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

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Robert Wehn, Peter Lunkenheimer and Alois Loidl

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Center of Electronic Correlations and Magnetism
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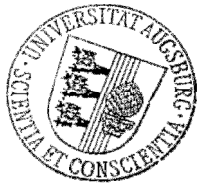


Outline

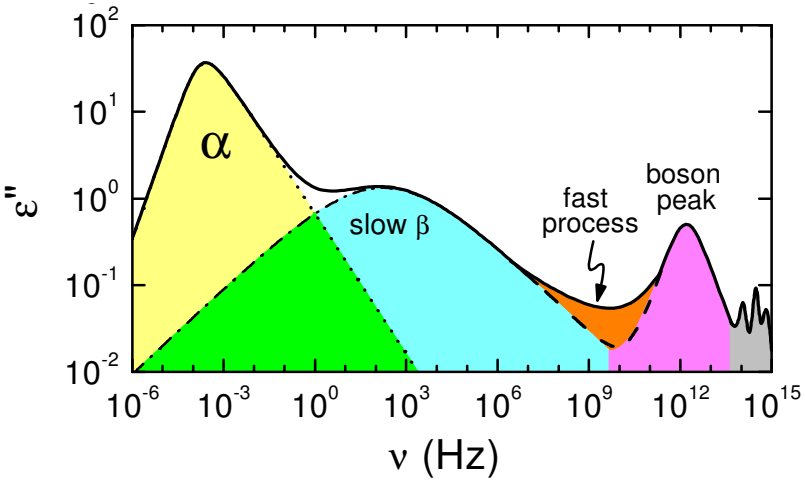
Introduction

- Disordered matter and hallmark features
- Characteristics of α and β relaxation

Results and Discussion

- Broadband spectra of propylene glycols
- α and β relaxation
- Mixed system of succino-glutaronitrile

Summary and Conclusion



Disordered matter

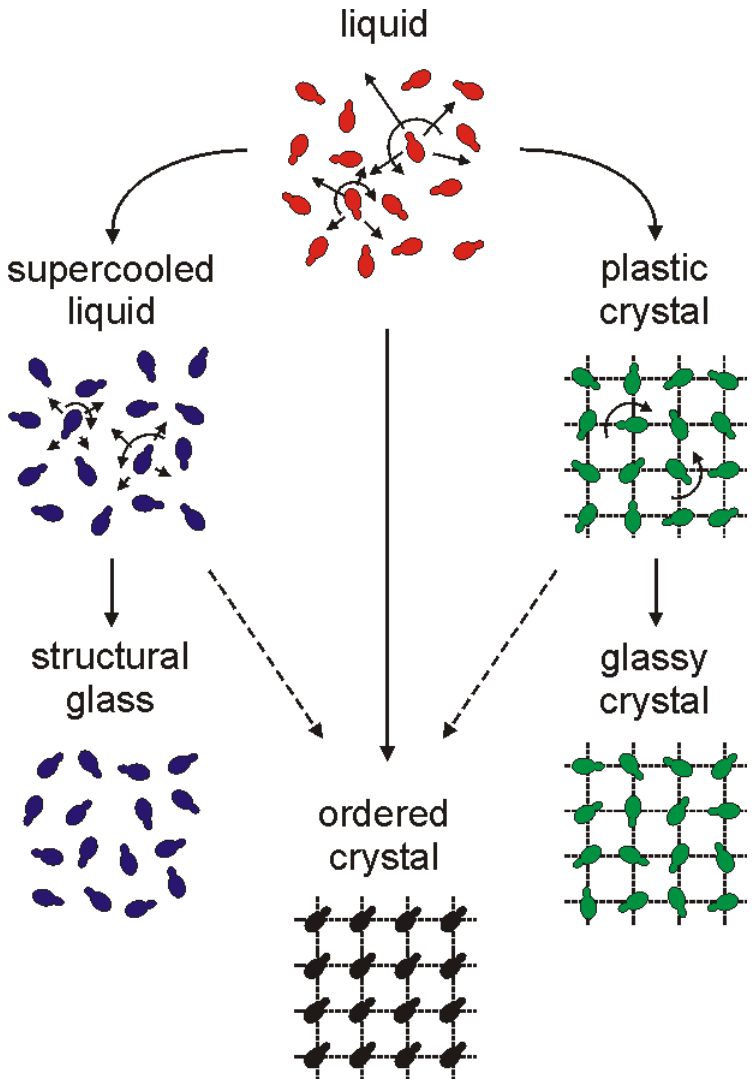
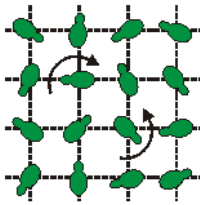


Figure from R. Brand et al. J. Chem. Phys. **116**, 10386 (2002)

Orientationally Disordered Systems



Pure molecular crystal

dominated by

Interaction
(IDC)

Anisotropy
(steric hindrance)
(ADC)

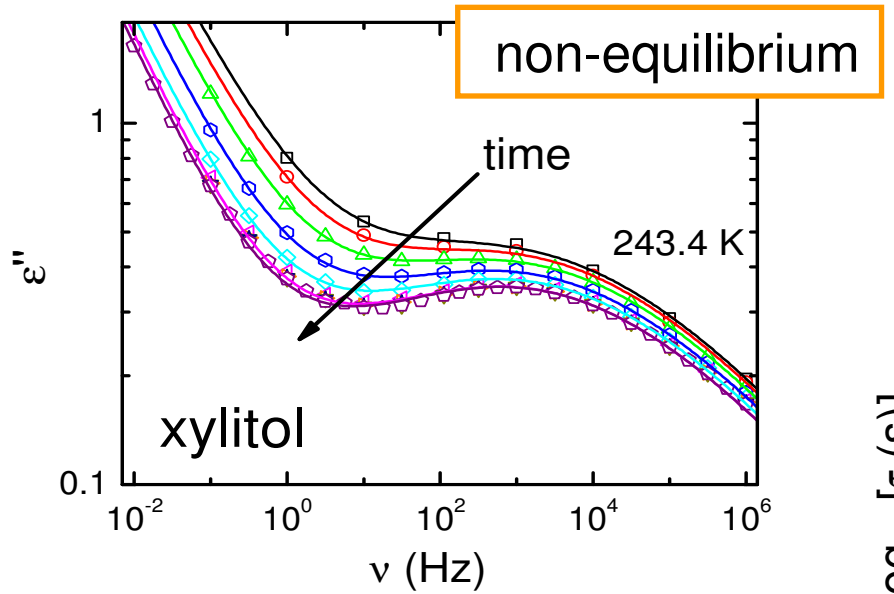
comparable

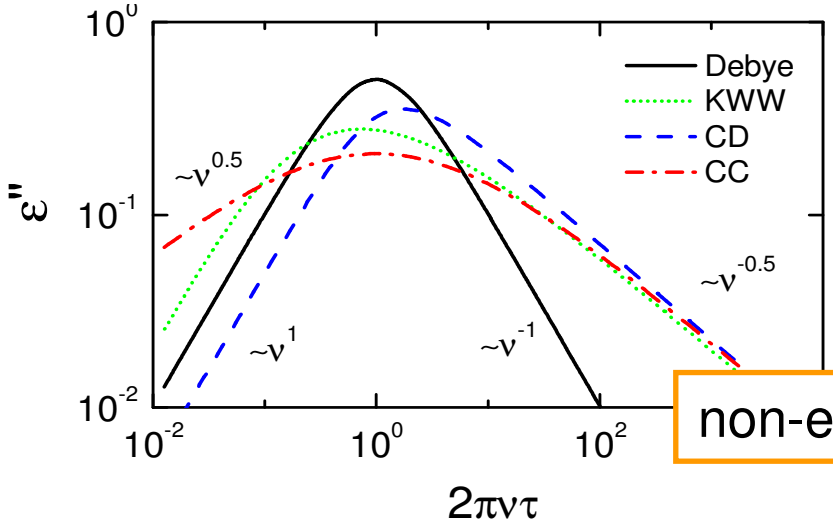
SPC
Supercooled plastic crystal

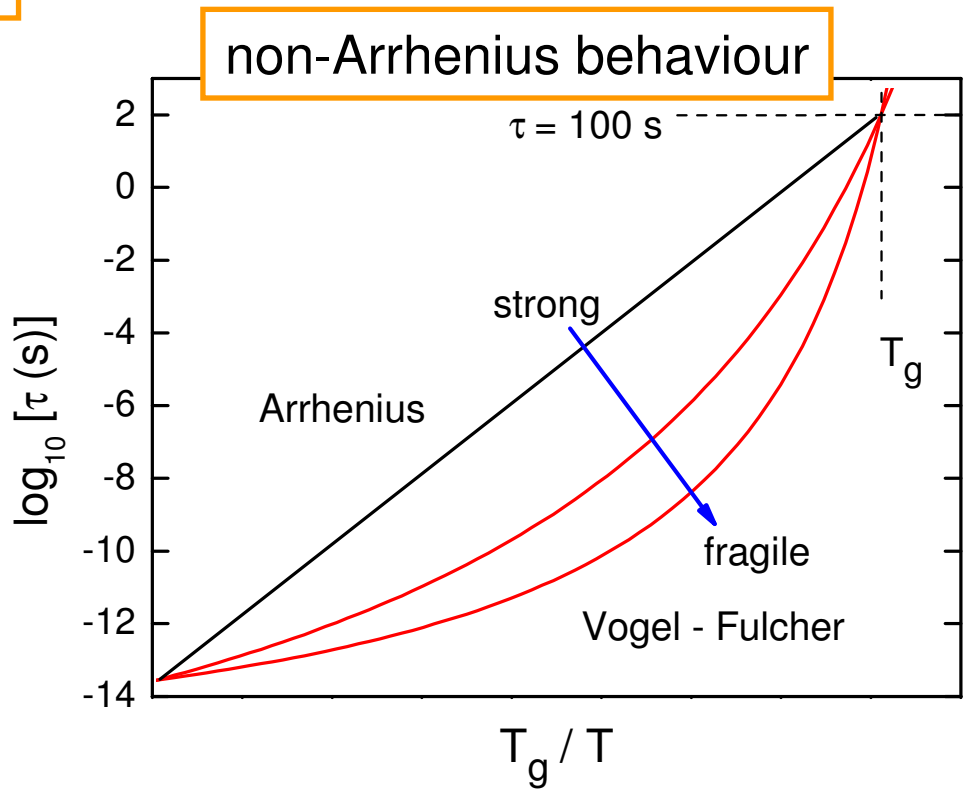
Mixed systems: complex situation!

A. Loidl and R. Böhmer, *Glass Transitions and Relaxation Phenomena in Orientational Glasses and Supercooled Liquids* (Springer, Berlin, 1994), p. 659ff

Hallmark features of glassy matter



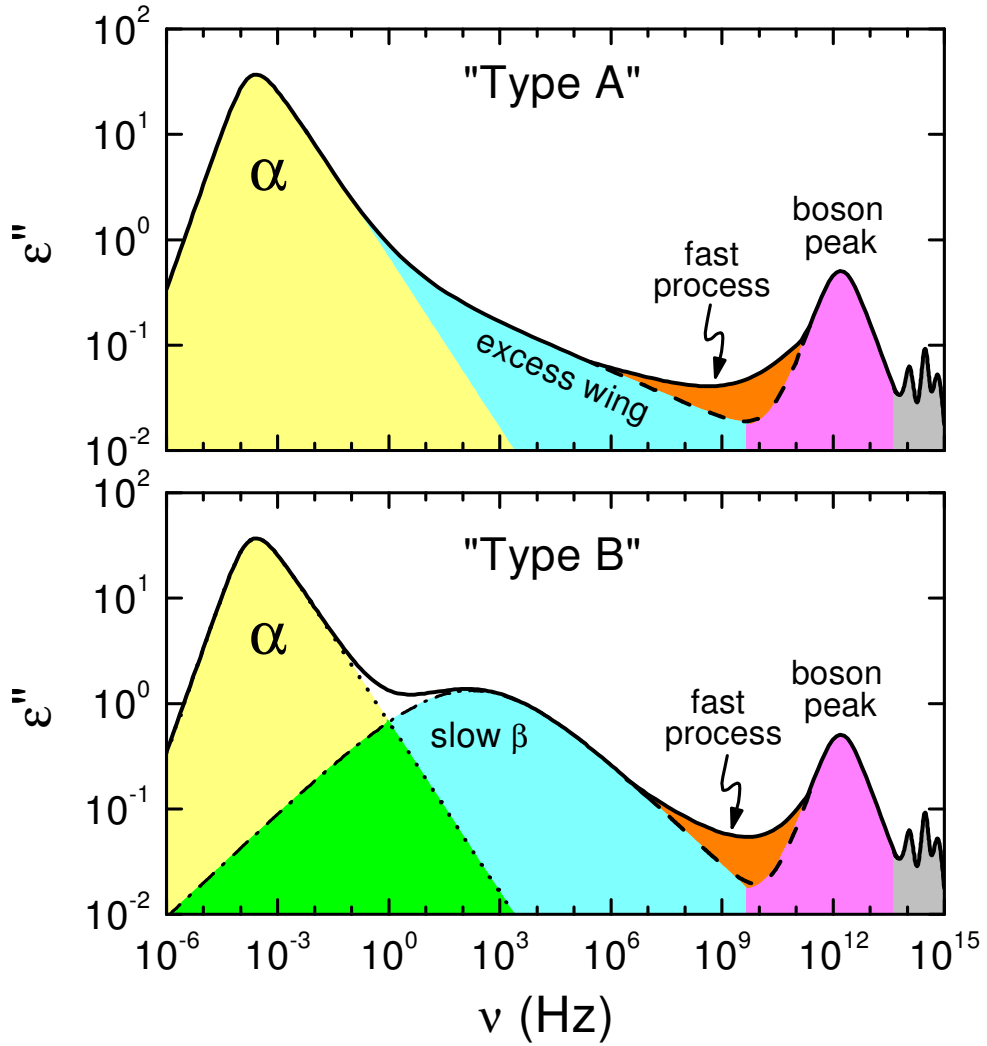




non-exponential relaxation

R. Wehn, P. Lunkenheimer and A. Loidl, *J. Non. Cryst. Solids*, **352**, 4941 (2006).
C.A. Angell and W. Sichina, *Ann. N. Y. Acad. Sci.,* **279**, 53 (1976).

Broadband dielectric response of glassforming liquids



α-relaxation – structural relaxation → viscosity

excess wing = slow β "Johari-Goldstein process"

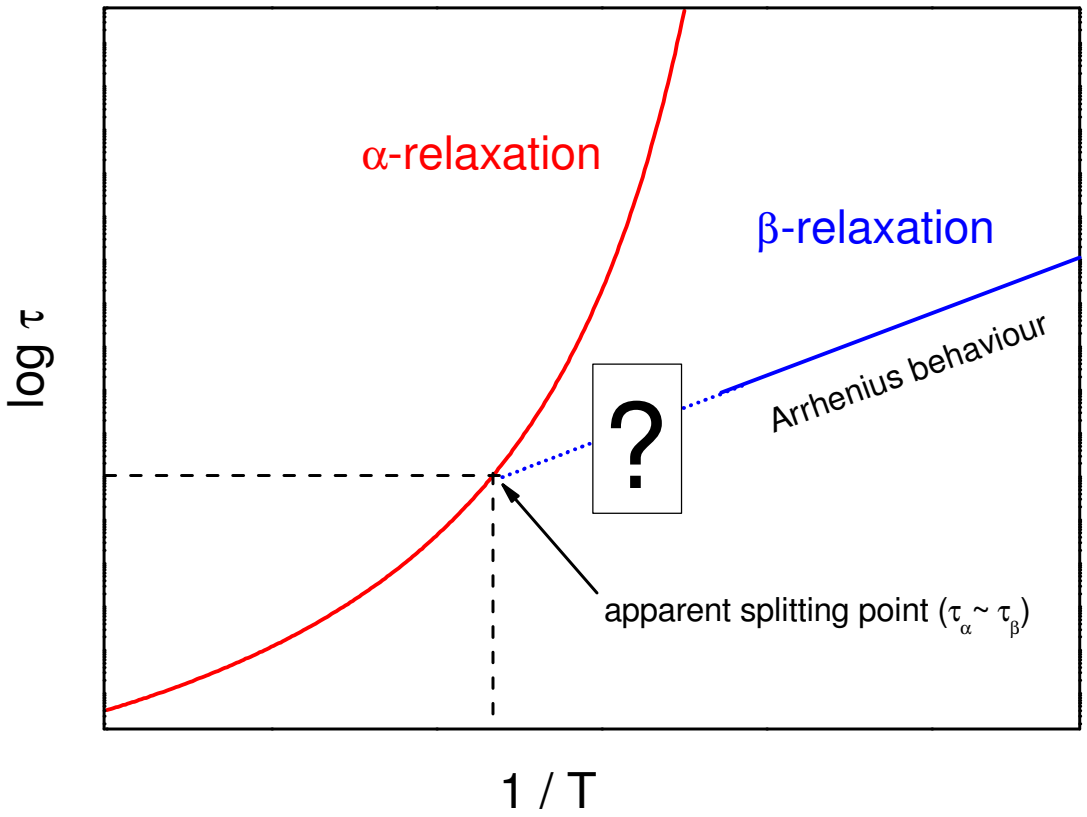
fast process: cage effect explained by mode-coupling theory (Götze *et al.*)

boson peak: vibrational excitations (?)

intramolecular modes

P. Lunkenheimer and A. Loidl, Contemp. Phys. **41**, 15 (2000);
Chem. Phys. **284**, 205 (2002).

Relaxation map of the α and β relaxation



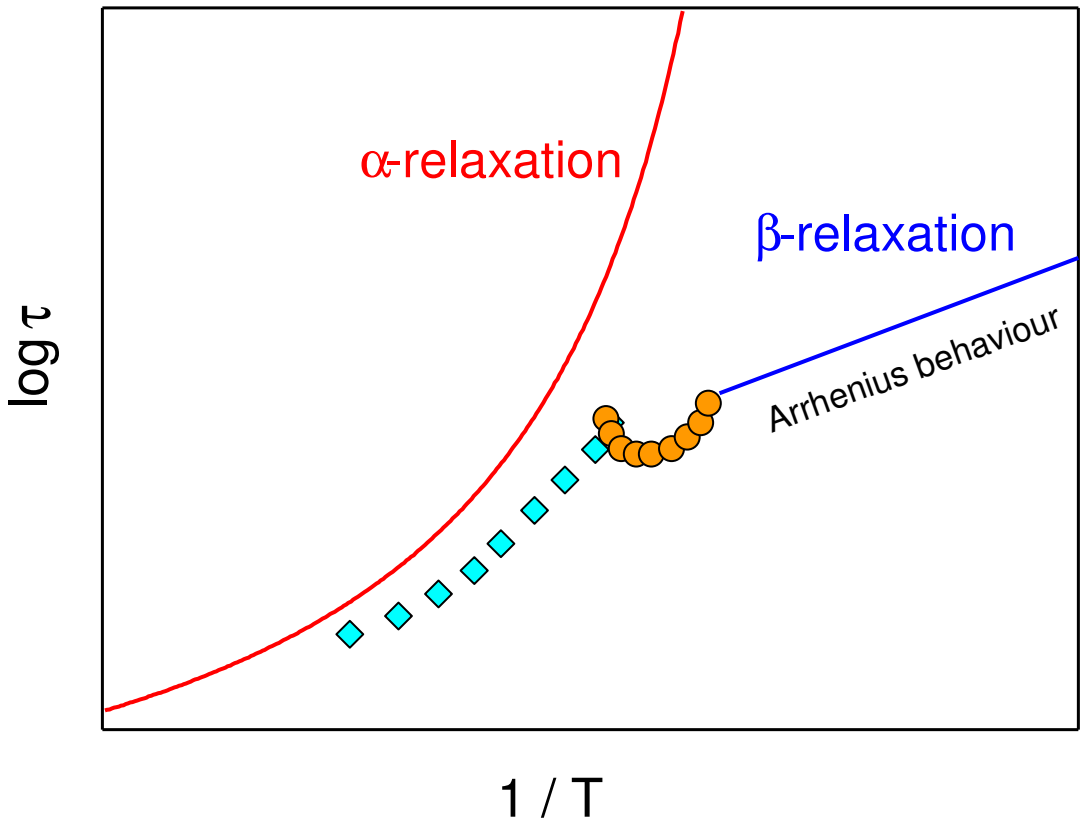
M. Paluch, C. M. Roland, S. Pawlus, J. Ziolo and K L. Ngai, Phys. Rev. Lett. **91**, 115701 (2003)

Explanations for the β 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…….

Relaxation map of the α and β relaxation



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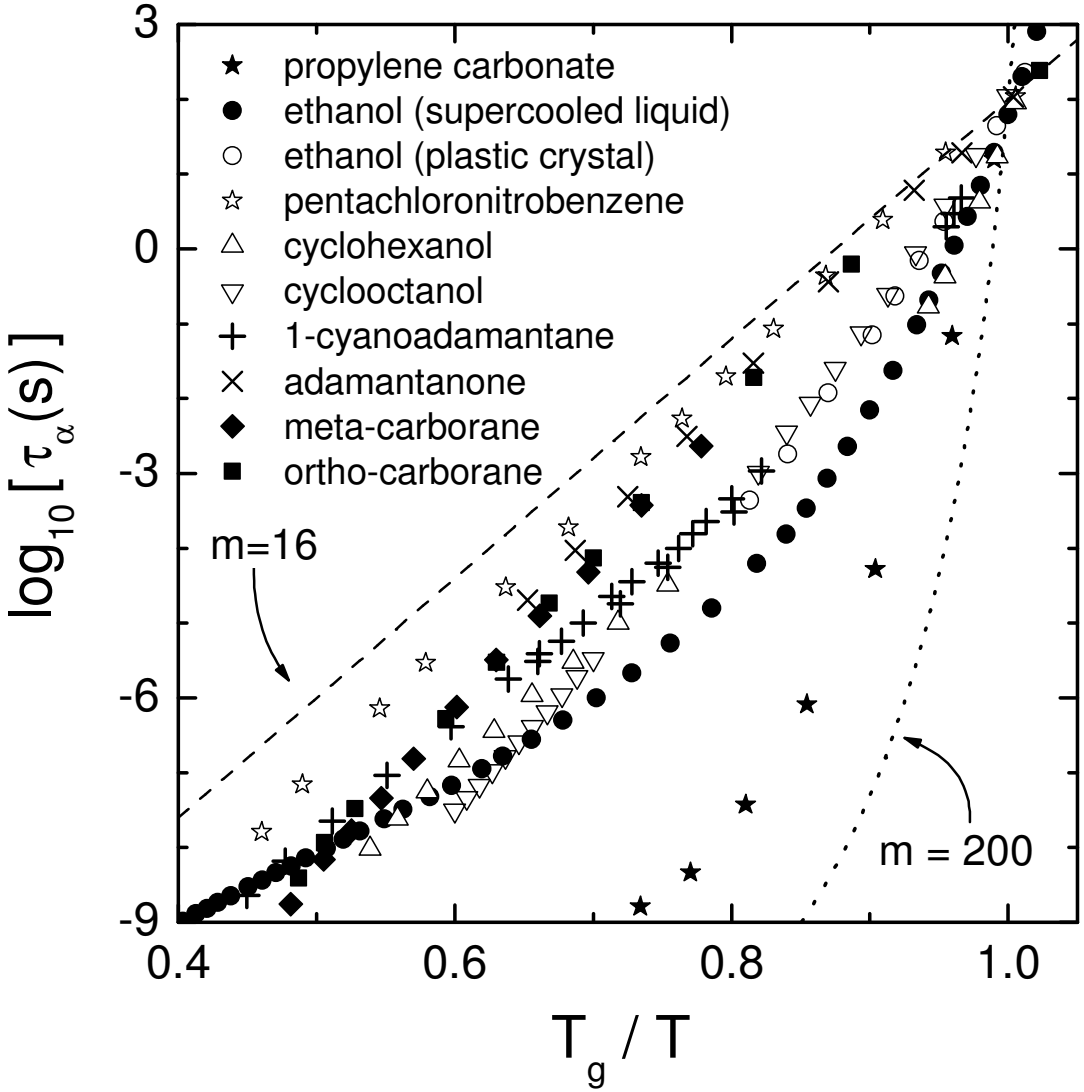
and many more…….

Angell plot of the α relaxation times



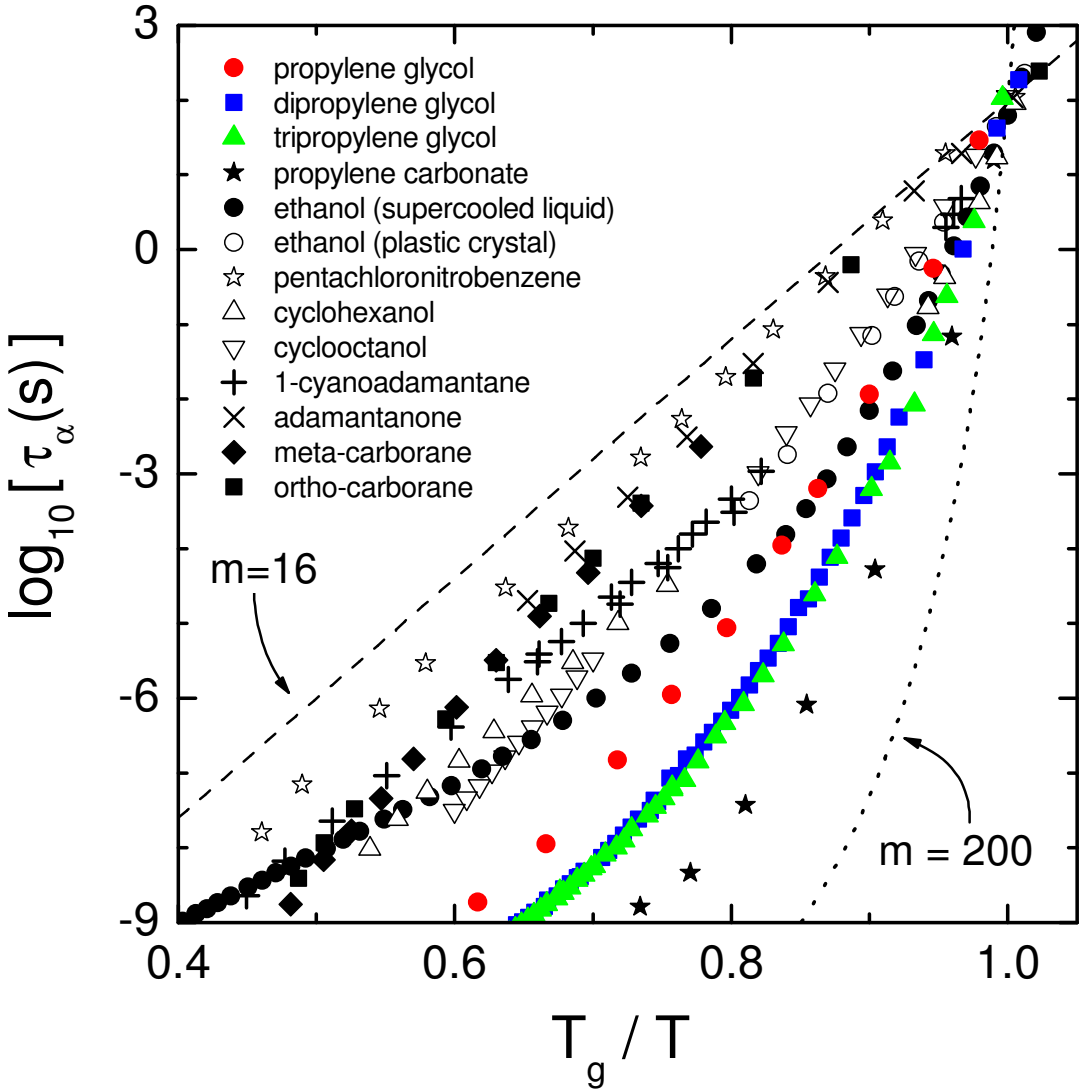
R. Brand, P. Lunkenheimer and A. Loidl, J. Chem. Phys. **116**, 23 (2002); **116**, 1038 (2002).

Fragility index m:

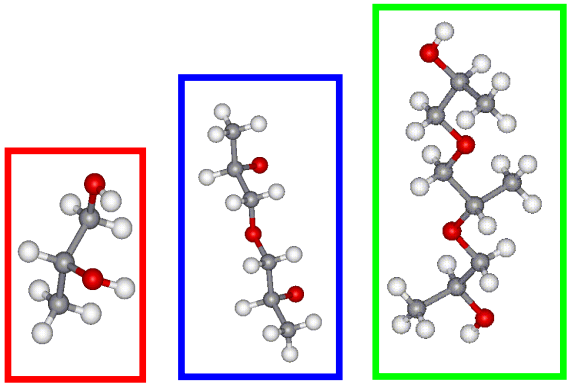
$$m = \left. \frac{d \log\langle \tau \rangle}{d(T_g / T)} \right|_{T=T_g}$$

D. J. Platzek, K. L. Ngai, Macromolecules **25**, 4911 (1991).
R. Böhmer, C. A. Angell, Phys. Rev. B **45**, 10091 (1992).

Angell plot of the α relaxation times



R. Brand, P. Lunkenheimer and A. Loidl, J. Chem. Phys. **116**, 23 (2002); **116**, 1038 (2002).



Investigation of

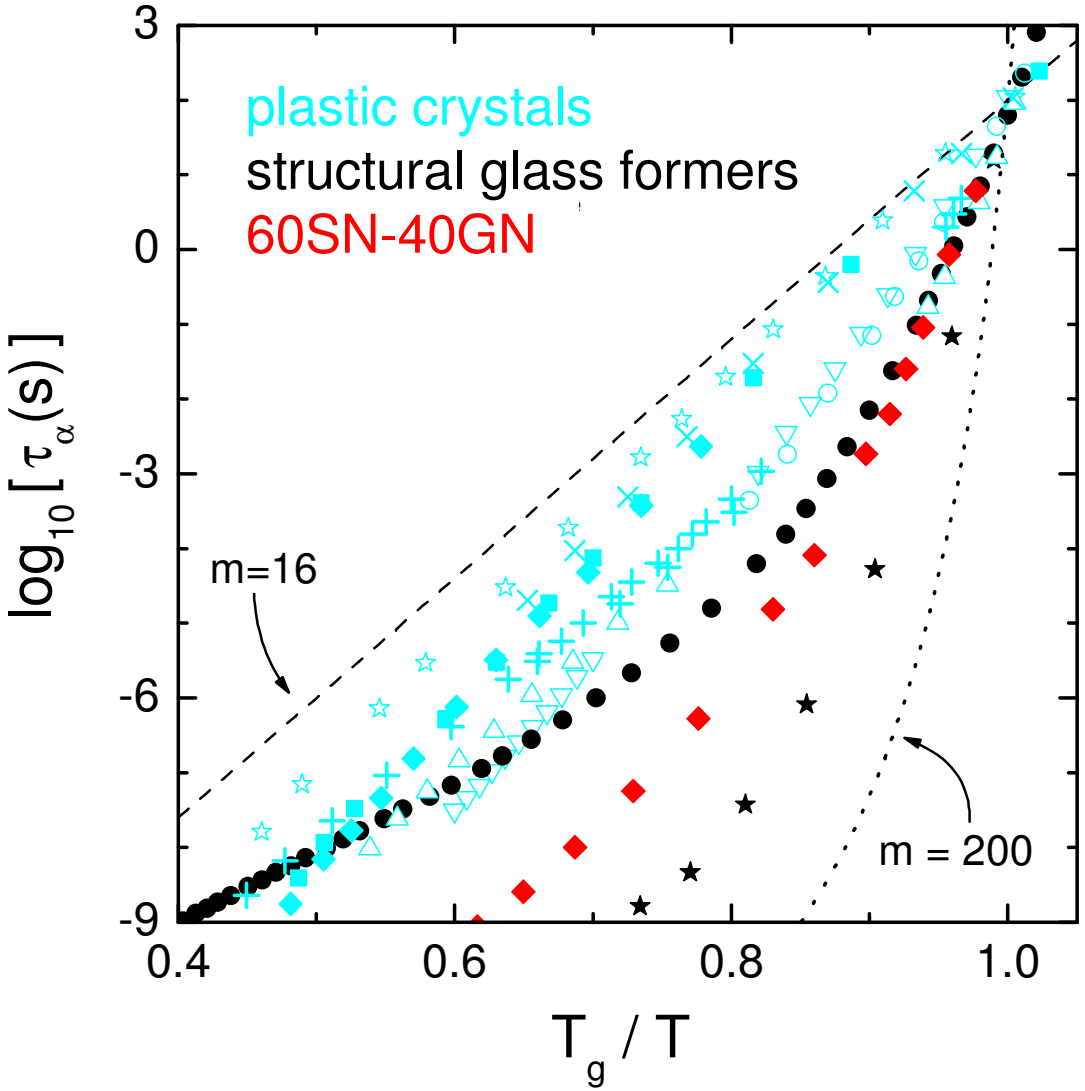
Propylene glycol

Dipropylene glycol

Tripropylene glycol

Molecular size effects?

Angell plot of the α relaxation times



R. Brand, P. Lunkenheimer and A. Loidl, J. Chem. Phys. **116**, 23 (2002); **116**, 1038 (2002).

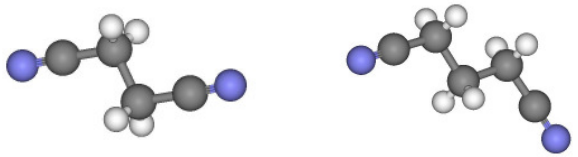
Exceptional:

High fragility

in

60%SN - 40%GN

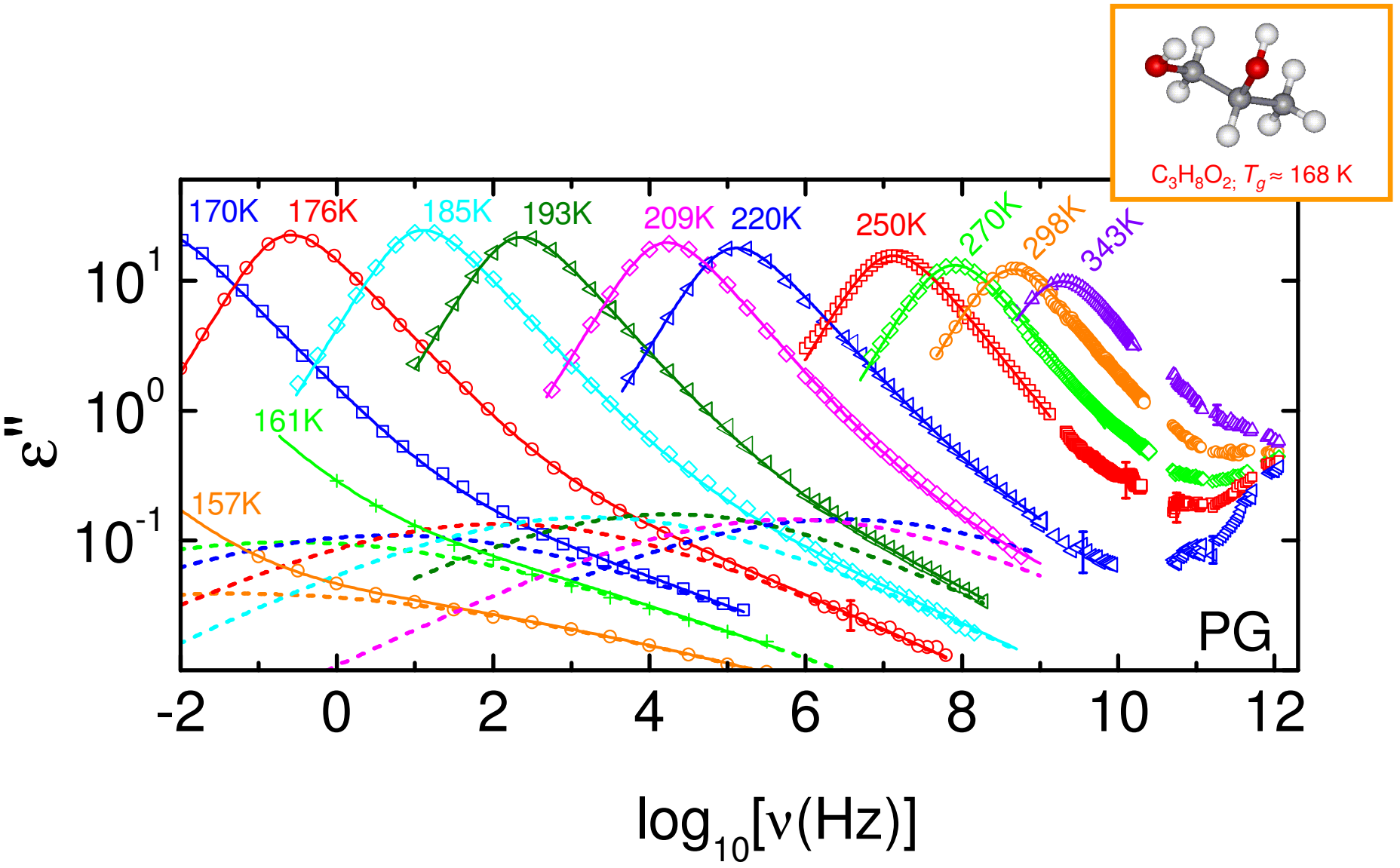
mixture



succinonitrile glutaronitrile

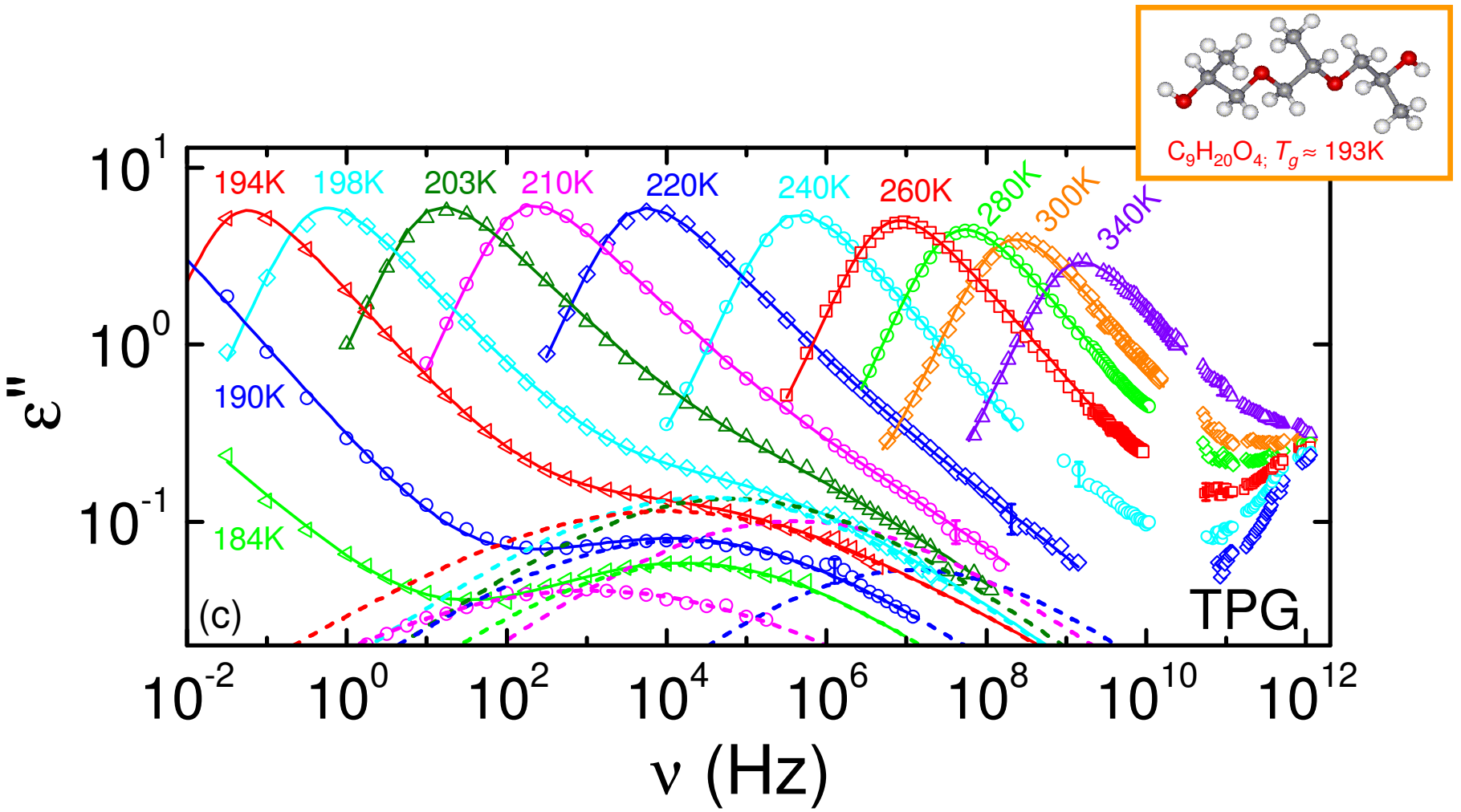
F. Mizuni *et al. J. Non-Cryst. Solids* **352**, 5147 (2006)

Dielectric loss spectra of propylene glycol



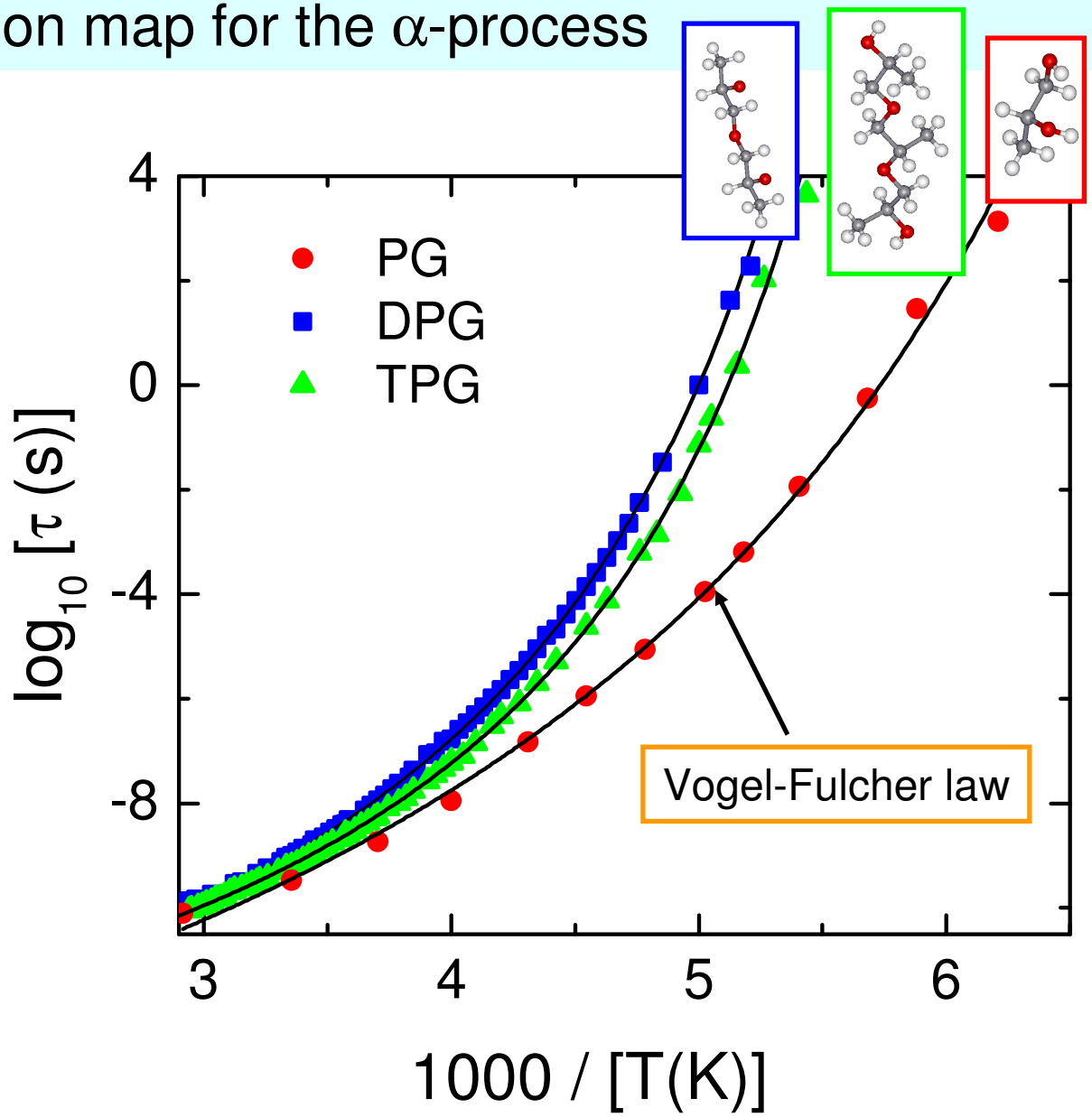
M. Köhler, Y. Goncharov, R. Wehn, P. Lunkenheimer, and A. Loidl, unpublished;
K.L Ngai, P. Lunkenheimer, C. León, U. Schneider, R. Brand, and A. Loidl, J. Chem. Phys. 115, 1405 (2001).

Dielectric loss spectra of tripropylene glycol

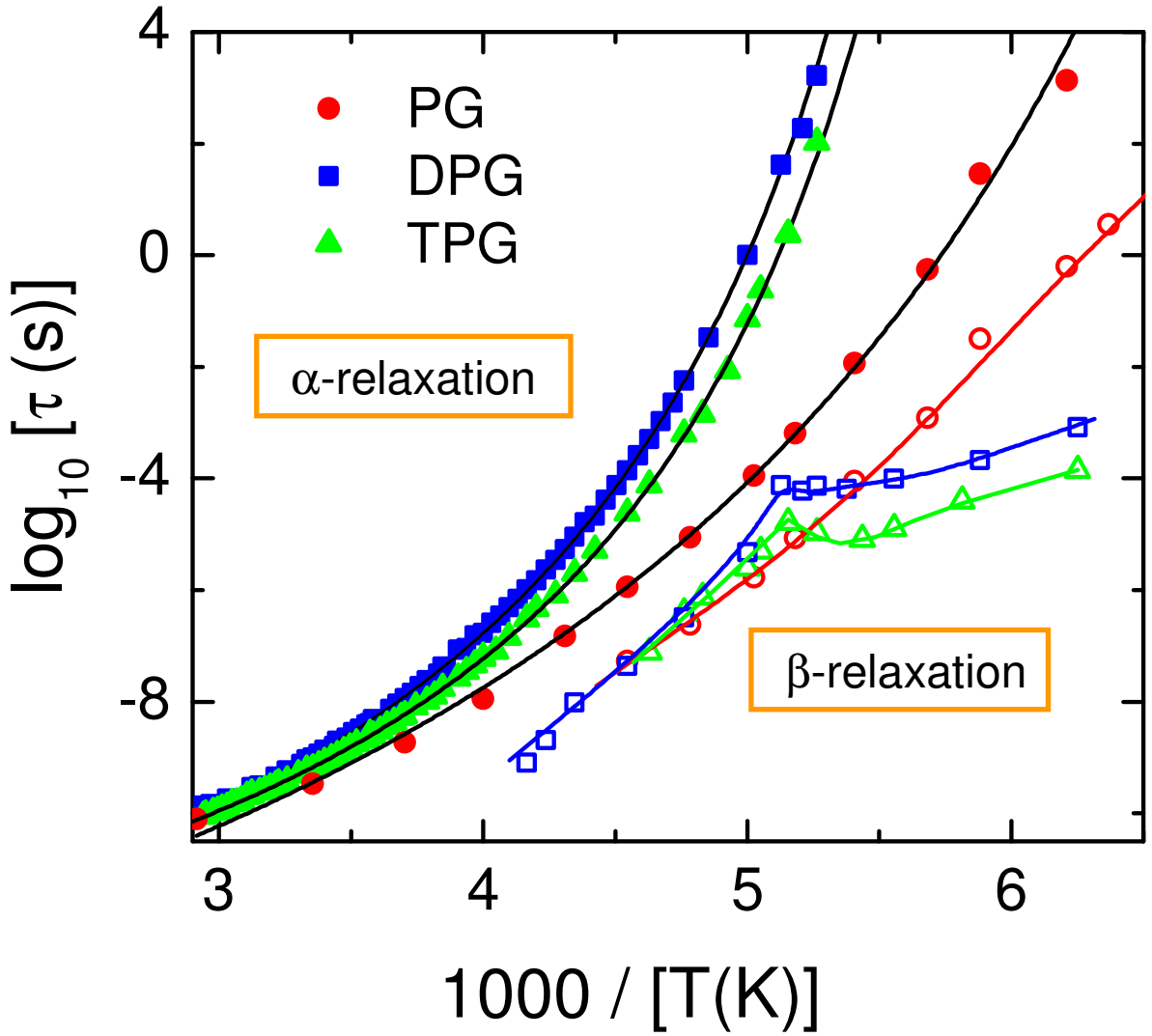


M. Köhler, Y. Goncharov, P. Lunkenheimer, and A. Loidl, unpublished.

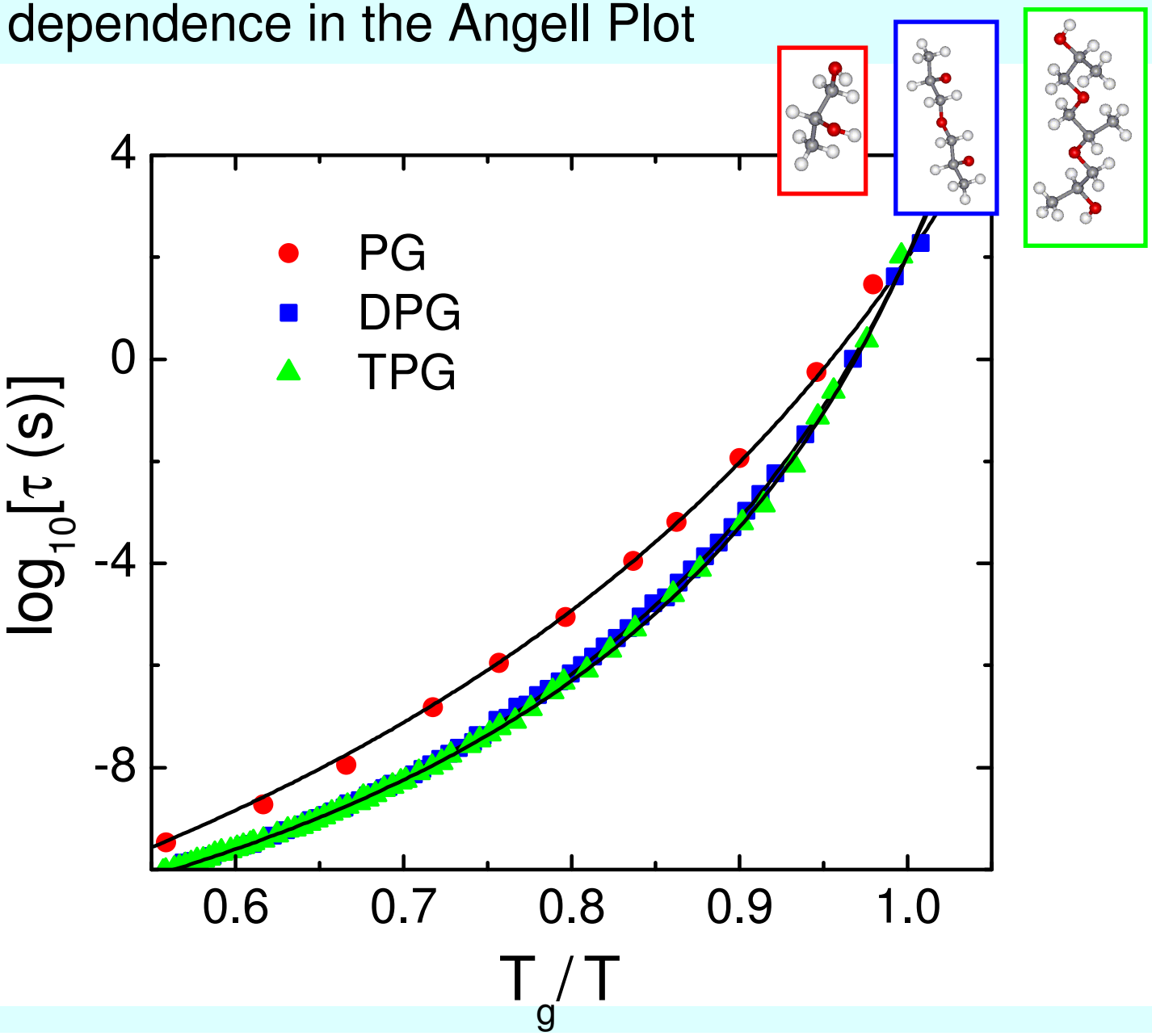
Relaxation map for the α-process



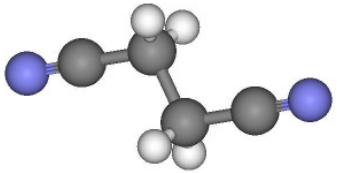
Relaxation map for α- and β-process



Size dependence in the Angell Plot

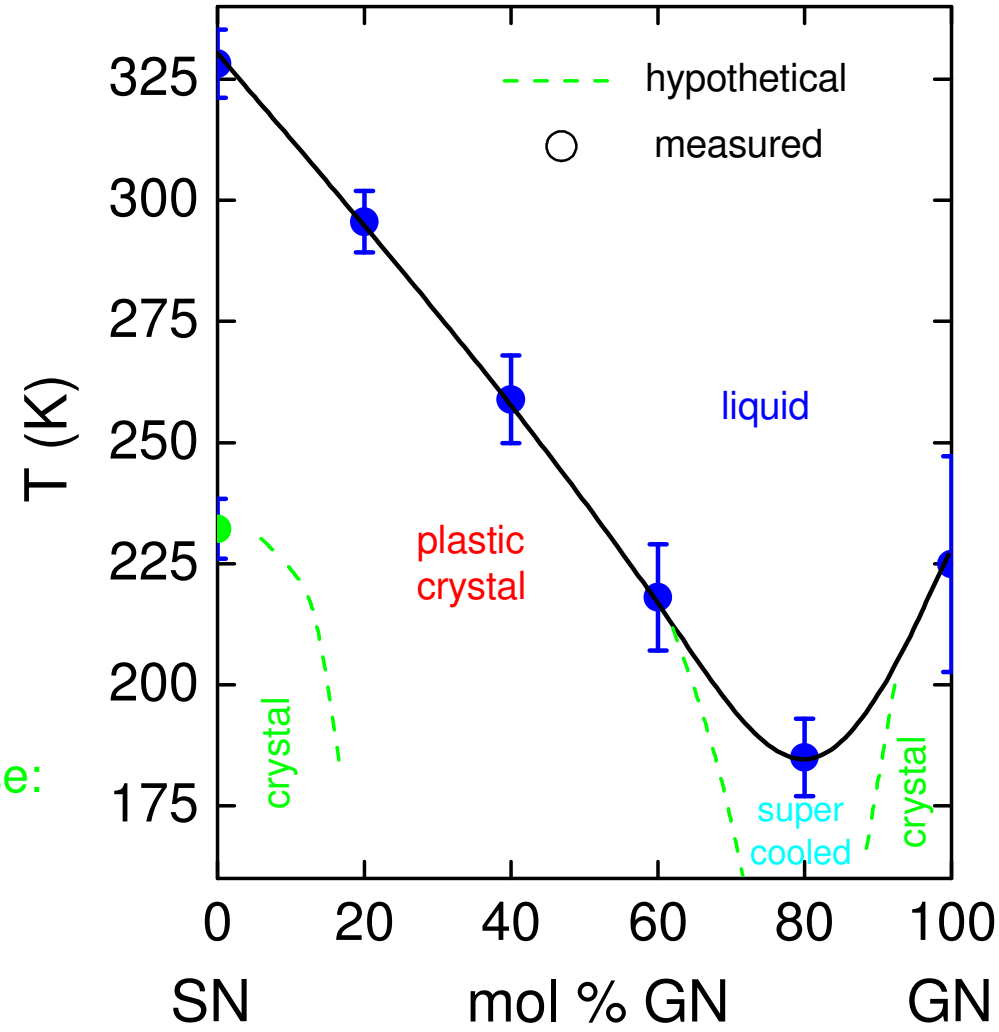


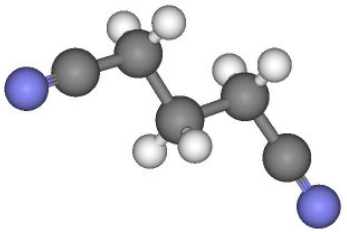
The system glutaro-succinonitrile



succinonitrile

Plastic phase:
BCC
Crystalline Phase:
monoclinic

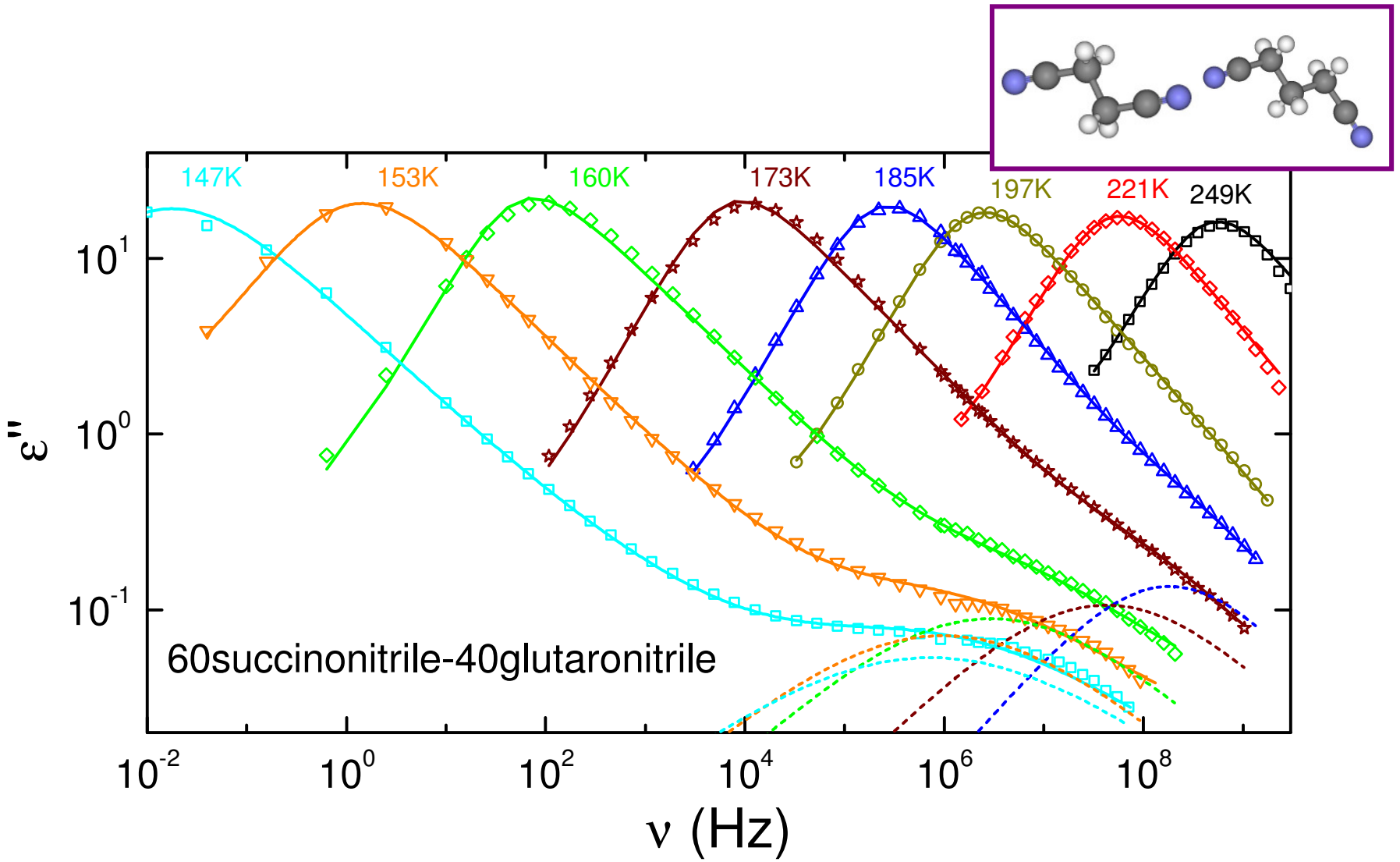




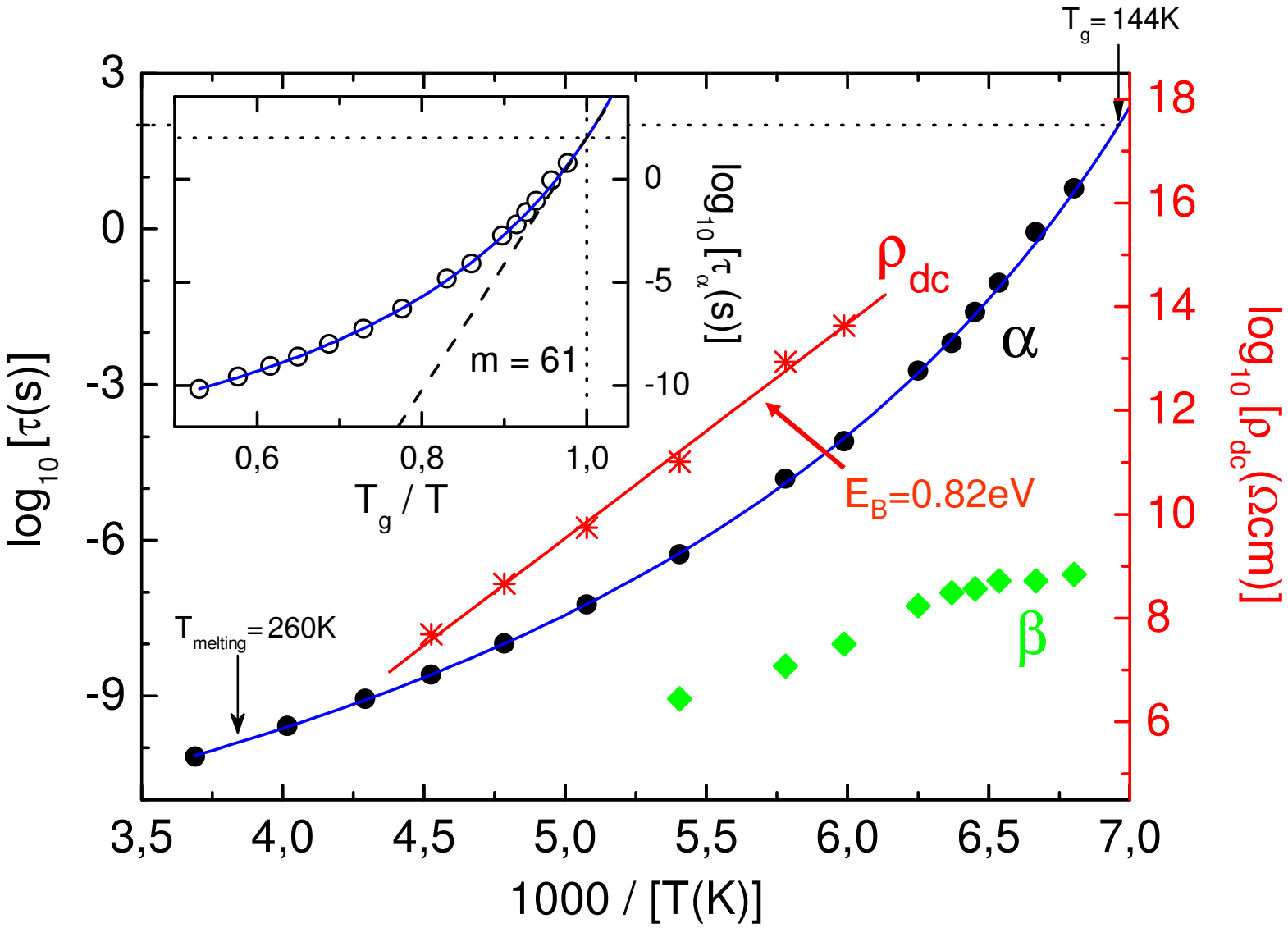
glutaronitrile

e.g.: F. Mizuni *et al. J. Non-Cryst. Solids* **352**, 5147 (2006); P. Derollez *et al. J. Phys.: Condens Matter* **2**, 6893 (1990);
P.J. Alarco *et al.*, *nature materials*, **3**, 476 (2004); G. Cardini *et al. J. Chem. Phys.* **95**, 679 (1991).

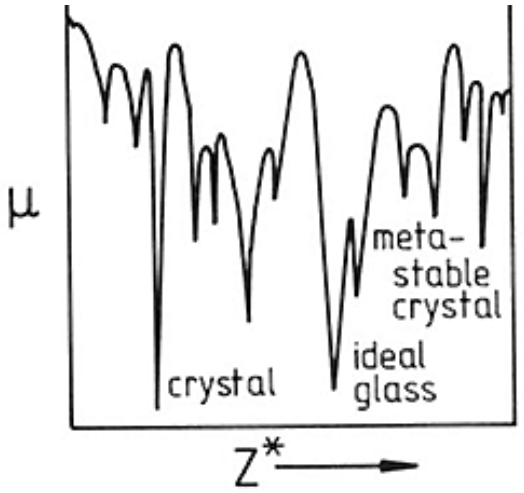
Dielectric loss spectra of 60%succinonitrile 40%glutaronitrile



Relaxation map for 60SN-40GN

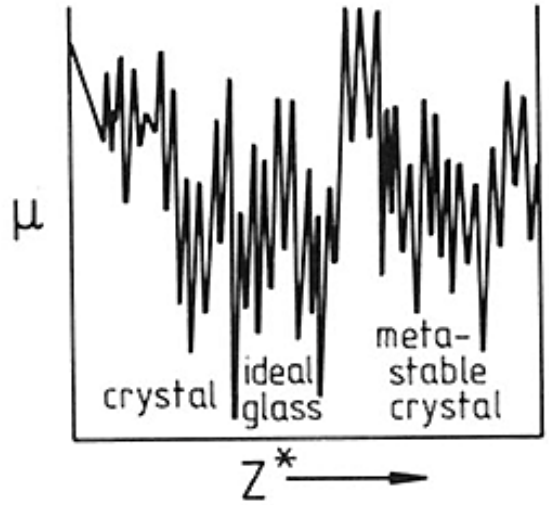


Potential energy in configuration space



Strong:

- Viscosity determined by
  thermal diffusion processes
- Nonhydrogen bonded network melts



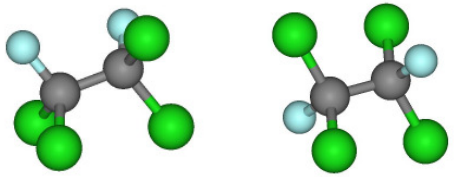
Fragile:

- Additional configurational states
- Nondirectional interatomic/intermolecular bonds

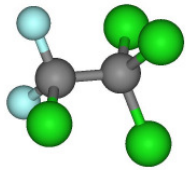
R. Böhmer and C. A. Angell, *Disorder Effects on Relaxational Processes* (Springer, Berlin, 1994), p. 11

Comparison to Freon

gauche trans

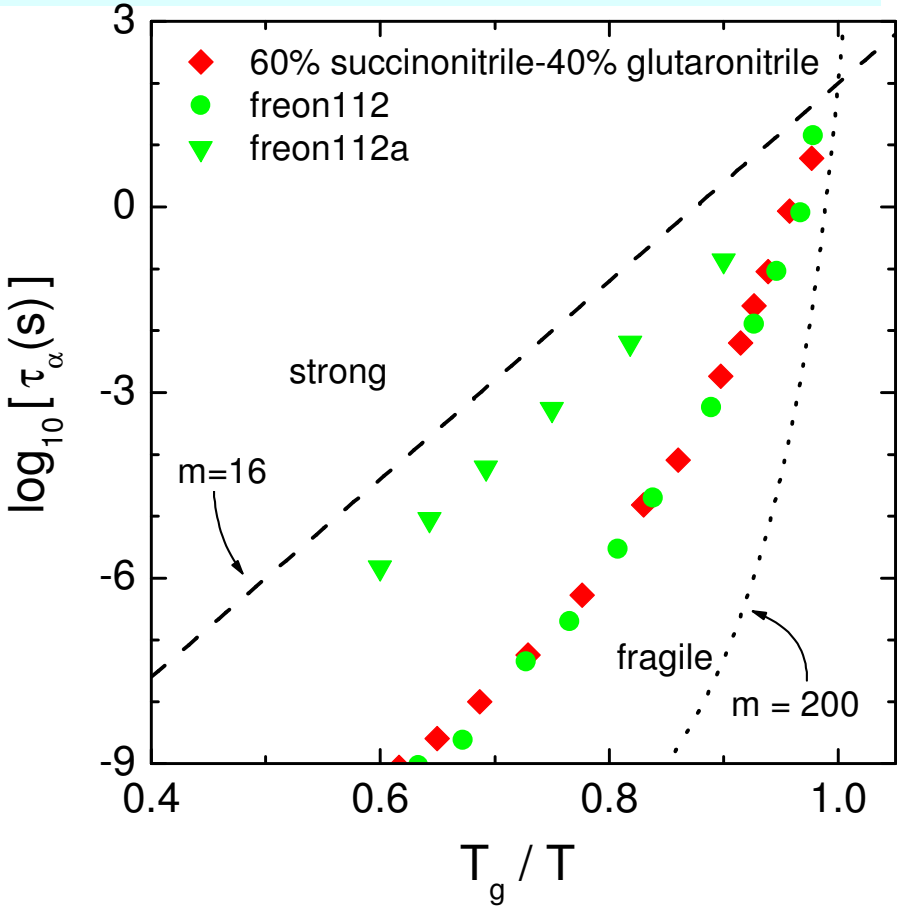


Freon 112
fragile



Freon 112a
strong

Trans and gauche:
Different molecular
potential energy landscape



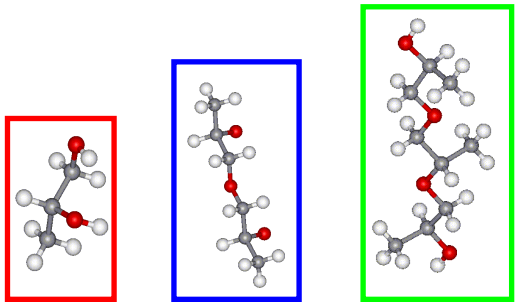
Is this also the cause of the high fragility in 60SN-40GN?

L.C. Pardo, P. Lunkenheimer and A. Loidl, J. Chem. Phys.. **124**, 124911 (2006)

Summary

GLYCOLS:

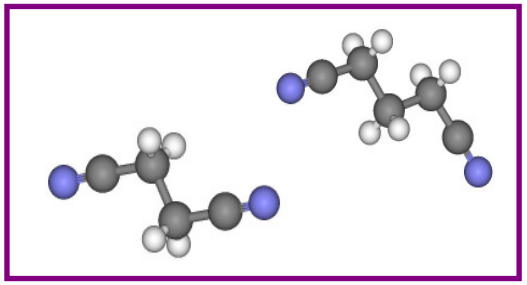
- Broadband dielectric measurements on glycols (10^{-2} – 10^{12} Hz)
- α relaxation time does not develop systematically with molecular size
- β relaxation times above T_g nearly identical



PG DPG TPG

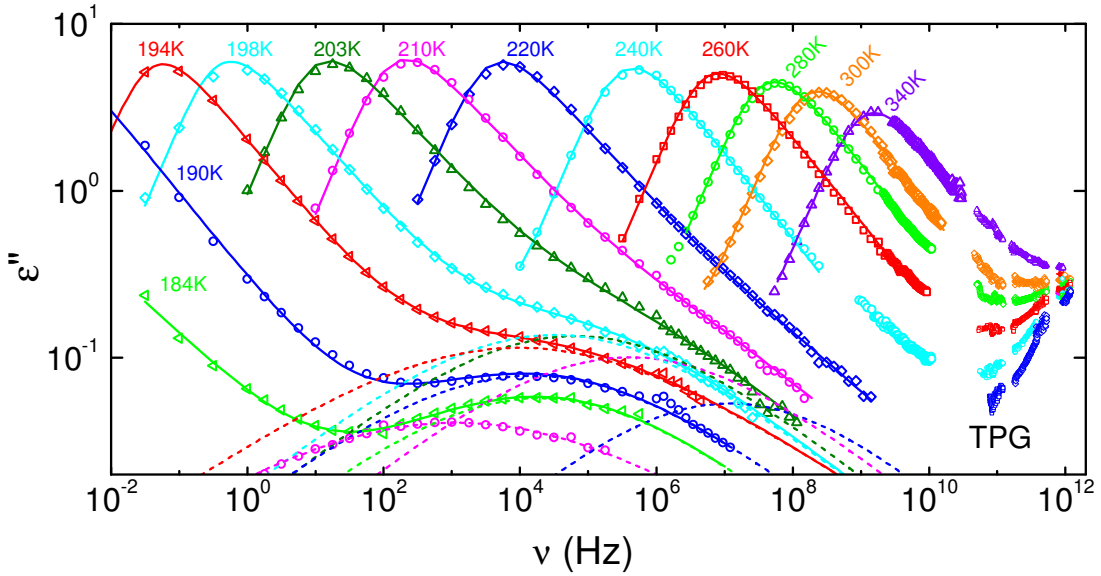
THE SYSTEM SN-GN:

- Unusually high fragility
- Good ionic conductor
- Additional relaxation instead of ac conductivity possible



succino-glutaronitrile

Thank you for your attention!



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Alois Loidl
Peter Lunkenheimer
Yurii Goncharov
Thomas Bauer
Robert Wehn

...and the EP V group