

CPP 5: Glasses and Glass Transition I (joint session DY/CPP)

Time: Monday 15:00–17:30

Location: H34

Invited Talk

CPP 5.1 Mon 15:00 H34

Intra- and inter-molecular dynamics in glass-forming liquids — ●PERIKLIS PAPAIOPOULOS¹, WILHELM KOSSACK², and FRIEDRICH KREMER² — ¹Max Planck Institute for Polymer Research, Mainz, Germany — ²Universität Leipzig, Germany

The intra- and inter-molecular interactions of salol and polystyrene, as low molecular weight and polymeric glass-forming model systems, are studied by Fourier-transform infrared (FTIR) spectroscopy and Broadband Dielectric Spectroscopy (BDS). By analysing the temperature dependencies of specific IR absorption bands it is demonstrated that each molecular moiety in the glass-formers has its own signature in the course of the dynamic glass transition: while some do not show any change at the calorimetric glass transition temperature, others exhibit a pronounced “kink”. The effects cannot be attributed solely to microscopic thermal expansion, but instead indicate gradual conformational changes. The ease of application of this approach to a variety of systems in different geometries and external conditions can assist the modelling of glasses and the understanding of the coupling between the glass transition and molecular-level dynamics.

[1] P. Papadopoulos, W. Kossack, and F. Kremer, *Soft Matter*, 2013, **9**, 1600 - 1603

CPP 5.2 Mon 15:30 H34

In-situ investigation of vapor-deposited thin films of toluene and ethylbenzene by AC chip-nanocalorimetry — ●MATHIAS AHRENBERG¹, KATIE R. WHITAKER², YEONG-ZEN CHUA¹, HEIKO HÜTH¹, MARK D. EDIGER², and CHRISTOPH SCHICK¹ — ¹Institut für Physik, Universität Rostock, Wismarsche Str. 43-45, 18051 Rostock, Germany — ²Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

Physical vapor deposition can be used to produce thin films with particular material properties. For example extraordinarily stable glasses can be obtained from organic molecules like toluene and ethylbenzene. We have investigated properties like packing efficiency and kinetic stability depending on substrate temperature and deposition rate by in-situ AC chip-nanocalorimetry. We have varied the substrate temperature covering the range from temperatures proven to yield high enthalpy glasses up to temperatures proven to yield low enthalpy glasses. This way the complete evolution of the mentioned stable glass properties is observed. Moreover AC calorimetry offers the possibility for isothermal measurements which enables to follow the transformation of the stable glass to the super-cooled liquid. Transformation experiments give suggestion of the transformation mechanism and its temperature dependence. The data are in agreement with a growth front for the transformation of the stable glass into the supercooled liquid.

CPP 5.3 Mon 15:45 H34

Calorimetric glass transition of ultrathin films of homopolymers and their blends — ●HUAJIE YIN and ANDREAS SCHÖNHALS — BAM Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin, Germany

Glass transition behavior of different ultrathin polymer films (down to around 10 nm) was investigated by specific heat spectroscopy using differential AC calorimetry. For thin homopolymer films like polystyrene (PS) and poly(vinyl methyl ether) (PVME), no thickness dependence of dynamic glass transition temperature was observed down to 10 nm. Furthermore, the width of the glass transition is independent of the film thickness which indicates that the extent of the cooperativity is essentially smaller than 10 nm. For polymer blend thin films in the case of PS/PVME with the weight fraction of 50/50, the dynamic glass transition temperature was found to be decreasing with reducing the film thickness. This phenomenon is explained in terms of surface enrichment of PVME in the polymer blend system where PVME has a lower surface energy than PS. X-ray photoelectron spectroscopy (XPS) was used to probe the surface composition in order to confirm such surface enrichment phenomena.

CPP 5.4 Mon 16:00 H34

Molecular dynamics of a discotic liquid crystal studied by Dielectric Relaxation and Specific Heat Spectroscopy — ●CHRISTINA KRAUSE¹, HUAJIE YIN¹, ANDREAS WURM², CHRISTOPH SCHICK², and ANDREAS SCHÖNHALS¹ — ¹BAM Federal Institute for

Materials Research and Testing, Unter den Eichen 87, D-12205 Berlin — ²Institute of Physics, University of Rostock, Wismarsche Straße 43-45, D-18051 Rostock

The molecular dynamics of the discotic liquid crystal pyrene-1,3,6,8-tetracarboxylic tetra(2-ethylhexyl)ester is investigated by dielectric relaxation and specific heat spectroscopy. The data from dielectric spectroscopy shows 3 processes: a β -relaxation at low temperatures and an α -relaxation in the temperature range of the mesophases followed by conductivity. In both phases the dielectric α -relaxation is assigned to restricted glassy dynamics. Glassy dynamics is also detected in the plastic crystalline phase by means of specific heat spectroscopy but with a different temperature dependence of the relaxation rates. This is discussed considering the different molecular restrictions of the fluctuations: close to the columns (dielectric spectroscopy) and more in the intercolumnar space (specific heat spectroscopy). In the frame of the fluctuation approach a correlation length of glassy dynamics is calculated to 0.78 nm which correlates well to the core-core distance estimated by X-ray scattering.

CPP 5.5 Mon 16:15 H34

Liquid to glass transition in a Wigner glass — ●FABIAN WESTERMEIER, MICHAEL SPRUNG, and GERHARD GRÜBEL — HASYLAB, Deutsches Elektronen-Synchrotron, 22607 Hamburg, Germany

One of the interesting problems of disordered systems is the nature of the liquid to glass transition. While the glass transition in molecular glass formers can be typically achieved by cooling down the system, in colloidal systems the glassy state is experimentally accessible by changing the strength of the direct particle interactions.

Colloidal systems can be distinguished by their type of interaction. While so called hard sphere systems interact via a repulsive, short range interaction potential, electrostatically stabilized systems are interacting via a long-range, screened Coulomb potential which depends inter alia on the charge of the particles and the concentration of additional ions in the solvent screening the direct particle interactions. As it is thus possible to tune the direct particle interaction strength of these systems, the glass transition can already occur at much lower volume fractions when compared to the hard sphere case.

We have used X-ray scattering techniques to investigate the glass transition of a charge stabilized system at a constant volume fraction, varying only the strength of the direct particle interactions. While the average structure of the colloidal suspensions shows only minor changes, the dynamics of the system vary strongly as a function of the direct particle interaction strength.

CPP 5.6 Mon 16:30 H34

Temporal evolution of structural and dynamical heterogeneities in a metastable colloidal fluid — ●SEBASTIAN GOLDE^{1,2}, MARKUS FRANKE², and HANS JOACHIM SCHÖPE^{2,3} — ¹Graduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany — ²Johannes Gutenberg-Universität Mainz, Institut für Physik, Staudinger Weg 7, 55099 Mainz, Germany — ³MPI für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

An interesting property of the metastable melt is that it exhibits spatial heterogeneous dynamics [1]. The dynamics can be understood as an accumulation of mobile and immobile particles. Recent work suggested that the local structure and dynamics of the metastable melt are correlated to each other [2]. In order to investigate these phenomena we used a hard sphere like colloidal model system. The local dynamics in the metastable colloidal melt were measured with our recently new designed multispeckle correlation spectroscopy setup which performs space- as well as time-resolved dynamic light scattering. The solidification kinetics was measured using an advanced time-resolved laser light Bragg scattering setup. The correlation between the particle dynamics and the solidification kinetics could be quantified by analyzing the temporal evolution of the local particle dynamics, the ensemble averaged dynamic structure factor and the solidification kinetics. Crossing the glass transition point we can show that there is fundamental link between crystallization and vitrification. [1] L. Berthier and G. Biroli, *Rev. Modern Physics* 83 (2011), [2] T. Kawasaki and H. Tanaka, *JCPM* 22 (2010)

CPP 5.7 Mon 16:45 H34

Multiple reentrant glass transitions in confined hard-sphere glasses — •SUVENDU MANDAL^{1,2}, SIMON LANG³, ROLF SCHILLING⁴, VITALIE BOTAN⁴, MARTIN OETTEL⁴, DIERK RAABE¹, THOMAS FRANOSCH³, and FATHOLLAH VARNIK^{1,2} — ¹Max-Planck Institut für Eisenforschung, Max-Planck Str. 1, 40237 Dusseldorf, Germany — ²Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, Stiepelers Strasse 129, 44801 Bochum, Germany — ³Institut für Theoretische Physik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstraße 7, 91058, Erlangen, Germany — ⁴Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudinger Weg 7, 55099 Mainz, Germany

We perform molecular dynamics simulations for a polydisperse, densely packed hard-sphere fluid confined between two parallel walls [1]. The diffusion coefficient parallel to the walls is observed to vary by orders of magnitudes upon changing the wall separation while keeping the packing fraction fixed. A striking multiple reentrance scenario emerges for the transition from liquid to glass as the wall separation becomes comparable to the particle diameter. The non-monotonic behavior of the phase diagram is rationalized in terms of a numerical solution of a recently developed mode-coupling theory [1,2].

[1] S. Mandal, S. Lang, R. Schilling, V. Botan, M. Oettel, D. Raabe, T. Franosch, and F. Varnik submitted [2] S. Lang, V. Botan, M. Oettel, D. Hajnal, T. Franosch, R. Schilling PRL 105, 125701 (2010).

CPP 5.8 Mon 17:00 H34

Shear banding in hard sphere glasses — SEGUN AYODELE¹, DIERK RAABE¹, INGO STEINBACH², and •FATHOLLAH VARNIK^{1,2} — ¹Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany — ²ICAMS, Ruhr Universität Bochum, Germany

When an amorphous solid is exposed to a simple shear such as a planar Couette flow, the flow may become heterogeneous despite the fact that the macroscopic stress is constant across the system [1,2]. However,

both in computer simulations [1,3] and experiments [2] the observed velocity profile is unsteady with significant spatio-temporal fluctuations. In this work, we address the question whether a steady shear banded solution may exist. For this purpose, we both perform an analysis of the underlying equations as well as lattice Boltzmann simulations, using as input the constitutive laws obtained from MD simulations [3].

[1] F. Varnik, L. Bocquet, J.-L. Barrat, L. Berthier, Phys. Rev. Lett. 90, 095702 (2003).

[2] R. Besseling, L. Isa, P. Ballesta, G. Petekidis, M.E. Cates, W.C.K. Poon, Phys. Rev. Lett. 105, 268301 (2010).

[3] S. Mandal, M. Gross, D. Raabe, F. Varnik, Phys. Rev. Lett. 108, 098301 (2012).

CPP 5.9 Mon 17:15 H34

Re-establishment of the equipartition theorem for small systems in molecular dynamics ensemble — •NIMA HAMIDI SIBONI^{1,2}, DIERK RAABE², and FATHOLLAH VARNIK³ — ¹AICES, RWTH-Aachen, Germany — ²Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany — ³ICAMS, Ruhr-Universität Bochum, Germany.

It has been reported recently that, in molecular dynamics (MD) simulations, periodic boundary condition leads to a violation of the equipartition theorem for systems containing particles with different masses [Shirts et al, J. Chem. Phys. **125** 164102 (2006)]. This effect is associated with the finite number of particles in MD simulations. Here, we propose a modification to MD simulation, which removes this problem. Our method is based on imposing Gaussian random fluctuations on the system's center of mass velocity. Using the analogy to a system exchanging momenta with impenetrable walls, we work out an analytical expression for the rate at which fluctuations are added to the system. The restoration of the equipartition is then demonstrated for small systems both at equilibrium as well as beyond equilibrium in the linear response regime.