

DYNAMICS OF GLASS-FORMING LIQUIDS:

will theory and experiment ever meet?

PROGRAM

5th-7th April 2017



Carlsberg Academy, Gamle Carlsbergvej 15, Copenhagen



DET FRIE FORSKNINGSRÅD
DANISH COUNCIL FOR
INDEPENDENT RESEARCH

08.00-08.50  **REGISTRATION** (coffee and croissant)

08.50-09.10  **WELCOME**

Chair: Jeppe Dyre

09.10-09.50 **Mark Ediger** · University of Wisconsin
Structure and dynamics of highly stable glasses prepared by physical vapor deposition

09.50-10.10 Discussion

10.10-10.30 **Ludovic Berthier** · Université de Montpellier
Equilibrium simulations of supercooled liquids beyond laboratory timescales: Will experiments ever catch up with theory?

10.30-10.40 Discussion

10.40-11.00  **COFFEE BREAK**

Chair: Jeppe Dyre

11.00-11.20 **Tullio Scopigno** · La Sapienza Università di Roma
A 100 Myr landscape exploration using a geologically hyperaged glass

11.20-11.30 Discussion

11.30-11.50 **Magdaleno Medina-Noyola** · Universidad Autónoma de San Luis Potosí
Physical gels, porous glasses, and the glass transition: Experimental tests of a unifying theory

11.50-12.00 Discussion

12.00-12.20 **Thomas Körber** · Universität Bayreuth
On the nature of the β -process in organic glass formers

12.20-12.30 Discussion

12.30-12.50 **Hao Liu** · Aalborg Universitet
A structural connection to the configurational heat capacity of borate-silicate glass-forming liquids

12.50-13.00 Discussion

13.00-14.00  **LUNCH**

Chair: Christoph Schick

14.00-14.40 **Christiane Alba-Simoniesco** · Laboratoire Léon Brillouin

The glass transition phenomenon:
When an experimental chemist meets with theoretical physicists

14.40-15.00 Discussion

15.00-15.20 **Timothy Ransom** · Naval Research Laboratory

Dielectric spectroscopy at extremely high pressure in a diamond anvil cell

15.20-15.30 Discussion

15.30-15.50 **Henriette Wase Hansen** · Roskilde Universitet

Isochronal superposition on second and picosecond timescales

15.50-16.00 Discussion

16.00-16.30  COFFEE BREAK

Chair: Christoph Schick

16.30-16.50 **Karolina Adrjanowicz** · Uniwersytet Śląski

Density scaling as a universal link between the dynamics of glass-forming liquids in the bulk and confined geometry

16.50-17.00 Discussion

17.00-17.20 **Denis Morineau** · Université de Rennes

Microphase separation and multiple glass transitions induced by nanoscale confinement

17.20-17.30 Discussion

17.30-17.50 **Friedrich Kremer** · Universität Leipzig

Glassy dynamics in one- and two-dimensional nanometric confinement – a comparison

17.50-18.00 Discussion

18.00-18.20 **Hua Tong** · University of Tokyo

Probing the structural origin of dynamic heterogeneity in glass-forming liquids

18.20-18.30 Discussion

19.00-20.00  DINNER (buffet) + POSTER SESSION

20.00-  POSTER SESSION continued with beer

Chair: Uli Buchenau

09.00-09.20 **Matthieu Wyart** · École Polytechnique Fédérale de Lausanne

Levy flight in mayonnaise

09.20-09.30 Discussion

09.30-09.50 **C. Patrick Royall** · University of Bristol

Particle-resolved studies of deeply supercooled liquids:
A means to test theories of the glass transition

09.50-10.00 Discussion

10.00-10.20 **Ulf Rørbæk Pedersen** · Roskilde Universitet

Theory of thermodynamics of freezing and melting

10.20-10.30 Discussion

10.30-11.00  COFFEE BREAK

Chair: Uli Buchenau

11.00-11.40 **Giulio Biroli** · CEA Saclay

Non-linear responses: a guide to discover the true nature
of the glass transition

11.40-12.00 Discussion

12.00-12.20 **François Ladieu** · Université Paris-Saclay

Unifying different interpretations of the nonlinear response
in glass-forming liquids

12.20-12.30 Discussion

12.30-12.50 **Ranko Richert** · Arizona State University

The effect of electric fields on the glass transition:
Theory versus experiment

12.50-13.00 Discussion

13.00-15.00  LUNCH + POSTER SESSION

Chair: Michael Wübbenhorst

- 15.00-15.20 **Gregor Diezemann** · Universität Mainz
 Nonlinear response in terms of simple stochastic models
- 15.20-15.30 Discussion
- 15.30-15.50 **Beatrice Ruta** · European Synchrotron Radiation Facility & Université de Lyon
 Anomalous microscopic dynamics in metallic glass formers
- 15.50-16.00 Discussion
- 16.00-16.20 **Chiara Cammarota** · King's College London
 Equilibrium random pinning and epsilon coupling:
 A unified picture where theory and experiments could possibly meet
- 16.20-16.30 Discussion

16.30-17.00  COFFEE BREAK

Chair: Michael Wübbenhorst

- 17.00-17.20 **Kenneth Schweizer** · University of Illinois
 Elastically collective activated relaxation in glass-forming liquids:
 Theory meets experiment
- 17.20-17.30 Discussion
- 17.30-17.50 **Johan Mattsson** · University of Leeds
 Chain-length dependent relaxation dynamics in glass-forming oligomers
 and polymers
- 17.50-18.00 Discussion
- 18.00-18.20 **Jörg Baschnagel** · Institut Charles Sadron
 Molecular dynamics simulations of supercooled polymer melts:
 Modeling of single-monomer dynamics by a continuous-time random walk
 approach
- 18.20-18.30 Discussion

19.00-  CONFERENCE DINNER

Chair: Tina Hecksher

09.00-09.40 **Peter Harrowell** · University of Sydney
The occurrence and consequence of constraint in supercooled liquids

09.40-10.00 Discussion

10.00-10.20 **Pierre Ronceray** · Princeton University
Suppression of crystalline order by competing liquid structures

10.20-10.30 Discussion

10.30-11.00  COFFEE BREAK

Chair: Tina Hecksher

11.00-11.20 **Paola Gallo** · Università di Roma Tre
The role of activated processes in the fragile to strong crossover of supercooled water

11.20-11.30 Discussion

11.30-11.50 **Fivos Perakis** · Stockholms Universitet
The liquid-liquid transition in ultraviscous deeply supercooled water

11.50-12.00 Discussion

12.00-12.20 **Catalin Gainaru** · Technische Universität Dortmund
Dielectric relaxation processes in glassy and liquid water

12.20-12.30 Discussion

12.30-13.30  LUNCH

14.00-15.00  Guided tour of the Carlsberg Brewery.

Structure and dynamics of highly stable glasses prepared by physical vapor deposition

Mark Ediger

University of Wisconsin-Madison

Glasses formed by cooling a liquid inherit both their structure and their marginal stability from the liquid state. In contrast, glasses prepared by vapor deposition need have neither of these limitations. By utilizing the high mobility present near the free surface of many organic glasses, one can prepared glasses that are likely similar to highly aged ordinary glasses, with low enthalpy and high thermal stability. Two recent experiments document additional features of these tightly packed glasses: 1) the beta relaxation can be suppressed by nearly a factor of four in vapor-deposited toluene glasses, and 2) the trans-cis isomerization in an azobenzene glassformer can be suppressed by a factor of fifty. On the other hand, we have recently learned that hydrogen-bonding reduces surface mobility and thus impedes the ability to form a highly stable glass.

Molecules at the free surface of the glass during deposition may prefer anisotropic packing arrangements – and these can be trapped into the glass by vapor deposition. For organic semiconductors such as the molecules used in OLEDs, anisotropic packing can improve device performance. Based upon a mechanism established by computer simulations, we can predict the anisotropy of vapor-deposited glasses from knowledge of the molecular arrangement preferred at the free surface. For molecules with a strong surface anchoring, such a liquid crystals, deposition can result in highly ordered solids that inherit their structure from the free surface structure. On the other hand, even a highly spherical molecule (carbon tetrachloride) can form stable glasses, indicating that molecular anisotropy is not required to access highly stable packing arrangements.

Equilibrium simulations of supercooled liquids beyond laboratory timescales:

Will experiments ever catch up with theory?

Ludovic Berthier

Université de Montpellier

Computer simulations give precious insight into the microscopic behavior of disordered and amorphous materials, but their typical timescales are orders of magnitude shorter than the experimentally relevant ones. In particular, ordinary simulations of supercooled liquids cover at most 4-5 decades of viscous slowing down, which falls far short of the 13 decades commonly accessible in experimental studies. We have closed this enormous gap for a class of realistic models of liquids, which we successfully equilibrate beyond laboratory time scales by means of a swap Monte Carlo algorithm. For some models, we achieve over 10 orders of magnitude speedup in equilibration timescale. This numerical advance allows us to address some outstanding questions concerning glass formation in a dynamical range that remains inaccessible in experiments, such as the relevance of an entropy crisis or the melting kinetics of ultrastable glasses.

A 100 Myears landscape exploration using a geologically hyperaged glass

Tullio Scopigno

La Sapienza Università di Roma

The way structure and dynamics of amorphous materials relate to their thermodynamic metastability is one of the current challenges for the glass transition understanding. From the experimental point of view, one of the major hurdles is the limited stability range conventionally accessible on the laboratory timescale. Fossil amber offers the unique opportunity of investigating an amorphous material which has been exploring its energy landscape for more than 110 Myears of natural ageing. By applying different x-ray scattering methods to fossil amber before and after rejuvenating it, we identify a link between the potential energy landscape and the structural and vibrational properties of glasses. Specifically, we find that hyperaging induces a depletion of the vibrational density of states in the THz region, also ruling the sound dispersion and attenuation properties of the corresponding acoustic waves. Critically, this is accompanied by homogeneous densification, peculiar of natural stabilization and different in nature from that caused by hydrostatic compression. Our results can be rationalized within the fluctuating elasticity theory, revealing that upon approaching the bottom of the potential energy landscape the elastic matrix becomes increasingly less disordered, though retaining the characteristic vibrational anomalies of glasses.

Physical gels, porous glasses, and the glass transition:

Experimental tests of a unifying theory.

Magdaleno Medina-Noyola, José Manuel Olais-Govea, and Leticia López-Flores

Instituto de Física "Manuel Sandoval Vallarta", Universidad Autónoma de San Luis Potosí, Álvaro Obregón 64, 78000 San Luis Potosí, SLP, México

In contrast with equilibrium crystalline solids, whose properties have no history dependence, non-equilibrium amorphous solids may exhibit aging and their properties do depend on their preparation protocol [1]. The non-equilibrium self-consistent generalized Langevin equation (NE-SCGLE) theory of irreversible processes in liquids [2], however, was recently shown to provide a simple and intuitive first-principles description [3] of the non-equilibrium relaxation of model glass-forming liquids with purely repulsive interparticle interactions near their high-density transition to repulsive, hard-sphere-like glasses. Still more recently [4] the same theory, applied to model liquids with repulsive plus attractive interactions, was shown to predict a still richer and more complex scenario including, in addition to hard-sphere glasses at high densities and temperatures, the formation of sponge-like gels and porous glasses by arrested spinodal decomposition at low densities and temperatures.

In this work we demonstrate the experimental relevance of the predicted kinetics of formation of these arrested disordered structures, which turns out to be equally complex and subtle. For example, contrary to the mild structural response characteristic of the formation of hard-sphere glasses, the structural evolution that follows a sudden quench of a liquid to the interior of its spinodal region is characterized by the dramatic amplification and eventual arrest of gigantic density (and hence, dynamical) heterogeneities. This is evidenced by the development of a small wave-vector peak in the predicted non-equilibrium static structure factor $S(k; t_w)$, similar to that observed in ordinary spinodal decomposition, whose height increases and whose position $k_{max}(t_w)$ decreases with waiting time t_w . The mean size $\xi(t_w) = 2\pi/k_{max}(t_w)$ of these heterogeneities, however, does not grow indefinitely, but saturates at a finite value $\xi_s(T)$. The dynamic and rheological properties are predicted to exhibit an amazing latency phenomenon: at a latency time $t_l(T)$ after the quench they cross over from a pseudo equilibration behavior to their sudden dynamic arrest. Both, $\xi_s(T)$ and $t_l(T)$ diverge as the final temperature T approaches the spinodal temperature T_s from below.

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[4] J. M. Olais-Govea *et al.*, *J. Chem Phys.* **143**, 174505 (2015).

On the nature of the β -process in organic glass formers

Th. Körber, B. Pötzschner, D. Bock, R. Kahlau, E.A. Rössler

Experimentalphysik II, Universität Bayreuth, 95447 Bayreuth, Germany

The nature of the secondary or β -relaxation in organic glasses is still an unsolved problem. Here, we investigate the β -process in binary glasses over the full concentration range by employing Dielectric and NMR spectroscopy, which allows to probe the dynamics of each component separately. The mixtures are made from a non-polymeric high- T_g ($M = 800$ g/mol) and a low- T_g component ($M = 200$ g/mol; so-called asymmetric binary glass former). The system is characterized by two glass transition temperatures (T_{g1} and $T_{g2} < T_{g1}$), and the β -process is monitored in the low temperature regime ($T < T_{g2}$). As in the case of neat molecular glass formers, the β -process introduced, *e.g.*, by the low- T_g component involves spatially highly hindered motions with an activation energy not changing over the entire concentration range. A very similar motion with the same time constant and similar angular displacements can be identified for the high- T_g component. In other words, the low- T_g component enslaves the large molecules of the high- T_g component. It only disappears at lowest concentration of the low- T_g component ($c < 10\%$). The spectroscopic features of the β -process are even absolutely the same for mixtures employing different high- T_g components [1]. We take these results as an indication that the β -process (as the α -process) is cooperative in nature [2].

Investigating the β -process in neat poly(ethylene-propylene) (PEP) we find, in contrast to molecular glass formers, indications that not all polymer segments participate. We speculate on the revival of the idea of “islands of mobility” [3].

[1] Pötzschner *et al.* JCP 2017, submitted

[2] Bock *et al.* JCP 2013, **139**, 064508

[3] Körber *et al.* Macromolecules 2017, **50**, 1554–1568

A structural connection to the configurational heat capacity of borate-silicate glass forming liquids

Hao Liu^{1,2*}, Morten M. Smedskjaer¹, Haizheng Tao², Lars R. Jensen³, Xiujian Zhao², and Yuanzheng Yue^{1,2}

1 Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark.

2 State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, PR China

3 Department of Mechanical and Manufacturing Engineering, Aalborg University, DK-9220 Aalborg, Denmark

* hal@bio.aau.dk

When a glass-forming liquid is supercooled to the glass transition temperature (T_g), the structural degree of freedom decreases, causing a loss of the configurational heat capacity ($C_{p,conf}$). In borate-silicate mixed glasses, the $C_{p,conf}$ exhibits a non-linear increase with substitution of B_2O_3 for SiO_2 [1]. However, its structural origin has not been well understood. In this work, through Raman spectroscopy measurements, we have found an implication for the intermediate range order (IRO) structural connection to the composition dependence of $C_{p,conf}$ in a series of $(75q)B_2O_3-(75(1-q))SiO_2-15Na_2O-10CaO$ glasses [2]. In the silica-rich composition, the increase of the content of B-O-Si network units ($[B_2Si_2O_8]^{2-}$) and 6-membered borate rings causes the rapid increase of the $C_{p,conf}$ with the addition of B_2O_3 . In the boron-rich composition, the $C_{p,conf}$ is almost constant, which is likely attributed to the counteraction between the decrease of the fraction of metaborate groups and the increase of the fraction of other borate superstructural units. Compared to short range order (SRO), the overall results suggest that the IRO structural change has a dominant contribution to the evolution of $C_{p,conf}$ with composition. Furthermore, IRO is also found to govern the composition dependence of dynamic fragility, implying that $C_{p,conf}$ can be seen as the thermodynamic fragility in the studied system.

[1] M. M. Smedskjaer, J. C. Mauro, R. E. Youngman, C. L. Hogue, M. Potuzak and Y.Z. Yue, *J. Phys. Chem. B*, **115**, 2011, 12930.

[2] H. Liu, M. M. Smedskjaer, H. Z. Tao, L. R. Jensen, X. J. Zhao and Y. Z. Yue, *Phys. Chem. Chem. Phys.*, **18** (16), 2016, 10887.

The glass transition phenomenon:

When an experimental chemist meets
with theoretical physicists

Christiane Alba-Simoniesco

Laboratoire Léon Brillouin

The title of this presentation illustrates the paradigm for scientists dealing with the glass transition phenomenon, where theoretical chemistry and experimental physics are combined at will. The extremely rich phenomenology and wide variety of materials associated required to classify them, establishing correlations, scaling approaches and disentangling the specific (as chemists like to work with) from the generic or universal (as physicists focus on). Experimentalists need theoretical laws to test and theoreticians well identified features. All work back and forth, sometimes converging or moving in parallel. I will first illustrate here some cases:

- when the MCT theory proposed scaling laws compatible with experiments done after but then revisited 20 years later limiting strongly its compatibility in the case of molecular liquids,
- when new experiments unravel the respective roles of control parameters such as temperature and density, leading to a formulation of the viscous slowing down in terms of a temperature-driven super-Arrhenius activated behavior rather than a density-driven congestion or jamming phenomenon,
- when correlations at the GT temperature between the fragility and the fast dynamics and the vibrational properties of the corresponding glass support models (shoving model) combining solid state and liquid state approaches.

However for an experimental chemist it becomes even more interesting when none of these approaches and correlations hold: then the non-adequacy enlightens new phenomena. Thus, in the second part, I will show trends of current works such as the Mw effect of the GT of polymers and the Adam-Gibbs theory, the effect of hydrogen bond network and the role of structural heterogeneities; either way additional constraints are identified that could help in other fields than the glass transition.

Dielectric spectroscopy at extremely high pressure in a diamond anvil cell

Timothy C. Ransom

Soft Matter Physics Code 6105, Naval Research Laboratory, Washington, DC 20375-5342

In order to fully understand glass-forming liquids and polymers, it is critically important to study them under conditions of very high pressure [1]. Though there is much that has been learned from high-pressure studies [2–8], it is experimentally challenging to employ standard dynamic measurement techniques at pressures higher than ~1 GPa.

Dielectric spectroscopy is one of the most powerful tools used for studying glass-forming systems due in part to its large frequency range over 9 orders of magnitude. Johari and Whalley obtained dielectric spectra on glycerol at pressures up to 5.3 GPa using piston cylinder and large anvil apparatuses [9]. Recently, Pronin et al. developed a similar anvil apparatus for dielectric spectroscopy up to 5–6 GPa [10,11]. However, it is greatly desirable to extend the ability to perform dielectric measurements at pressures much higher than this. Several molecular dynamic simulation studies predict that power law density scaling breaks down in the high-density limit [12,13]. It is thus necessary to test these predictions with physical measurements at ultra-high pressures over 10 GPa to achieve such large density changes.

This work presents the development of a new technique which adapts a diamond anvil cell (DAC), which is easily capable of reaching 10 GPa, for measurements using dielectric spectroscopy. Preliminary results are shown on polyurea, a glass-forming polymer which has shown interesting dynamic properties [14]. With the successful development of this new tool, we test density scaling over large compression ranges and explore behaviors under these extreme conditions.

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Isochronal superposition on second and picosecond timescales

Henriette Wase Hansen¹, Alejandro Sanz¹, Karolina Adrjanowicz²,
Bernhard Frick³, Kristine Niss¹

- 1 Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Denmark
- 2 Institute of Physics, University of Silesia, Katowice, Poland
- 3 Institut Laue-Langevin, Grenoble, France

We present a combined high-pressure cell for doing simultaneous dielectric spectroscopy and neutron scattering in the range 1-300 K, 0.1-500 MPa. We study both the fast and slow dynamics simultaneously in glass-forming liquids and are able to see signal with both techniques. We follow the fast and slow dynamics along isobars, isotherms, and in particular along isochrones, i.e. constant relaxation time $\tau_{\alpha}(T,P)$.

We use the cell to test the isomorph theory. The fundamental prediction of the isomorph theory is the existence of isomorphs, which are curves in the phase diagram along which all dynamical phenomena and structure are invariant [1]. The alpha relaxation, both its time and spectral shape, is one of the properties that is invariant along an isomorph, and we can therefore experimentally identify the isomorphs by the isochrones. We therefore expect to see isochronal superposition along the isochrones, i.e. all types of spectra should collapse.

We investigate the dynamics on picosecond timescale and show the difference for a van der Waals liquid and a H-bonded liquid along the glass transition isochrone, i.e. $\tau_{\alpha} = 100$ s, and higher temperature isochrones found from dielectric spectroscopy.

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Density scaling as a universal link between the dynamics of glass-forming liquids in the bulk and confined geometry

Karolina Adrjanowicz, Kamil Kaminski, Marian Paluch

Institute of Physics, University of Silesia, Uniwersytecka 4, 40-007 Katowice, Poland

The properties of a molecular liquid confined at the nanometer length scale can be very distinct from the bulk. For that reason, the macro- and the nanoscopic behaviors of glass-forming liquids are regarded as two nonconnected realms. In this presentation, we will demonstrate that the glassy dynamics in molecular liquids confined to nanometer pores might obey the density scaling relation, ρ^γ/T , just like in bulk fluids. Even more surprisingly, the same value of the scaling exponent γ superposes the α -relaxation time measured at different state points in nanoscale confinement and on increased pressure. Tested liquids are van der Waals liquids tetramethyl-tetraphenyl-trisiloxane (DC704) and polyphenyl ether (5PPE), considered as simple, single-parameter liquids. The validity of the density scaling idea in both environments opens an exciting possibility to predict the dynamic features of the nanoconfined system close to its glass-transition temperature from the high-pressure studies of the bulk liquid. Likewise, we can describe the viscous liquid dynamics at any given combination of temperature and pressure based on the analysis of its behavior in nanopores.

Microphase separation and multiple glass transitions induced by nanoscale confinement

D. Morineau¹, R. Lefort¹, A. R. Abdel Hamid¹, R. Mhanna^{1,3}, S. Dutta¹, A. Ghoufi¹, L. Noirez², C. Alba-Simionesco² and B. Frick³

¹ Institute of Physics of Rennes, CNRS-University of Rennes 1, France

² Laboratoire Léon Brillouin, CEA-CNRS, Gif-Sur-Yvette, France

³ Institut Laue-Langevin, Grenoble, France

The properties of liquids confined in nanometric cavities can be very different from their bulk counterparts, which raises exciting new questions for basic condensed matter physics. Among many fascinating confinement effects, we focus on the formation of new liquid structures of glassforming binary systems confined in nanochannels

Glassforming H-bonding liquids are especially interesting candidates because of their tendency to develop both supramolecular order and cooperative dynamics, which might be particularly sensitive to confinement at the nanoscale. Indeed it is striking that the ability of alcohols to spontaneously form mesoscopic ordered structures could be tuned, either by dispersion in an aprotic solvent [1], or by confinement in porous silicates [2-4].

We will discuss how this study went one step further recently, with the observation of confinement induced micro-phase separation of fully miscible low-molecular-weight binary mixtures confined in different types of straight, mono-disperse, rigid channels of mesoporous MCM-41 and SBA-15 silicates ($D = 3.6, 8.3$ nm) [5-7].

Neutron diffraction experiments with selective isotopic compositions have been performed to vary systematically the scattering length density of the different compounds. It resulted in an apparently anomalous modulation of the intensity of the Bragg peaks of the mesoporous system, which demonstrates that the liquids are really inhomogeneous at the nanoscale. The predictions from a specifically designed core-shell model confirm the existence of a micro-phase-separated tubular structure, with the segregation of alcohol that forms a layer at the pore surface, which surrounds a rich-apolar solvent core.

We addressed the molecular relaxations at play on the different timescales that govern the individual molecular dynamics of the segregated components on the one hand, and the glass transition of the whole binary system on the other hand by dynamical studies (Quasielastic Neutron Scattering, Dielectric Spectroscopy, and Calorimetry).

This core-shell phenomenon is probably more general. We believe it is related to different interfacial interactions that have been quantified by Dynamical Vapor Sorption experiments: a situation which is awaited for a variety of other complex fluids in nanopores [8].

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Glassy dynamics in one- and two-dimensional nanometric confinement – a comparison

Friedrich Kremer

Institute of Experimental Physics I, University of Leipzig, 04103 Leipzig, Germany

Glassy dynamics of polymers (e.g. poly(methylphenylsiloxane) (PMPS) or poly(*cis*-1,4-isoprene) (PI)) is studied by broadband dielectric spectroscopy (BDS) in one-(1D)- and two-(2D)-dimensional nanometric confinement; the former is realized in thin layers having thicknesses down to 5 nm, the latter in unidirectional (length 50 nm) nanopores with diameters varying between 4–8 nm. Based on dielectric measurements carried out in a broad spectral range at widely varying temperatures glassy dynamics is analyzed in detail in 1D and in 2D confinement with the following results, (i) the segmental dynamics (dynamic glass transition) of the polymer in 1D confinement down to thicknesses of 5 nm is identical to the bulk in the mean relaxation rate and the width of the relaxation time distribution function; (ii) additionally a well separated surface induced relaxation is observed, being assigned to adsorption and desorption processes of polymer segments with the solid interface; (iii) in 2D confinement with native inner pore walls the segmental dynamics shows a confinement effect, i.e. the segmental dynamics becomes faster the smaller the pores are; on silanization this dependence on the pore diameter vanishes, but the mean relaxation rate is still faster than in 1D confinement; (iv) in 2D confinement a pronounced surface induced relaxation process is found the strength of which increases with decreasing pore diameter; it can be fully removed by silanization of the inner pore walls; (v) the surface induced relaxation depends in its spectral position only negligibly on the pore diameter; (vi) comparing 1D and 2D confinement, the segmental dynamics in the latter is by about two orders of magnitude faster. All these findings can be comprehended by considering the density of the polymer; in 1D it is assumed to be the same as in the bulk, hence the dynamic glass transition is not altered, in 2D it is reduced due to a frustration of packaging resulting in a higher free volume, as proven by ortho-positronium annihilation lifetime spectroscopy.

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Probing the structural origin of dynamic heterogeneity in glass-forming liquids

Hua Tong

University of Tokyo

If a liquid is supercooled approaching the glass transition, the drastic slowing down of its dynamics is accompanied by growing spatial heterogeneity. The pursuit of physical factors controlling the dynamic heterogeneity has triggered intensive studies but a coherent understanding remains elusive. Here we introduce a new approach to probe the structural origin of the heterogeneous dynamics which works in two model glass-forming liquid of very different natures. We find that the development of dynamic heterogeneity can be well predicted in the way of progressive coarse graining of the initial static structure, in case the many-body (orientational) correlations are properly included in the structural order parameter. The predictive power maximizes at a specific coarse-graining length and time scale for the mobility to develop, which are in accord with the dynamic correlation length and the α relaxation time. Our results hence unveil an intrinsic link of the important spatial and temporal scales between the static structure and the glassy slow dynamics. We further show that the close correlation between short- and long-time dynamics emerges as a natural result of their connections with the underlying structure.

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Levy flight in mayonnaise

Matthieu Wyart

EPFL, Lausanne

Glassy systems with long-range interactions often present avalanche type-response under slow driving, as well as a vanishing density of excitation at low energy or “pseudo gap”. I will explain why these facts must come together, and discuss in particular the plasticity of amorphous solids (for example, how does a mayonnaise flow when one slowly pushes it with a spoon). In that case a pseudo-gap characterizes the density of vibrational modes that are close to a saddle node bifurcation. I will argue that the mean-field description of plasticity maps into the problem of Levy Flights near an absorbing boundary. Using this analogy I will show that the pseudo-gap exponent characterizing the solid stability is not universal, except when the applied stress is zero, and depends non-monotonically on the stress level. If time permit, I will discuss a scaling description of the liquid phase above the yield stress, connections to other type of glassy systems (spin, hard spheres and electron glasses), as well as open questions.

Particle-resolved studies of deeply supercooled liquids:

A means to test theories of the glass transition

C. Patrick Royall

H.H. Wills Physics Laboratory, Tyndall Avenue, Bristol, BS8 1TL, UK
Centre for Nanoscience and Quantum Information, Tyndall Avenue, Bristol, BS8 1FD, UK
School of Chemistry, University of Bristol, Cantock's Close, Bristol, BS8 1TS, UK
Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

One promising route to discriminating theoretical descriptions of the glass transition is to probe the supercooled regime beyond the mode-coupling transition. However, the corresponding dynamics are inaccessible to conventional computer simulation and particle resolved studies of colloids [1,2,3]. Here we present two approaches to probe the dynamics of very deeply supercooled liquids at the particle level: "nano"-particle resolved studies and a hybrid theory-simulation approach to probe "cooperatively rearranging regions" or "excitons".

Nano-particle resolved studies exploits the fact that the diffusion time of nanoparticles scales with the cube of their diameter. By imaging particles ten times smaller than the state-of-the-art, with stimulated emission by depletion (STED) "nanoscopy" [4], we probe three decades in relaxation time past the mode-coupling transition. Our results show that the role of local structure appears to become more significant at deep supercooling: the coupling between structure and dynamic heterogeneity is stronger. Unlike previous studies [2,5,6], two distinct populations are identified: a population of fast-moving particles emerges which is not found in the locally favoured structure of the system. We further see hints of a long-sought [2,3,7,8] coupling between structural and dynamical lengthscales. Finally, by measuring so-called "overlaps", we see that the high-overlap and low-overlap regions have a distinct local structure.

Our second approach is to consider "cooperatively rearranging regions" or "excitons" to be droplets immersed in a bulk medium. The bulk hard sphere fluid we treat with the morphometric approach (a geometrical method for computing solvation free energies) [9]. We use the morphometric approach and energy landscape calculations for small systems [10] to obtain free energy barrier heights to relaxation in regimes of supercooling inaccessible to other approaches. Elucidating these "cooperatively rearranging regions" or "excitons" at a particulate level at unprecedented degrees of supercooling is expected to enable discrimination between theories such as Random-First Order Transition Theory/Adam Gibbs and Dynamic Facilitation [2,3].

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Theory of thermodynamics of freezing and melting

U. R. Pedersen, L. Costigliola, N. P. Bailey, T. B. Schröder, J. C. Dyre

Glass and Time, IMFUFA, Dep. of Science and Environment, Roskilde Uni., Roskilde, Denmark

Freezing of liquids are well known by laymen and are fundamental for many areas of the sciences. We present a theoretical framework [1] for the thermodynamics of freezing. Properties of the crystal and liquid at a single state-point allow one to predict the coexistence pressure as a function of melting temperature, as well as the variation along the melting/freezing lines of quantities such as the reduced crystalline vibrational mean-square displacement (the Lindemann ratio), the liquid diffusion constant or the viscosity. The fundamental assumption is hidden scale-invariance of liquid and crystalline states [2,3]. An analytical expression is available for systems of particles interacting via pair potentials that are differences of two inverse power laws. The theory is validated by computer simulations of the freezing and melting properties [4] of the 6-12 Lennard-Jones system.

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Non-linear responses:

a guide to discover the true nature of the glass transition

Giulio Biroli

CEA Saclay

In this talk I will discuss how theoretical results on non-linear responses of glassy systems combined with experiments on non-linear dielectric susceptibilities of super-cooled liquids allowed us to gain substantial new insights on the nature of the glass transition. Our results provide strong evidence that compact amorphously ordered domains grow approaching the glass transition, as predicted by thermodynamic theories of the glass transition, and challenge explanations based on purely dynamical or local physical mechanisms.

Unifying different interpretations of the nonlinear response in glass-forming liquids

François Ladieu

SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay Bat 772, 91191 Gif-sur-Yvette Cedex, France.

This talk aims at reconsidering several interpretations coexisting in the recent literature concerning non-linear susceptibilities in supercooled liquids. We present experimental results on glycerol and propylene carbonate showing that the three independent cubic susceptibilities have very similar frequency and temperature dependences, both for their amplitudes and phases. This strongly suggests a unique physical mechanism responsible for the growth of these non-linear susceptibilities. We show that the framework proposed by two of us [1], where the growth of non-linear susceptibilities is intimately related to the growth of "glassy domains", accounts for all the salient experimental features. We then review several complementary and/or alternative models, and show that the notion of cooperatively rearranging glassy domains is a key (implicit or explicit) ingredient to all of them. This paves the way for future experiments which should deepen our understanding of glasses.

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The effect of electric fields on the glass transition:

Theory versus experiment

Ranko Richert

School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, U.S.A.

Only in the limit of small fields are the results of dielectric relaxation experiments independent of the amplitude of the electric field. At large fields, deviations from the linear response regime become noticeable, either as altered susceptibilities or as the appearance of higher order Fourier components. Various sources of non-linear dielectric effects exist: saturation, chemical effects, energy absorption, and the consequence of field induced entropy changes. While the occurrence of chemical effects is highly material specific, the other three features will occur in any system that displays orientational polarizability.

Dielectric saturation leads to a reduction of the dielectric constant or relaxation amplitude because polarization has an upper bound. The strong static polarization that is associated with dielectric saturation also leads to a reduction of entropy. This, in turn, impacts the structural relaxation time and thus the glass transition, as implied in the Adam-Gibbs model.

Experimental results will be presented on the extent to which relaxation times depend on external electric fields [1]. Using experimental techniques that facilitate time-resolved studies of non-linearity, it is shown that a liquid requires considerable time to reach equilibrium with regard to the external high electric field [2]. As in the case of electro-optical Kerr studies, the rise and decay behavior of the field induced effect is asymmetric, i.e., the rise appears to be slow compared with the decay. This dependence on the time that field has been switched on (or off) constitutes a structural recovery process, just like in a physical aging situation, but with the field step replacing the temperature jump.

The observations will be discussed in light of theoretical approaches that relate dynamics to external electric fields [3]. More specifically, it will be demonstrated that changing the excess entropy of the system by the same amount but using temperature versus electric field as control parameter leads to different changes in the structural relaxation times. As a result, the Adam-Gibbs model provides only very limited input to this problem [4,5].

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Nonlinear response in terms of simple stochastic models

Gregor Diezemann

Universität Mainz

The effect of large electric fields on the relaxation of supercooled liquids and also other systems like ionic liquids and crystals has been studied intensively during the last decade [1].

Due to the formal lack of an analogue to the well known fluctuation dissipation theorem valid for linear response, one essentially relies on model calculations for the interpretation of the experimental results [2].

There are a number of different models that are used to compute the nonlinear response of glassforming systems, such as the so-called box model, the model of isotropic dipole reorientations or the dipole flips in an asymmetric double well potential (ADWP) [3,4].

In the present contribution I will discuss the results of model calculations of the nonlinear response for simple stochastic models for the dynamics. In particular, I will consider the ADWP model which is known to exhibit a peak in the modulus of the third-order response in a narrow temperature range around some characteristic temperature. I will present results of calculations for various different nonlinear susceptibilities and discuss the observed behavior in the light of recent experimental observations.

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Anomalous microscopic dynamics in metallic glass formers

Beatrice Ruta

ESRF – The European Synchrotron, Grenoble, France
Institut Lumière Matière, Université Lyon 1 & CNRS, Lyon, France

In recent years, the x-ray photon correlation spectroscopy technique has provided an unprecedented look into the relaxation dynamics of glasses by probing the density fluctuations on the atomic length scale. Studies on metallic glass formers have revealed the existence of a dynamical crossover at the glass transition temperature, T_g , between an equilibrium-like liquid state characterized by stretched exponential decays of the intermediate scattering function (ISF), to a highly unstable glassy state with compressed ISF and multiple aging regimes [1-4]. Depending on the nature and the previous thermal history of the system, the microscopic structural relaxation time is found to depend exponentially on the annealing time [1,2] or to jump through intermittent aging regimes [3]. This behavior appears connected to ordering processes involving density changes at the medium range [4]. Furthermore, the spontaneous temporal equilibration toward the corresponding supercooled liquid results strongly impeded by up temperature jumps from the glassy state, in marked contrast with down temperature jumps from the viscous liquid and macroscopic measurements. All these features suggest a complex microscopic picture of metallic glasses, not reflected in measurements of macroscopic quantities and in theoretical studies.

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Equilibrium random pinning and epsilon coupling a unified picture where theory and experiments could possibly meet

C. Cammarota (in collaboration with G. Biroli and J.P. Garrahan)

King's College London

A number of methods [1,2] involving the introduction of well tailored thermodynamic biases have been proposed in recent times to study the origin and the mechanism of the slowing down of the dynamics in glass forming liquids.

The proposed procedures, even though potentially quite telling about the nature of the glass transition, were not always thought to be straightforwardly experimentally realisable.

In this talk I will present a detailed comparison of these procedures and of the feature they are able to reveal on the physics of glass formation.

I will propose a unified picture where the original biases, as they were described in the literature, represent the limiting cases and a full range of interpolating cases appears.

Most importantly I will show how these intermediate mixed bias procedures could be used as a playground where theory and experiment would finally meet in this field.

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Elastically collective activated relaxation in glass-forming liquids:

Theory meets experiment

Kenneth Schweizer

University of Illinois

We have formulated a predictive and quantitative force-level theory of activated relaxation based on density fluctuations as the slow dynamical variable [1]. The approach combines elements of mode coupling theory, the dynamic free energy concept, and collective elastic fluctuation physics. The irreversible re-arrangement event is of a mixed local-nonlocal character involving coupled large amplitude hopping on the cage scale and a facilitating longer range spontaneous elastic distortion of the surrounding liquid, resulting in two related, but physically distinct, contributions to the total barrier. The theory addresses in a unified manner the apparent Arrhenius, dynamic crossover and deeply supercooled regimes. The emergence of the more strongly temperature and density dependent elastic barrier heralds the crossover to the deeply supercooled regime. The approach is devoid of fit parameters, and has no divergences at finite temperature or below jamming. Quantitative comparisons with experiment and simulation for the alpha relaxation time of hard sphere systems reveals good agreement over 5-6 decades [1]. A quasi-universal theory for thermal liquids is constructed via an a priori mapping to an effective hard sphere fluid based on matching the material and thermodynamic state dependent amplitude of equilibrium long wavelength dimensionless density fluctuations. The theory accurately captures the key features of the alpha time in molecular liquids over 12-14 decades, including the quasi-universalities experimentally observed by Rossler and coworkers [1]. Extension to polymer liquids is achieved based on the statistical Kuhn length as the elementary length scale [2]. Unique polymeric features such as a nonuniversal chain length dependence of the vitrification temperature and exceptionally low and high dynamic fragilities can be understood. The longer range collective elastic effect has large and unique consequences on how confinement and interfaces induce strong spatial gradients of mobility, accelerate relaxation, reduce fragility and suppress T_g in free-standing thin films [3].

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Chain-length dependent relaxation dynamics in glass-forming oligomers and polymers

D. Baker¹, M. Reynolds¹, R. Masurel², P. D. Olmsted², **J. Mattsson**¹

¹ School of Physics and Astronomy, University of Leeds, Leeds, U.K.

² Department of Physics, Georgetown University, Washington, D.C., U.S.

We here discuss new experimental and computational results focusing on the effect of molecular size and chain-connectivity on the relaxation behaviour in glass-forming oligomers and polymers. We show experimental results from broadband dielectric spectroscopy, calorimetry and oscillatory rheology together with results from Monte Carlo and Molecular Dynamics computer simulations. We discuss the detailed development of molecular relaxation dynamics (structural relaxation and secondary relaxations) as well as chain conformations and overall chain size with chain-length for oligomeric and polymeric systems of different chain characteristics. We particularly focus on the role of secondary relaxations in glass-formations and show results on the nature and inter-relationship of secondary relaxations for oligomeric and polymeric systems and discuss their link to the structural relaxation and thus the glass transition temperature. Moreover, we discuss the link between glass-formation in small molecular and oligomeric/polymeric glass-formers and discuss our results in the light of models/theories that can be used to understand the observed behaviour.

MD simulation of supercooled polymer melts:

Modeling of single-monomer dynamics by a continuous-time random walk approach

J. Helfferich ¹, F. Ziebert ¹, H. Meyer ², J. Farago ², A. Blumen ¹, J. Baschnagel ²

¹ Physikalisches Institut, Albert-Ludwigs-Universität, Freiburg, Germany

² Institut Charles Sadron, Strasbourg, France

We present results of molecular-dynamics (MD) simulations for supercooled polymer melts. Prompted by work on simple liquids we analyze the trajectories of individual monomers. In the supercooled state near the critical temperature of mode-coupling theory the single-monomer trajectories display long periods of localization interrupted by “fast moves”. This observation suggests a modeling by a continuous-time random walk (CTRW), i.e. by a series of random jumps separated by random waiting times. We introduce an algorithm allowing to filter the “fast moves” so as to retain only those “moves” which comply with the conditions of a CTRW.

These moves are called “jumps” in the following; the remaining analysis is based on them. As a function of temperature and chain length we then examine key distributions of the CTRW: the jump length distribution (JLD) and the waiting time distribution (WTD) for the jumps.

For the equilibrium (polymer) liquid under consideration the WTD and JLD suffice to model the single-monomer dynamics by the CTRW. For the mean-square displacement (MSD) of a monomer the results of this modeling are compared with MD data. The MD results exhibit two regimes of subdiffusive behavior, one for the early α process and another at later times due to chain connectivity. By contrast, the analytical solution of the CTRW yields diffusive behavior for the MSD at all times. We can account for the effect of chain connectivity by modifying the JLD. The resulting polymer-specific CTRW is solved numerically by Monte Carlo simulations. The results of these simulations are then in good agreement with the MD data in the connectivity-dominated regime, but not in the early α regime where they systematically underestimate the MSD from the MD. The comparison between MD and CTRW simulations is extended to the self-part of the van Hove function, showing that the CTRW can also provide a reasonable description for the spatial dependence of the van Hove function [3].

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The occurrence and consequence of constraint in supercooled liquids

Shibu Saw, Gang Sun and **Peter Harrowell**

School of Chemistry, University of Sydney, Sydney NSW Australia

Any disordered configuration can, in principle, be analysed in terms of the degree to which it exerts constraint on the motion of the particles that make it up. In an amorphous configuration, these constraints will be heterogeneously distributed and their definition presents a challenge. At $T = 0$ they can be identified by Maxwell constraint counting, at least when particle interactions do not extend far beyond the particle radius. It has been proposed that the individual particle Debye-Waller factor provides a more general measure of constraint. In this talk we examine the T dependence of the spatial distribution of the Debye-Waller factors, the relationship between this distribution and that of relaxation kinetics, the general relation between constraint and rigidity and the relationship between mobility enhancement at glass surfaces and the general decrease of constraint at a free surface.

Suppression of crystalline order by competing liquid structures

Pierre Ronceray¹ and Peter Harrowell²

¹ Princeton Center for Theoretical Science, Princeton University, USA

² School of Chemistry, University of Sydney, Sydney N.S.W. 2006, Australia

In a molecular liquid, the local structure characteristic of the crystal is likely to be particularly stable, and one can expect that it will accumulate on cooling. However, other non-crystalline structures can also be stable in the liquid, and compete with the accumulation of crystalline order. On what conditions can such a competition stabilize the supercooled liquid to the point of dynamical arrest?

We tackle this question using a lattice model where both the crystalline order and the non-crystalline structures are explicitly specified in terms of local configuration of binary spins. We demonstrate the crucial importance of geometrical interactions between the crystalline local order and its competing structures: aside from stabilizing thermodynamically the liquid, non-crystalline structures can either geometrically antagonize crystallinity, or help accumulating it. We introduce the crystal affinity, a new structural quantity $Q = \frac{\partial c_x}{\partial T} |_{T=\infty}$ where c_x is the concentration of crystalline local structures, and demonstrate that it correlates remarkably well with the non-thermodynamic component of the nucleation rate at low temperature: crystal-“agonist” structures with good overlap with the crystal tend to facilitate crystallization, while crystal-antagonist ones tend to impede it dramatically by increasing the surface tension.

The role of activated processes in the fragile to strong crossover of supercooled water

Paola Gallo

Dipartimento di Matematica e Fisica, Università Roma Tre, Roma, Italy.

A crossover from a fragile behaviour to a strong behaviour is a typical change of behaviour that many glass formers undergo upon supercooling. In water this crossover, observed in translational relaxation time, has been connected to the thermodynamics water and in particular to the possible existence of a liquid-liquid critical point laying in the supercooled region of water.

The dynamics crossover was observed in experiments on confined water, in simulations on bulk water, confined water and aqueous solutions at low concentrations and very recently in an experiment on bulk water.

In order to inquire on the microscopic origin of this behaviour in water I will show results from an accurate analysis of the density self correlation functions of TIP4P/2005 supercooled water on approaching the region of the liquid-liquid critical point [1]. In previous simulation works [2] evidence was provided for this potential of a fragile to strong crossover of the translational relaxation time in the deep supercooled region. The structural relaxation follows the Mode Coupling Theory in the fragile region and then upon further supercooling it deviates from Mode Coupling regime to a strong Arrhenius behavior.

The van Hove Self Correlation Functions can show the presence and the role of the hopping phenomena, that are responsible of the fragile to strong crossover in simple liquids. We analyze how they depend on temperature and density in TIP4P/2005 close to the fragile to strong crossover and to the Mode Coupling ideal crossover temperature.

In particular in the deep supercooled regime our analysis clearly indicates that activated processes dominate the dynamics. A comparison between the van Hove functions and the Radial Distribution Functions allows to better understand the mechanism of hopping phenomena in supercooled water and to connect their onset directly with the crossing of the Widom Line, an important thermodynamic line that signals the presence of the liquid liquid critical point.

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The liquid-liquid transition in ultraviscous deeply supercooled water

F. Perakis^{1,2}, K. Amann-Winkel¹, F. Lehmkuhler^{3,4}, M. Sprung³, D. Pettersson¹, J. A. Sellberg⁵, H. Pathak¹, A. Späh¹, F. Cavalca^{1,2}, D. Schlessinger¹, A. Ricci³, A. Jain³, B. Massani⁶, F. Aubree⁶, C. J. Benmore⁷, T. Loerting⁵, G. Grübel^{3,4}, L. G. M. Pettersson¹ and A. Nilsson¹

- 1 Department of Physics, Stockholm University, Sweden
- 2 SLAC National Accelerator Laboratory, Menlo Park, California, USA
- 3 Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany,
- 4 Hamburg Centre for Ultrafast Imaging, Hamburg, Germany
- 5 Biomedical and X-ray Physics, KTH Royal Institute of Technology, Sweden
- 6 Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria
- 7 X-ray Science Division, Advanced Photon Source Argonne National Laboratory, USA

Despite the simple structure of the individual water molecule, water is a very complex and anomalous liquid, due to the ability of the molecules to form a hydrogen bond network. This highly heterogeneous and disordered three-dimensional network is hypothesized to exist in two different forms: a high- and low-density [1]. A liquid-liquid transition has recently been established for a molecular model of water [2], whereas there is no direct experimental evidence as of yet. It has further been postulated that the observed high- and low-density amorphous ice forms of water can be related to the hypothesized liquid forms through the ultraviscous regime [3]. The experimental challenge in these investigations relates to the preparation of truly equilibrated amorphous ice states [4], as well as to the thermodynamically metastable and hard-to-explore area of the phase diagram (so-called “no-man’s land”), where crystallization occurs very rapidly [5].

Here, we investigate an equilibrated high-density amorphous ice form at atmospheric pressure, where by increasing the temperature it can be transformed to the low-density form [6]. The question is whether this is a transition between two amorphous ice forms, or whether this is a liquid-liquid transition. By using x-ray diffraction in highly coherent synchrotron sources we investigate the local molecular structure, as well as the dynamics over several nanometer regions, during the aforementioned transition. Our results indicate the coexistence of high and low-density domains, giving rise to spatial heterogeneities. In addition, we observe the appearance of a faster component over $T = 115$ K while still in the high-density form, which we interpret as a high-density liquid state with diffusive dynamics. Furthermore, the corresponding low-density form exhibits diffusive character as well, corresponding to the low-density liquid form of deeply supercooled water at $T = 130$ K.

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Dielectric relaxation processes in glassy and liquid water

J. S. Hansen,¹ K. Köster,² T. Loerting,³ A. Sokolov,⁴ R. Böhmer,² and C. Gainaru²

- 1 "Glass and Time," IMFUFA, Department of Science and Environment, Roskilde University, Denmark
- 2 Faculty of Physics, TU Dortmund University, D-44221 Dortmund, Germany
- 3 Institute of Physical Chemistry, University of Innsbruck, A-6020 Innsbruck, Austria
- 4 Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA

Water exhibits a plethora of fascinating anomalies and continues to generate numerous controversies. Among them is the existence of different metastable states at low temperatures, namely the low-density and the high-density amorphous ices [1]. In this contribution we will present the dielectric responses of these two states [2]. Based on recent experimental findings we will discuss whether their underlying dynamics reflects truly structural fluctuations or merely proton motion as in crystalline ices [3]. Additionally, we will focus on the kinetics of the transitions between the two amorphous states, on their subsequent crystallization, and on the role played by quantum effects for the dynamics of ultracold water [4]. Regarding the other side of its "no man's land", several recent studies revisited the relaxation behavior of water above its melting point [5]. Here research is stimulated by the progress in understanding gained from the investigation of monohydroxy alcohols. In this respect we performed a comparative analysis of the relaxation patterns of 1-propanol and water which allowed us to clearly identify the dielectric signature of the relaxation process for the latter [6]. Our findings vindicate the apparent inconsistency between the dielectric and rheological properties of water and shed new light on the microscopic origin of its anomalously large polarization exploited in microwave heating.

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Crystallization kinetics along isomorphs

N. P. Bailey¹, Ulf. R. Pedersen¹, Karolina Adrjanowicz², Kristine Niss¹

1 "Glass and Time", IMFUFA, Department of Science and Environment, Roskilde University, Denmark

2 Institute of Physics, University of Silesia, Poland

It has been known for some years that many condensed matter systems have isomorphs in their phase diagram—curves along which structure and dynamics are essentially invariant when expressed in appropriate reduced units. Considering crystallization as a dynamical process, one can ask whether its kinetics are isomorph invariant. This is non-trivial because two phases are involved, and isomorph invariance generally applies to a single phase. We consider supercooled liquid isomorphs and the corresponding crystalline phases with the same temperature and pressure. Because liquid dynamics are invariant along an isomorph, the kinetic factor in the crystallization rate is fixed, and any variation must be due to thermodynamic effects. Experimental data suggest that the kinetics vary weakly along such an isomorph [1]. Theoretical analysis based on recent developments of the isomorph theory [2] allows calculation of the driving force $\Delta\mu$ along isomorphs for Lennard-Jones systems, and provides a framework for understanding experimental results [3]. A side-effect of the analysis is that one must take variation of the scaling exponent γ into account even though it cannot be directly detected. Computer simulations of the nucleation rate for a single-component super-cooled Lennard-Jones fluid show the opposite behavior from that expected from the variation of $\Delta\mu$, suggesting that the variation of the interface energy along isomorphs must also be taken into account.

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Compressed exponential decays in correlation experiments:

The influence of temperature gradients and convection

T. Blochowicz, J. Gabriel, B. Stühn

TU-Darmstadt, 64289 Darmstadt, Germany

In a wide range of correlation experiments, e.g., with laser light or partially coherent X-rays, so called compressed exponential correlation functions were reported, i.e., $c(t) \propto \exp(-(t/\tau)^\beta)$, with $\beta > 1$. This phenomenon is seen in soft matter systems like gels, microemulsions or foams but also in the density correlation of ageing metallic glasses [1] or in solutions of colloidal particles in supercooled liquids [2]. While in many cases the source of this phenomenon can be traced back to internal stresses in a sample out of equilibrium [3], in some cases the reasons are not well understood, like for example for colloidal particles in supercooled liquids close to T_g [4] or for concentration fluctuations in binary glass formers [5].

We performed multi speckle-dynamic laser light scattering experiments in a system of polystyrene spheres in supercooled propanediol. At low temperatures compressed exponential decays are observed in a multispeckle experiment, in agreement with literature findings in similar systems. At the same time, due to the fact that in our setup the scattered light contains near field contributions, clear indication for convection in the sample can be derived from the speckle pattern, which is due to a slight temperature gradient across the sample cuvette mounted in a cold finger cryostat. These effects increase with decreasing temperature and after a temperature jump and in some cases can be corrected for by assuming convective flow at constant velocity. Such corrections reduce or remove compressed exponential behavior in our experiment [6]. Finally we compare different experimental setups and geometries with respect to their sensitivity towards flow effects.

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Dynamic light scattering in monoalcohols:

Debye relaxation and β -process

T. Blochowicz, J. Gabriel

TU-Darmstadt, 64289 Darmstadt, Germany

The relaxation behaviour in monohydroxy alcohols shows peculiar features, in particular a pronounced Debye-like relaxation process. The latter is mainly observed in the dielectric spectra on the low frequency side of the α -relaxation, and is generally ascribed to transient supramolecular structures forming due to hydrogen bonding in the liquid [1]. For a long time it was thought that the Debye type relaxation is only observed in dielectric spectra but recently its signature was also found, e.g., in dynamic shear modulus experiments [2]. Therefore, the question arises, to what degree this process is observed by other methods as well, in particular by depolarized light scattering, which probes reorientational motion similar to dielectric spectroscopy.

In the present contribution we investigate monoalcohols by depolarized dynamic light scattering (DDLS) and time domain dielectric spectroscopy. In particular we revisit 1-propanol [3] in DDLS with improved accuracy, which enables us to compare in detail the Debye contribution in both techniques. Moreover, we focus on the β -process, which is well resolved in the dielectric spectra of many glass forming systems, also in propanol. The role of the β -relaxation in light scattering, however, is far less clear, and it was even argued that the β -process may not be visible in DDLS at all [4]. For propanol we show, that not only is the β -process well resolved in DDLS, but it also has the same temperature dependent strength and shape as observed in dielectric spectroscopy.

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Modeling the nonlinear dielectric response of glass formers

U. Buchenau

Jülich Center for Neutron Science, Forschungszentrum Jülich Postfach 1913, D-52425 Jülich, Federal Republic of Germany

The recently developed pragmatical model of asymmetric double-well potentials with a finite lifetime is applied to nonlinear dielectric data in polar undercooled liquids [1–7]. The viscous effects from the finite lifetime provide a crossover from the cooperative jumps of many molecules at short times to the motion of statistically independent molecules at long times. One gets good general agreement with experiments in glycerol, propylene carbonate and two mono alcohols. The model is compared to the alternative box model.

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A Grüneisen model for melts

U. Buchenau

Jülich Center for Neutron Science, Forschungszentrum Jülich Postfach 1913, D-52425 Jülich, Federal Republic of Germany

According to a recent numerical finding [1], the dynamics of a glass former is exclusively due to the forces within the first coordination shell. This suggests to treat the melt in terms of a Grüneisen γ given by the nearest-neighbor potential, to be able to calculate the increases of the volume and of the vibrational entropy on increasing the structural energy.

Angell's pragmatism description [2] suggests that the structural entropy of the liquid is limited. On this basis, a Grüneisen model with a limited structural entropy and three structural degrees of freedom per atom is proposed. It is able to describe numerical data [3], able to calculate the heat capacity of liquid selenium and able to explain the surprising difference in the low-temperature dynamics of the Lennard-Jones potential if one replaces its attractive part by an external pressure [4,5].

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Applications of the Moens-Korteweg modes in the expansion tube of the piezoelectric bulk modulus transducer

Tage Christensen

"Glass and Time," IMFUFA, Department of Science and Environment, Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark

The resonances of the bulktransducer in the spectrum between the Helmholtz mode and the standing spherical waves in the liquid sphere are identified as Moen-Kortewig standing waves in the expansion tube.

They have the expected frequency dependence on the liquid column height, liquid density and tube wall thickness.

The shift in the resonances can be used for determining the expansivity of the liquid taking due account of the temperature dependence of the Young modulus of the wall material (by calibration).

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Viscosity of the Lennard-Jones fluid

L. Costigliola¹, D. M. Heyes², T. B. Schröder¹, J. C. Dyre¹

- 1 "Glass and Time", IMFUFA, Department of Science and Environment, Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark
- 2 Department of Mechanical Engineering, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, United Kingdom

The steady-state shear viscosity of the Lennard-Jones (LJ) fluid has been evaluated at more than one hundred state points using the SLLOD algorithm, covering number densities ρ varying between 0.9 and 3.4 and temperatures T from the triple point temperature to several hundred (LJ units). Most of the state points studied are supercritical. The data are well described by the following equation for the (macroscopically) reduced viscosity, $\tilde{\eta} = \tilde{\eta}_0 \exp[B(T_F(\rho)/T)^{2/3}]$ in which $T_F(\rho)$ is the freezing temperature as a function of density and $B = 2.37$. This equation may be justified in part by reference to the isomorph theory [1,2], but the exponent $^{2/3}$ remains to be derived theoretically. The paper also reports data for the diffusivity, which violate the Stokes-Einstein relation at high temperatures. The findings are discussed in light of other representations of the LJ viscosity's variation throughout the phase diagram.

This work has not been published yet but is part of the PhD thesis in [3].

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Non-equilibrium phase behavior of confined molecular films under pressure

David M. Heyes

Department of Mechanical Engineering, Imperial College London
d.heyes@imperial.ac.uk

Glassy and other forms of structurally arrested state can be formed from liquids and solids on the rapid application of a large pressure, such as may be found in Elastohydrodynamic Lubrication. The range of these different types of state increases when this is accompanied by shear and confinement. To explore this behaviour, Non-equilibrium Molecular Dynamics (NEMD) simulations of molecularly thin confined Lennard-Jones films at high pressure and large shear rates have been carried out [1], which follows on from our previous work [2-5]. The nonequilibrium phase and tribological diagrams are mapped out as a function of applied pressure, wall sliding speed and atomic scale surface roughness. Hysteresis effects are also explored. The friction coefficient depends strongly on the nonequilibrium phase adopted by the confined region of molecules, and in general does not follow the classical friction relations between macroscopic bodies.

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Instability in the Kob-Andersen binary Lennard Jones mixture

Trond S. Ingebrigtsen¹, **Jeppe C. Dyre**², **Thomas B. Schroeder**², **C. Patrick Royall**³

- 1 Institute of Industrial Science, University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
- 2 "Glass and Time," IMFUFA, Department of Science and Environment", Roskilde University, DK-4000 Roskilde, Denmark
- 3 H.H. Wills Physics Laboratory, Tyndall Avenue, Bristol, United Kingdom
School of Chemistry, University of Bristol, Cantock's Close, Bristol, United Kingdom
Centre for Nanoscience and Quantum Information, Tyndall Avenue, Bristol, United Kingdom
Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

A glass is formed upon rapid cooling of a liquid through the supercooled liquid region and produces an amorphous solid. Glass formation is, however, obstructed if crystallization takes place as the liquid is cooled. A standard computer model for glass formation is the Kob-Andersen (KA) binary Lennard Jones mixture and was proposed as a model for a metallic liquid. We detail in this study that the KA model possesses an inherent flaw that unfortunately makes this model prone to crystallization and not as good a glass former as is commonly believed. More specifically, we find that the KA model gives rise to A-particle-rich fluctuations in the supercooled liquid. These fluctuations ultimately lead to a single-component-like crystallization kinetics and seals the fate of this model system. We expect our results not only to be relevant for binary metallic glass formers but also to mixtures with several components.

Huginn: Peltier-based temperature controlled sample platforms for neutron scattering

Bo Jakobsen¹, **Alexander T. Holmes**², **Harald Schneider**², **Anders Petterson**², **Arno Hiess**², and **Kristine Niss**¹

¹ Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Denmark

² European Spallation Source ERIC, Lund, Sweden

The main goal of the RUC/ESS Huginn project is to utilize Peltier elements for improving temperature stability and decreases thermalization time compared to conventional sample environments used in neutron scattering. The ability to change temperature fast, has the general advantage that more temperatures can be investigated in a given time interval. This becomes increasingly important at the ESS with the greater neutron brightness and therefore shorter measurement time.

Furthermore, the ability for fast temperature change of the sample will open new possibilities such as: Studies involving time resolved measurements which are performed on processes that start when the sample is moved to a given temperature, i.e. physical aging, crystallization, water uptake or chemical reactions. It also becomes possible to access new meta-stable phases of the investigated substances. Finally, studies of glass-forming liquids and other system with strong temperature dependence will benefit greatly by the the increased stability and precision of the sample temperature.

We present design and prototype tests of two Peltier element based sample holders:

- A sub-cryostat insert for top loading cryostats, for use with general purpose sample cells.
- A multiple temperature SANS sample environment based on individually controlled Peltier elements.

The sub-cryostat insert has the following key performance parameters:

- Very fast temperature changes, typically a few minutes for 10–20 K temperature changes.
- The possibility to change the sample temperature by at least 10 K from the main-cryostat (at overall temperatures down to 150 K).
- An improved temperature stability compared to the main-cryostat by at least an order of magnitude (in most cases two orders of magnitude).
- A working temperature range from 100 K to 370 K.

The multiple temperature SANS sample environment has the following performance parameters:

- Individual cuvettes can have a temperature difference from the base temperature of at least 30 K.
- Temperature changes of up to 30 K can be achieved within a few minutes.
- The temperature is stabilized within 10–100 mK.

Altogether we demonstrate that Peltier element based sample environments is able to decreases thermalization time and improve temperature stability. The two sample environments presented will be available at the ESS, and can easily be adopted to other facilities.

Avalanche dynamics in the so called elastic region of the glassy $\text{Cu}_{50}\text{Zr}_{50}$ system by means of molecular dynamics simulation

A. E. Lagogianni and K. Samwer

I. Physikalisches Institut, Universitaet Goettingen, Friedrich-Hund-Platz 1, 37077 Goettingen, Germany

We present results on the study of the avalanche dynamics of a 3D $\text{Cu}_{50}\text{Zr}_{50}$ system by means of molecular dynamics simulations. The system is subjected to a finite strain rate deformation scheme and to the athermal quasistatic protocol. We find that the avalanches occur from the beginning of the so called elastic region. The critical exponents obtained by the stress drop sizes and time duration distributions for the elastic and plastic region are similar, indicating that the difference in the deformation mechanisms that govern the two regions are not depicted in the statistical profiles of the avalanches. The two regions differ in the way that the number of the avalanches, their average size and the instantaneous shear modulus evolves with strain. Additionally the avalanches, depicted as stress drops, are accompanied by the appearance of regions in the systems that undergo shear transformations and consist of characteristic categories of clusters. The percentage of the clusters in these regions evolves upon deformation in a correlated way with the stress and the energy of the system. The overall decrease/increase of their number upon deformation is taking place by a continuous structural loop where an initial type of cluster transforms into an intermediate one of the same coordination number and consecutively this new type transforms back again to the initial state.

Nonlinear glassy modes

Edan Lerner

Institute for Theoretical Physics, University of Amsterdam, Amsterdam, Netherlands

The disordered microstructure of glassy solids gives rise to a population of quasi-localized low-energy excitations whose statistical properties determine various mechanical, dynamic and thermodynamic properties of glasses. In my poster I will present a micromechanical definition of these glassy excitations [1], which accounts for nonlinearities of the potential energy landscape. I will show that these excitations, coined nonlinear glassy modes, are useful in disentangling delocalized low-frequency vibrational modes from localized ones, and play a key role in the micromechanics of plastic instabilities encountered upon deforming a glass [2].

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Low alkaline borosilicate glasses with different thermal history

– a multi spectroscopic study of preferential bonding, phase-separation and dopant sites

D. Möncke¹, D. Palles¹, G. Tricot², D. Ehr³, E.I. Kamitsos¹

¹ Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

² LASIR, UMR CNRS 8516, USTL, Villeneuve d'Ascq Cedex, France

³ Otto-Schott-Institut für Glaschemie, Friedrich-Schiller-Universität Jena, Germany

Low alkaline borosilicate (NBS) glasses are known to exhibit phase separation, though the addition of small amounts (~1mol%) of Al_2O_3 can prevent visible phase separation. In Al-containing and Al-free NBS glasses, vibrational and 2D NMR spectroscopy shows a preference for B-O-B and Si-O-Si bonds over mixed B-O-Si bonds. However, quenching of the glasses can increase the number of mixed B-O-Si bonds considerably. Furthermore, as the number of mixed bonds decreases significantly upon careful annealing, the remaining mixed bonds are of the $\text{B}_3\text{-O-Si}$ type. $\text{B}_4\text{-O-Si}$ bonds are observed by 2D NMR in quenched samples, but are absent in annealed low alkali borosilicate glasses (B_4 and B_3 denote four- and three-fold coordinated boron, respectively) [1,2].

In the glass NBS2 ($74 \text{ SiO}_2 - 20.7 \text{ B}_2\text{O}_2 - 1 \text{ Al}_2\text{O}_3 - 4.3 \text{ Na}_2\text{O}$), a combination of different melting temperatures (1650 to 1750 °C) with various annealing temperatures (from splat quenching to annealing at 700°C) results in a series of glasses with the same composition but different connectivities.

DSC measurements show two distinct glass transition temperatures, T_g , corresponding to the borate and the silica-rich phases. The two T_g values are in closer proximity for quenched glasses, and shift apart as the annealing temperature increases for constant melting temperature. Density and some mechanical properties vary also with the thermal history, as does the coordination of dopants such as Co^{2+} or Ni^{2+} [3]. Transition metal doping results in a clustering of the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+}) in sodium borate-rich sites, seeking out $[\text{B}\text{O}]_4^-$ tetrahedra as complexing ligands, which in turn increases the tendency of preferential bonding of the glass network [4].

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Study of the crystallization process of a barium-free glass-ceramic for SOFCs

Ilaria Ritucci¹, Wolff-Ragnar Kiebach¹, Henrik Lund Frandsen¹, Federico Smeacetto², Antonio Gianfranco Sabato², Karsten Agersted¹

¹ Department of Energy Conversion and Storage, Technical University of Denmark

² Department of Applied Science and Technology, Politecnico di Torino, Italy

A new silica-based barium-free composition of glass has been designed for solid oxide fuel cell applications. The capacity of some glass compositions to crystallize into a glass-ceramic material over certain temperature and pressure conditions has been used to tailor the heat treatment and the final properties of the material. The effect of the particle size and the heating rate have been studied using different approaches and thermal analyses. Differential thermal analysis (DTA) have been used to determine the characteristic thermal transactions that take place during the heating of the glass. This technique has been used for a calculation of the activation energy for the crystallization to understand which type of crystal growth takes place [1-3]. The heat stage microscope (HSM) has been used to evaluate the sintering behavior of the glass related to the shrinkage and viscosity values [4-6]. In situ x-ray diffraction (XRD) measurements have been performed in order to identify which crystalline phases and at which temperatures crystallize. These analyses have been used for an optimization of the heat treatment to obtain the desired glass-ceramic properties and understand what happens during the crystallization. A possible "freeze" effect that stops the viscous flow and the sintering of the glass has been observed and supposed, as found in literature [7-8]. Moreover different theories will be take in account for the study of this crystallization phenomenon of the glass in order to explain which final densification can be obtained.

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Coupling between molecular mobility and kinetics of crystal growth in a hydrogen-bonded liquid

Alejandro Sanz and Kristine Niss

"Glass and Time", IMFUFA, Department of Science and Environment, Roskilde University, Postbox 260, DK-4000 Roskilde, Denmark

The connection between liquid's dynamics and crystalline development in a hydrogen-bonded liquid is studied by means of dielectric spectroscopy. We monitored the kinetics of crystallization in glycerol by isothermal treatment at temperatures between 220 and 240 K ($T_g = 185$ K). Given the thermal protocol employed, we stimulated the growth of the crystalline phase at the expense of pre-existed molecular aggregates, in such a way that the observed kinetics correspond principally to the crystal growth step. The experimental results are discussed in terms of the classical theory of crystallization which predicts a significant correlation between the liquid's diffusion and the crystal growth rate. The coupling between dynamic properties, such as dielectric α relaxation time, viscosity and self-diffusion coefficient, and the characteristic crystal growth time is commented on. Although not perfect, we found a strong correlation between crystal growth kinetics and glycerol's self-diffusion coefficient ($\tau_{\text{crys}} \propto D^{-0.85}$). This confirms that liquid's dynamics is the principal factor governing the crystal growth in glycerol at the proximities of T_g .

Pseudoisomorphs in liquids with intramolecular degrees of freedom

Thomas B. Schröder

Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Denmark

Computer simulations show that liquids of molecules with harmonic intramolecular bonds may have “pseudoisomorphic” lines of approximately invariant dynamics in the thermodynamic phase diagram. We demonstrate [1] that these lines can be identified by requiring scale invariance of the inherent-structure reduced-unit low-frequency vibrational spectrum evaluated for a single equilibrium configuration. This rationalizes why generalized excess-entropy scaling, density scaling, and isochronal super-position apply for many liquids with internal degrees of freedom.

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Comparative molecular simulation study of low and high density polymer glasses: Competing attractive and repulsive interactions

J. Singh and P. P. Jose

Indian Institute of Technology Mandi, Kamand, H.P.(175005), India

Results of molecular dynamics simulations of Kremer and Grest linear polymer melts system are presented at moderate and high number density [1,2,3]. A detailed study of molecular pair distribution function shows that potential of mean force between the molecules have form of Gaussian with an attractive tail at moderate number density $\rho = 0.85$ (in Lennard-Jones units), which is due to the dominating attractive interactions from temperature $T = 0.7$; this system shows formation of gel like structures [4,5], which is inferred from peaks of molecular structure factor at small wave-numbers and dynamical analysis. At low temperature, this system phase separate to form dense domains whose local density is high. These collection of polymer chains at low temperatures show many dynamical features of glass transition in monomer and molecular level of relaxation indicating glass transition is assisted by gel-like structures in this system [10]. In the same system, at $\rho = 1.0$, repulsive interactions dominate, structure does not change even at low temperatures; the system exhibits dynamic heterogeneity and known to undergo glass transition. In this work we compare and contrast the structure and dynamics of the system near the state points where system undergo glass transition. We computed correlation length of each system from the peak value of four-point structural dynamic susceptibility [7,8,9], which shows that the correlation length of the system is greater at $\rho = 1.0$, which is due to the enhanced cooperatively rearranging regions.

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Short time dynamics determine glass forming ability in a glass transition two-level model:

a stochastic approach using Kramers' escape formula

Javier Quetzalcoatl Toledo-Marin

Instituto de Fisica, UNAM, Circuito de la Investigación Científica, Ciudad Universitaria, CP. 04510 México

The relationship between short and long time relaxation dynamics is obtained for a simple solvable two-level energy landscape model of a glass. This is done through means of the Kramers transition theory, which arises in very natural manner to calculate transition rates between wells. Then the corresponding stochastic master equation is analytically solved to find the population of metastable states. A relation between the cooling rate, the characteristic relaxation time and the population of metastable states is found from the solution of such equation. From this, a relationship between the relaxation times and the frequency of oscillation at the metastable states, i.e., the short time dynamics is obtained. Since the model is able to capture either a glass transition or a crystallization depending on the cooling rate, this gives a conceptual framework in which to discuss some aspects of rigidity theory, for example, a floppy mode implies larger relaxation times and better glass-forming ability.

Liquid fluxing method application for HLW vitrification

N. Musatov, Yu. Volchok, T. Smelova, D. Suntsov, I. Shestoporov, A. Tuchkova

Bochvar Institute (SC "VNIINM"), Moscow, Russia

For the conditioning of liquid radioactive waste resulting from spent nuclear fuel reprocessing, a method of radionuclides incorporation in silicate and borosilicate glasslike matrices is considered.

In the currently existing commercial installations of high-level radioactive waste vitrification, prefabricated glass frit containing the necessary components to produce glass is used as borosilicate glass-forming flux. Before feeding to the melter, glass frit in powder or granular form is mixed with the precalcinated high-level radioactive waste. Various types of batch chargers are used to load a glass-forming mixture into the melter.

When charging dry flux there are a number of disadvantages. These disadvantages can be eliminated by using glass-forming substances which form a fluid mixture when combined with liquid radioactive waste.

Bentonite, silica sol or a mixture of bentonite and silica sol can be used as reagents for liquid fluxing for glassmaking. They are also the source of the required glass-forming substances.

In this paper feasibility of liquid fluxing method application for the vitrification of high-level radioactive waste arisen from the hydrometallurgical reprocessing of spent nuclear fuel was shown.

Borosilicate and sodium-silicate glasslike matrices were produced. Hydrolytic stability of these matrices produced by liquid fluxing method meets requirements to solidified high-level radioactive waste. And molten glass flow characteristics (viscosity) allow easily to carry on the process in induction or resistance melter.

In comparison with the method of charging the flux in the form of glass frit liquid fluxing method has the following advantages:

- simplicity and reliability of the design and a wide range of commercially available dosing apparatuses for liquid fluxing;
- light wear of dosing apparatuses and corresponding increase of operating life;
- method implementation of liquid flux preparation is much simpler than the one of glass frit preparation;
- significant reduction of the dust discharge.

Connecting local yield stresses with plastic activity in a model amorphous solid

S. Patinet¹, Michael L. Falk², **Damien Vandembroucq**¹

- 1 Laboratoire de Physique et Mécanique des Milieux Hétérogènes (PMMH), UMR CNRS 7636 ; PSL - ESPCI, 10 rue Vauquelin, 75005 Paris, France; Sorbonne Université – UPMC, Univ. Paris 06; Sorbonne Paris Cité - UDD, Univ. Paris 07
- 2 Departments of Materials Science and Engineering, Mechanical Engineering, and Physics and Astronomy, Johns Hopkins University, Baltimore, MD 21218

In a model atomic glass, a strong correlation is established between the low shear stress thresholds measured locally and the plastic rearrangements observed during a mesoscopic loading. This purely local yield stress field shows a better prediction power of the plastic activity location in comparison with more conventional structural properties. Most importantly, the soft zones thus defined are shown to be persistent with the plastic deformation, after several plastic rearrangements. This direct and non-perturbative approach gives access to explicit physical quantities characterizing the stability of amorphous solids down to atomic-scale. Our results reinforce the relevance of modelling plasticity in amorphous solids based on discrete and local zones pre-existing in the structure.

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Enthalpy relaxation of a metal-organic framework glass

Chao Zhou^{1*}, Thomas D. Bennett², Yuanzheng Yue¹

1 Department of Chemistry and Bioscience, Aalborg University, DK-9220 Aalborg, Denmark

2 Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, University of Cambridge, CB3 0FS, UK

* czh@bio.aau.dk

Metal-organic frameworks (MOFs) or coordination polymers, have been investigated intensively in recent decades owing to their functional properties for applications such as gas absorption, catalysis and sensing. A subset of MOFs called zeolitic imidazolate frameworks (ZIFs), has been found to be of particular interest because of their ability to melt prior to decomposition, and hence, be converted to glasses upon quenching [1–3]. This new family of glasses can be used to understand fundamental glass problems such as melting mechanism, glass formation, and glass transition. In the present work, we study, for the first time, enthalpy relaxation and the thermodynamic properties of a MOF-glass, formed from ZIF-62 [$\text{Zn}(\text{Im})_{1.75}(\text{blm})_{0.25}$]. The enthalpy relaxation time described by the Kohlrausch model demonstrates a broad distribution range, with values of the stretching exponent β of 0.4 to 0.8 with increasing annealing temperature, accompanied by a steady characteristic relaxation time. This unusual relaxation is attributed to stable structural domains with medium-range ordering, and a wide distribution of short-range order structures. The temperature dependences of the enthalpy, entropy and Gibbs free energy of ZIF-62 are also determined. The small thermodynamic values of the differences of the enthalpy, entropy and Gibbs free energy close to the glass transition temperature thermodynamically support the high thermal stability of ZIF-62 glass.

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Organized by Kristine Niss kniss@ruc.dk with the "Glass and Time" Research Center.

Workshop secretary: Phd-stud. Henriette Wase Hansen hwase@ruc.dk