CPP 4: Glasses I (joint session with DY)

Time: Monday 15:00–17:30 Location: C 243

Invited Talk CPP 4.1 Mon 15:00 C 243

Glass transition by molecular network topology freezing and discovery of vitrimers — •Ludwik Leibler, Damien Montarnal, Mathieu Capelot, and François Tournilhac — Matière Molle et Chimie, ESPCI, 10, rue Vauquelin, 75005 Paris, France

We will discuss a concept and practical realizations of a glass transition by reversible topology freezing of a molecular network. Permanently cross-linked materials, like thermosets or rubbers, have outstanding mechanical properties and solvent resistance, but they cannot be processed and reshaped once synthesized. Non-cross-linked polymers and those with reversible cross-links are processable, but they are soluble. We design epoxy networks able to rearrange their topology by exchange reactions without depolymerization and show that they are insoluble and processable. Unlike organic compounds and polymers whose viscosity varies abruptly near glass transition, these networks, vitrimers, show Arrhenius-like gradual viscosity variations just like vitreous silica. Like silica, the vitrimers can be wrought and welded to make complex objects by local heating without the use of molds. The concept of a glass, made by reversible topology freezing in epoxy networks can be readily scaled up for applications and generalized to other chemistries.

Topical Talk CPP 4.2 Mon 15:30 C 243

Elastic Properties of 2D amorphous solids — •Peter Keim — Universität Konstanz

Using positional data from video-microscopy of a two-dimensional colloidal system and from simulations of hard discs we determine the wave-vector-dependent normal mode spring constants in the supercooled fluid and glassy state, respectively. The emergence of rigidity and the existence of a displacement field in amorphous solids is clarified. Continuum elastic theory is used in the limit of long wavelengths to analyze the bulk and shear modulus of this amorphous system as a function of temperature. The onset of a finite static shear modulus upon cooling marks the fluid/solid transition. This provides an opportunity to determine the glass transition temperature T_G in an intuitive and precise way.

CPP 4.3 Mon 16:00 C 243

Heterogeneous shear in hard sphere glasses — •Fathollah Varnik[1,2], Suvendu Mandal[2], and Dierk Raabe[2] — [1]ICAMS, Ruhr University Bochum, Germany — [2]Max-Planck-Institut fuer Eisenforschung, Duesseldorf, Germany

There is growing evidence that the flow of driven amorphous solids is not homogeneous, even if the macroscopic stress is constant across the system [1,2]. Via event driven molecular dynamics simulations of a hard-sphere glass, we provide first direct evidence for a correlation between the fluctuations of the local volume-fraction and the fluctuations of the local shear rate [3]. Higher shear rates do preferentially occur at regions of lower density and vice versa. The temporal behavior of fluctuations is governed by a characteristic time scale, which, when measured in units of strain, is independent of shear rate in the investigated range. Interestingly, the correlation volume is also roughly constant for the same range of shear rates. A possible connection between these two observations is discussed.

[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, submitted to Phys. Rev. Lett.

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Effect of cross-link density on re-entrant melting of microgel colloids — •Malte Wiemann[1], Norbert Willenbacher[2], and Eckhard Bartsch[1,3] — [1]University of Freiburg, Department of Physical Chemistry, Freiburg, Germany — [2]Karlsruhe Institute of Technology, Department of Mechanical Process Engineering and Mechanics, Karlsruhe, Germany — [3]University of Freiburg, Department of Macromolecular Chemistry, Freiburg, Germany

Fluid states of colloidal dispersions at volume fractions above the glass transition can be accessed by introducing short-ranged depletion attraction [1]. For a binary mixture of PS-microgel particles (crosslinking density 1:50) in a good organic solvent DLS-measurements revealed a fluidization up to a volume fraction ϕ=0.69 when linear nonadsorbing polymer is added. The high packing fraction up to which fluid states could be observed raised the question whether the magnitude of this effect is a specialty of the microgel system. We prepared microgels with a much higher crosslinking density (1:10) which should be a good approximation of hard sphere colloids. Fluid states could again be obtained above ϕg, however, up to a significantly smaller packing fraction. The amount of free polymer needed to fluidize the dispersion was much lower as compared to the previous mixture [2]. The existence of fluid states up to high volume fractions for the 1:50 crosslinked particles is - at least partially - a microgel effect which is at present not fully understood and possible origins will be discussed. [1] K. Dawson etal., Phys. Rev. E 63, 011401 (2000) [2] M. Wiemann, N. Willenbacher, E. Bartsch, Colloid Surface A, 10.1016/j.colsurfa.2011.11.029

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Epoxy resins in confined geometry — •Anna Silex, Jörg Baller, and Roland Sanctuary — Laboratory of Physics of Condensed Matter and Advanced Materials, University of Luxembourg, 162A, Avenue de la Faiencerie, L-1511 Luxembourg

In order to exemplarily study the influence of confinement on the behavior of a widely used epoxy resin (Diglycidil Ether of Bisphenol A, DGEBA), we have filled mesoporous glasses with different pore radii with the low molecular weight liquid. Several confinement effects are known to take influence on the glass transition of small molecule liquids. Firstly, interactions between the glass former and the large internal surface of the porous glass lead to a slowing down of the molecular dynamics. Secondly, the confinement of the liquid molecules by the pores and the layer is generally known to accelerate the molecular dynamics. Finally, negative pressure building up in the pores due to the mismatching thermal expansion coefficients of the liquid and the porous glass is discussed to lead to a lower glass transition temperature compared to the pure materials. We present experimental results obtained for DGEBA-porous glass systems with stochastically modulated calorimetry and thermo-mechanical analysis. Thereby the focus is on the influence of the pore size on the glass transition behavior of the guest material but also on the macroscopic characteristics of the complete system as a result of the confinement. Differences between the thermal expansion of the empty and DGEBA filled samples are highlighted.

CPP 4.6 Mon 16:45 C 243

Glassy dynamics of isolated polymer coils — •Martin Tress, Emmanuel Mapesa, and Friedrich Kremer — Universität Leipzig, Leipzig

For the first time, the glassy dynamics of randomly distributed, isolated poly(2-vinylpyridine) (P2VP) polymer coils is studied by means of Broadband Dielectric Spectroscopy (BDS). This is achieved by recently developed nano-structured electrode arrangements where isolated polymer coils are deposited onto ultra-flat, highly conductive silicon electrodes. Atomic Force Microscopy scans of the identical sample before and after the BDS measurement prove that the volume of the coils matches, within a factor of 10 (reflecting the broad molecular weight distribution), with the expected volume of a single chain (considering bulk density and the respective molecular weight). The observed dynamics compares well with that of bulk but is slowed down by a factor of about 10. This is attributed to attractive interactions of the P2VP segments with the supporting silica surface.

CPP 4.7 Mon 17:00 C 243

Reduced Glass Transition Temperatures of Thin Polymer Films - Confinement Effect or Artifact? — •Oliver Bäumchen[1], Joshua D. McGraw[1], James A. Forrest[2], and Kari Dalnoki-Veress[1] — [1]Department of Physics & Astronomy and the Brockhouse Institute for Materials Research, McMaster University, Hamilton, ON, Canada, L8S 4M1 — [2]Department of Physics and Astronomy and Guelph-Waterloo Physics Institute, University of Waterloo, Waterloo, ON, Canada, N2L 3G1

For two decades there have been reports of measurements of reduced glass transition temperatures (T_g) in polymer, and in particular polystyrene, films. These results have motivated theoretical models and a variety of sophisticated experiments probing interfacial polymer properties. While the much larger reductions in T_g for free standing films have suggested the importance of the free surface, a significant concern has been raised about a possible correlation between anomalous dynamics and incomplete equilibration of the sample. Here, we present new ellipsometry measurements which unambiguously address this concern. The glass transition in free standing and supported films can be changed by many 10's of degrees by manipulating the interfacial properties. Taken together with previous work the results clearly reveal the importance of free interfaces as we transition from two, to one, to zero free interfaces.

CPP 4.8 Mon 17:15 C 243

Molecular Mobility and Glass Transition of Thin Poly(Bisphenol A Carbonate) Films — •Huajie Yin and Andreas Schönhals — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

Glass transition behavior of thin poly(bisphenol A carbonate) (PBAC) films (down to 10 nm) was investigated using capacitive dilatometry (CD), broadband dielectric spectroscopy (BDS) and differential ac-chip calorimeter (DACC) accompanied by contact angle measurements. In the BDS measurements of the thin PBAC films capped between two Al layers, no thickness dependence of the segmental dynamics was detected down to a critical thickness of 20 nm. For thickness below 20 nm, an increase of the relaxation time at a fixed temperature was observed. The thickness dependence of the thermal glass transition temperature determined by CD is in agreement with BDS results. Dynamic glass transition temperature of the ultra-thin PBAC films (10-55 nm) supported on SiO2 layer, with one free surface, was studied by means of differential ac-chip calorimeter as well. No thickness dependence of the dynamic glass transition temperature was observed within an uncertainty of +/-3 K for each frequency. These experimental results are discussed in terms of the different interactions of polycarbonate segments with the different substrates and/or different preparation conditions.