundamentally different from the athermal jamming transition. Finally, we explore the relation to spatial percolation transitions.

[1] L. Milz and M. Schmiedeberg, Connecting the random organization transition and jamming within a unifying model system, *Phys. Rev. E* 88, 062308 (2013).

CPP 66.3 Fri 10:30 ZEU 118

NMR and BDS Experiments on Water confined in MCM-41 — •EDDA KLOTZ, MATTHIAS SATTIG, CHRISTINA LEDERLE, and MICHAEL VOGEL — TU Darmstadt Solid State Physics, Darmstadt, Germany

The investigation of the dynamics of water in confinement is relevant for various fields of interest, from biological applications to geological ones. It is well established that confined water undergoes a dynamic crossover upon supercooling. However, the origin of the crossover is controversially discussed. To further study this issue, we focus on water in MCM-41 silica nanopores and use pore diameters for which well defined partial freezing occurs. Calorimetric studies are performed to characterize this freezing behavior. Moreover, nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy (BDS) are applied to ascertain the dynamics of the non-freezing water fraction cross the freezing transition. The dielectric spectra exhibit several processes that are sensitive to an appearance of a solid water fraction. ²H-NMR allows us to show that one of the processes can be identified with the rotational motion of water, exhibiting a kink in the temperature dependence at the freezing-transition. Moreover, ¹H static field gradient NMR yields self-diffusion coefficients of water, which can be linked to freezing-affected polarization processes in BDS. Thus, these combined studies clearly show a dynamic crossover due to formation of a solid water fraction.

CPP 66.4 Fri 10:45 ZEU 118

Water Dynamics in Mesoporous Silica Confinement — •MAX SCHÄFER, EDDA KLOTZ, ALEXANDER HARIRI, and MICHAEL VOGEL — Institut für Festkörperphysik, TU-Darmstadt, Germany

Confinement effects on the dynamics of water are examined using mesoporous silica MCM-41 with various pore diameters. Additionally the size of these pores are systematically modified by atomic layer deposition with Al₂O₃. To explore rotational motion, we combine different ²H NMR technics that are sensitive to molecular reorientations. Applying spin-lattice-relaxation, line shape analyzes and stimulated echo experiments, we cover the dynamical range down to very slow dynamics in a deeply supercooled temperature regime. ¹H diffusion measurements in an ultra high static field gradient were performed also. These experiments were supplemented by broadband dielectric spectroscopy and differential scanning calorimetry. We find that the temperature dependence of the structural alpha-relaxation exhibits a kink, which is strongly related to the pore size. We show that this kink is not associated to a proposed liquid-liquid phase transition of water, but to partial freezing. Furthermore we study confinement effects on dynamics and phase behavior in binary mixtures of water and glycerol for various concentrations. The properties of the hydrogen bond network and an eventually phase separation initiated by the confinement are of great interest. Glycerol dynamics for confined mixtures show an Arrhenius behavior at low temperatures in contrast to bulk mixtures and to pure glycerol confined in MCM-41. The similarity to water dynamics in confinement suggests a cooperative motion of water and glycerol.

CPP 66.5 Fri 11:00 ZEU 118

Dynamical coexistence in a polydisperse hard-sphere liquid — •MATTEO CAMPO^{1,2}, CHRISTOPHER PATRICK ROYALL³, and THOMAS SPECK¹ — ¹Institut für Physik, Johannes Gutenberg-Universität, Mainz, Germany — ²Graduate School Materials Science in Mainz, Germany — ³H. H. Wills Physics Laboratory, University of Bristol, United Kingdom

The glass transition is a long-standing challenge of condensed matter physics. One of the problems is that no significant change in the global structure seems to arise upon vitrification [1]. Recent studies however have recovered the old idea of Frank according to which geometric motifs which minimise the local free energy, so-called locally favoured structures (LFS), would grow in correlation with the slow regions of the glass and thus play an important role in the transition [2]. Among the key insights is the identification of a non-equilibrium phase transition in trajectory space, which implies phase coexistence between a slow phase rich in LFS and the normal supercooled liquid. Here we present a study of a polydisperse hard-sphere model glassformer and its LFS properties upon crystallization [3] and vitrification. We combine our numerical simulations with experimental observations that support the picture of the non-equilibrium phase transition in trajectory space.

[1] Ludovic Berthier and Giulio Biroli. *REV MOD PHYS*, 2011.

[2] C Patrick Royall and Stephen R Williams. *PHYS REP*, 2015.

[3] Matteo Campo and Thomas Speck. *JSTAT*, 2016.

15 min. break

CPP 66.6 Fri 11:30 ZEU 118

Electro-diffusion versus chemical diffusion in alkali calcium phosphate glasses - implication of structural changes — •ANNELI HEIN, JOHANNES MARTIN, MARTIN SCHÄFER, and KARL-MICHAEL WEITZEL — Philipps-Universität Marburg

A long term transport experiment has been performed on a bioactive calcium phosphate glass of the molar composition 30 CaO *25 NaO *45 P₂O₅ using the technique of bombardment induced ion transport (BIIT) with potassium as foreign bombardier ion. Ion transport due to gradients of the electrical potential and the concentration lead to incorporation of K⁺ and depletion of both Na⁺ and Ca⁺⁺ by electro-diffusion in forward direction. The resulting concentration profile has been quantitatively analyzed by ToF-SIMS. Further analysis of the P⁺ and PO_x⁺ signals (x = 1-4) shows characteristic changes of the structure of the local glass network. Since the concentration profiles imprinted by the BIIT constitute pronounced concentration gradients, these depletion profiles further evolve on a much longer time scale due

to chemical diffusion (absence of electric potential gradients). The former depletion zone is partially refilled by chemical diffusion. At the same time the structural changes of the glass network are demonstrated to be reversible. Numerical simulations on the basis of the coupled Nernst-Planck-Poisson equations allow deriving the diffusion coefficients of sodium, potassium and calcium for both cases, i.e. electrodiffusion and chemical diffusion. The two experiments are sensitive to different aspects of the diffusion coefficients and thus are complementary.

CPP 66.7 Fri 11:45 ZEU 118

Confinement effects on the correlation of plasticity in amorphous solids — ●MUHAMMAD HASSANI, PHILIPP ENGELS, and FATHOLLAH VARNIK — Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr Universität, Bochum, Germany

In amorphous solids, spatio-temporal correlations of plastic deformation are known to be mediated by the elastic medium [1]. Solid walls may strongly alter this elastic propagator and are thus expected to also influence these correlations. We study this issue via large scale molecular dynamics (MD) simulations. Spatial correlations of plastic activity are found to decay more slowly when approaching a wall. This observation is paralleled by a similar trend in the case of the strain field around a spherical inclusion placed at various distances from a wall. Results obtained from MD simulations are in quantitative agreement with numerical solution of continuum mechanics equations in the presence of an inclusion [2,3].

[1] F. Varnik, S. Mandal, V. Chikkadi, D. Denisov, P. Olsson, D. Vagberg, D. Raabe, and P. Schall, Correlations of plasticity in sheared glasses, *Phys. Rev. E* 89, 040301 (2014)

[2] A. Nicolas and J.-L. Barrat, A mesoscopic model for the rheology of soft amorphous solids, with application to microchannel flows, *Faraday Discuss.* 167, 567 (2013)

[3] M. Hassani, P. Engels, and F. Varnik, Confinement effects on the correlation of plasticity in amorphous solids (in preparation)

CPP 66.8 Fri 12:00 ZEU 118

Glass transitions, semiconductor-metal (SC-M) transitions and fragilities in Ge-V-Te (V=As, or Sb) liquid alloys: the difference one element can make — ●SHUAI WEI¹, GARRETT COLEMAN², PIERRE LUCAS², and C.AUSTEN ANGELL¹ — ¹Arizona State University — ²University of Arizona

Glass transition temperatures (T_g) and liquid fragilities are measured along a line of constant Ge content in the system Ge-As-Te, and contrasted with the lack of glass-forming ability in the twin system Ge-Sb-

Te at the same Ge content. The one composition established as free of crystal contamination in the latter system shows a behavior opposite to that of more covalent system. Comparison of T_g vs bond density in the three systems Ge-As-chalcogen differing in chalcogen i.e. S, Se, or Te, shows that as the chalcogen becomes more metallic, the bond density effect on T_g becomes systematically weaker, with a crossover at $\langle r \rangle = 2.3$. When the more metallic Sb replaces As at $\langle r \rangle$ greater than 2.3, incipient metallicity rather than directional bond covalency apparently gains control of the physics. This leads us to an examination of the electronic conductivity and, then, semiconductor-to-metal (SC-M) transitions, with their associated thermodynamic manifestations, in relevant liquid alloys. The thermodynamic components control liquid fragility and cause fragile-to-strong transitions during cooling. We tentatively conclude that liquid state behavior in phase change materials (PCMs) is controlled by liquid state SC-M transitions that have become submerged below the liquidus surface. The analogy to supercooled water phenomenology is highlighted.

CPP 66.9 Fri 12:15 ZEU 118

Glass structure and quantum efficiency of luminescent borate glass — ●A. CHARLOTTE RIMBACH¹, BERND AHRENS^{1,2}, FRANZISKA STEUDEL², and STEFAN SCHWEIZER^{1,2} — ¹South Westphalia University of Applied Sciences, Luebecker Ring 2, 59494 Soest — ²Fraunhofer Application Center for Inorganic Phosphors, Branch Lab of Fraunhofer Institute for Microstructure of Materials and Systems IMWS, Luebecker Ring 2, 59494 Soest

Luminescent glasses have gained more importance in the last decades, in particular for lasers, optical fibres, and optical amplifiers. For optical applications, borate glass is very versatile in shape and a suitable host for luminescent lanthanide ions due to its good lanthanide ion solubility. The borate glass system possesses a high transparency, low melting point as well as high mechanical, chemical, and thermal stability. Various luminescent borate glasses using boron oxide as network former and lithium oxide as network modifier are prepared. Here, the ratio between network former and network modifier determines the mechanical and chemical properties of the glass. An important parameter for the evaluation of luminescent materials is the absolute photoluminescence quantum efficiency (QE), i.e. the ratio of emitted to absorbed photons. While the ratio between network former and network modifier affects the QE only slightly, additional doping with aluminium oxide to reduce hygroscopicity results in a significant decrease in QE. Raman and Fourier transform infrared spectroscopy are used to analyze the structure of the glass network; the results are correlated with the QE measurements.