

CPP 78: Glasses and Glass Transition (joint session CPP, DF, DY)

Time: Friday 9:30–11:15

Location: C 243

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Stable glasses from strong liquids — ●YEONG ZEN CHUA¹, MATHIAS AHRENBURG¹, MICHAEL TYLINSKI², MARK D. EDIGER², and CHRISTOPH SCHICK¹ — ¹Institute of Physics, University of Rostock, Wismarsche Str. 43-45, 18051 Rostock, Germany — ²Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706 USA

To date, only several materials have been observed to form ultra-stable glasses by vapor deposition. Some authors have suggested that fragility might be a controlling factor in the ability to form stable glasses by vapor deposition, with highly stable glasses only being possible for highly fragile liquids. Glasses of ethylcyclohexane, fragility index 56.5, and 1-pentene, a very small molecule, produced by physical vapor deposition have been characterized by in situ AC chip nanocalorimetry. Since the fragility index of 1-pentene was not available, it was determined as 52 from the calorimetric glass transition temperatures measured in the frequency range from 0.2 Hz to 4 kHz. Ethylcyclohexane and 1-pentene are both strong glass formers, for which possibility of stable glass formation has been questioned. On the contrary, we observed formation of highly stable glasses of ethylcyclohexane and 1-pentene. The results on ethylcyclohexane and 1-pentene will be presented and compared with literature data of other known glass formers.

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Broadband dielectric spectroscopy of ionic liquids — ●PIT SIPPEL¹, MICHAEL AUMÜLLER¹, STEPHAN KROHNS^{1,2}, PETER LUNKENHEIMER¹, and ALOIS LOIDL^{1,2} — ¹Experimental Physics V, University of Augsburg, Germany — ²Institute for Materials Resource Management, University of Augsburg, Germany

Due to their high potential for applications, e.g., in energy-storage devices such as supercapacitors or batteries, during recent years ionic liquids have come into the focus of research [1]. Ionic liquids are composed of organic cations and weakly coordinating anions. An essential method for the study of ionic transport is dielectric spectroscopy. Our results on a large variety of ionic liquids cover a broad frequency and temperature range. This allows obtaining valuable information on phenomena like dc charge transport, the glass transition, electrode polarization, and relaxation. We analyze the dielectric spectra using an equivalent-circuit approach [2]. Amongst others, this enables the deduction of the relaxation times of the involved dynamic processes. We conclude that the main reorientational relaxation process of these ionic liquids, the α relaxation, is closely linked to the dc-conductivity. This provides insight into the underlying conductivity mechanisms and, thus, the mobility of the ionic charge carriers. Moreover, a number of secondary relaxation processes is found, including hints at the presence of a Johari-Goldstein relaxation process [3].

[1] M. Armand *et al.*, Nat. Mat. **8**, 621 (2009). [2] S. Emmert *et al.*, Eur. Phys. J. B **83**, 157 (2011). [3] G.P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

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Dielectric spectroscopy on glycerol and water confined in metal-organic frameworks — ●JONAS FISCHER¹, PIT SIPPEL¹, PETER LUNKENHEIMER¹, DMYTRO DENYSENKO², DIRK VOLKMER², and ALOIS LOIDL¹ — ¹Experimental Physics V, University of Augsburg, Germany — ²Chair of Solid State and Material Chemistry, University of Augsburg, Germany

Approaching the glass transition, the slowing down of molecular dynamics generally proceeds much stronger than expected for thermally activated motions. This can be ascribed to a temperature-dependent activation energy arising from the cooperative motion of increasing numbers of molecules at low temperatures [1]. The number of correlated molecules can be controlled by confining the glass-forming liquid in small pores. Previously, glass formers have been confined in porous glasses, zeolites and other silicates [2]. Recently, metal-organic frameworks (MOFs) have become available. This class of porous coordination polymers consists of metal-containing units and organic linkers. MOFs are tunable in many regards [3], thus allowing confinement in pores of different inner surfaces and varying sizes. Here, we present broadband dielectric spectroscopy data of glycerol and water confined in different MOFs, of the MFU-type [4]. It is shown that MOFs are well-suited for the measurement of confined liquids.

- [1] T. Bauer *et al.*, Phys. Rev. Lett. **111**, 225702 (2013).
 [2] A. Huwe *et al.*, Phys. Rev. Lett. **82**, 2338-2341 (1999).
 [3] H. Furukawa *et al.*, Science **341**, 1230444 (2013).
 [4] D. Denysenko *et al.*, Chem Commun. **48**, 1236 (2012).

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Dynamics of the glass transition in confined glycerol under hard and soft confinement, investigated by ²H NMR — ●MICHAEL LANNERT, MATTHIAS SATTIG, THOMAS BLOCHOWICZ, and MICHAEL VOGEL — Hochschulstraße 6-8, 64289 Darmstadt, Germany
²H NMR allows us to access correlation times of molecular rotational dynamics, ranging from $\tau=10^{-12}$ s to $\tau=10^{-1}$ s, by using longitudinal relaxation, solid echo, and stimulated echo sequences. Findings for confined glycerol, which is subjected to spherical soft confinement (using AOT/toluene micro-emulsions) and cylindrical hard confinement (using microporous silica, namely MCM-41) are compared, and a shift in correlation times to shorter times is observed for the hard confinement, but not for the soft confinement. Various diameters (2nm to 9nm) were used in order to gain a comprehensive understanding of the finite size effect. Investigation of the dynamics of the glycerol in the supercooled regime proved to be a challenging enterprise in soft confinement, because of the onset of rotational diffusion of the whole microemulsion droplet, which exceeds the contribution of molecular rotational dynamics. Therefore droplet size-dependence and viscosity-dependence of the dynamics were investigated additionally, in order to evaluate the impact of these results.

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Structure and Dynamics of Asymmetric Poly(styrene-*b*-1,4-isoprene) Diblock Copolymer under 1D and 2D Nanoconfinement — ●WYCLIFFE K. KIPNUSU¹, MAHDY M. ELMAHDY¹, EMMANUEL U. MAPESA¹, JIANGI ZHANG², DETLEF-M. SMILGIES³, CHRISTINE M. PAPADAKIS⁴, and FRIEDRICH KREMER¹ — ¹Institute of Experimental physics I, Linnstr.5, 04103, Leipzig — ²National Center for Nanoscience and Technology (NCNST), No.11 ZhongGuanCun BeiYiTiao, 100190 Beijing, P.R. China. — ³Cornell High Energy Synchrotron Source (CHESS), Wilson Laboratory, Cornell University, Ithaca, NY 14853, USA — ⁴Technische Universität München, Physik-Department, Physik weicher Materie, James-Frank-Straße 1, 85748 Garching, Germany.

The impact of 1- and 2-dimensional (2D) confinement on the structure and dynamics of poly(styrene-*b*-1,4-isoprene) P(S-*b*-I) diblock copolymer is investigated by a combination of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), Atomic Force Microscopy (AFM) and Broadband Dielectric Spectroscopy (BDS). 1D confinement is achieved by spin coating the P(S-*b*-I) to form nanometric thin films on silicon substrates, while in the 2D confinement, the copolymer is infiltrated into cylindrical anodized aluminum oxide (AAO) nanopores. GISAXS and AFM reveal hexagonally packed cylinders of PS in a PI matrix. The dynamic glass transition of the styrene and isoprene blocks is independent of the dimensionality and the finite sizes (down to 18 nm) of confinement but the normal mode is influenced by both factors with 2D geometrical constraints exerting greater impact.

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High frequency laser heated AC-chip calorimeter for dynamic glass transition investigation in room temperature ionic liquids — ●EVGENI SHOIFET^{1,2,3,4}, HEIKO HUTH¹, SERGEY VEREVKIN^{2,4}, CHRISTOPH SCHICK^{1,4}, and EGON HASSEL³ — ¹Institute of Physics, University of Rostock, 18057 Rostock, Germany — ²Institute of Physical Chemistry, University of Rostock, 18059 Rostock, Germany — ³Department of Technical Thermodynamics, Faculty of Mechanical Engineering and Marine Technology, Rostock, 18051 Rostock, Germany — ⁴Faculty of Interdisciplinary Research, Department "Life, Light and Matter", University of Rostock, Germany

Many ionic liquids are good glass formers. Nevertheless, for the relaxation behavior only a few studies of the dynamic glass transition in ionic liquids are available so far. Particularly the frequency dependence of the dynamic glass transition (α -relaxation) is not known for most ionic liquids. The standard technique for such studies - dielectric spectroscopy - is not easily applicable to ionic liquids because of the high electrical conductivity. In addition, dielectric spectroscopy is equally

sensitive to the segmental relaxation (α -relaxation) and secondary relaxation but calorimetry is sensitive solely to segmental relaxation.

We try to use calorimetric techniques to obtain complex heat capacity and to investigate the dynamic glass transition of room temperature ionic liquids (RTILs) in a wide frequency range. This can give an insight in cooperative motions of ions and ion clusters in RTILs. Particularly the influence of alkyl chain length on the α -relaxation in the frequency range from 1 mHz to 0.1 MHz [Shoifet. E. et. al. (2013)].

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Dynamic glass transition measurements on nm-thin films of Indomethacin using AC chip-nanocalorimetry — •MATHIAS AHRENBURG, CHRISTOPH SCHICK, and GUNNAR SCHULZ — Institut für Physik, Universität Rostock

We are using AC chip nano-calorimetry for the in-situ investigation of

the dynamic glass transition of vapor-deposited thin films of toluene and indomethacin of thicknesses between several hundred nm down to ten nm. With these experiments on low molecular mass substances we complement our data on similar thin polymer films. Firstly, the deposition-related thermodynamic state (stable glass) of each film is erased by transforming them into ordinary glasses. Secondly, upon reheating the thin ordinary glass films a direct comparison of the subsequently measured frequency-dependent dynamic glass transition temperatures becomes possible. The frequency of temperature modulation can be varied from 1 Hz up to about 1000 Hz. Film thicknesses for indomethacin are measured ex-situ with an atomic force microscope directly on the membrane of the chip-sensors. Similar to the thin polymer films no thickness dependence of the dynamic glass transition temperature (main relaxation) is seen. The results are in agreement with the explanation given by Cangialosi et al.