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

Melanie Köhler, Yurii Goncharov, Thomas Bauer, Robert Wehn, Peter Lunkenheimer and Alois Loidl

Experimental Physics V
Center of Electronic Correlations and Magnetism
University of Augsburg
Outline

**Introduction**
- Disordered matter and hallmark features
- Characteristics of $\alpha$ and $\beta$ relaxation

**Results and Discussion**
- Broadband spectra of propylene glycols
- $\alpha$ and $\beta$ relaxation
- Mixed system of succino-glutaronitrile

**Summary and Conclusion**
Disordered matter

Figure from R. Brand et al. J. Chem. Phys. 116, 10386 (2002)
Orientationally Disordered Systems

Mixed systems: complex situation!

Pure molecular crystal

dominated by

Interaction (IDC)

Anisotropy (steric hindrance) (ADC)

comparable

SPC
Supercooled plastic crystal

Mixed systems: complex situation!

Hallmark features of glassy matter

non-equilibrium

non-Arrhenius behaviour

non-exponential relaxation

\begin{align*}
\varepsilon'' &\sim \nu^{0.5} \\
&\sim \nu^1 \\
&\sim \nu^{-0.5}
\end{align*}

Debye
KWW
CD
CC

\[ \varepsilon'' \sim 2\pi\nu\tau \]

xylitol

\[ \tau = 100 \text{ s} \]

Tg

\[ T_g / T \]

Arrhenius

Vogel - Fulcher

Strong

Fragile

Broadband dielectric response of glassforming liquids

\[ \begin{align*}
\text{Type A} & \quad \alpha \text{-relaxation} \rightarrow \text{viscosity} \\
\text{excess wing} & \quad \text{"Johari-Goldstein process"} \\
\text{fast process: cage effect} & \quad \text{explained by mode-coupling theory (Götze et al.)} \\
\text{boson peak} & \quad \text{vibrational excitations (?)} \\
\text{intramolecular modes} & 
\end{align*} \]

\[ \begin{align*}
\text{Type B} & \quad \alpha \text{-relaxation} \\
\text{excess wing} & \quad \text{fast process: cage effect} \\
\text{boson peak} & \quad \text{vibrational excitations (?)} \\
\text{intramolecular modes} & 
\end{align*} \]

Explanations for the $\beta$ relaxation:

- islands of mobility
  [G. P. Johari et al.]
- small angle reorientations
  [e.g. F. H. Stillinger]
- coupling model
  [K. L. Ngai]
- minimal model
  [J. C. Dyre et al.]
- mode coupling theory
  [W. Götze and M. Sperl]

and many more…….
Explanations for the $\beta$ relaxation:

- islands of mobility
  [G. P. Johari et al.]
- small angle reorientations
  [e.g. F. H. Stillinger]
- coupling model
  [K. L. Ngai]
- minimal model
  [J. C. Dyre et al.]
- mode coupling theory
  [W. Götze and M. Sperl]

and many more…….
Angell plot of the $\alpha$ relaxation times

$\log_{10} [\tau_\alpha (s)]$

propylene carbonate
ethanol (supercooled liquid)
ethanol (plastic crystal)
pentachloronitrobenzene
cyclohexanol
cyclooctanol
1-cyanoadamantane
adamantanone
meta-carborane
ortho-carborane

$m=16$
$m = 200$

Fragility index $m$:

$$m = \frac{d \log \langle \tau \rangle}{d (T_g / T)} \bigg|_{T=T_g}$$


Angell plot of the $\alpha$ relaxation times

$\log_{10}[\tau_\alpha(s)]$

$m=16$

$m=200$

$T_g / T$


Investigation of Propylene glycol Dipropylene glycol Tripropylene glycol

Molecular size effects?
Angell plot of the $\alpha$ relaxation times

- Logarithmic plot of $\log_{10}[\tau_\alpha(s)]$ vs. $T_g / T$
- Various data points for different substances
- Dashed lines indicating $m=16$ and $m=200$
- Exceptional: High fragility in 60%SN - 40%GN mixture


Dielectric loss spectra of propylene glycol

C₃H₈O₂; T_g ≈ 168 K

M. Köhler, Y. Goncharov, R. Wehn, P. Lunkenheimer, and A. Loidl, unpublished;
Dielectric loss spectra of tripropylene glycol

\[ \varepsilon''(\nu) \]

\[ C_9H_{20}O_4; T_g \approx 193K \]

M. Köhler, Y. Goncharov, P. Lunkenheimer, and A. Loidl, unpublished.
Relaxation map for the $\alpha$-process

\[ \log_{10} [\tau (s)] \]

\[ \frac{1000}{[T(K)]} \]

- PG
- DPG
- TPG

Vogel-Fulcher law
Relaxation map for $\alpha$- and $\beta$-process

![Graph showing relaxation times vs. inverse temperature for different samples: PG, DPG, and TPG. The graph compares $\alpha$-relaxation and $\beta$-relaxation.](image-url)
Size dependence in the Angell Plot

\[ \log_{10} [\tau(s)] \]

- \( T_g/T \)

- PG
- DPG
- TPG
The system glutaro-succinonitrile

Plastic phase: BCC
Crystalline Phase: monoclinic

Dielectric loss spectra of 60%succinonitrile 40%glutaronitrile
Relaxation map for 60SN-40GN

- $T_g = 144K$
- $T_{\text{melting}} = 260K$
- $E_B = 0.82eV$

$log_{10}[\tau(s)]$

$log_{10}[\rho_{dc}(\Omega\text{cm})]$

$m = 61$

$\beta$

$\alpha$

$\rho_{dc}$
Potential energy in configuration space

**Strong:**
- Viscosity determined by thermal diffusion processes
- Nonhydrogen bonded network melts

**Fragile:**
- Additional configurational states
- Nondirectional interatomic/intermolecular bonds

Comparison to Freon

Trans and gauche: Different molecular potential energy landscape

Freon 112 fragile
Freon 112a strong

Is this also the cause of the high fragility in 60SN-40GN?

Summary

GLYCOLS:
• Broadband dielectric measurements on glycols (10^{-2} – 10^{12} Hz)
• α relaxation time does not develop systematically with molecular size
• β relaxation times above T_g nearly identical

THE SYSTEM SN-GN:
• Unusually high fragility
• Good ionic conductor
• Additional relaxation instead of ac conductivity possible
Thank you for your attention!

Special thanks to:
Alois Loidl
Peter Lunkenheimer
Yurii Goncharov
Thomas Bauer
Robert Wehn

...and the EP V group