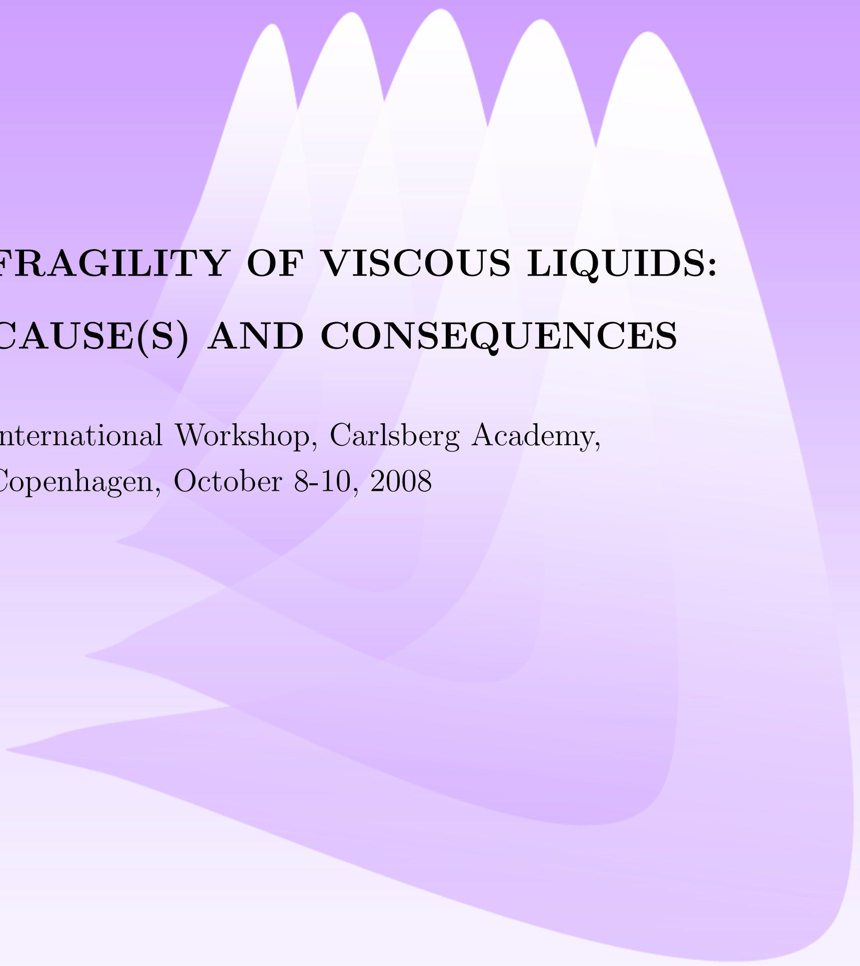

# FRAGILITY OF VISCOUS LIQUIDS: CAUSE(S) AND CONSEQUENCES

International Workshop, Carlsberg Academy,
Copenhagen, October 8-10, 2008

**Glass and Time** - DNRF Centre for Viscous Liquid Dynamics,
Roskilde University

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Organized by **Glass and Time -**
DNRF Centre for Viscous Liquid Dynamics,
Roskilde University

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# INFORMATION

INFORMATION

### Venue

*The Carlsberg Academy*
*Gamle Carlsberg Vej 15*
*2500 Valby*

The Carlsberg Academy is located in Copenhagen adjacent to the Carlsberg Brewery, between Enghave and Valby S-train stations. It is only a short distance from downtown Copenhagen with frequent bus and train connections.
The Carlsberg Academy is now a conference venue owned by Carlsberg Brewery, but in his Will, the former owner - J. C. Jacobsen - stated that, after he and his immediate family had passed away, his house should be used as an honorary residence for a deserving man or woman within the fields of science, literature or art. Since then, the house has been home to many famous guests, including Albert Einstein. Its first resident was the philosopher Harald Høffding. He was followed by the physicist Niels Bohr, who lived here from 1931 to 1962.
The house is built in the classical Italian villa style and J. C. Jacobsen himself designed its heating/ventilation system. The English-inspired park dates from 1848 and was planned by landscape gardener Rudolph Rothe in accordance with J. C. Jacobsen's ideas. It includes many rare plants and trees which J. C. Jacobsen brought back from his foreign trips.

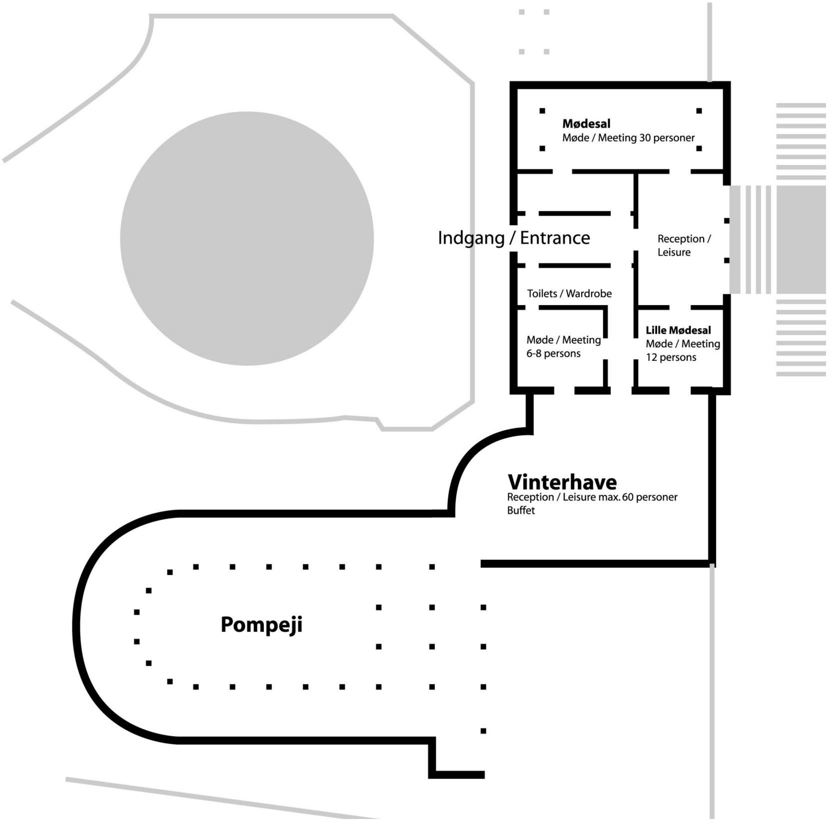
For more information:

`http://carlsbergfondet.dk/`
`http://www.carlsberggroup.com/Experience/Footprints/Valby/Pages/Carlsberg.aspx`

### Registration/Conference Information desk

*Opening Hours:*

| | |
|---|---|
| Wednesday, October 8: | 8:00-9:00 and 14:00-16:00 |
| Thursday, October 9: | 13:00-14:30 |
| Friday, October 10: | 10:00-11:00 and 12:00-14:00 |



### Oral Presentations

Oral presentations take place in "Pompeji". Most talks are of 20 minutes. For details see the program. After each talk, 10 minutes is set aside for discussion.

### Poster Session

Posters should be mounted on the designated poster boards that are placed around the perimeter of "Pompeji". Posters are left throughout the duration of the meeting. Adhesive tape and pins will be available for mounting the posters. During the poster session, beer, soft drinks and snacks will be available in "Vinterhaven".

### Instruction to Speakers

Talks are presented in Powerpoint or pdf format. Please make sure your presentation has been copied to the conference computer in one of the breaks preceding the session. It is important that you finish in time, because the success of the meeting depends on there being plenty of time for discussion of each talk. We would like to publish all presentations on our website after the meeting; if your presentation contains material not to be published now, please provide a "public" version of the presentation, also. It is a good idea to include relevant references in the presentation.

### Coffee Breaks

Coffee and tea will be available in "Vinterhaven".

### Lunches

A simple buffet lunch is provided.

### Conference Dinner

The conference dinner takes place Thursday, October 9.

### Internet Access

Wireless internet access is available at the academy. No password is required.

### Public Transport

**by train:** The Carlsberg Academy is located close to Valby and Enghave S-train stations. From Copenhagen Central Station take S-train lines H, H$^+$, C, B, B$^+$ or Bx towards Frederiksund, Ballerup or Høje Taastrup (H and H$^+$ lines stop only in Valby). A single ticket for the train between Copenhagen Central Station (København H) and Valby or Enghave Station costs DKK 17, and the train ride takes approximately 5 minutes.

**by bus:** Bus number 1A, 4A, 18 and 26 have stops near the Carlsberg Academy. Check the schedules and stops at `http://www.rejseplanen.dk/` and `http://www.moviatrafik.dk/`.

# PROGRAM

## Program

| | **Wednesday, October 8, 2008** | |
|---|---|---|
| **08:00-09:00** | *REGISTRATION* | |
| **09:00-09:05** | *Welcome* | Jeppe Dyre |
| **09:05-09:20** | *The Danish National Research Foundation* | Klaus Bock (DNRF) |
| | **Morning Session** | |
| | *Chair: Aleksandar Matic* | |
| **09:20-09:50** | *Fragility of Viscous Liquids: The Phenomenon and the many Ideas to Explain It* | Austen Angell (Arizona State University) |
| **09:50-10:00** | Discussion | |
| **10:00-10:30** | *Coherent MHz and GHz Longitudinal and Shear Acoustic Phonons in Glass-Forming Liquids* | Keith Nelson<br>Jeremy Johnson &<br>Christoph Klieber<br>(MIT) |
| **10:30-10:40** | Discussion | |
| **10:40-11:00** | **Coffee Break** | |
| | *Chair: Ernst Rössler* | |
| **11:00-11:20** | *Little Evidence for Dynamic Divergences in Ultraviscous Molecular Liquids* | Tina Hecksher (Roskilde University) |
| **11:20-11:30** | Discussion | |
| **11:30-11:50** | *Viscosity, Entropy and Fragility* | Isak Avramov (Bulgarian Academy Academy of Sciences) |
| **11:50-12:00** | Discussion | |
| **12:00-12:20** | *The Dynamic Crossover in o-Terphenyl* | Nikolaus Petzold (Universität Bayreuth) |
| **12:20-12:30** | Discussion | |
| **12:30-12:50** | *Prevalence of $\sqrt{t}$ Relaxation for the Dielectric $\alpha$-process in Viscous Organic Liquids* | Albena Nielsen (Roskilde University) |
| **12:50-13:00** | Discussion | |
| **13:00-14:00** | **Lunch** | |

| | **Wednesday, October 8, 2008** | |
|---|---|---|
| **14:00-16:00** | **Poster Session** | |
| | **Afternoon Session** | |
| | *Chair: Andrea Mandanici* | |
| **16:00-16:20** | *Long-lived Structural Fluctuations and Crystallization of Binary Mixture* | Ulf R. Pedersen (Roskilde University) |
| **16:20-16:30** | Discussion | |
| **16:30-16:50** | *A Fragile Monodisperse Lennard-Jones Liquid on the Hyperbolic plane: Dynamical Heterogeneities and Topological Defects* | Francois Sausset (Université Pierre et Marie Curie) |
| **16:50-17:00** | Discussion | |
| **17:00-17:20** | *Universal Scaling Between Structural Relaxation and Caged Dynamics in Glass-Forming Liquids, Polymers and Binary Mixtures* | Alistar Ottochian (Università di Pisa) |
| **17:20-17:30** | Discussion | |
| **17:30-17:50** | *Breakdown of the Stokes-Einstein Relation in Lennard-Jones Glass-Forming Mixtues with different Interation Potentials* | Frederic Affouard (Université Lille) |
| **17:50-18:00** | Discussion | |
| **18:00-20:00** | **Dinner (Buffet)** | |

| | | |
|---|---|---|
| | **Wednesday, October 8, 2008** | |
| | **Evening Session** | |
| | *Chair: Marc Descamps* | |
| **20:00-20:20**<br>**20:20-20:30** | *Ageing of Dielectric and Mechanical Properties*<br>Discussion | Niels Boye Olsen (Roskilde University) |
| **20:30-20:50**<br>**20:50-21:00** | *Memory Effects in the Gaussian Trap Model*<br>Discussion | Gregor Diezemann (Universität Mainz) |

| | **Thursday, October 9, 2008** | |
|---|---|---|
| | **Morning Session** | |
| | *Chair: Christ Glorieux* | |
| **09:00-09:20**<br>**09:20-9:30** | *Electrode Polarisation and its Scaling: A Microscopic Model*<br>Discussion | Friedrich Kremer (Universität Leipzig) |
| **09:30-09:50**<br>**09:50-10:00** | *Charge Transport and Mass Transport in Ionic Liquids*<br>Discussion | Joshua Sangoro (Universität Leipzig) |
| **10:00-10:20**<br>**10:20-10:30** | *Frequency-Dependent Specific Heat from Thermal Effusion in Spherical Geometry*<br>Discussion | Bo Jakobsen (Roskilde University) |
| **10:30-11:00** | **Coffee Break** | |
| | *Chair: Ulirich Buchenau* | |
| **11:00-11:20**<br>**11:20-11:30** | *Shear-Mechanical and Dielectric Dynamic Heterogeneity in Supercooled Liquids*<br>Discussion | Claudio Maggi (Roskilde University) |
| **11:30-11:50**<br>**11:50-12:00** | *Dynamics of Structurally and Orientationally Disordered Materials Investigated by Broadband Dielectric Spectroscopy*<br>Discussion | Melanie Köhler (Universität Augsburg) |
| **12:00-12:20**<br>**12:20-12:30** | *Dynamics Slower than the Structural Relaxation in Viscous Liquids*<br>Discussion | Catalin Gainaru (Universität Dortmund) |
| **12:30-14:30** | **Lunch & Leisure** | |

| | **Thursday, October 9, 2008** | |
|---|---|---|
| | **Afternoon Session** | |
| | *Chair: Tullio Scopigno* | |
| **14:30-14:50**<br>**14:50-15:00** | *Influence of Chemical Structure on Fragility in Polymers: A Qualitative Picture*<br>Discussion | Kumar Kunal (University of Akron) |
| **15:00-15:20**<br>**15:20-15:30** | *Fragility and Thermodynamics in Complex Glass-formers*<br>Discussion | Daniele Cangialosi (University of the Basque Country) |
| **15:30-15:50**<br>**15:50-16:00** | *Positron Annihilation Lifetime Response and the Fragility Concept*<br>Discussion | Josef Bartos (Slovak Academy of Sciences) |
| **16:00-16:20**<br>**16:20-16:30** | *Structure and Dynamics in Hydrogen-Bonded Liquids*<br>Discussion | Aleksander Matic (Chalmers University) |
| **16:30-17:00** | **Coffee Break** | |
| | *Chair: Burkhard Geil* | |
| **17:00-17:20**<br>**17:20-17:30** | *Understanding non-exponentiality and non-Arrhenius Temperature Dependence through Memory Functions*<br>Discussion | Nicholas P. Bailey (Roskilde University) |
| **17:30-17:50**<br>**17:50-18:00** | *On the Relationship Between Fragility and Stretching*<br>Discussion | John C. Mauro (Corning Incorporated) |
| **18:00-18:20**<br>**18:20-18:30** | *Fragility as Explained from the Landscape Persepctive*<br>Discussion | Andreas Heuer (Universität Münster) |
| **18:30-18:50**<br>**18:50-19:00** | *Fragility and its (Proposed) Correlation to other Properties - What Can We Learn from High-Pressure Experiments?*<br>Discussion | Kristine Niss (Roskilde University) |
| **Conference Dinner** | | |
| **Piano Music Played by Friedrich Kremer** | | |

| | **Friday, October 10, 2008** | |
|---|---|---|
| | **Morning Session** | |
| | *Chair: Morten Eldrup* | |
| **9:00-9:20** | *The Fragility of Bulk Metallic Glasses* | Wei-Hua Wang (Chinese Academy of Sciences) |
| **9:20-9:30** | Discussion | |
| **9:30-9:50** | *On Fragility of Bulk Metallic Glass-Forming Liquids* | Ralf Busch (Universität des Saarlandes) |
| **9:50-10:00** | Discussion | |
| **10:00-10:20** | *Kinetic and Thermodynamic Studies of the Fragility of Bulk Metallic Glass-Forming Liquids* | Isabella Gallino (Universität des Saarlandes) |
| **10:20-10:30** | Discussion | |
| **10:30-11:00** | **Coffee Break** | |
| | *Chair: Søren Toxværd* | |
| **11:00-11:20** | *Strong Forever - Supercooled Hydration Water in Connective Tissue* | Roland Böhmer (Univertät Dortmund) |
| **11:20-11:30** | Discussion | |
| **11:30-11:50** | *What Can Thermal Fluctuations Tell Us about Fragility?* | Thomas B. Schrøder (Roskilde University) |
| **11:50-12:00** | Discussion | |
| **12:00-12:20** | *Single-Parameter Description of the Overall Dynamics of Glass-Forming Liquids under Temperature and Density Variations* | Simone Capaccioli (University of Pisa) |
| **12:20-12:30** | Discussion | |
| **12:30-13:30** | **Lunch** | |

| | | |
|---|---|---|
| | **Friday, October 10, 2008** | |
| | **Afternoon Session** | |
| | *Chair: Dorthe Lybye* | |
| **13:30-13:50**<br>**13:50-14:00** | *Dynamic Light Scattering in Glass-Forming Ultraphosphate Liquids*<br>Discussion | David Sidebottom (Creighton University) |
| **14:00-14:20**<br>**14:20-14:30** | *Link between Liquid Fragility and Glass Iso-structure Viscosity*<br>Discussion | Yuanzheng Yue (Aalborg University) |
| **14:30-14:50**<br>**14:50-15:00** | *Fragility of High BaO-Containing Glasses*<br>Discussion | Ralf Keding (Aalborg University) |
| **15:00-15:20**<br>**15:20-15:30** | *Low Entropy Glasses from Zeolite Amorphisation*<br>Discussion | Neville Greaves (Aberystwyth University) |
| **15:30** | **Meeting Ends** | |

# ABSTRACTS FOR ORAL PRESENTATIONS

# Fragility of Viscous Liquids: The Phenomenon and the many Ideas to Explain It

Austen Angell

*Dept. of Chemistry and Biochemistry,*
*Arizona State University*

We start by defining the territory of the problem, stressing that fragility is not a phenomenon of the *supercooled* liquid state, but rather a problem of the low temperature liquid state. To emphasize this point we define the "*ideal glass-former*" as distinct from the "ideal glass" as a liquid that reaches the glassy state without ever becoming metastable with respect to crystals, and give examples (that are so far limited to multicomponent systems). To broaden the target, we make a second emphasis - that the fragility problem, usually associated with the accelerating temperature dependence of relaxation times, is equally a problem of low temperature liquid thermodynamics - specifically in the "excess" thermodynamic properies. This is a useful correlation because thermodynamic behavior is more easily interpreted, and the difference between constant volume and constant pressure excess thermodynamic properties, is brought into focus. The Adam-Gibbs theory, the free-volume model, and the "shoving" model featuring the $G_\infty$ shear modulus, are all bridges that connect thermodynamics to relaxation. We examine the possible links to vibrational dynamics. Finally the possibility that fragility is a reflection of proximity to a submerged liquid-liquid (or rather liquid-to-glass) first order phase transition is "floated", and related to recent observations on "stable glasses" from the Ediger group.

In the course of presenting these ideas, and with the aim of broadening the empirical base, we review the range of fragilities that has been observed, and the range of liquids in which high fragilities have been observed.

# Coherent MHz and GHz Longitudinal and Shear Acoustic Phonons in Glass Forming Liquids

Darius H. Torchinsky, Jeremy A. Johnson,
Christoph Kleiber and Keith A. Nelson

*Massachusetts Institute of Technology*
*77 Massachusetts Ave., Cambridge, MA 02139*

We have performed experiments in which MHz and GHz frequency longitudinal and shear acoustic phonons are coherently generated and probed in glass forming liquids, allowing direct tests of mode coupling theory (MCT) as well as the shoving model.

Shear acoustic waves in a previously inaccessible MHz spectral region have been observed using depolarized impulsive stimulated Brillouin scattering. We present a test of the shoving model [1] and of the correlation between the fragility index and Poisson ratio [2] of eight supercooled liquids: triphenyl phosphite (TPP), tetramethyl-tetraphenyl trisiloxane (DC704), m-fluoroaniline, $Ca(NO_3)_2 \cdot 4H_2O$, diethyl phthalate, m-toluidine, phenyl salicylate (salol), 2-benzylphenol, and Santovac 5 (5-phenyl 4-ether). We also present comprehensive studies of the longitudinal acoustic spectrum of DC704, as well as comparisons between the shear acoustic spectrum and previously obtained longitudinal spectrum [3] of TPP. This allows tests of MCT and comparison between structural and shear relaxation dynamics [4, 5, 6]. A novel method of shear acoustic wave generation has been developed [7] and employed in conjunction with our Death Star spectroscopy [8] so that we can generate and probe tunable longitudinal and shear acoustic waves in the GHz regime. This allows a direct look at beta relaxation dynamics, significantly extending the range of MCT tests.

## References

[1] J. C. Dyre, N. B. Olsen, T. Christensen, Phys. Rev. B **53** (5), 2171-2174, 1996.

[2] V. N. Novikov, A. P. Sokolov, Nature **431** (7011), 961-963, 2004.

[3] S. M. Silence, A. R. Duggal, L. Dhar and K.A. Nelson, J. Chem. Phys. **96** (7), 5448-5459, 1992.

[4] W. Götze, J. Phys.: Condens. Matter **11**, A1-A45, 1999.

[5] R. Ahluwalia, S. P. Das; J. Non-Cryst. Solids **235-237**, 115-120, 1998.

[6] M. Priya, S. P. Das, Phys. Rev. E **76**, 061501, 2007.

[7] T. Pezeril, P. Ruello, S. Gougen, N. Chigarev, D. Mounier, J. M. Breteau, P. Picart and V. Gusev, Phys. Rev. B **75** (17), 2007.

[8] J. D. Choi, T. Feurer, M. Yamaguchi, B. Paxton, K.A.Nelson, App. Phys. Lett. **87**, 081907, 2005.

# Little Evidence for Dynamic Divergences in Ultraviscous Molecular Liquids

Tina Hecksher, Albena I. Nielsen,
Niels Boye Olsen, and Jeppe C. Dyre

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

The physics of the ultraviscous liquid phase preceding glass formation continues to pose major problems that remain unsolved [1]. It is actively debated, for instance, whether the marked increase of the relaxation time reflects an underlying phase transition to a state of infinite relaxation time [2-4] or if it has a different origin [5-7]. We present an analysis of the temperature dependence of the dielectric relaxation time for 42 organic liquids just above the glass transition [8]. We defined the relaxation time as the inverse dielectric loss-peak frequency which was determined by fitting a second order polynomial to the imaginary part of the dielectric response in a log-log plot. All datasets were fitted by two well known equations with the same number of parameters: the VFT equation $\tau = \tau_0 \exp[A/(T - T_0)]$ (which has a divergence) and Avramov equation $\tau = \tau_0 \exp[B/T^n]$ (which does not). In the fitting procedure the pre-factor was kept fixed at a physically reasonable value, $\tau_0 = 10^{-14}s$. On average the VFT equation fits data better. The success of the VFT equation can be explained by its prediction of an increasing temperature index (defined as $I_{\Delta E} = -d \ln \Delta E / d \ln T$ [9]) with decreasing temperature in accordance with the behavior 9 out of 10 liquids, whereas the Avramov equation predicts a constant temperature index. Two other equations with increasing temperature index, the same number of parameters, and no divergence, are shown to fit the data just as well as the VFT-equation. Our analysis shows that the VFT-equation remains an excellent fitting function, however there is no compelling evidence for the prediction that the relaxation time diverges at a finite temperature. We conclude that theories with a dynamic divergence of the VFT form lack a direct experimental basis [8, 10].

## References

[1] C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys., **88**, 3113 (2000).

[2] G. Adams and J. H. Gibbs, J. Chem. Phys., **43**, 139 (1965).

[3] J. Bouchaud and G. Biroli, J. Chem. Phys., **121**, 7347 (2004).

[4] V. Lubchenko and P. G.Wolynes, An. Rev. Phys. Chem., **58**, 235 (2007).

[5] W. Götze and L. Sjögren, Rep. Prog. Phys., **55**, 241-376 (1992).

[6] F. H. Stillinger, J. Chem. Phys., **88**, 7818 (1988).

[7] J. C. Dyre, N. B. Olsen, and T. Christensen, Phys. Rev. B., **53**, 2171 (1996).

[8] T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nature Physics, **4**, 737 (2008).

[9] J. C. Dyre and N. B. Olsen, Phys. Rev. E, **69**, 042501 (2004).

[10] G. B. McKenna, Nature Physics, **4**, 673 (2008).

# Viscosity, Entropy and Fragility

Isak Avramov

*Institute of Physical Chemistry, 1113 Sofia, Bulgaria*

A model of viscosity $\eta$ of glass-forming melts is discussed in an attempt to predict the dependence of $\eta$ on chemical composition as well as on temperature $T$ and on pressure $P$. It describes well all existing experimental viscosity data including those of glass-forming melts, igneous materials and polymers. It is demonstrated that the activation energy $E(T_g)$ can be expressed through the glass transition temperature $T_g$ as $E(T_g) = \varepsilon RT$ where $\varepsilon R = 260 \pm 10\%$ in $[J/(molK)]$. The fragility parameter, $F$, depends on the molar fraction, $x$, of network modifiers according to $F = 1 + 6x$. It is demonstrated that $F$ is correlated to the fragility parameter, $m$, derived by Angell.

# The Dynamic Crossover in o-Terphenyl

N. Petzold, A. Brodin, R. Kahlau,
J. Hintermeyer and E. A. Rössler

*Universität Bayreuth, Germany*

o-Terphenyl (OTP) is a glass former investigated by many techniques to unravel the evolution of molecular dynamics while cooling from well above the melting point down to the glass transition temperature T$_g$. Recent findings by electron paramagnetic resonance spectroscopy (EPR)[1] demonstrate a clear-cut dynamic crossover for the rotational non-ergodicity parameter f$_{rot}$ at T$_c$ = 297.5±0.5 K (cf. Fig. 1).

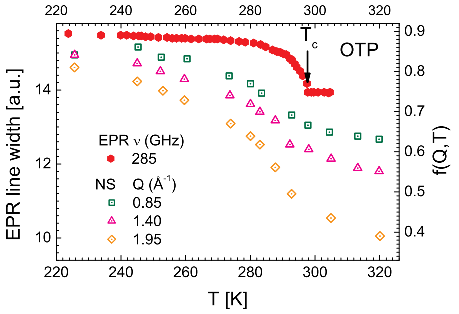


Figure 1: Results on o-terphenyl: temperature dependence of EPR-linewidth as a measure of the rotational non-ergodicity parameter f$_{rot}$(T) (red hexagon)[1] compared with temperature and q-dependence of Debye-Waller factor as a measure of density fluctuations f(Q,T) obtained by neutron scattering[3]

In contrast, attempting to identify this crossover by other techniques, it appears much more smeared (cf. Fig. 1) which has led to the conclusion that the transition may be masked by further relaxation processes or even might not exist. To resolve this unclear experimental situation we re-visit the spectral analysis carried out on OTP by depolarized light scattering (DLS), dielectric spectroscopy (DS) and optical Kerr effect (OKE)[2]. We present new DLS spectra avoiding spectral artifacts which spoiled previous studies. Figure 2 shows the rotational correlation function from Fourier transforming the DLS spectra. The inset demonstrates the validity of time-temperature superposition up to highest temperatures. We will show that analyzing DLS as well as OKE data the excess-wing (EW), the latter well known from DS, has to be accounted for when separating the contributions from fast and slow dynamics, for example, to get $f_{rot}$(T) also from DLS spectra. In any case, a pronounced change in $f_{rot}$(T) can be identified in the DLS data. It is common belief that fragility $m$ and non-exponentiality $\beta_K$ are correlated: The more fragile a system the more stretched is the structural relaxation ($\alpha$-process) [4]. Analyzing the relation between $m$ and $\beta_K$ for several glass formers at temperatures well above $T_c$ where no secondary relaxations contribute to the DLS spectra we find no correlation between $m$ and $\beta_K$. Testing the above mentioned conjecture at $T \sim T_g$ any statement on this relation depends on the way $\alpha$- and secondary relaxation processes (EW, $\beta$-process) are separated. Starting from that, we revisit our DS, DLS and NMR results to test several approaches to disentangle $\alpha$- and secondary processes and demonstrate again that there is no correlation between $m$ and $\beta_K$.

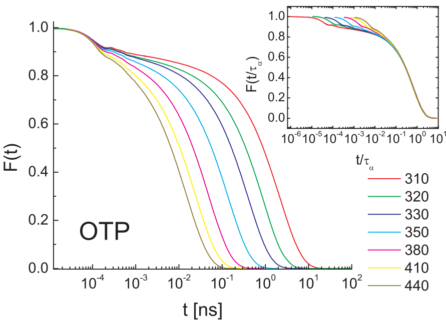


Figure 2: Depolarized light scattering data of o-terphenyl for several temperatures between 310 and 440 K: Fourier-transformed into step-response representation; **inset:** step-response spectra versus reduced time $t/\tau_\alpha$

## References

[1] V. Bercu, M. Martinelli, C. A. Massa, L. A. Pardi, E. A. Rössler, and D. Leporini, submitted (2008);
*see also* T. Blochowicz, A. Brodin, and E. Rössler, Ad. C. P. **133**, 127 (2006).

[2] S. Gottke, D. Brace, G. Hinze, and M. Fayer, J. P. C. **105**, 238 (2001).

[3] A. Tölle, H. Schober, J. Wuttke, and F. Fujara, Phys. Rev. E **56**, 809 (1997).

[4] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. C. P. **99**, 4201 (1993).

# Prevalence of approximate $\sqrt{t}$ relaxation for the dielectric $\alpha$ process in viscous organic liquids

Albena I. Nielsen[1], Tage Christensen[1], Bo Jakobsen[1],
Kristine Niss[1], Niels Boye Olsen[1],
Ranko Richert[2] and Jeppe C. Dyre[1]

[1] *DNRF Centre "Glass and Time", IMFUFA, Department of Sciences, Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*
[2] *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85387-1604, USA*

We present an analysis of dielectric relaxation data for organic glass-forming liquids compiled from different groups and supplemented by new measurements. The main quantity of interest is the "minimum slope" of the dielectric loss plotted as a function of frequency in a log-log plot. The data (294 spectra) for 52 liquids show prevalence of minimum slopes close to -1/2, corresponding to approximate $\sqrt{t}$ dependence of the dielectric relaxation function at short times. There are considered studies of possible correlations between minimum slopes and: i) Temperature, quantified via the loss-peak frequency; ii) How well an inverse power law fits data above the loss peak; iii) Degree of time-temperature superposition; iv) Loss-peak half width; v) Deviation from non-Arrhenius behavior via the "activation energy temperature index" [1-3]; vi) Loss strength. The first two points yield correlations that support a conjecture that there is something special about liquids with minimum slopes close to -1/2 [4, 5]. For the last four points only fairly insignificant correlations are found for liquids with minimum slopes close to -1/2. Large-loss liquids have minimum slopes that are numerically significantly larger than 1/2 and loss peak widths that are significantly smaller than those of most other liquids. We conclude that − excluding large-loss liquids − approximate $\sqrt{t}$ relaxation appears to be a generic property of the $\alpha$ relaxation of organic glass formers. To ensure, however, that there are some unconscious bias in the selection of liquids, the analysis must be done on bigger number of liquids before a firm conclusion can be drawn.

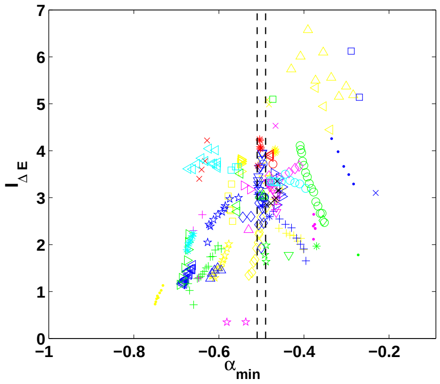


Figure 1: The activation energy temperature index $I_{\Delta E}$ versus $\alpha_{min}$ for all data sets. The quantity $I_{\Delta E}$ is the "activation energy temperature index". A broad range of non-Arrhenius behaviors is represented among liquids exhibiting approximate $\sqrt{t}$ relaxation the temperature index varies by no less than a factor of 2.5, or in terms of fragility − between 50 and 125.

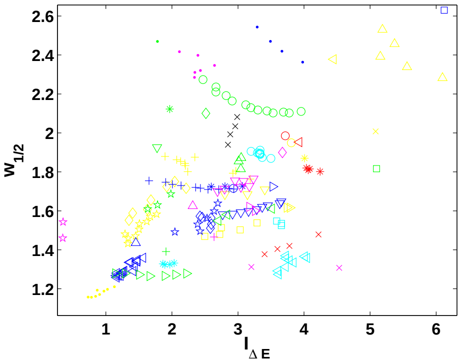


Figure 2: Temperature index $I_{\Delta E}$ versus the modified width $\omega_{1/2}$ plot does not show a clear correlation.

# References

[1] K. U. Schug, H. E. King, and R. Bhmer, J. Chem. Phys. **109**, 1472 (1998).

[2] J. C. Dyre and N. B. Olsen, Phys. Rev. E **69**, 042501 (2004).

[3] T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nature Physics (`www.nature.com/naturephysics`, doi:10.1038/nphys1033) (2008)

[4] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001).

[5] B. Jakobsen, K. Niss, and N. B. Olsen, J. Chem. Phys. **123**, 234511 (2005).

# Long-Lived Structural Fluctuations and Crystallization of a Binary Mixture

Ulf R. Pedersen[1], Thomas B. Schrøder[1],
Jeppe C. Dyre[1] and Peter Harrowell[2]

[1] *DNRF Center "Glass and Time", IMFUFA, Dept. of Sciences,
Roskilde University, P.O. Box 260, DK-4000 Roskilde, Denmark*
[2] *School of Chemistry, University of Sydney, Sydney, Australia*

A supercooled liquid has two possible fates - to crystallize as a consequence of an unstable structural fluctuation (the critical crystal nucleus in classical nucleation theory) or, as the temperature is decreased, to become a rigid amorphous solid through the accumulation and stabilization of long-lived structural fluctuations. The glass-forming liquid must, in other words, have access to stable fluctuations sufficiently different from those of the crystalline state to avoid crystallization. In this paper we analyze the results of simulations of a binary Lennard-Jones mixture, suggested by Wahnström [1] as a model glass-former, which can freeze into the $MgZn_2$ crystal, a Laves phase [2]. At suitable temperatures, the supercooled liquid persists for a long time before the onset of crystallization allowing us to analyze the geometry and composition of the long-lived transient fluctuations. By differentiating those that produce only transient stability from those that result in crystallization we can understand the differences between those structures capable of stabilizing an amorphous solid and those that result in crystal nucleation.

## References

[1] G. Wahnström, J. Phys. Rev. A **44**, 3752 (1991).

[2] U. R. Pedersen, N. P. Bailey, J. C. Dyre, T. B. Schrøder, arXiv:0706.0813v2 (2007).

# A Fragile Monodisperse Lennard-Jones Liquid on the Hyperbolic Plane: Dynamical Heterogeneities and Topological Defects

François Sausset and Gilles Tarjus

*Laboratoire de Physique Théorique de la Matière Condensée,*
*Université Pierre et Marie Curie, 75252 Paris, France.*

Motivated by the frustration-based approach of the glass transition, we have investigated by MD simulation what seems to be the simplest yet tractable frustrated liquid model: a Lennard-Jones fluid on a hyperbolic plane. The system of disks on a Euclidean plane is not frustrated, but placing it in hyperbolic geometry introduces frustration, whose strength is associated with the curvature of the plane. Having generalized the standard MD algorithm to hyperbolic geometry, we have monitored the properties of the model, as a function of both the temperature and the degree of frustration. We find that the one-component liquid does not crystallize and forms a glass on the hyperbolic plane. The "fragility" creases with increasing frustration, and one can tune fragility by changing the space curvature. The cooperative nature of the slowing down (super-Arrhenius, stretched relaxation, dynamic heterogeneities) shows up below a crossover temperature near the "avoided singularity" associated with ordering in flat space. We have also studied the (point) topological defects that are present in the liquid. This provides a means to describe the interplay between structure and dynamics and investigate the connection between dynamical heterogeneities and topological defects. More quantitatively, we have also investigated the four-point dynamical susceptibility and the link between the growing dynamical correlation length and the static correlation length characteristic of hexatic ordering. We find two regimes as temperature decreases: one dominated by collective ordering effects controlled by the avoided transition and one dominated by the dynamics of the few intrinsic topological defects.

## References

[1] G. Tarjus, S. A. Kivelson, Z. Nussinov, and P. Viot, *The frustration-based approach of supercooled liquids and the glass transition: a re-*

*view and critical assessment*, J. Phys.: Condens. Matter, **17**: R1143-R1182, December 2005.

[2] F. Sausset, G. Tarjus, and P. Viot, *Tuning the fragility of a glass-forming liquid by curving space*, arXiv:0805.1475, May 2008.

[3] F. Sausset and G. Tarjus, *Self-diffusion in a monatomic glassforming liquid embedded in the hyperbolic plane*, arXiv:0805.2819, May 2008.

# Universal Scaling between Structural Relaxation and Caged Dynamics in Glass-Forming Liquids, Polymers and Binary Mixtures

A. Ottochian, C. De Michele, D. Leporini
*Università di Pisa*

When cooled or compressed, several systems can avoid crystallization and freeze into a glass. Close to the glass transition (GT) structural relaxation becomes extremely difficult and the kinetic units rattle into the cage of their first neighbors for increasingly longer periods. Despite the huge difference between the relaxation and the vibrational timescales, a number of studies addressed to the cage motion to reach a better understanding of the viscous flow (see [1] for a review).

We show simulation results that, when compared with the available experimental data for systems spanning a very large fragility range, reveal the universal correlation of the structural relaxation time and the rattling amplitude for mixtures, molecular liquids and polymers over about eighteen decades of relaxation times [2]. The scaling holds for several different routes to approach GT in addition to the customary temperature scan, e.g. under isothermal conditions by increasing either the density or the connectivity.

According to the emerging picture the glass softens when the rattling amplitude exceeds a critical value, in agreement with the Lindemann criterion for the melting of crystalline solids [3] and the free-volume model for polymers [4].

## References

[1] J. C. Dyre, N. B. Olsen and T. Christensen, Phys. Rev. B **53**, 2171-2174 (1996).

[2] L. Larini, A. Ottochian, C. De Michele and D. Leporini, Nature Physics **4**, 42 (2008).

[3] X. Xia and P. G. Wolynes; Proc. Natl. Acad. Sci. **97**, 42 (2000).

[4] U. W. Gedde, Polymer Physics (Chapman and Hall, London, 1995).

# Breakdown of the Stokes-Einstein Relation in Lennard-Jones Glass-forming Mixtures with Different Interaction Potential

F. Affouard and M. Descamps

*Laboratoire de Dynamique et Structure des Matériaux Moléculaires*
*UMR CNRS 8024, Université Lille I, 59655 Villeneuve d'Ascq cedex, France*

Three models composed of mixtures of Lennard-Jones A-B particles have been constructed by modifying the shape of the interaction potential between A particles. By performing molecular dynamics simulations, we show that these systems intrinsically possess different homogeneities due to the mixing which are shown to directly affect the breakdown of the Stokes-Einstein relation. This latter particularly occurs at different temperatures for each type of particles and it is directly related to the dynamical decoupling between A and B particles and the formation or not of paths where particles show jump-like motions. Similarity with silicate glasses including mixed alkali effect is discussed.

## References

[1] P. Bordat, F. Affouard, M. Descamps, and K. L. Ngai, Phys. Rev. Lett. **93**, 105502 (2004).

[2] P. Bordat, F. Affouard, and M. Descamps, J. Non-Cryst. Solids **353**, 3924 (2007).

# Ageing of Dielectrical and Mechanical Properties

Niels Boye Olsen

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

A scaling procedure is presented, leading to a master curve in a Kovac-McKenna mapping of the relaxation rate as function of the normalized relaxation function. Both linear- and non-linear scaling procedures are discussed. It is concluded that all measured physical properties age in the same way, suggesting that all physical properties follow the same glass specific internal clock. The temperature- and time dependence of the internal clock-rate, giving the fragility, is discussed in terms of a linear network model for the thermal expansivity. It is demonstrated how this model allows for a non-vanishing relaxation strength of the frequency dependent isocoric heat capasity, the loss peak frequency being non-Arrhenius.

# Memory Effects in the Relaxation of the Gaussian Trap Model

Gregor Diezemann

*Institut für Physikalische Chemie, Universität Mainz,*
*Welderweg 11, 55099 Mainz, FRG*

The so-called memory or Kovacs effect is found in a variety of complex (model) systems undergoing heterogeneous dynamics. If a glass-forming liquid is cooled from some high temperature $T_0$ to a low temperature $T_1$, one-time quantities like the volume or the energy change continuously until the equilibrium value at the destination temperature is reached. Usually, the equilibrium values of such quantities decrease with decreasing temperature. If the system now after the cooling process is kept at a low temperature $T_1$ until the quantity under consideration has reached the equilibrium value at an intermediate temperature $T_2$ with $T_1 < T_2 < T_0$ and one then immediately jumps to $T_2$, the naive expectation would be that nothing changes. This is because the quantitiy already has the correct equilibrium value by construction. In all experimental and theoretical investigations, however, it is found that as a function of time the observed quantity first increases, then reaches a maximum and finally decreases towards the equilibrium value again. This is the so-called Kovacs hump. This behavior has been attributed to the distribution of relaxation times relevant for the heterogeneous $\alpha$-relaxation in the system. In the present contribution, I will consider a trap model (also known as the energy master equation) with a Gaussian density of states. This model shows relaxation to equilibrium at all finite temperatures along with a broad distribution of relaxation times. All aging effects are of a transient nature, similar to what is typically observed experimentally. This fact distinguishes the model from the trap model with an exponential density of states or coarsening models. For the study of the Kovacs effect, the energy is used as the relevant one-time quantity. After a quench from a high temperature to a low temperature $T_1$, the time to reach the equilibrium value of the energy at an intermediate temperature $T_2$, passes through a minimum if considered as a function of $T_1$. This completely unexpected behavior can be understood via an analysis of the relaxation behavior of the energy. The maximum of the Kovacs hump increases with increasing difference in temperatures, $T_1$-$T_2$, whereas the

time of its occurence decreases. If instead of a quench from a high initial temperature, a temperature jump from a low initial temperature is considered (now with $T_1 > T_2$), again a hump is observed. It is found that the qualitative behavior is similar to the situation after a quench. This shows that the memory of the initial conditions has only a quantitative effect on the results. In particular, the drastically different behavior of the relaxation of the trap populations, which is a bimodal distribution at intermediate times in case of a temperature jump, shows no strong effect. Some implications of these findings are discussed.

# Electrode Polarisation and its Scaling: A Microscopic Model

A. Serghei, M. Tress, J. R. Sangoro and F. Kremer

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

A quantitative theory is suggested for the scaling of electrode polarization − an ubiquitous phenomenon taking place at the interface between a metallic and an ionic conductor − its dependence on frequency of the external electrical field, on temperature (resp. concentration of charge carriers) and the geometrical length of the sample cell. It is based on the fact that the mobility of ionic charge carriers is slowed down by many orders of magnitude at the metal/ionic conductor interface and enables one to deduce − by use of a novel formula − the bulk conductivity of the ionic charge carriers under study.

# Charge Transport and Mass Transport in Ionic Liquids

J. R. Sangoro[1], A. Serghei[1], S. Naumov[1], P. Galvosas[1],
J. Kärger[1], C. Wespe[2], F. Bordusa[2] and F. Kremer[1]

[1] *Institute for experimental physics I, University of Leipzig,*
*Leipzig, Germany*
[2] *Martin-Luther University Halle-Wittenberg,*
*Halle, Germany*

The mechanism of charge transport in a series of ionic liquids is analyzed by combining Broadband Dielectric Spectroscopy (BDS) and Pulsed Field Gradient Nuclear Magnetic Resonance (PFG NMR). The dielectric spectra are dominated – on the low-frequency side – by electrode polarization effects while, for higher frequencies, charge transport in a disordered matrix is the underlying physical mechanism. Using the Einstein and Einstein-Smoluchowski equations enables one to determine – in excellent agreement with direct measurements by PFG NMR – the diffusion coefficients of the charge carriers. By that, it becomes possible to extract from the dielectric spectra separately the number density and the mobilities of the charge carriers and the type of their thermal activation. It is shown that the observed Vogel-Fulcher-Tammann (VFT) dependence of the DC conductivity can be traced back to a similar temperature dependence of the mobility while for the number density an Arrhenius-type thermal activation is found.

## References

[1] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Krger, C. Wespe, F. Bordusa, and F. Kremer, Phys. Rev. E **77**, 051202 (2008).

[2] J. R. Sangoro et al, J. Chem. Phys. **128**, 214509 (2008).

[3] W. Xu, C. A. Angell, Science **302**, 422 (2003).

[4] J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, C. Wespe, F. Bordusa, and F. Kremer, submitted to Phys. Rev. Lett.

# Frequency-dependent Specific Heat from Thermal Effusion in Spherical Geometry

Bo Jakobsen, Niels Boye Olsen and Tage Christensen

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University, Denmark*

The studies of frequency-dependent specific heat in liquids close to the glass transition temperature dates back to 1985 where two independent studies of glycerol were published [1,2]. Since then a number of different techniques have been introduced, but the full thermo-viscoelastic problem is normally not taken into account. For thin liquids this is not a problem, but for liquids close to the glass transition temperature where stresses generated by thermal expansion relax on the same time scale as the enthalpy, thermo-viscoelastic coupling has to be taken into account. Some of us have recently given such a theoretical solution in the case of a true 1-dimensional planar geometry [3] and a spherical geometry [4]. Here we present a novel method for measuring the frequency dependent specific heat at the glass transition utilizing a spherical geometry [5]. Working in the spherical geometry has the advantage that the mechanical boundary condition can be taken into account. This is not the case in a planar experiment where no full solution exists which takes the boundaries into account. The method is based on thermal effusion. A small spherical thermistor bead is used as the heater and detector at the same time utilizing what is known as the $3\omega$-method for finding the thermal impedance that the bead "sees". The thermal impedance is the ratio, $\delta T(r_1)/P(r_1)$ between the heat flow, $P(r_1)$, through the surface of the bead and the accompanying temperature response, $\delta T(r_1)$. The thermistor is placed in a large sphere (compared to the thermal diffusion length) filled with the liquid under investigation. In such a geometry the thermal impedance is given by

$$Z_{liq} = \frac{1}{4\pi\lambda r_1 (1 + \sqrt{i\omega r_1^2 c_l/\lambda})},$$

where $r_1$ is the radius of the bead, $\lambda$ is the thermal conductivity, and $c_l$ is the longitudinal specific heat $-$ a quantity between $c_p$ and $c_v$. That it is $c_l$ and not $c_p$ that is measured even if the outer surface of the liquid is free to expand is a consequence of the thermo-viscoelastic interaction.

A merit of the method is that the thermal conductivity and specific heat can be found independently. We present first data on a five-ring polyphenyl ether (5-polyphenyl-4-ether), the Santovac 5 vacuum pump fluid. An account of the $3\omega$-technique used including higher order terms in the temperature dependence of the thermistor and in the power generated is furthermore given. And it is discussed how the thermal properties of the thermistor bead itself can be modelled.

## References

[1] T. Christensen, J. Phys. (Paris) Colloq. **46**, C8-635 (1985).

[2] N. O. Birge and S. R. Nagel, Phys. Rev. Lett. **54**, 2674 (1985).

[3] T. Christensen, N. B. Olsen, and J. C. Dyre, Phys. Rev. E **75**, 041502 (2007).

[4] T. Christensen and J. C. Dyre, Phys. Rev. E **78**, 021501 (2008).

[5] B. Jakobsen, N. B. Olsen, and T. Christensen, arXiv:0809.4617v1 [cond-mat.soft] (2008).

# Shear-Mechanical and Dielectric Dynamic Heterogeneity in Supercooled Liquids

C. Maggi

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

We report the dynamic heterogeneity [1] extracted from shear mechanical and dilectric measurement on several supercooled liquids. Our broad-band mechanical spectroscopy-technique [2] allows us to follow the structural heterogeneity in a wide dynamic window and to compare it with the one taken from the dielectric response. We find that the heterogeneity, at a given temperature, is sensitively smaller when computed through the shear-mechanical probe. We apply the same analysis to classify the relaxation processes in some mono-alcohols exhibiting a strong low-frequency Debye-type process in their dielectric spectrum [3].

## References

[1] L. Berthier, G. Biroli, J. P. Bouchad, et al. Science **310**, 1797 (2005).

[2] T. Christensen and N. B. Olsen, Rev. Sci. Instrum. **66**, 5019 (1995).

[3] B. Jakobsen, C. Maggi, et al. arXiv:0805.4519v1.

# Dynamics of Structurally and Orientationally Disordered Materials Investigated by Broadband Dielectric Spectroscopy

Melanie Köhler[1], Yurii Goncharov[2], Thomas Bauer[1],
Robert Wehn[1], Peter Lunkenheimer[1] and Alois Loidl[1]

[1] *Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany*
[2] *Institute of General Physics, Russian Academy of Sciences, 119991 Moscow, Russia*

In the present contribution, we report broadband dielectric spectra of three related structural glass formers, propylene glycol and its di- and trimer. In addition, very recent results on 60succinonitrile - 40glutaronitrile (60S40GN), a binary mixture showing an orientationally disordered (OD) plastic-crystal phase with relatively high fragility [1], will be presented. In both studied systems, the relaxation times of the $\alpha$ relaxation can be parameterized by the Vogel-Fulcher-Tammann (VFT) equation [2, 3, 4]. Within the strong-fragile classification scheme by Angell [5], all three investigated glycols can be characterized as intermediate glass formers. Contrary to naive expectation, the relaxation of the trimer seems to be faster than that of the dimer. However, this contradiction disappears when scaling the data by the corresponding glass temperature in the "Angell-Plot"[5]. Based on earlier works [6], the relaxation dynamics of OD materials generally seem to show rather strong characteristics. However, the plastic crystalline phase of 60S40GN behaves unconventionally in this respect and can be characterized as fragile. This unusually high fragility may be ascribed to a higher density of minima in the potential energy landscape, caused by substitutional disorder effects. In addition, while most other plastic crystalline phases show no or only a very weak secondary process [6], 60S40GN exhibits a well developed $\beta$ relaxation. Concerning the slow $\beta$ relaxation, the monomer of propylene glycol reveals an excess wing only [7], whereas the di- and trimer show a JG $\beta$ relaxation [8]. The data are discussed in the framework of various models such as the coupling model [9] and the minimal model [10]. In addition, very recent results in the high frequency regime up to $THz$ will be shown and analyzed in terms of the fast $\beta$ process of MCT.

## References

[1] F. Mizuni, J. P. Belieres, N. Kuwata, A. Pradel, M. Ribes, and C. A. Angell, J. Non-Cryst. Solids **352**, 5147 (2006).

[2] H. Vogel, Phys. Z. **22**, 645 (1921).

[3] G. S. Fulcher, J. Am. Ceram. Soc. **8**, 339 (1923).

[4] G. Tammann and W. Hesse; Z. Anorg. Allg. Chem. **156**, 245 (1926).

[5] C. A. Angell, in K. L. Ngai and G. B. Wright (eds.), *Relaxations in Complex Systems*, (National Technical Information Service, Springfield, 1985).

[6] *See, e.g.*, R. Brand et al., Phys. Rev. Lett. **82**, 1951 (1999); R. Brand et al., J. Chem. Phys. **116**, 10386 (2002).

[7] K. L. Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, J. Chem. Phys. **115**, 1405 (2001).

[8] K. Grzybowska, A. Grzybowski, J. Ziolo, M. Paluch and S. Capaccioli, J. Chem. Phys. **125**, 044904 (2006).

[9] K. L. Ngai, Comments Solid State Phys. **9**, 127 (1979).

[10] J. C. Dyre and N. B. Olsen, Phys. Rev. Lett. **91**, 155703 (2003).

# Dynamics Slower than the Structural Relaxation in Viscous Liquids

C. Gainaru and R. Böhmer

*T.U. Dortmund, Experimentelle Physik III,*
*Otto-Hahn-Straße 4, 44221 Dortmund*

Monohydroxy alcohols exhibit a peculiar relaxational behavior with respect to other simple molecular glass formers. In particular, for such systems the process responsible for the ultimate decay of the dielectric function appears exponential [1]. Moreover, the spectral contribution associated with this so-called "Debye process" is anomalously high, apparently unrelated to the magnitude of the dipole moment of the molecular constituents [1]. This process is accompanied by a smaller relaxation feature at higher frequencies. The latter shows characteristics similar to the primary ($\alpha$-) relaxation process governed by the glass transition in typical viscous liquids. Remarkably, the prominent Debye dielectric feature shows no distinguishable thermodynamical and mechanical fingerprints [2, 3].

Relaxation patterns similar to those of the monohydroxy alcohols are observed also for some linear polymers. In addition to the $\alpha$-process, arising from the reorientation of the monomeric units, a slower relaxation process can be identified for type A polymers [4]. In type A polymers a large dipole moment is formed along their chain by the superposition of the individual monomeric contributions (normal mode). While the $\alpha$-process (segmental mode) is governed by the structural relaxation and exhibits a clear thermodynamic signature, the normal mode mainly determines the mechanical properties of the polymer, e.g., the flow.

In the present contribution the dielectric normal relaxation modes are measured for a series of polypropylene glycol (PPG) samples, with different molecular weights. The results are compared with those for the Debye process observed in monohydroxy alcohols. All in all, this comparison points to a possible existence of large structures sustained by hydrogen bonds in alcohols with similar dynamics as observed for polymers. In addition, for PPG the crossover from the monomer to the polymer dynamics is discussed within the spirit of new phenomenological approaches [5, 1].

# References

[1] L-M. Wang, R. Richert, J. Chem. Phys., **121**, 11170 (2004)

[2] L-M. Wang, R. Richert, Phys. Chem. B, **109**, 11091 (2005).

[3] B. Jakobsen et al., cond-mat/08054519 (2008).

[4] G. Strobl, *The physics of polymers*, Springer, 1996.

[5] S. Kariyo et al., Phys. Rev. Lett., **97**, 207803 (2006).

[6] Y. F. Ding et al., Macromolecules, **37**, 161 (2004).

# Influence of Chemical Structure on Fragility in Polymers: A Qualitative Picture

Kumar Kunal[1], Christopher G. Robertson[2],
Sebastian Pawlus[3] and Alexei P. Sokolov[1]

[1] *Department of Polymer Science, The University of Akron,*
*Akron, OH 44325-3909, USA*
[2] *Saint-Gobain High Performance Materials, Northboro R&D Center,*
*Northboro, MA 01532-1545, USA*
[3] *Institute of Physics, Silesian University, ul. Uniwersytecka 4,*
*40-007, Poland*

Many polymers exhibit very high fragility ($> 100$), much higher than most of the non-polymeric systems [1, 2]. Understanding structural parameters that control fragility and the glass transition in polymers remains a challenge. It seems that there is some *polymer specific* contribution that leads to such high fragility in polymers. Analysis of literature reveals that most polymers with rigid and sterically hindered backbones show high fragility. On the other hand, polymers with flexible backbones and side groups are relatively strong [3]. These observations are in accordance with the Generalized Entropy theory suggested by Dudowicz et al [4]. However, many deviations have been found from this trend [5, 6], and a unified approach to explain these deviations, and to predict the fragility of all polymers, is still lacking.

We have studied a wide range of polymer structures and analyzed them in the framework of the molecular packing efficiency, as suggested by the above-mentioned model [4]. Our analysis reveals that the flexibility of side groups relative to the flexibility of the backbone is the most important factor controlling fragility in polymers. On the other hand, glass transition temperature $T_g$ primarily depends on the backbone flexibility and the side group bulkiness (occupied volume). Based on these results we propose a modified approach to understand the effect of chemical structure on polymeric fragility: (i) polymers with stiff backbones always have high $T_g$ and fragility, while (ii) polymers with flexible backbones and no side-groups are the strongest; (iii) however, for the most common type of polymeric structure-flexible C-C or Si-O backbone with side groups, fragility increases with increasing “relative” stiffness of side groups versus the backbone. In this class of polymers, lowest fragility

is expected when the side groups are of similar chemical structure (or flexibility) as the backbone, as in the case of polyisobutylene, one of the strongest polymers known. This scenario is consistent with the idea of the packing efficiency as the main parameter controlling fragility.

## References

[1] Böhmer et al., J. Chem. Phys. 1993, **99**, 4201.

[2] Huang D. and McKenna G. B., J. Chem. Phys. 2001, **114**, 5621.

[3] Sokolov et al., J. Phys. Condens. Matter 2007,**19**, 205116.

[4] Dudowicz J., Freed K. F.; J. Chem. Phys. 2006, **124**, 21350.

[5] Kunal et al., J. Poly Sci B 2008, **46**,1390.

[6] Kunal et al., Macromolecules, 2008 (submitted).

# Fragility and Thermodynamics in Complex Glass-Formers

D. Cangialosi[1], A. Alegría[1,2] and J. Colmenero [1,2,3]

[1] *Centro de Física de Materiales Centro Mixto (CSIC-UPV/EHU),*
*Edificio Korta,20018 San Sebastián, Spain*
[2] *Departamento de Física de Materiales,*
*Universidad del País Vasco (UPV/EHU), Facultad de Qumica,*
*Apartado 1072, 20080 San Sebastián, Spain*
[3] *Donostia International Physics Center, Paseo Manuel de Lardizabal 4,*
*20018 San Sebastián, Spain*

A liquid cooled down below its melting temperature undergoes an increase of the relaxation time (and the viscosity), which eventually leads to the glass transition. Depending on the steepness of the relaxation time variation, supercooled liquids are classified into strong and fragile, respectively displaying mild and rapid variation of the relaxation time with temperature. The connection between the steepness of the relaxation time variation of the $\alpha$ process, the so-called dynamic fragility, with other properties of the glass-former, such as thermodynamic, has been the subject of intense debate within the scientific community.

In this contribution, we have connected the dynamic fragility, namely the steepness of the relaxation time variation upon temperature reduction, to the excess entropy and specific heat of a large number of glass-forming polymers and low molecular weight glass formers possessing internal degrees of freedom. The connection was obtained in a natural way from the Adam-Gibbs equation, relating the structural relaxation time to the configurational entropy. We find a clear correlation only for a group of polymers. For another group of polymers and all investigated low molecular weight glass formers, for which this correlation does not work, we emphasise the contribution of relaxation processes unrelated to the $\alpha$ process and attributed to internal degrees of freedom to macroscopic thermodynamic properties. Once the residual excess entropy at the Vogel temperature, attributed to these degrees of freedom, is removed from the total excess entropy, the correlation between dynamic fragility and thermodynamic properties is re-established.

# References

[1] C. A. Angell, *In Relaxations of Complex Systems*, edited by K. L. Ngai, G. B. Wright (National Technical Information Service, U.S. Department of Commerce, Springfield, VA 1985).

[2] K. Ito, C. T. Moynihan, and C. A. Angell, Nature **398**, 492 (1999).

[3] D. Cangialosi, A. Alegría, and J. Colmenero, J. Chem. Phys. **124**, 024906 (2006).

# Positron Annihilation Lifetime Response and the Fragility Concept

Josef Bartoš[1] and Jozef Krištiak[2]

[1] *Polymer Institute of SAS, Dúbravksá cesta 9, 842 36 Bratislava*
[2] *Institute of Physics of SAS, Dúbravská cesta 9, 842 28 Bratislava, Slovak Republic*

The structure-property relationships belong to long-standing topics of physics, chemistry and materials sciences of condensed matter. In the case of disordered glass-forming systems, a classical diffraction approach is not very effective at characterization of the physical microstructure, so that their physical microstructure is often treated using the pseudo-molecular free volume concept being very useful because of its conceptual simplicity and physical plausibility in interpretation of the thermodynamic, dynamic and transport behavior. At present, positron annihilation lifetime spectroscopy (PALS) based on the annihilation of the bound system of positron and electron, the so called ortho-positronium (o-Ps), is an effective tool for the free volume characterization. The o-Ps probe is a very sensitive indicator of the presence of local regions of the reduced electron density, such as quasi-static vacancies in real crystals or more or less static depending free volume holes in amorphous phases.

In general, the PALS response of glass-forming systems, i.e. o-Ps lifetime $\tau_3$, being a measure of free volume size as a function of temperature T, exhibits a typical quasi-sigmoidal course. Phenomenological model-free analysis of these $\tau_3$-T plots in a series of small molecular and polymeric glass-formers revealed the existence of several characteristic PALS temperatures marked according to a unified notation as $T_g^{PALS}$, $T_{b1}$ and, $T_{b2}$ the two latter being located at $T_{b1}^L \sim$ 1.2-1.4 $T_g^{PALS}$ or $T_{b2}^L \sim$ 1.4-1.7 $T_g^{PALS}$, respectively. Evidently, the full utilization of PALS method for the characterization of any disordered system requires not only to describe the whole $\tau_3$-T dependence, but also to understand the physical origin of and the observed trends in these PALS temperatures as completely as possible. In this respect, it was found that both the temperature ratios $T_{b1}/T_g^{PALS}$ and $T_{b2}/T_g^{PALS}$ are closely related to the corresponding fragilities. Thus, the higher fragility of a given liquid is, the larger their values of the T ratios are. In addition, the expansivity of the o-Ps lifetime in the vicinity of the liquid-glass transition increases with the respective fragility. In our attempt to explain these empirical findings, the two-order parameter (TOP) model of disordered systems suggests that these trends might be related to the mutual relationship between the solid-like and liquid-like domains in supercooled liquid, especially to the temperature evolution of the solid-like domains on cooling the originally normal liquid state through its supercooled liquid state down to the final glassy state.

# Structure and Dynamics in Hydrogen-Bonded Liquids

Per Sillrén, Aleksandar Matic and Johan Mattsson

*Department of Applied Physics, Chalmers University of Technology*
*Göteborg, Sweden*

Hydrogen (H-) bonding plays an essential role in materials of importance for a wide range of applications including pharmaceutical, food, paint, hygiene and cosmetics industry. In fact, life largely relies on H-bonding, in water itself and in between water and other H-bonding biomolecules. H-bonding liquids, as other liquids, generally show different dynamics above and below a crossover temperature $T^* \approx 1.1$ - $1.6\,T_g$, where $T_g$ is the glass-transition temperature. This crossover is observed in a range of different dynamic properties, such as the temperature dependence of the structural relaxation time and the relationship between diffusional and rotational motion [1]. The main difficulty in modelling and understanding these liquids lies in the high directionality and intermediate strength of the hydrogen bonds. In this contribution we report results from a systematic investigation of the structure and dynamics of liquids with varying degrees of hydrogen bonding. Using oligomeric liquids (glycols) and some related alcohols, we obtain a dilution of the hydrogen bond concentration via variations in chain length or size of the molecules. With dielectric spectroscopy we follow the structural relaxations [2-4] and with vibrational spectroscopy we monitor the hydrogen-oxygen (OH) stretch vibrations, which are strongly influenced by the degree and nature of the hydrogen bonds, from the boiling temperature down to the glass temperature. In general we observe for increasing hydrogen bond concentration a decreased fragility of the liquid and that the dynamic crossover in the super cooled regime becomes more pronounced. We also find that there is a marked shift in both position and shape of the OH-stretch vibrational band as a function of temperature (see figure 1). The aim is to relate this change of bond-strength to the structure and dynamics of these liquids, especially in the supercooled regime.

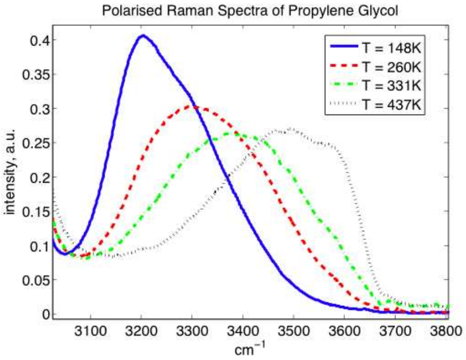


Figure 1: Raman spectrum of propylene glycol in the OH-stretch region as a function of temperature. The spectral weight is shifted to lower wave-numbers with decreasing temperature indicating an increased tendency for stronger hydrogen bonding.

# References

[1] Angell, C.A. et al., J. Appl. Phys. **88**, 3113 (2000).

[2] J. Mattsson et al., arXiv:0803.3374v2.

[3] J. Mattsson et al., Phys. Rev. Lett. **90**, 075702-1-4 (2002).

[4] J. Mattsson et al., Phys. Rev. Lett. **94**, 165701-1-4 (2005).

# Understanding Non-Exponentiality and Non-Arrhenius Temperature Dependence Through Memory Functions

Nicholas P. Bailey

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

We present analysis of correlation functions describing viscous liquid dynamics using the memory function, which on time scales greater than about 10 ps turns out to be surprisingly simple: a delta function at zero time and a negative inverse power law at finite times. An obvious application is fitting the correlation function, although we do not have a general analytic expression for the correlation function associated with such a memory function. The growth of the amplitude of the power-law tail as temperature decreases explains both non-exponential relaxation and the non-Arrhenius temperature dependence, while the short time behavior shows near-Arrhenius behavior. The negative tail can be understood as a consequence of disorder, which heightens the probability of reverse transitions, at time intervals up to the relaxation time. In principle the low-temperature limit corresponds to the negative tail growing to the point that the time integral of the memory function vanishes and the relaxation time diverges. It is hypothesized that this divergence is cut off by elastic coupling between spatially separated regions which acts as a noise source, reducing the effective memory of a given region.

# On the Relationship Between Fragility and Stretching

John C. Mauro[1] and Prabhat K. Gupta[1,2]

[1] *Science and Technology Division, Corning Incorporated,*
*Corning, NY 14831, USA*
[2] *Department of Materials Science and Engineering,*
*The Ohio State University, Columbus, OH 43210, USA*

We derive an analytical expression showing the relationship between fragility and the exponent $\beta$ of the stretched exponential (KWW) relaxation function. We show that the fragility can be described as a product of (i) a thermodynamic term depending on configurational heat capacity and entropy and (ii) a kinetic term depending only on the value of $\beta$ at the glass transition temperature. Our result indicates that there is not a 1:1 correlation between the value of $\beta$ and the fragility of a supercooled liquid. Rather, the value of $\beta$ provides a lower limit for fragility, which can be increased through changes in the configurational heat capacity and entropy. In the limit of zero configurational heat capacity and $\beta$ = 1, we recover the fragility of a strong liquid (m = 17). Our result explains the apparent contradiction between those researchers showing a correlation between $\beta$ and fragility - and those who question such a correlation due to the noisiness and spread of the data . In addition, we show that only one particular value of $\beta$ influences fragility, viz., that at the glass transition temperature.

## References

[1] *Correlations of the nonexponentiality and state dependence of mechanical relaxations with bond connectivity in Ge-As-Se supercooled liquids*, R. Böhmer and C. A. Angell, Phys. Rev. B **45**, 10091 (1992).

[2] *On the correlation between fragility and stretching in glass-forming liquids*, K. Niss, C. Dalle-Ferrier, G. Tarjus, and C. Alba-Simionesco, J. Phys.: Condens. Matter **19**, 076102 (2007).

[3] *Ten themes of viscous liquid dynamics*, J. Dyre, J. Phys.: Condens. Matter **19**, 205105 (2007).

# Fragility as Explained from the Landscape Perspective

A. Heuer

*Institute of Physical Chemistry, D-48149 Münster*

Via a numerical study of two systems as different as the binary Lennard-Jones system and the BKS-model of silica it turns out that the density of inherent structures of the potential energy landscape (PEL) can be described as a Gaussian [1, 2, 3]. The only difference between both systems is the emergence of a low-energy cutoff for silica. Furthermore for both systems a well-defined crossover energy $e_{cross}$ is observed between regions of the PEL which serve as traps for the system and regions where the system behaves more liquid-like. Finally a direct relation between energy and mobility can be identified. Using this input one can formulate a model of the glass transition for the so-called *ideal Gaussian glass-forming system* [1, 4].

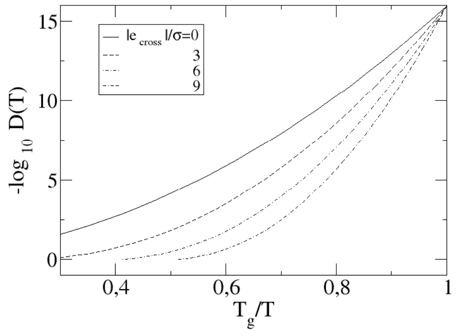


Figure 1: Temperature dependence of the diffusion constant for an ideal Gaussian glass-forming system for different values of the cross-over energy $e_{cross}$ relative to the width $\sigma$ of the Gaussian inherent structure energy distribution.

Now fragility can be expressed in terms of the relevant landscape parameters, thereby yielding a deeper understanding of what fragility really is.

In particular one can calculate the temperature-dependence of the diffusion constant and thus the kinetic fragility (see Figure 1)

Several questions can be approached within this model: Is fragility related to the non-exponentiality of relaxation? What is the origin of the correlation between thermodynamic and kinetic fragility? Is fragility an appropriate concept to characterize glass-forming systems?

## References

[1] A. Heuer, *Exploring the potential energy landscape of glass-forming systems: from inherent structures via metabasins to macroscopic transport*, J. Phys. Cond. Mat. (in press).

[2] A. Saksaengwijit, J. Reinisch, A. Heuer, *The origin of the fragile-to-strong crossover in liquid silica as expressed by its potential energy landscape*, Phys. Rev. Lett. **93**, 235701/1-4 (2004).

[3] A. Saksaengwijit, A. Heuer, *Silica dynamics as explained by properties of the potential energy landscape*, Phys. Rev. E **73**, 061503/1-4 (2006).

[4] A. Heuer, A. Saksaengwijit,*Properties of ideal Gaussian glass-forming systems* Phys. Rev. E (in press); arXiv: 0802.3515.

# Fragility and Its (Proposed) Correlation to Other Properties - What Can We Learn from High Pressure Experiments?

Kristine Niss[1,2] and Christiane Alba-Simionesco[1]

[1] *Laboratoire de Chimie Physique, Bâtiment 349, Université Paris-Sud, 91405 Orsay, France*
[2] *DNRF Centre "Glass and Time", IMFUFA, Department of Sciences, Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

Within the past decades a lot of experimental effort has been put into correlating isobaric fragility at atmospheric pressure with other properties of the liquid and the glass. However, the isobaric fragility can be decomposed in an isochoric fragility and a term related to the expansion coefficient. Based on this observation we develope a scheme for analyzing correlations between fragility and other properties [1]. Using this scheme we show how correlations to the isobaric fragility in some cases reflect the effect of density on the relaxation time while they in other cases are related to the intrinsic effect of temperature on the relaxation time. We specifically consider the correlations proposed between fragility and the stretching parameter $\beta_{KWW}$ [2] and the correlation proposed by Scopigno [3] between fragility and the temperature dependence of slope $\alpha$ of the inverse nonergodicity factor as a function of $T/T_g$, measured in the glassy state [4].

## References

[1] *Effects of density and temperature on correlations between fragility and glassy properties*, K. Niss and C. Alba-Simionesco, Phys. Rev. B. **74** 024205, (2006).

[2] *On the correlation between fragility and stretching in glassforming liquids*, K. Niss, C. Dalle-Ferrier, G. Tarjus, and C. Alba-Simionesco, J. Phys-Cond. Mat. **19** 076102 (2007).

[3] *Is the fragility of a liquid embedded in the properties of its glass?*, T. Scopigno, G. Ruocco, F. Sette, and G. Monaco. Science **302**, 849 (2003)

[4] *Glassy properties and viscous slowing down : an analysis of the correlation between nonergodicity factor and fragility*, K. Niss, C. Dalle-Ferrier, V. M. Giordano, G. Monaco, B. Frick, and C. Alba-Simionesco, J. Chem. Phys. (in press).

# The Fragility of Bulk Metallic Glasses

Wei Hua Wang

*Institute of Physics, Chinese Academy of Sciences,*
*Beijing 100080, China*

The fragility of various bulk metallic glass-forming alloys was determined using thermodynamic and kinetic way. A survey of the relation between fragility and elastic, mechanical, and thermodynamic properties, glass-forming ability of various bulk metallic glasses (BMGs) is presented. We discuss the possible correlation between the liquid fragility and the Poissons ratio (alternatively the ration of the bulk and shear moduli, B/G) in various bulk metallic glasses based on all available relevant data. The studies of the relationships among fragility and elastic, mechanical, and thermodynamic properties, glass-forming ability in BMGs could assist in understanding the long-standing issues of metallic glass formation and the nature of glass and stimulate the work of theorists.

# On the Fragility of Bulk Metallic Glass Forming Liquids

Ralf Busch

*Universität des Saarlandes, Lehrstuhl für Metallische Werkstoffe,*
*Campus C63 66123 Saarbrücken, Germany*

This presentation gives an overview of the kinetic properties of bulk metallic glass forming liquids. Good bulk glass forming liquids are rather strong liquids and a general trend is found that the strength increases with the number of components in the liquid [1, 2, 3]. The kinetic strength is associated with a high degree of short and medium range order. For very strong liquids such as the five component Vitreloy 1, this pronounced structure in the melt even leads to shear thinning behavior in the equilibrium liquid above the liquidus temperature [4]. In the case of Vitreloy 1 the shear thinning causing structure gets destroyed far above the liquidus temperature. The liquid becomes more fragile but is still much stronger than pure metals or binary alloys. When undercooled the fragile Vitreloy 1 undergoes a re-transformation into a strong liquid. Other five-, and four- component bulk glass forming alloys such as Vitreloy 106 and 105 do not show pronounced shear thinning above the liquidus and exhibit viscosities that are similar to the fragile Vitreloy 1. However viscosity and relaxation time measurements close to the glass transition for these alloys suggest that they are also much stronger at low temperatures similar to Vitreloy 1.

## References

[1] L. Shadowspeaker and R. Busch, *On the fragility of Nb-Ni-based and Zr-based bulk metallic glasses*, Appl. Phys. Lett. **85**, 2508 (2004).

[2] R. Busch, *Thermophysical Properties of Bulk Metallic Glass Forming Liquids*, J. Min. Met. Mater. S. (JOM) **52** (7), 39 (2000).

[3] R. Busch, J. Schroers, and W. H. Wang, *Thermodynamics and kinetics of bulk metallic glass*, MRS Bulletin **32**, 620 (2007).

[4] C. Way, P. Wadhwa und R. Busch, *The influence of shear rate and temperature on the viscosity and fragility of the*

$Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10.0}Be_{22.5}$ *metallic-glass-forming liquid*, Acta Mater. **55**, 2977 (2007).

# Kinetic and Thermodynamic Studies of the Fragility of Bulk Metallic Glass-Forming Liquids

Isabella Gallino, Christopher D. Way, Ralf Busch

*Universität des Saarlandes, Lehrstuhl für Metallische Werkstoffe,*
*Campus C63 66123 Saarbrücken, Germany*

Viscosity and specific heat capacity measurements of several bulk metallic glass-forming liquids are analyzed to study the connection between kinetic and thermodynamic fragility [1]-[5]. For each alloy, consistent Vogel-Fulcher-Tammann (VFT) fits $[(\eta = \eta_0 \cdot \exp(D^* T_0/T - T_0)]$ of the viscosity measurements are established. This leads to the determination of $T_g^*$ as the glass transition temperature for which the viscosity of the undercooled liquid is $10^{12}$ Pa·s, and of $T_m^*$ as the temperature for which the viscosity of the liquid is about 1 Pa·s. From the thermodynamic data the change in configurational entropy, $S_c$, with undercooling is calculated for each alloy, leaving the configurational entropy at $T_m^*$ as a fit parameter. Besides the VFT fits, fits to the Adam-Gibbs equation $[(\eta = \eta_0 \cdot \exp(C/S_c \cdot T)]$ are performed using this configurational entropy change. Under these assumptions we find remarkable agreement between the Adam-Gibbs and VFT fits. The $T_0$, in the VFT fits, matches very well the temperature, where the configurational entropy vanishes in the Adam-Gibbs fits.

## References

[1] L. M. Martinez, C. A. Angell, *A thermodynamic connection to the fragility of glass-forming liquids*, Nature vol. **410** (2001) 663-667.

[2] C. A. Angell, *Glass Former, and viscous liquid slowdown since David Turnbull: enduring Puzzles and new twists*, MRS Bulletin, vol. **33**, 544- 555 May 2008.

[3] R. Busch, W. Liu, W. L. Johnson, *Thermodynamics and kinetics of the* $Mg_{65}Cu_{25}Y_{10}$ *bulk metallic glass forming liquid*, J. Appl. Phys. 83(8) 4134-4141 (1998).

[4] I. R. Lu, G. Wilde, G. P. Görler, R. Willbecker, *Thermodynamic properties of Pd-based glass-forming alloys*, J. Non-Cryst. Solids vol.**250-252** (1999) 577-581.

[5] G. J. Fan, J. F. Löffler, R. K. Wunderlich, H.J. Fecht, *Thermodynamics, enthalpy relaxation and fragility of the bulk metallic glass-forming liquid* $Pd_{43}Ni_{10}Cu_{27}P_{20}$, Acta Mater. **52** (2004) 667-674.

# Strong Forever - Supercooled Hydration Water in Connective Tissue

Roland Böhmer, Catalin Gainaru,
Burkhard Geil and Ariane Fillmer

*Fakultät für Physik, TU Dortmund, 44221 Dortmund, Germany*

Hydrated proteins are interesting from various points of view. On the one hand, the dynamics of water in the hydration shell of proteins is crucial for their biological function. On the other hand, water confined in that shell fails to crystallize and, unlike bulk water, can be easily supercooled. This may offer new clues to unravel some of the complexities related with the vitrification of bulk water, the first liquid for which a fragile to strong transition was proposed [1]. When the motion of the hydration water comes to rest upon cooling, then also the conformational changes of the protein cease. This statement has been phrased by saying that the bio-macromolecules are the slaves of water [2]. Currently, there is much discussion about how this water-protein interplay should be properly viewed [3,4].

In this talk we focus on nominally dry and on hydrated elastin and collagen which are responsible for the elasticity and the tensile strength, respectively, of the connective tissue of vertebrates. Broadband dielectric measurements were carried out to identify the contributions of the hydration water as well as that of other dipolar degrees of freedom. We discuss to what extent the hydration water performs a decoupled relaxation [5,6] below the glass transition of the solvated protein.

## References

[1] C. A. Angell, Science **319**, 582 (2008)

[2] P. W. Fenimore, H. Frauenfelder, B. H. McMahon, R. D. Young, PNAS **101**, 14408 (2004).

[3] J. Swenson, H. Jansson, R. Bergman, Phys. Rev. Lett. **96**, 247802 (2006); J. Svenson, H. Jansson, J. Hedström, R. Bergman, J. Phys.: Condens. Matter **19**, 205109 (2007).

[4] S. Pawlus, S. Khodadadi, A. P. Sokolov, Phys. Rev. Lett. **100**, 108103 (2008); S. Khodadadi, S. Pawlus, J. H. Roh, V. Garcia Sakai, E. Mamontov, A. P. Sokolov, J. Chem. Phys. **128**, 195106 (2008).

[5] K. L. Ngai, S. Capaccioli, N. Shinyashiki, J. Phys. Chem. B **112**, 3826 (2008).

[6] S. Cerveny, A. Alegría, J. Colmenero, Phys. Rev. E **77**, 031803 (2008).

# What Can Equilibrium Thermal Fluctuations Tell Us about Fragility?

Thomas B. Schrøder, Ulf R. Pedersen, Nicoletta Gnan,
Nicholas P. Bailey and Jeppe C. Dyre

*DNRF Centre “Glass and Time”, IMFUFA, Department of Sciences,
Roskilde University, Postbox 260, DK-4000, Roskilde, Denmark*

Any macroscopic system approaches thermal equilibrium at long times if left undisturbed. Even in equilibrium there are fluctuations of variables that are not strictly conserved. E.g. in the NVT-ensemble (constant particle number, volume and temperature), the chemical potential, pressure, internal energy, and instantaneous temperature fluctuate as a function of time. For large systems thermal fluctuations are small and apparently insignificant. That this is not the case was first pointed out by Einstein, who showed that for any system in equilibrium with its surroundings, the specific heat is determined by the magnitude of the energy fluctuations.

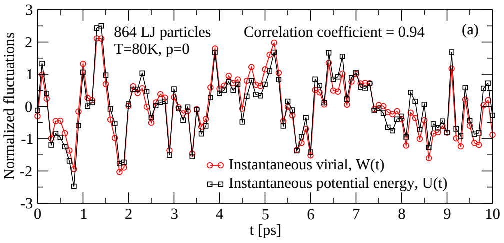


Figure 1: Correlations between instaneous values of potential energy, $U(t)$, and the configurational part of the pressure, the virial $W(t)$ [$p(t) = Nk_BT(t)/V + W(t)/V$]. Normalized fluctuations at $T = 80K$ and zero average pressure (density = 34.6 mol/l) of the virial, W, $\Delta W(t)/\sqrt{\langle \Delta W2 \rangle}$ where $\Delta W(t) \equiv W(t) - \langle W \rangle$, and of the potential energy, $\Delta U(t)/\sqrt{\langle \Delta U2 \rangle}$. The equilibrium fluctuations of virial and potential energy are strongly correlated, as quantified by the correlation coefficient: $R \equiv \langle \Delta W \Delta U \rangle / \sqrt{\langle \Delta W^2 \rangle \langle \Delta U^2 \rangle} =$ 0.94.

One expects few new insights or surprises to come from studies of fluctuations in equilibrated systems. However, in the present contribution we report strong correlations between equilibrium fluctuations in the configurational parts of pressure and energy. This is illustrated in

Fig. 1 for the single component Lennard-Jones Liquid, and is seen also in a number of other liquids, the class of “strongly correlating liquids” [1].

In the present contribution I will give the physical explanation for these correlations [1], and discuss their consequences for viscous liquids [2-4]. I will conclude by explaining what the correlations can tell us about fragility.

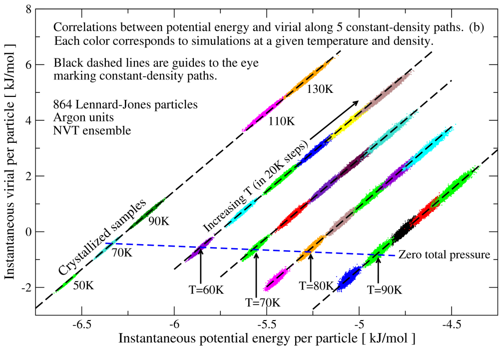


Figure 2: Correlations between instantaneous values of potential energy, $U(t)$, and the configurational part of the pressure, the virial $W(t)$ $[p(t) = Nk_BT(t)/V + W(t)/V]$. Each color represents simulations at one particular temperature and density where each data point marks instantaneous values of virial and potential energy from a 10ns simulation run taken after 10ns of equilibration. The black dashed lines mark constant density paths with the highest density to the upper left. State points on the blue dashed line have zero average total pressure. The plot includes three crystallized samples (lower left corner). Reproduced from [1].

## References

[1] Ulf R. Pedersen, Nicholas Bailey, Thomas B. Schrøder, Jeppe C. Dyre, *Strong Pressure-Energy Correlations in van der Waals Liquids*, Phys. Rev. Lett. 100, 015701 (2008).

[2] Ulf R. Pedersen, Tage Christensen, Thomas B. Schrøder, Jeppe C. Dyre, *Feasibility of a single-parameter description of equilibrium viscous liquid dynamics*, Phys. Rev. E 77, 011201 (2008).

[3] Thomas B. Schrøder, Ulf R. Pedersen, Jeppe C. Dyre, *Density scaling as a property of strongly correlating viscous liquids*, arXiv:0803.2199 [cond-mat.soft] (2008).

[4] N. P. Bailey et al., *Glass-forming liquids: One or more "order" parameters?*, J. Phys.: Condens. Matter 20, 244113 (2008).

# Single Parameter Description of the Overall Dynamics of Glass-Forming Liquids under Temperature and Density Variations

Simone Capaccioli

*Dipartimento di Fisica, Università di Pisa,*
*Largo Pontecorvo 3, I-56127, Pisa, Italy*

The dramatic dynamic slowing down driving to the glass formation is usually governed by the simultaneous effects of decreasing volume and thermal energy, whose contributions can be singled out only by measurements carried out under different thermodynamic paths (isothermal compression and isobaric cooling). Recent studies showed that structural dynamics is a functional of a unique key parameter $\mathbf{\Gamma} = \rho^x/T$, where both the density and temperature contributions are included [1, 2, 3]. Such relation has been proven valid for experiments on more than 70 glass-formers, including molecular and polymeric systems, ionic liquids and liquid crystals. The parameter x, characteristic of the system, was linked to the steepness of the intermolecular repulsive potential [4]. Accordingly, recent numerical simulation studies [5] showed that energy and volume fluctuations correlate strongly in the constant-pressure, constant-temperature ensemble for a number of model systems. Usually different glass-forming systems show qualitatively different T dependencies of $\tau_\alpha$, on approaching the glass transition, and they are classified by the concept of steepness index or "fragility", defined as m= $\partial \log(\tau_\alpha)/\partial(T_g/T)|_{T=T_g}$. Since, for the above mentioned relation, $\tau_\alpha$ is an unique function of $\rho^x/T$, the isochoric fragility, m$_V$, is also a material constant, independent on T, P. It can be demonstated that m$_V$ is inversely correlated with x [6]. From these experimental facts, by normalizing material-specific quantities related to x and suitably choosing $T_g$, a universal function for the dynamics can be obtained for several glass-formers over the supercooled regime. Moreover, a recent study showed that the dispersion (i.e. the line shape) of the structural $\alpha$-relaxation, under different conditions of temperature T and pressure P, depends only on the characteristic relaxation time and not on T and P separately [7]. In fact, not only the timescale, but also the shape of the structural relaxation is a function of $\mathbf{\Gamma}$ only. Recently we found that also the intermolecular, Johari-Goldstein (JG), $\beta$-relaxation (related to local rotation of the whole molecule), when well resolved and identified is affected by pressure both in the supercooled liquid and glassy state and scales with the parameter $\mathbf{\Gamma}$ [8]. Our evidence from broadband dielectric spectroscopy show that the dynamics of the primary $\alpha$- and the secondary Johari-Goldstein (JG) $\beta$- processes are strongly correlated in different glass-forming systems over a wide temperature T and pressure P range, in contrast with the widespread opinion of statistical independence of these processes. The $\alpha$-$\beta$ mutual dependence is quantitatively confirmed by: a) the overall superposition of spectra measured at different T, P combinations but with an invariant $\alpha$- relaxation time; b) the contemporary scaling of the isothermal-pressure and isobaric-temperature dependences of the $\alpha$-and $\beta$-relaxation times as plotted versus the reduced variable $\mathbf{\Gamma}$. This novel and model-independent evidence indicates the relevance of the JG relaxation phenomenon in glass transition, often overlooked by most current theories. Moreover, these results indicate that the single parameter $\mathbf{\Gamma}$, able to describe the structural relaxation scaling, it is also driving the local intermolecular JG relaxation.

# References

[1] R. Casalini et al., Phys.Rev.E**69**, 062501 (2004).

[2] R. Casalini et al., Phys.Rev.B, **71**, 014210 (2005).

[3] C. Alba-Simionesco et al., Europhys.Lett., **68**, 58 (2004).

[4] D. Coslovich and C. M. Roland, JPCB, **112**, 1329 (2008).

[5] U. R. Pedersen, N. P. Bailey, T. B. Schrøder, and J. C. Dyre, Phys. Rev. Lett. **100**, 015701 (2008).

[6] R. Casalini, S. Capaccioli and C. M. Roland, J. Phys. Chem. B, **110**, 11491 (2006).

[7] K. L. Ngai, R. Casalini, S. Capaccioli, M. Paluch and C. M.Roland, J. Phys.Chem.B, **109**, 17356 (2005).

[8] K. Kessairi, S. Capaccioli, D. Prevosto, M. Lucchesi, S. Sharifi, P. A. Rolla, J. Phys. Chem. B **112**, 4470 (2008).

# Dynamic Light Scattering in Glassforming Ultraphosphate Liquids

R. L. Fabian, J. R. Changstrom and D. L. Sidebottom

*Creighton University, Omaha, NE 68178 USA*

Phosphate glasses feature prominently in many technological applications [1] and yet the viscoelastic response of the glass forming liquid has not received much attention. Here we report results of an ongoing dynamic light scattering study [2, 3] of the viscoelastic relaxation in sodium ultraphosphate liquids, $(Na_2O)_x(P_2O_5)_{1-x}$. The compositional range extends from pure $P_2O_5$, whose bridging oxygens form a three dimensional network of covalent bonds, to the metaphosphate ($x = 0.5$) which forms 2-dimensional chains of covalent bonds. Properties of the time decay of the dynamic structure factor, including the average structural relaxation time and the stretching exponent, were obtained for a series of compositions at temperatures near the glass transition using photon correlation spectroscopy. We find that both the fragility index and the stretching exponent display systematic changes with respect to the average number of bridging oxygens per phosphate unit. Furthermore, the variation in the fragility is virtually identical with that seen in chalcogenide glass formers [4], suggesting a common origin in the level of connectivity present in the network of covalent bonds.

## References

[1] R. K. Brow, J. Non-Cryst. Sol., **263** and **264**, 1 (2000).

[2] D. L. Sidebottom and J. R. Changstrom, Phys. Rev. B,**77**,020201 (2008).

[3] J. R. Changstrom and D. L. Sidebottom, J. Phys: Cond. Matter, in press (2008).

[4] R. Boehmer and C. A. Angell, Phys. Rev. B **45**, 10091 (1992).

# Link between Liquid Fragility and Glass Iso-Structure Viscosity

Yuanzheng Yue

*Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark*

The fragility index of a silicate glass melt is obtained by fitting its equilibrium viscosity data to the Avramov- Milchev (AM) equation. The iso-structure viscosities as a function of temperature are determined by converting the AM equation into an Adam-Gibbs fashion, in which the configurational entropy is frozen-in by cooling. Then, two kinds of activation energies can be derived from the converted equation: one is the activation energy for equilibrium viscous behavior and another is that for iso-structural behavior. Interestingly, it is found that the ratio of the former energy to the latter energy is exactly the fragility index of the AM equation. Thus, a straightforward link between fragility and iso-structure viscosity has been established. This link means that the ratio between the two types of activation energies remains constant with changing temperature. A further implication of this link is that the configurational contribution to the activation energy for the equilibrium flow behavior is proportional to the non-configurational (e.g. vibrational) contribution. Understanding of this link will shed light on the physical origin of liquid fragility. Here it should be noted that the link applies only to a melt that does not show the strong-to-fragile transition. Furthermore, it is found that the activation energy ratio derived from other viscosity models (except for the AM model) varies with temperature. The origin for this is discussed in this work. In addition, the iso-structure viscosities derived from the AM model below the glass transition temperature are compared with those measured and reported in the literature, and the former viscosities well agree with the measured ones.

## References

[1] C. A. Angell, Science **267** (1995) 1924.

[2] I. Avramov and A. Milchev, J. Non-Cryst. Solids **104** (1988) 253.

[3] G. Adam and J. H. Gibbs, J. Chem. Phys. **43** (1965) 139.

[4] Y. Z. Yue, (2008) manuscript to be submitted.

# Fragility of High BaO-Containing Glasses

Ralf Keding

*Section of Chemistry*
*Department of Biotechnology, Chemistry and Environmental Engineering,*
*Aalborg University*

The investigation of viscosity in network modifier rich glasses is usually limited by the strong crystallisation tendency. Bulk glass samples can be obtained by a conventional casting process from melts with the composition 45BaO $40SiO_2$ $5B_2O4_3$ $5ZrO_2$ $2.5La_2O_3$. For glasses with such a high content of network modifiers this is a quite unique property. A change in the BaO / $SiO_2$ ratio will allow to adjust the network modifier content in a comparably broad range without changing other parameters in the system fundamentally. All compositions can be obtained as a glass by conventional casting processes. The viscosity of the melts is investigated by rotation viscometer at elevated temperatures and by beam bending viscometer at low temperatures. DSC is used to determine $T_g$. The fragility parameter is calculated from these viscosities. The average degree of polymerisation of the silicate network formers is varied between 1.6 and 3.6 and results in a fragility parameter between 2.7 and 3.5. The link between average degree of polymerisation and fragility is discussed by structural models. The unexpected low value of the fragility for the highly depolymerized melts is linked with the formation of an invert glass with a cation network.

## References

[1] C. A. Angell, *Formation of glasses from liquids and biopolymers*, Science **267** (5206), 1924-1923, (1995).

[2] I. Avramov, R. Keding and C. Rüssel, *Crystallisation kinetics and rigidity percolation in glass forming melts*, J. non-Cryst. Solids, **272**, 147-153, (2000).

[3] M. Solvang, Y. Yue, S. L. Jensen and D. B. Dingwell, *Rheological and thermodynamic behaviour of different calcium aluminosilicates melts*

*with the same non-bridging oxygen content*, J. non-Cryst. Solids **336**, 179-188, (2004).

[4] I. Avramov, R. Keding and C. Rüssel, *Effect of chemical composition on viscosity of oxide glasses*, J. non-Cryst. Solids, **324**, 29-35, (2003).

# Low Entropy Glasses from Zeolite Amorphisation

Neville Greaves

*Institute of Mathematics and Physics, Aberystwyth University,*
*Aberystwyth SY23 3BZ, UK*

By using in situ X-ray diffraction, inelastic X-ray scattering and magic angle spinning NMR we have identified low entropy glasses formed during the collapse of zeolite crystals [1]. By approaching the glass transition from below rather than from above, the crystallisation problems that face melt-quenching procedures in the search for "perfect glasses" can be minimised [2]. Also starting from the crystalline state rather than the melt, the Kauzmann Paradox should be avoided. The amorphisation process separates into a displacive crystalline-amorphous transition resulting in the low entropy phase followed by a disordering amorphous-amorphous transition leading to a higher entropy phase equivalent to a melt-quenched glass [3]. From the relaxation time which governs microporous collapse the kinetic fragility of the low entropy phase is found to be much lower than for a conventional melt and the glass transition temperature higher. Moreover the degrees of non-ergodicity, mechanical non-deformability and chemical order obtained spectroscopically for the low entropy glass are significantly greater than for melt-quenched glasses. In particular Poisson's ratio for the glass is close to zero and hence to the auxetic limit, whilst the fragility during amorphisation is Arrhenian and virtually twice the strength of liquid $SiO_2$.

## References

[1] N. Greaves, F. Meneau, F. Kargl, D. Ward, in preparation.

[2] Greaves N. and Sen S., *Inorganic glasses, glass-forming liquids and amorphising solids*, Advances in Physics, 2007, **56** 1-166.

[3] N. Greaves, F. Meneau, F. Kargl, D. Ward, P. Holliman, F. Albergamo, *Zeolite collapse and polyamorphism*, J. Phys.: Condens. Matter, 2007, **19**, 415102.

# ABSTRACTS FOR

# POSTER PRESENTATIONS

# Exponential Distributions of Flow Event Properties in Supercooled Liquids

Nicholas Bailey, Thomas Schrøder and Jeppe Dyre

*DNRF Centre "Glass and time", IMFUFA, Department of Sciences,*
*Roskilde University, Denmark*

Understanding the equilibrium dynamics of supercooled liquids means understanding the temperature and time/frequency dependence of dynamical response functions. For long times all information is contained in the time correlation functions defined on the inherent structures—the local minima explored by the system. Equivalently we may consider "flow events"—transitions from one minimum to another. This information consists of (1) distributions of the changes of relevant quantities (e.g. energy $E$, pressure $p$, shear stress $\sigma_s$, etc.); (2) correlations between these for a given event (3) distributions of inter-event times; (4) correlations between successive changes of a given quantity. We have investigated (1) in 2D and 3D models. The distributions are very well described by an exponential. We find also that $S$, the sum of squared displacements in an event, is exponentially distributed. $S$ is shown to control the other quantities in the sense that for fixed $S$ the others have gaussian distributions with width proportional to $S$. Looking at the particle displacements, we observe an exponential tail for values greater than about 0.2 (inter-particle spacings), with characteristic length around 0.1, suggesting a Lindemann-type interpretation. Taking this to define "active particles" we find their number is also exponentially distributed. Finally we present a simple probabilistic model which naturally generates exponential distributions of all quantities.

# The Effect of Cooling Rates on the Apparent Fragility of Bulk Metallic Glasses

Zachary Evenson, Isabella Gallino and Ralf Busch

*Universität des Saarlandes, Lehrstuhl für Metallische Werkstoffe,*
*Campus C63 66123 Saarbrücken, Germany*

The effect of various enthalpic states on the glass transition of the $Zr_{57}Nb_5Al_{10}Cu_{15.4}Ni_{12.6}$ and $Zr_{58.5}Nb_{2.8}$ $Cu_{15.6}Ni_{12.8}Al_{10.3}$ bulk metallic glass forming alloys are studied. The amorphous samples are heated into the supercooled liquid region using Differential Scanning Calorimetry (DSC) and cooled back down into the glassy state using a series of different cooling rates $C_i$. The relative shifts in the glass transition region are assessed by determining the onset glass transition temperature $T_g$ upon re-heating with a series of heating rates $R_i$. Analysis of the fictive temperature $T_f$ is carried out using methods adopted by Moynihan [1] and Angell [2]. The data are modelled assuming a Vogel-Fulcher-Tammann (VFT) type behavior in the structural relaxation time $\tau$. Shifts in the glass transition region are observed as being influenced, in part, by the thermal histories of the samples. These changes also showed evidence of an apparent increase in the kinetic fragility parameter, $D^*$, for lower cooling rates. The VFT fits are compared with viscosity data obtained by three point beam bending and rotating cup viscometry, where a crossover in kinetic fragilities was observed from the low- to high-temperature regions. This strong-to-fragile transition is thought to be attributed to the decrease in entropy through the destruction of short-range order as the high-temperature region is reached.

## References

[1] C. T. Moynihan, A. J. Easteal, and M. A. DeBolt, *Dependence of the Fictive temperature of glass on cooling rate*, Journal of the American Ceramic Society **59**, 12-16, (1976).

[2] V. Velikov, S. Borick, and C. A. Angell, *Molecular glasses with high Fictive temperatures for energy landscape evaluations*, J. Phys. Chem. B **106**, 1069-1080, (2002).

# Temperature Dependence of the Electrical Conductivity of Imidazolium Ionic Liquids

Jan Leys[1], Michael Wübbenhorst[1],
Chirukandath P. Menon[1], Ravindran Rajesh[1],
Jan Thoen[1], Christ Glorieux[1], Peter Nockemann[2],
Ben Thijs[2], Koen Binnemans[2] and Stéphane Longuemart[3]

[1] *Laboratorium voor Akoestiek en Thermische Fysica,*
*Departement Natuurkunde en Sterrenkunde,*
*Katholieke Universiteit Leuven, Celestijnenlaan 200D,*
*PO 2416, B-3001 Leuven, Belgium*
[2] *Laboratorium voor Cordinatiechemie, Afdeling Moleculair*
*Design en Synthese, Departement Chemie,*
*Katholieke Universiteit Leuven, Celestijnenlaan 200F,*
*PO 2404, B-3001 Leuven, Belgium*
[3] *Laboratoire de Thermophysique de la Matire Condense*
*(UMR CNRS 8024), Universit du Littoral Cte d'Opale,*
*145 avenue M. Schumann, F-59140 Dunkerque, France*

We will present results on the temperature dependence of the electrical conductivity of 1-alkyl-3-methylimidazolium tetrafluoroborate ionic liquids and of 1-hexyl-3-methylimidazolium ionic liquids with different anions. The values were fitted with the VFT equation. The glass transition temperatures are increasing with increasing length of the alkyl chain. The fragility is weakly dependent on the alkyl chain length, but is highly sensitive to the structure of the anion. An attempt is done to explain the observations in the framework of interactions on the ionic level.

# Charge Transport and Glassy Dynamics in Imidazole-Based Liquids

M. C. Iacob[1], J. R. Sangoro[1], A. Serghei[1], S. Naumov[1], P. Galvosas[1], J. Kärger[1], C. Friedrich[2] and F. Kremer[1]

[1] *Institute of Experimental Physics I, University of Leipzig, Leipzig, Germany*
[2] *Freiburger Materialforschungszentrum (FMF) und Institute für Makromolekulare Chemie der Albert-Ludwigs Universitt Freiburg i. Br., Germany*

Broadband Dielectric Spectroscopy, Pulsed Field Gradient Nuclear Magnetic Resonance, differential scanning calorimetry and rheology are combined to investigate the correlation between translational and rotational diffusion in an homologous series of imidazole-based liquids. Physical quantities as dc conductivity, self-diffusion coefficient, viscosity, calorimetric glass transition temperature and alpha relaxation process are investigated in a broad frequency and temperature range upon systematic variation of the chemical structure. A strong correlation between the translational component of the molecular dynamics (as manifested in the dc conductivity and self-diffusivity) and the rotational one (as revealed by viscosity, calorimetric and dynamic glass transition) is found, demonstrating that the charge transport mechanism is assisted by the glassy dynamics.

## References

[1] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F.Bordusa, and F. Kremer, Phys. Rev. E **77**, 051202 (2008).

[2] J. R. Sangoro et al, J. Chem. Phys. **128**, 214509 (2008).

[3] W. Xu , C. A. Angell, Science **302**, 422 (2003).

[4] J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, C. Wespe, F. Bordusa, and F. Kremer, submitted to Phys. Rev. Lett.

# Broadband Shear Mechanical and Dielectric Investigation of Monohydroxy Alcohols Close to the Glass Transition Temperature

Bo Jakobsen, Claudio Maggi,
Tage Christensen and Jeppe Dyre

*DNRF Centre "Glass and time", IMFUFA, Department of Sciences,
Roskilde University, Denmark*

Liquids close to the glass transition temperature generally show two relaxation processes which can be observed by dielectric and shear mechanical relaxation spectroscopy (e.g. [1]): the main structural (alpha) relaxation, and the (Johari-Goldstein) beta relaxation.

In monohydroxy alcohols an additional low frequency relaxation process (alpha-prime) is known to be observed by dielectric spectroscopy. The dielectric relaxation strength of this alpha-prime process is around 100 times larger than that of the alpha relaxation and it is Debye.

In this work [2] we present broadband (1mHz-50kHz) shear mechanical measurements on monohydroxy systems, along with complementary dielectric data. The shear mechnical data are obtained using the piezoelectric shear modulus gauge (PSG) [3].

Data on the spectral shapes and relaxation times are compared between the two techniques. Shear mechanical spectroscopy allows for a clear identification of the structural relaxation process of the liquid, and its signature in the dielectric spectrum.

## References

[1] B. Jakobsen, K. Niss, and N. B. Olsen, J. Chem. Phys., **123**, 234511, (2005).

[2] B. Jakobsen, C. Maggi, T. Christensen, and J. C. Dyre, J. Chem. Phys., Accepted for publication, (2008). arXiv:0805.4519v2 [cond-mat.soft]

[3] T. Christensen and N. B. Olsen, Rev. Sci. Instrum., **66**, 5019, (1995).

# Universal Scaling of Charge Transport in Glass-Forming Ionic Liquids

F. Kremer, J. R. Sangoro, A. Serghei
and M. C. Iacob

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

Charge transport and glassy dynamics of a variety of glass-forming ionic liquids (ILs) are investigated in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy, Differential Scanning Calorimetry and Rheology. While the absolute values of dc conductivity and viscosity vary over more than 11 decades with temperature and upon systematic structural variation of the ILs, quantitative agreement is found between characteristic frequency indicating the onset of dispersion in conductivity and the structural $\alpha$-relaxation. This is traced back to dynamic glass transition assisted hopping as the underlying mechanism of charge transport.

## References

[1] J. R. Sangoro, A. Serghei, S. Naumov, P. Galvosas, J. Kärger, C. Wespe, F. Bordusa, and F. Kremer, Phys. Rev. E **77**, 051202 (2008).

[2] J. R. Sangoro et al, J. Chem. Phys. **128**, 214509 (2008).

[3] J. R. Sangoro, C. Iacob, A. Serghei, C. Friedrich, C. Wespe, F. Bordusa, and F. Kremer, submitted to Phys. Rev. Lett.

# Supercooled Liquids Dyamics Studied in Shear-Mechanical Spectroscopy

Claudio Maggi, Bo Jakobsen,
Tage Christensen, Niels Boye Olsen
and Jeppe Dyre

*DNRF Centre "Glass and time", IMFUFA, Department of Sciences,*
*Roskilde University, Denmark*

The study of the slow dynamics in supercooled liquids is one of the central topics in glass-physics. Experimentally the tool that is mainly used to analyze the relaxation processes associated with this dynamics is dielectric spectroscopy. However other response functions could be potentially very interesting to measure. It is not well understood, in fact, if the various observables display some universal features approaching the glass transition and how they are related to each other. Furthermore the mechanical properties of these ultra-viscous liquids are deeply interesting from a pratical and theoretical point of view.

These motivations lead us to exploit a recently-developed experimental technique to access the frequency-resolved shear modulus of several glass-forming liquids. We report dynamical shear modulus measurements for five glass-forming liquids (silicon oil, diethyl phthalate, dibutyl phthalate, 1,2-Propanediol, 1,3-Propanediol). The shear mechanical spectra are obtained by the piezoelectric shear modulus gauge (PSG) method [1]. This technique allows us to measure the shear moduls (100 kPa - 10 GPa) of the supercooled liquid close to the glass transition temperature within a wide frequency range: 1 mHz - 50 kHz.

We analyze the frequency-dependent response functions checking if time temperature superposition (TTS) is obeyed. We also study the shear loss peak position and its high-frequency part. It has been suggested indeed that, when TTS applies, the high frequency side of the imaginary part of the dielectric response decreases like power law of the frequency with an exponent equal to -1/2 [2]. This is also supported by a recent theoretical work [3]. This conjecture is analyzed on the basis of the shear mechanical data. A model for viscous liquids dynamics that relates the shear modulus and the alpha relaxation time has been proposed [4]. A test of this model is made possible by these mechanical measurements so its prediction is compared with the experimental data.

# References

[1] T. Christensen and N. B. Olsen, Rev. Sci. Instrum. **66**, 5019 (1995).

[2] N. B. Olsen, T. Christensen, and J. C. Dyre, Phys. Rev. Lett. **86**, 1271 (2001)

[3] J. C. Dyre, Europhys. Lett. **71**, 646 (2005).

[4] J. C. Dyre, N. B. Olsen, and T. Christensen, Phys. Rev. B **53**, 2171 (1996)

# An Apparent Exception to the General Correlation Between the Fragility and the Shape of the $\alpha$-Relaxation: Problem and Solution

A. Mandanici[1], W. Huang[2], M. Cutroni[1]
and R. Richert[2]

[1] *Dipartimento di Fisica, Universit di Messina,*
*Salita Sperone, 31, 98100 Messina, Italy*
[2] *Department of Chemistry and Biochemistry, Arizona State University,*
*Tempe, AZ 85287-1604, USA*
*E-mail: `andrea.mandanici@unime.it`

Very broad relaxation peaks, corresponding to low values of the stretching exponent $\beta_{KWW}$ for the Kohlrausch-Williams-Watts (KWW) response function in the time domain, are mainly observed in liquids characterized by a high kinetic fragility [1] as in the case of neat decalin [2]. An apparent exception to this general rule is found for ethylcyclohexane: the estimated fragility of this glass-former [3,4] corresponds to the intermediate character of molecular liquids, as found for some alcohols and polyols [5] but the main relaxation observed in supercooled ethylcyclohexane in the 50 Hz - 20 kHz frequency range using high resolution dielectric spectroscopy displays a broad relaxation shape. Exploiting the scaling properties of the experimental spectra we show that the apparently anomalous behaviour is due to the superposition of a secondary process to the dielectric $\alpha$-process [6]. The results obtained with this approach reconcile the behavior of ethylcyclohexane with the common dynamical properties of glass-forming liquids and are in agreement with a possible intramolecular nature of the observed $\beta$-relaxation.

## References

[1] R. Böhmer, K. L. Ngai, C. A. Angell, and D. J. Plazek, J. Chem. Phys. **99**, 4201 (1993).

[2] K. Duvvuri and R. Richert, J. Chem. Phys. **117** 4414 (2002).

[3] A. Mandanici, W. Huang, M. Cutroni and R. Richert, J. Chem. Phys. **128**, 124505 (2008).

[4] A. Mandanici, M. Cutroni, A. Triolo, V. Rodriguez-Mora and M. A. Ramos, J. Chem. Phys. **125**, 054514 (2006).

[5] D. Huang and G. B. McKenna, J. Chem. Phys. **114**, 5621 (2001).

[6] A. Mandanici, W. Huang, M. Cutroni and R. Richert, Phil. Mag., submitted.

# Fragility in the Enthalpy Landscape Approach

John C. Mauro[1] and Roger J. Loucks[2]

[1] *Science and Technology Division, Corning Incorporated,*
*Corning, NY 14831, USA*
[2] *Department of Physics and Astronomy, Alfred University,*
*Alfred, NY 14802, USA*

The macroscopic properties of a glass are continually relaxing toward their equilibrium supercooled liquid values. Experimentally, the shape of the relaxation function is known to depend on the fragility of the supercooled liquid. In this presentation, we investigate the impact of fragility on relaxation behavior in the enthalpy landscape approach. We derive an expression for fragility in the statistical mechanical framework of continuously broken ergodicity. Our approach is applied to selenium, a simple but realistic glass-former for which we have derived an enthalpy landscape from ab initio physics, without any experimental fitting parameters.

We show that the fragility of a supercooled liquid is a direct result of the interplay of enthalpic and entropic effects in the enthalpy landscape. Through proper adjustment of the landscape parameters, the fragility of a system can be varied while maintaining the same equilibrium properties and also holding the glass transition temperature constant.

Using selenium as the base glass composition, we adjust the landscape parameters to model a set of systems with identical glass transition temperatures but different values of fragility. The computed volume-temperature diagrams show that the sharpness of the glass transition increases with higher fragility, indicating a more sudden breakdown of ergodicity. We subject each of the simulated glasses to a variety of heat treatment cycles and show that the magnitude of enthalpy relaxation is much lower in the higher fragility systems.

Finally, we show that while there is an inherent lower limit to fragility governed by the entropy of the landscape, there is no theoretical upper limit to fragility. In the limit of infinite fragility the glass transition becomes an ideal second-order phase transition where no relaxation is possible in the glassy state.

# References

[1] R. Böhmer and C. A. Angell, *Correlations of the nonexponentiality and state dependence of mechanical relaxations with bond connectivity in Ge-As-Se supercooled liquids*, Phys. Rev. B **45**, 10091 (1992).

[2] K. Niss, C. Dalle-Ferrier, G. Tarjus, and C. Alba-Simionesco, *On the correlation between fragility and stretching in glass-forming liquids*, J. Phys.: Condens. Matter **19**, 076102 (2007).

[3] L. Hornbøll and Y. Yue, *Enthalpy relaxation in hyperquenched glasses of different fragility*, J. Non-Cryst. Solids **354**, 350 (2008).

[4] J. C. Mauro, P. K. Gupta, and R. J. Loucks, *Continuously broken ergodicity*, J. Chem. Phys. **126**, 184511 (2007).

[5] J. C. Mauro and R. J. Loucks, *Selenium glass transition: A model based on the enthalpy landscape approach and nonequilibrium statistical mechanics*, Phys. Rev. B **76**, 174202 (2007).

# Viscous Behavior, Fragility and Glass-Forming Ability of Calcium Aluminosilicate Melts

Mette Moesgaard and Yuanzheng Yue

*Section for Chemistry, Aalborg University, Sohngaardsholmsvej 57,*
*DK-9000 Aalborg*

The viscous behavior of two series of calcium aluminosilicate (CAS) melts is studied by measuring the viscosity-temperature relationship. One series is positioned on the joining line connecting the two eutectic compositions of tridymite-anorthite-wollastonite and anorthite-wollastonite-gehlenite. Another is positioned parallel to the joining line at larger alumina concentrations. The viscosity-temperature relation in the low (approx. $10^0$-$10^3$ Pa $\cdot$ s) and high (approx. $10^8$-$10^{13}$ Pa $\cdot$ s) viscosity range is determined by means of concentric cylinder viscometry and micro penetration viscometry, respectively. The fragility parameter is obtained by fitting the viscosity data to the Avramov equation. The glass forming ability (GFA) is defined here as the resistance of a melt to crystallization during cooling. This resistance can be determined from concentric cylinder viscometry measurements. In addition the GFA is in this work quantified as the resistance of a glass towards crystallization during reheating. This resistance can be determined using the Hrubÿ parameter obtained from calorimetric measurements. The results show a correspondence between the two above-mentioned approaches of defining the GFA. In this work, it is found that the GFA increases with a decrease of fragility for the CAS systems. The origin of this correlation is discussed in terms of structural changes of the glasses.

## References

[1] C. A. Angell, Science **267** (1995) 1924.

[2] I. Avramov, J. Non-cryst. Solids **351** (2005) 3163.

[3] A. Hrubÿ, Czech. J. Phys. **B220** (1972) 1187.

[4] M. Moesgaard, Y. Z. Yue, (2008) manuscript to be submitted.

# A Circuit Model for the Merging of Dielectric Alpha- and Beta-Relaxation

Nesli Saglanmak, Kristine Niss,
Jeppe Dyre and Niels Boye Olsen

*DNRF Centre "Glass and time", IMFUFA, Department of Sciences,
Roskilde University, Denmark*

The dielectric relaxation spectra of liquids close to the glass transition is dominated by the structural alpha relaxation. However, many liquids also exhibit a clearly resoluted secondary relaxation, referred to as the slow beta relaxation or the Johari-Goldstein process. The role of the beta relaxation including its relation to the alpha relaxation is not well understood and a subject to active studies. The first question in this context is whether it is possible to make a meaningful separation of the two processes in order to be able to study the "pure" individual processes. There are two traditional routes to such a separation, either to consider the total spectrum as a sum of two processes or to consider it as a convolution of the two processes. In this work we present an electrical network model which results in a new view on the merging of the alpha and the beta processes. We compare the model to new dielectric data on two glass-formers and get good fits with reasonable parameters. We moreover discuss the charecteristic features of the alpha-beta seen in the new model and in data.

# Are All Liquids Strongly Correlated at High Pressure?

Jon Papini

*DNRF Centre “Glass and time”, IMFUFA, Department of Sciences, Roskilde University, Denmark*

*E-mail: `papini@ruc.dk`

In a recent numerical simulation study of a number of model systems, thermal equilibrium fluctuations of the non-kinetic parts of energy and pressure were monitored in the NVT-ensemble [1]. The results showed that the correlation between the fluctuating quantities was strong (correlation coefficient greater than 0.9) in a Lennard-Jones liquid as well as in other simple liquids, whereas in hydrogen bonding liquids, such as SPC/E water [3] and methanol [4], the correlations were weak, owing to competing Lennard-Jones and Coulomb interactions. Furthermore the studies showed that the correlation increased with increasing temperature. The results also suggested that as the density is increased along an isotherm, the not so strongly correlating liquids also become more correlated. This reflects the Lennard-Jones potential increasingly dominating the fluctuations and the Coulomb potential becoming less important, as argued in [4].

In the present work, numerical classical molecular dynamics simulations were made. In addition to the systems mentioned above (Single Component Lennard-Jones liquid, SPC/E water, methanol), more model liquids were included in the study: TIP5P, Silicate, and 1-Butyl-3methylimidazolium Nitrate [5-7]; the aim was to cover liquids belonging to different chemical classes: Van der Waals, hydrogen and covalent bonded liquids, as well as Ionic liquids.

Here we study the aforementioned pressure dependence of the correlation between fluctuating thermal quantities, with pressures ranging from 0 Gpa to 12 Gpa along isotherms.

The simulations showed that the correlations increased with increasing pressure for all studied systems.

# References

[1] U. R. Pedersen, N. P. Bailey, T. B. Schrøder, and J. C. Dyre, Phys. Rev. Lett. **100**, 015701 (2008).

[2] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987)

[3] W. F. Van Gunsteren, S. R. Billeter, A. A Eising, P. H. Hünenberger, P. Krüger, A. E. Mark, W. R. P. Scott, and I. G. Tironi, *Biomolecular Simulation: The GROMOS96 manual and user guide*, (Hochschulverlag AG an der ETH Zürich), Zürich, Switzerland, 1996.

[4] N. P. Bailey, U. R. Pedersen, N. Gnan, T. B. Schrder, and J. C. Dyre (2008), to appear in J. Chem. Phys.

[5] M. W. Mahoney and W. L. Jorgensen, J. Chem. Phys. **112**, 8910 (2000).

[6] A. Carré, J. Horbach, S. Ispas, and W. Kob, EPL, **82**, 17001 (2008).

[7] N. M. Micaelo, A. M. Babtista, and C. M. Soares, J. Phys. Chem. B, **110**, 14444-14451 (2006).

# Coupling Effects in Macroscopic Glass-Forming Systems

Christian Rehwald

*Universität Münster*

As described in [1], transitions between inherent structures in the potential energy landscape (PEL) dominate the dynamics of a supercooled liquid, even above the glass transition. This connection allows one to derive macroscopic observables like fragility, diffusion constant or the Stokes-Einstein relation from PEL properties. Our approach to describe macroscopic glass-forming systems places emphasis on the location and definition of subsystems and corresponding interaction. We try to achieve our aims by applying three methods:

1. During the last decade many simulations were performed to investigate the PEL of different small glass-forming systems with periodic boundary conditions [2] (especially Lennard-Jones and BKS-$SiO_2$ liquids). Common features were identified, giving rise to the notion of ideal Gaussian glass formers [3]. In agreement with the experiment this model system displays deviations from the Stokes-Einstein relation which are, however, too large. We introduce a phenomenological model of interacting elementary subsystems of ideal Gaussian glass formers to reproduce macroscopic glass-formers. The interaction reduces the long tails of the waiting time distribution and renders the relaxation function $S_0(t)$ less non-exponential. In particular, the violation of the Stokes-Einstein relation is now close to experimental observations. Furthermore we check the model with respect to finite size effects and discuss the relation to facilitated spin models [4].

2. To verify the assumption of hopping dynamics of subsystems, we investigate a binary mixture Lennard-Jones liquid by molecular dynamics simulation with respect to finite size effects. The goal is a detailed understanding of the completely different $N$ dependencies of the diffusion constant $D(N)$ and the $q$-dependent structural relaxation time $\tau(N, q)$. While $D(N)$ shows no relevant finite size effects for $N = 60$, $\tau(N, q)$ shows a strong, non-intuitive and non-trivial behavior [5]. The analysis is based on particle coordinates, inherent structures and metabasins including their comparison.

3. Another promising approach for studying finite size effects is the distribution of waiting, persistence and exchange times generated by

particle displacements [6]. In contrast to PEL properties and the corresponding CTRW in terms of metabasin transitions, the particle displacement is a local quantity and therefore more sensitive. These functions have a bigger potential to show non-trivial finite-size effects on the large $\tau$ regime than the global metabasin waiting time distribution $\varphi(\tau)$.

## References

[1] F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982).

[2] B. Doliwa, Shaker Verlag (2002).

[3] A. Saksaengwijit, A. Heuer, Phys. Rev. E in press, arXiv:0802.3515v1.

[4] Y. Jung, J. Garrahan, D. Chandler, Phys. Rev. E **69** (2004).

[5] D. A. Stariolo and G. Fabricius, J. Chem. Phys. **125** (2006).

[6] Hedges *et al.*, J. Chem. Phys. **127**, 211101 (2007).

# Why Chain and Segmental Relaxation in Polymers Show Different Temperature Dependence (Fragility)?

Alexei Sokolov
*Department of Polymer Science, The University of Akron, Akron, OH, USA*

The presence of chain relaxation differentiates the dynamics of polymers from dynamics of other glass forming systems. Temperature variations of chain and segmental modes in polymers are traditionally described through corresponding friction coefficients. It is usually assumed that the same friction mechanism controls dynamics of both processes. As a result, their temperature dependence is expected to be the same. It is known, however, that segmental relaxation in many polymers varies faster than the chain one when temperature approaches the glass transition, $T_g$. We present an analysis of temperature variations of segmental and chain modes for different polymers. The analysis shows very clear difference in the behavior of the two processes and the difference increases in polymers with higher chain rigidity or fragility. We demonstrate [1] that the chain relaxation shows rather universal temperature dependence for many polymers when it is presented vs $T_g/T$. Even polymers with strongly different temperature behavior of segmental dynamics (fragility) exhibit similar behavior for the chain relaxation. These results indicate strong decoupling in behavior of chain and segmental modes and emphasize our deficiency in understanding the microscopic mechanism of the chain friction coefficient. We speculate that chemical specificity of polymeric molecules that influence fragility of their segmental relaxation is averaged out on the length and time scale of the chain modes. As a result, these polymeric molecules behave as long and flexible chains with a single energetic parameter (probably related to their flexibility) that controls their temperature dependence and is scaled with $T_g$. The role of dynamic heterogeneity and molecular cooperativity in chain and segmental relaxation are discussed at the end.

## References

[1] Ding Y., Sokolov A. P., Macromolecules 2006, **39**, 3322.

# Modeling and Simulation of Supercooled Liquids

Søren Toxværd

*DNRF Centre "Glass and Time", IMFUFA, Department of Sciences,*
*Roskilde University,Postbox 260, DK-4000,Roskilde, Denmark*

As computers get faster, simulations of the highly viscous liquid phase preceding glass formation become increasingly realistic. In this context it is nice to have a standard model system, something like the Ising model for critical phenomena. For several years binary Lennard-Jones (LJ) mixtures have served this purpose - in particular the Wahnström and Kob-Andersen systems [1,2], because they are easy to simulate and were never found to crystallize. Recently, however, both the Wahnström and the Kob-Andersen (KA) systems were shown to crystallize in lengthy computer runs [3] This motivated the present investigation that has three purposes. First, we briefly detail the crystallization of the KA system. Secondly, we review the general theory of thermodynamic and kinetic stability of supercooled binary mixtures. Finally, we introduce a modification of the interactions in binary systems that ensures stability against nucleation; in fact, we have not been able to crystallize the new systems even in month long simulations. The stability is obtained by ensuring a large negative mixing enthalpy, which not only increases the melting point depression; but also increases the size of the critical nucleus in accordance with the revised theory. In the case of a modified KA mixture this is easily ensured by removing the AA and BB attractions by adopting purely repulsive (Weeks-Chandler-Andersen) LJ potentials between like particles; but maintaining the AB attraction. The modified binary mixture is stable against crystallization and faster to simulate, and it has been simulated for $10^{10}$ time steps ($\approx 100\mu s$) in the highly viscous regime.

## References

[1] G. Wahnström, Phys. Rev. A **44**, 3752 (1995).

[2] W. Kob and H. C. Andersen, Phys. Rev. E **51**, 4626 (1993); ibid. 52, 4134 (1995).

[3] U. R. Pedersen, N. P. Bailey, J. C. Dyre, and T. B. Schrøder, arXiv:0706.0813 (2007); S. Toxvaerd, T. B. Schrøder, and J. C. Dyre, arXiv:0712.0377 (2007).

[4] S. Toxværd, U. R. Pedersen, T. B. Schrøder, and J. C. Dyre, Submitted to J. Chem. Phys.

# PARTICIPANTS

## **List of Participants** (alphabetically after first name)

Albena Nielsen, Roskilde University
Aleksander Matic, Chalmers University
Alexei Sokolov, University of Akron
Alistar Ottochian, Pisa University
Andrea Mandanici, University of Messina
Andreas Heuer, Universität Münster
Austen Angell, Arizona State University
Bo Jakobsen, Roskilde University
Burkhard Geil, Technische Universität Dortmund
Catalin Gainaru, Universität Dortmund
Christ Glorieux, Katholieke Universiteit Leuven
Christian Rehwald, Universität Münster
Christoph Klieber, MIT
Claes Hedberg, Blekinge Institute of Technology
Claudio Maggi, Roskilde University
Cormac Byrne, Risø
Daniele Cangialosi, University of the Basque Country
David Sidebottom, Creighton University
Ditte Gundermann, Roskilde University
Dorthe Lybye, Rockwool International
Ernst Rössler, Universität Beyruth
Francois Sausset, LPTMC Universite Pierre et Marie Curie
Friedrich Kremer, Universität Leipzig
Gregor Diezemann, Universität Mainz
Iacob Ciprian, Universität Leipzig
Isabella Gallino, Universität des Saarlandes
Isak Avramov, Bulgarian Academy of Sciences
Jeppe Dyre, Roskilde University
Jeremy Johnson, MIT
John Mauro, Corning Incorporated
Jon Papini, Roskilde University
Josef Bartos, Polymer Insitute of SAS
Joshua Rume Sangoro, Universität Leipzig
Keith Nelson, MIT
Klaus Boch, DNRF
Kristine Niss, Roskilde University
Kumar Kunal, University of Akron
Ludovic Berthier, Université Montpellier

Melanie Köhler, Universität Augsburg
Mette Moesgaard, Aalborg University
Mette Solvang, Rockwool International
Morten Eldrup, Risø
Neville Greaves, Aberystwyth University
Nicholas Bailey, Roskilde University
Nicoletta Gnan, Roskilde University
Niels Boye Olsen, Roskilde University
Nikolaus Petzold, Universität Bayreuth
Per Sillren, Chalmers University
Ralf Busch, Universität des Saarlandes
Ralf Keding, Aalborg University
Robbe Salenbien, Katholieke Universiteit Leuven
Roland Böhmer, Technische Universität Dortmund
Simone Capaccioli, University of Pisa
Stefan Eibl, ILL Grenoble
Søren Toxværd, Roskilde University
Tage Christensen, Roskilde University
Thomas B. Schrder, Roskilde University
Tina Hecksher, Roskilde University
Tullio Scopigno, University of Rome
Ulf R. Pedersen, Roskilde University
Ulrich Buchenau, Jülich
Wei-Hua Wang, Chinese Academy of Sciences
Yuanzheng Yue, Aalborg University
Zachary Evenson, Universität des Saarlandes

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