

CPP 11: Poster: Glasses and Glass Transition (joint session DY/CPP)

Time: Monday 17:30–19:30

Location: Poster C

CPP 11.1 Mon 17:30 Poster C

Room temperature ionic liquid's (RTILs) dynamic glass transition by calorimetric methods. — ●EVGENI SHOIFET^{1,2}, HEIKO HUTH¹, SERGEY VEREVKIN², and CHRISTOPH SCHICK¹ — ¹Institute of Physics, Rostock University, Rostock, 18051, Germany — ²Institute of Chemistry, University of Rostock, 18051 Rostock, Germany

Many of the ionic liquids are good glass formers. Nevertheless, only a few studies of the 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. 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. The techniques that were used are DSC, TMDSC, and AC-chip calorimeter[5] covering a frequency range from 0.001 Hz to 10000 Hz. Similar fragility was found not only in series of RTILs with different alkyl chain length in the cation ([Cnmim]), but also for two different anions ([Co(NCS)2],[NTf2]). Also the decrease in thermal glass transition temperature (T_g) and add/even effect have been observed in cobalt RTIL, while the T_g in RTIL with sulfonic anion is increasing, with increase of alkyl chain length.

CPP 11.2 Mon 17:30 Poster C

Nanoscale confinement of a low molecular weight liquid — ●ANNA DJEMOUR, JÖRG BALLER, CARLO DI GIAMBATTISTA, MARLENA FILIMON, JENS-PETER BICK, ANDREAS MICHELS, and ROLAND SANCTUARY — Laboratory for the Physics of Advanced Materials, University of Luxembourg, 162A, Avenue de la Faiencerie, L-1511 Luxembourg

The enormous change of the molecular dynamics of glass formers when approaching the thermal glass transition temperature is usually attributed to the increase of the size of cooperative rearranging regions (CRR). Spatial confinement is known to take influence on the glass transition behaviour when the scale of confinement is in the same order as the size of the CRRs. In this work we present investigations of the glass transition of a low molecular weight epoxy resin (Diglycidil Ether of Bisphenol A, DGEBA) filled in different nanoporous silica glasses. The effect of confinement is studied by two different ways: i) properties of the glass former are investigated by modulated calorimetry, dielectric spectroscopy and X-ray scattering. ii) properties of the whole system, i.e. porous glasses filled with the glass former are investigated by thermo-mechanical analysis and dynamic mechanical analysis. Combining the results from both approaches contributes to the understanding of the glass former DGEBA under confinement.

CPP 11.3 Mon 17:30 Poster C

Local Thermal Analysis as a Tool for Morphological Investigation of Polypropylene — THOMAS FISCHINGER, ●LISA MARIA UIBERLACKER, and SABINE HILD — Institute for Polymer Science, Johannes Kepler University, Altenbergerstraße 69, 4040 Linz, Austria

A basic understanding of physical and chemical properties of polymers is of fundamental importance for the development of advanced polymers. Thermal analysis methods are generally used to provide important and reliable data. However, up to now mainly bulk properties of polymers have been detected. Conventional methods reach a limit for applications such as the investigation of crystal structures. Therefore, a method is proposed for nano-thermal characterization of polymers using scanning probe microscopy (SPM) in combination with heatable cantilever probes. This method is based on an appropriate temperature calibration, which provides a reliable correlation between applied voltage and the temperature at the tip. LTA measurements were applied to high molecular isotactic polypropylene with varying lamellar thicknesses. Furthermore, the structure and morphology of randomly distributed isotactic propylene-1-hexene-copolymer (PHCP) were investigated with a focus on local thermal properties. In this study it will be shown that it is possible to investigate the differences in softening of α - and γ - structure of PHCP.

CPP 11.4 Mon 17:30 Poster C

Bestimmung der molekularen Dynamik von Polyvinylpyrrolidon mittels NMR und DS — ●MICHAEL LANNERT und MICHAEL VOGEL — Technische Universität Darmstadt, Institut für Festkörperphysik

Die molekulare Dynamik von Wasser in Polymer-Matrizen (D₂O-Polyvinylpyrrolidon-Mischung) wurde mittels Deuteronen NMR untersucht. Fragestellung ist, ob sich anhand der temperaturabhängigen Korrelationszeit der Rotation der C-D-Bindungen ein starkes oder fragiles Verhalten ausmachen lässt. Eine Theorie, welche die Existenz einer hochdichten (HDL) und niederdichten (LDL) Flüssigphase des Wassers im unterkühlten Regime voraussagt, legt einen "Fragil-Stark-Übergang" bei $T \approx 220\text{K}$ nahe. Zusätzlich zu den NMR-Messungen wurden Daten aus Dielektrischer Spektroskopie ausgewertet. Unter Annahme spezieller empirischer Modelle für die spektrale Dichte der unterliegenden Prozesse, namentlich einer Cole-Davidson Verteilung, kann so aus den DS Daten die mittlere Relaxationsrate der NMR-Experimente vorausgesagt und mit den tatsächlich erhaltenen Werten verglichen werden. Interpolationen der Temperaturabhängigkeit der Wasserdynamik mit einem Arrheniusgesetz ergeben eine Aktivierungsenergie von $E_A = 0.5\text{eV}$, welche von der Wasserkonzentration unabhängig ist. Durch Kombination von NMR und DS sowie Abdeckung eines breiten Zeitfensters gelingt es somit, ein konsistentes Bild der Dynamik im untersuchten System zu zeichnen.

CPP 11.5 Mon 17:30 Poster C

Thermomechanical Properties of Organic-Coatings: A scanning force microscopy study — ●BERNHARD JACHS¹, BERNHARD STRAUSS², and SABINE HILD¹ — ¹Institute of Polymer Science, JKU Linz, Altenbergerstraße 69, 4040 Linz, — ²voestalpine Stahl GmbH, 4020 Linz

Coil Coating is a continuous industrial process where one or more polymeric layers with thicknesses ranging from 5 up to 50 μm are applied on steel coils to protect them against environmental impacts. For further processing of the coated material, the knowledge of thermal and mechanical properties of the coating is crucial. Widely used analytical techniques (DSC, DMA) require special sample preparation where the coating has to be removed from the substrate or is prepared as a free standing coating film. In this work a SFM equipped with a heating stage was used to directly investigate mechanical properties of coatings as a function of temperature by performing nanoindentation measurements. Static measurements were carried out at different displacement rates and temperatures. By taking into account contact-mechanical models, which describe the tip-sample-interaction, the Elastic Modulus can be obtained as a function of temperature and displacement rate. Shifting the curves according to the Williams-Landel-Ferry equation yields a mastercurve which allows extrapolating mechanical properties beyond the measuring range. In addition, dynamic measurements have been carried out modulating the tip position at different frequencies and temperatures. Using proper viscoelastic models, Storage and Loss Moduli as well as loss tangent can be determined.

CPP 11.6 Mon 17:30 Poster C

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 HUTH¹, 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 11.7 Mon 17:30 Poster C

Triplet-Solvatationsdynamik an unterkühlten Wassermischungen in hartem und weichem Confinement — ●VINCENTO TALLUTO¹, CARL BÖHMER¹, THOMAS WALTHER¹ und THOMAS BLOCHOWICZ² — ¹Institut für Angewandte Physik, Technische Universität Darmstadt, Schlossgartenstr. 7, 64289 Darmstadt — ²Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstraße 8, 64289 Darmstadt

Die Triplet-Solvatationsdynamik ist eine Methode, mit der Relaxation in unterkühlten Flüssigkeiten nahe des Glasübergangs untersucht werden kann. Hierzu wird der Flüssigkeit ein Farbstoff beigemischt, welcher mittels eines UV-Laserpulses in einen langlebigen Tripletzustand angeregt wird. Über den zeitlichen Verlauf der Emissionswellenlänge des Farbstoffes kann die Relaxation der Solvatationshülle in einem Zeitbereich von 0.1 ms bis 1 s verfolgt werden. Je nach Farbstoff kann dabei eine dielektrische oder mechanische Response auf die Anregung des Farbstoffmoleküls beobachtet werden.

Der Vorteil dieser lokalen Methode liegt u.a. darin, dass z. B. Glasbildner in Confinement untersucht werden können. In gefüllten Porensystemen sind hier z. B. die Ergebnisse der herkömmlichen dielektrischen Spektroskopie nur schwer zu interpretieren. Wir präsentieren erste Messungen an Wasser-Alkohol-Mischungen als Bulk-Material, sowie im Confinement von Vycor-Poren und Mikroemulsionströpfchen mit dem Ziel, Oberflächen-, Dichte- und Finite-Size-Effekte voneinander zu trennen, deren Überlagerung eine eindeutige Interpretation dynamischer Daten bisher erschwert.

CPP 11.8 Mon 17:30 Poster C

The interplay between inter- and intramolecular dynamics in a series of alkylcitrate — ●WYCLIFFE KIPNUSU¹, WILHELM KOSSACK¹, CIPRIAN IACOB¹, JOSHUA SANGORO², and FRIEDRICH KREMER¹ — ¹Institute of Experimental Physics I, University of Leipzig, Linnestr. 5, 04103 Leipzig, Germany — ²Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830-6197, United States.

The inter- and intra-molecular dynamics in a series of glass-forming alkylcitrate is studied by a combination of Broadband Dielectric (BDS), Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR), Dynamic Mechanical (DMS), and Fourier-Transform Infrared (FTIR) Spectroscopy. Analyzing the temperature dependencies of specific IR absorption bands in terms of their spectral position and the corresponding oscillator strengths enables one to unravel the intramolecular dynamics of specific molecular moieties and to compare it with the intermolecular dynamics. With decreasing temperature, the IR band positions of carbonyls and H-bonded moieties of citrates, show a red shift with a kink at T_g while other moieties whose dynamics are decoupled from those of the core units, exhibit a blue shift with nominal changes at T_g. The oscillator strength of the ester linkage and H-bonded units show a kink at a temperature where structural and faster secondary relaxations merge. By that, a wealth of novel information is obtained proving the fundamental importance of intramolecular mobility in the process of glass formation, beyond coarse-grained descriptions. Reference: Papadopoulos P. et al. *Softmatter* 2012 In press.

CPP 11.9 Mon 17:30 Poster C

First Thermal Conductivity and Elastic Susceptibility measurements of Zr-based Bulk Metallic Glasses at Ultra Low Temperatures — ●MARIUS HEMPEL, DANIEL ROTHFUSS, ANDREAS FLEISCHMANN, and CHRISTIAN ENSS — Kirchhoff-Institut für Physik, Heidelberg

The thermal conductivity and the elastic susceptibility of Zr-based superconducting bulk metallic glasses have been measured the first time in the temperature range down to 6 mK in order to study the interaction of atomic tunnelling systems with phonons and conducting electrons. Additional susceptibility measurements reveal a superconducting transition around 1 K.

Both, the elastic susceptibility and the thermal conductivity measurements use a novel SQUID-based contact free detection technique below 1 K which allows to dispense with a bias voltage in the case of the elastic measurements and reduces parasitic heat input during the thermal conductivity measurements.

The thermal conductivity of the bulk metallic glass Zr_{52.5}Ti₅Cu_{17.9}Ni_{14.6}Al₁₀ scales nearly quadratically with temperature as expected from the tunnelling model. The change of sound

velocity of the of the bulk metallic glass Zr₅₅Cu₃₀Al₁₀Ni₅ shows a temperature dependence which is governed by resonant and relaxational processes. The latter are caused by the interaction with thermal phonons and quasi-particles in the vicinity of the superconducting transition.

CPP 11.10 Mon 17:30 Poster C

Non-universal dielectric and elastic properties of glasses at very low temperatures — ●ANNINA LUCK, MARIUS HEMPEL, ANDREAS FLEISCHMANN, and CHRISTIAN ENSS — Kirchhoff-Institut für Physik, Universität Heidelberg

Based on many experimental observations the low temperature properties of glasses, governed by atomic tunneling systems, have long been viewed as being universal. In the last years, however, measurements of dielectric two-pulse polarization echoes have revealed that nuclear electric quadrupole moments involved in atomic tunneling systems can cause large material-dependent effects in magnetic fields.

To study the possible influence of nuclear electric quadrupoles in two level systems on the low frequency dielectric and elastic properties of glasses down to a temperature of 10 mK, we measured vitreous silica and the multicomponent glass N-KZFS11, which contains 25 mass percent of tantalum oxide. As ¹⁸¹Ta carries a very large nuclear electric quadrupole moment, N-KZFS11 seems to be an ideal candidate to determine the influence of nuclear electric quadrupole moments on the physical properties of glasses at low temperatures.

Our measurements not only show a non-universal dielectric and elastic behaviour for these two glasses, but the results also differ significantly from various predictions of the standard tunneling model. We discuss these new findings and possible implications in terms of the tunneling model.

CPP 11.11 Mon 17:30 Poster C

1/f flux noise induced by spin glasses in superconducting qubits — ●JUAN ATALAYA — Institut für Theoretische Festkörperphysik, Karlsruher Institut für Technologie, Karlsruhe, Deutschland.

Recently, it has been realized that the coherence time of flux qubits is limited by unknown sources of flux noise, which exhibits a 1/f spectrum at low frequencies $f \lesssim 10$ kHz and at low temperatures $\lesssim 5$ K. Experiments suggest that the main contribution to the flux noise may be produced by paramagnetic spins located on the surface of the superconducting loop. We consider a spin glass system of classical Heisenberg spins and investigate the low frequency dynamics of the total magnetization at temperatures near the spin glass freezing temperature. We discuss the role of anisotropy and temperature on the shape of the noise spectrum.

CPP 11.12 Mon 17:30 Poster C

Glassy dynamics of orientation fluctuations in modulated phases — ●CHRISTIAN RIESCH, GÜNTER RADONS, and ROBERT MAGERLE — Institut für Physik, Technische Universität Chemnitz, D-09107 Chemnitz

We report on glassy dynamics and aging behavior in a 2D stripe-forming system free of topological defects. Numerical simulations based on model B with Coulomb interactions were performed for a wide range of noise strengths. The autocorrelation function of the local stripe orientation obeys the scaling form $C_\theta(t, t_w) \sim t_w^{-b} \cdot f(t/t_w)$, typical for glassy dynamics, and we argue that the relaxation time of the orientation fluctuations diverges. Spatial correlations are anisotropic, exhibiting a fast decay parallel to the stripes and an emerging power-law behavior in the perpendicular direction. We also investigate aging effects in other modulated phases, such as a hexagonal system in 2D and a lamellae-forming system in 3D.

CPP 11.13 Mon 17:30 Poster C

Theoretical methods to analyse scattering patterns in the systems of self-assembling anisotropic particles — ●SOFIA KANTOROVICH^{1,2}, ELENA PYANZINA¹, CRISTIANO DE MICHELE², and FRANCESCO SCIORTINO² — ¹Ural Federal University, Lenin av. 51, 620000, Ekaterinburg, Russia — ²Sapienza, University of Rome, Piazzza A. Moro 5, 00185, Rome, Italy

Self-assembly is a phenomena which can be observed on the broad range of scales: starting from simple molecules to colloidal particles. This effect of spontaneous equilibrium formation of reversible aggregates might serve as a key to the synthesis of new smart materials, once self-assembly mechanisms are well understood. The aggregates formed in the systems might lead to significant changes in macroscopic

responses of the systems, thus, becoming very important in soft matter and biophysics. One of the examples of self-assembling building blocks is short blunt-ended DNA duplexes which form chains. At low densities these chains form an isotropic phase, whereas, at high densities, these particular DNA solutions are known to order into the nematic liquid crystal phases. Here, we put forward a theoretical approach, which suggests how to predict the average chain length and the stacking free energy, based on the experimental scattering patterns. We show that the proposed method is rather general and might be used for any self-assembling anisotropic particles, as long as the chain-size distribution is exponential.

CPP 11.14 Mon 17:30 Poster C

Dissociation behavior of pyridine coordination compounds in aqueous solutions — ●MANUEL GENSLER¹, CHRISTIAN EIDAMSHAUS², ARTUR GALSTYAN², ERNST-WALTER KNAPP², HANS-ULRICH REISSIG², and JÜRGEN P. RABE¹ — ¹Institut für Physik, Humboldt-Universität zu Berlin — ²Institut für Chemie und Biochemie, Freie Universität Berlin

The pyridine core is ubiquitous in natural products and widely used for the construction of supramolecular structures [1]. We analyzed coordination compounds of mono- and bivalent pyridines with Cu(II) and Zn(II) by SFM based single molecule force spectroscopy (SMFS) in aqueous solutions. Using the Bell-Evans-Kramers model we determined surprisingly long rupture lengths from 0.25 nm for the mono-valent pyridin with Cu(II) up to 0.52 nm for the bivalent pyridine with Cu(II). DFT calculations suggest a stepwise dissociation through an intermediate product in which a water ligand inserts in between the pyridine and metal ion. Such process is different to the known solvent-ligand-exchange mechanism of a pyridine-palladium complex in DMSO with a rupture length of only 0.17 - 0.19 nm [2]. Therefore additional water ligands may attribute to the mechanical properties

of metallosupramolecular compounds and their corresponding natural systems.

[1] L.E. Kapinos and H. Sigel *Inorg. Chim. Acta* **2002**, *337*, 131-142. [2] F.R. Kersey et al. *J. Am. Chem. Soc.* **2006**, *128*, 3886-3887.

CPP 11.15 Mon 17:30 Poster C

Probing the electronic structure of gas phase methanol by soft RIXS — ●ANDREAS BENKERT^{1,2,3}, FRANK MEYER¹, MONIKA BLUM⁴, REGAN G. WILKS⁵, MARCUS BÄR^{4,5}, WANLI YANG⁶, FRIEDRICH REINERT^{2,3}, CLEMENS HESKE^{1,4,7}, and LOTHAR WEINHARDT^{1,4,7} — ¹Inst. for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology (KIT) — ²Exp. Physik VII, Universität Würzburg — ³Gemeinschaftslabor für Nanoanalytik, KIT — ⁴Dept. of Chemistry, University of Nevada, Las Vegas — ⁵Solar Energy Research, Helmholtz-Zentrum Berlin f. Mat. u. Energie — ⁶Advanced Light Source, Lawrence Berkeley National Laboratory — ⁷ANKA Synchrotron Radiation Facility Karlsruhe, KIT

We have investigated methanol in gas phase at atmospheric pressure using resonant inelastic soft x-ray scattering (RIXS). RIXS maps of both, the O K and C K edge, will be presented, and it will be shown that the observed emission lines can be attributed to different molecular orbitals in accordance to DFT-based calculations of isolated methanol molecules. This demonstrates the local character of the RIXS process.

In detail, we observe strong spectator shifts of up to 0.9 eV upon excitation into different absorption resonances at the O K edge. Furthermore, we find evidence for nuclear dynamics on the time scale of the x-ray emission process, leading to a dissociation of the hydrogen atom from the hydroxyl group. In addition, measurements of deuterated methanol allow us to separate the contributions of intact and dissociated methanol molecules in the emission spectra.