# New Approach to the Old Problem: Cooperativity and Heterogeneity in Dynamics of Glassforming Systems

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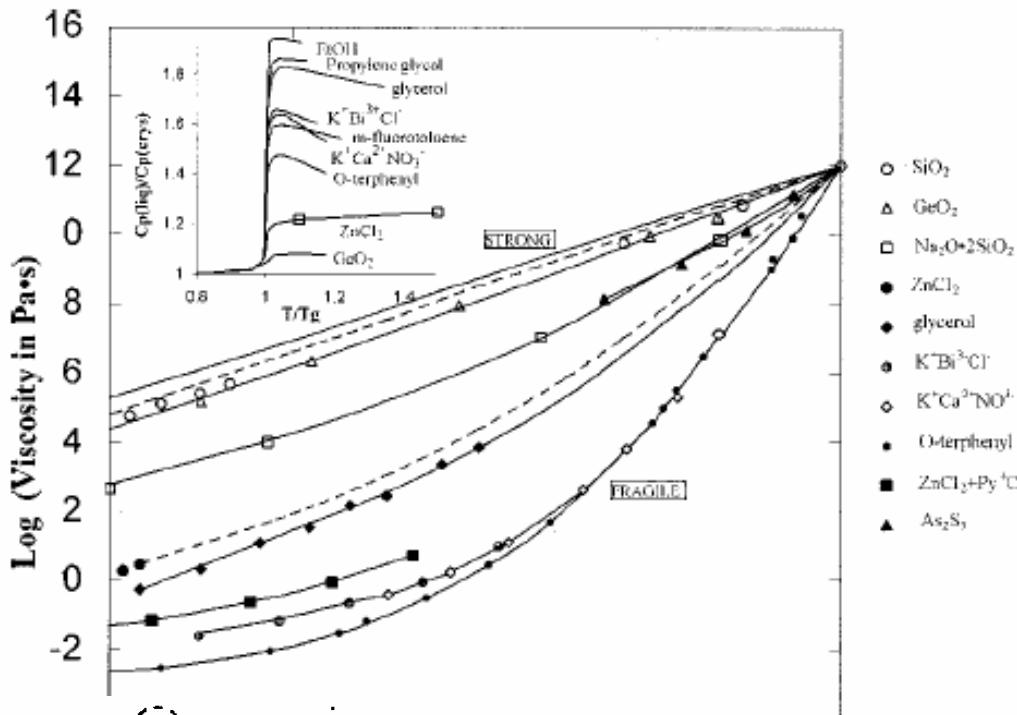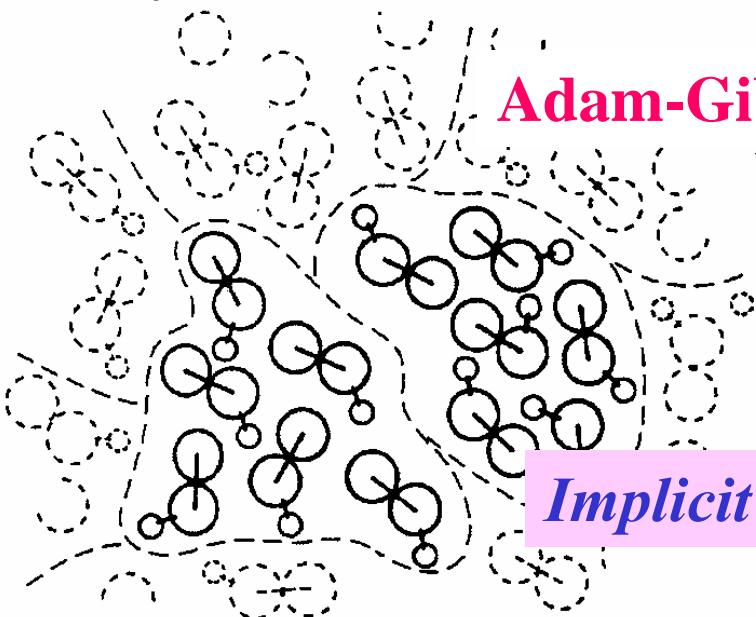
Non-Arrhenius temperature dependence of structural relaxation. Fragility Index

$$m = \frac{\partial \log \eta(T)}{\partial (T_g / T)}\Bigg|_{T=T_g}$$

m characterizes apparent activation energy at Tg normalized by Tg.

Adam-Gibbs Picture

Traditional view:

Sharp increase in apparent activation energy is caused by increase in cooperativity.

*Implicit assumption:* **Fragility → Cooperativity**

How do we define Cooperativity?

> *The amount of atoms (particles) involved in a single relaxation event?*
> *Size of dynamic heterogeneities?*
> *…?*
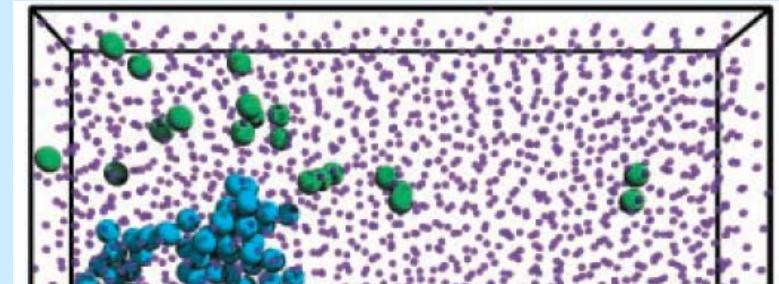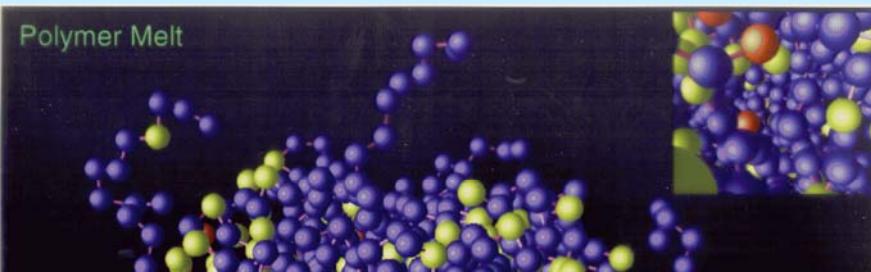
But should we care about the fastest particles?
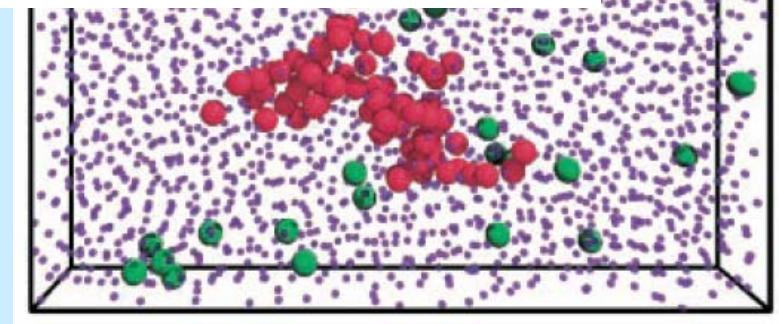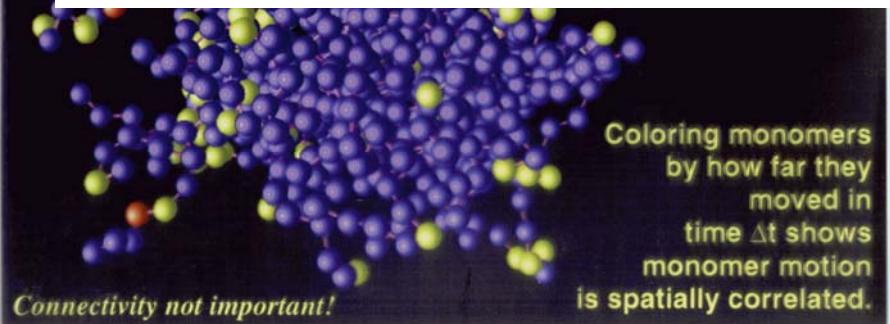
Analysis of the fastest 5% of particles in MD-simulations demonstrates existence of clusters – 'strings' [Bennemann, et al. **Nature 399**, 246 (1999)]

Similar picture emerges from optical microscopy of colloids [Weeks, et al. **Science 287**, 627 (2000)].
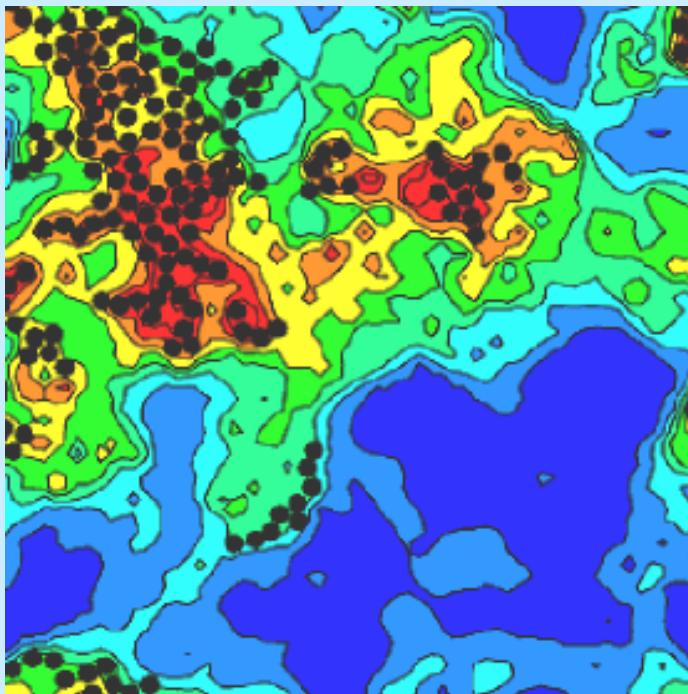
Matching heterogeneities in fast and slow dynamics [Widmer, Harrowell, **PRL 96**, 185701(2006)]
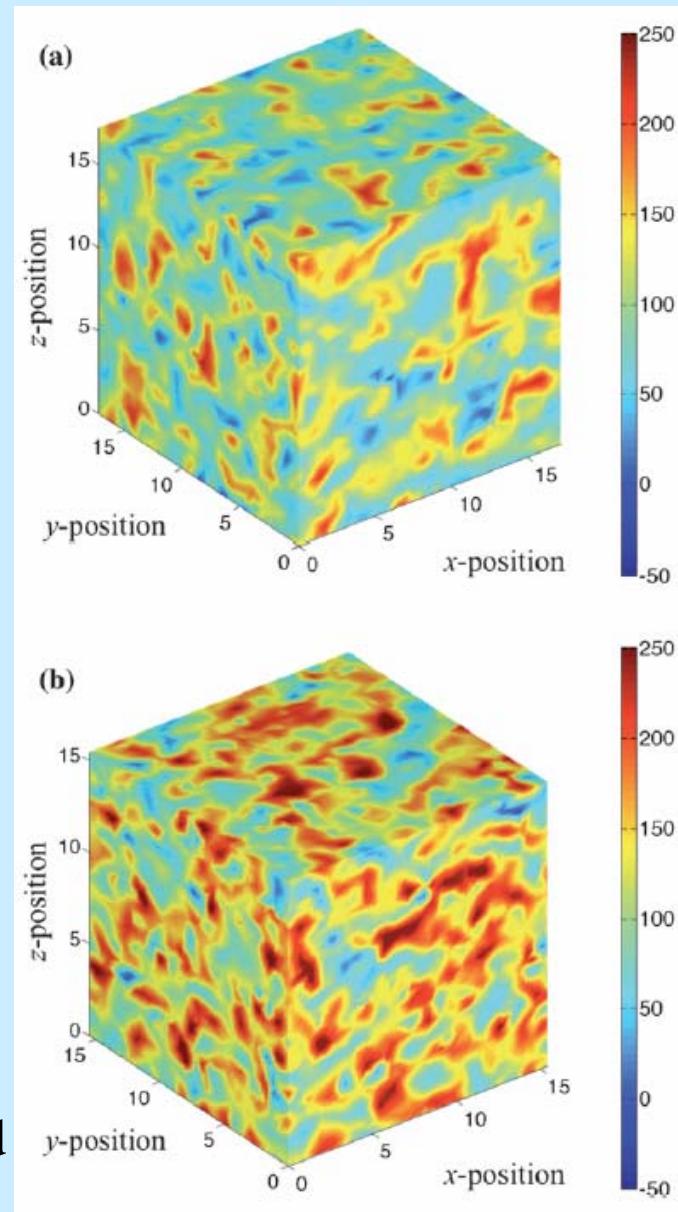
Elastic constants fluctuations in fragile (a) and stronger (b) systems [Riggleman, et al. **Soft Matter 6**, 292 (2010)].
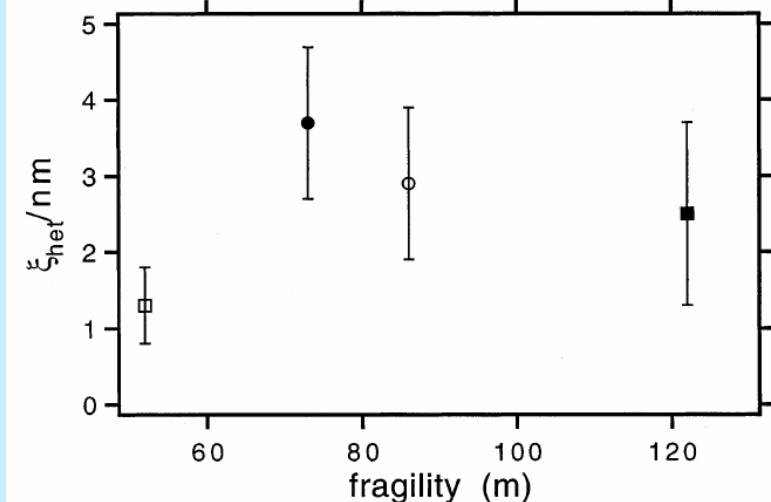
4D-NMR provided estimates of the size of slow-relaxing domains [Qiu, Ediger, **JPC B 107**, 459 (2003)].

No connection to fragility???
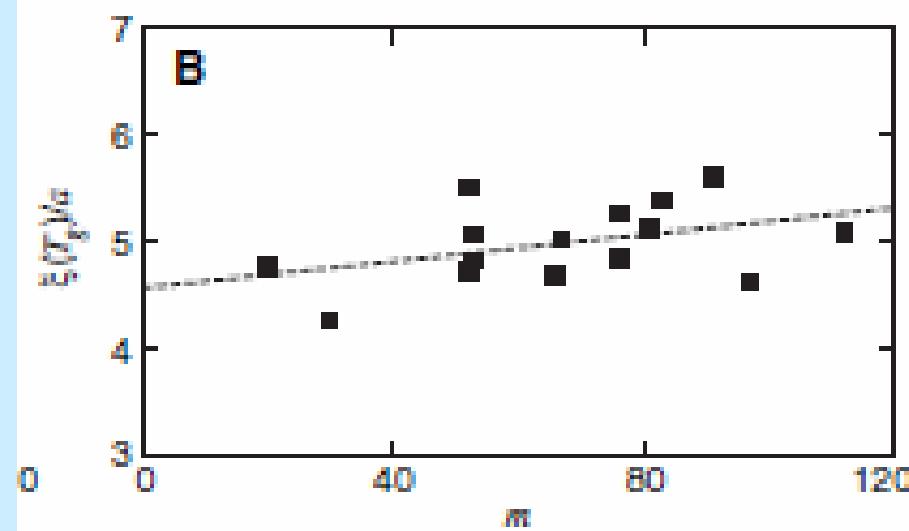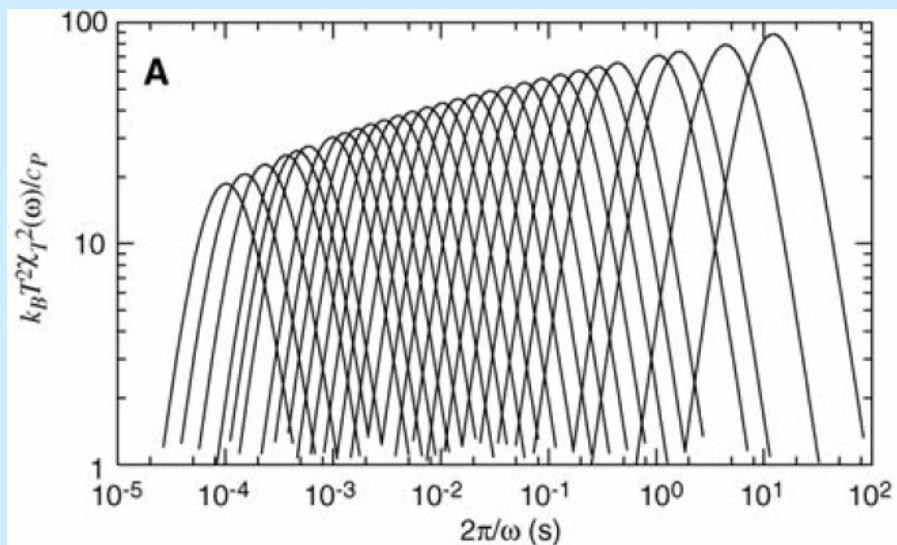
Attempts to estimate cooperativity (4-point correlation function) from 2-point susceptibility [Berthier, et al., **Science 310**, 1797 (2005)]

This analysis also did not find the cooperativity -> fragility connection.
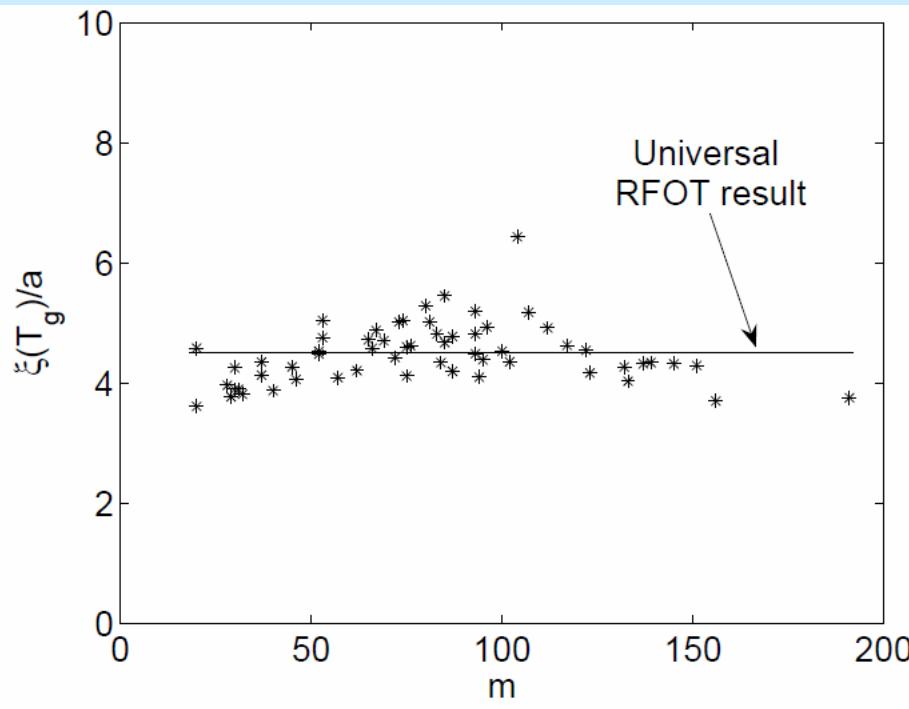
Stevenson and Wolynes analyzed existing experimental data in framework of RFOT and found *the characteristic length scale ξ at Tg* scaled by interatomic distance **a** to be almost universal number independent of m [cond-matt/0609677].

Schweizer and Saltzman also came to a similar conclusion in the framework of Entropy Barrier Theory [JPC B 108, 19729 (2004)].

For dense atomic and flexible polymer liquids interacting via repulsive forces, both integral equation theory and molecular dynamics simulations[41] find $\xi_\rho/\sigma \approx 0.5-1$. Equation 16 thereby yields a domain diameter of $\xi_d/\sigma \approx 3-4$. Although this estimate

$$\xi \approx \lambda_{BP} = V_{TA}/\nu_{BP}$$

Sample	Boson Peak ξ (BP) (nm)	ξ (4D NMR)* (nm)
Glycerol	1.4 ± 0.1	1.3 ± 0.5
Sorbitol	1.5 ± 0.1	2.5 ± 1.2
OTP	2.5 ± 0.2	2.5 ± 1
PVAc	2.9 ± 0.2	3.4 ± 1
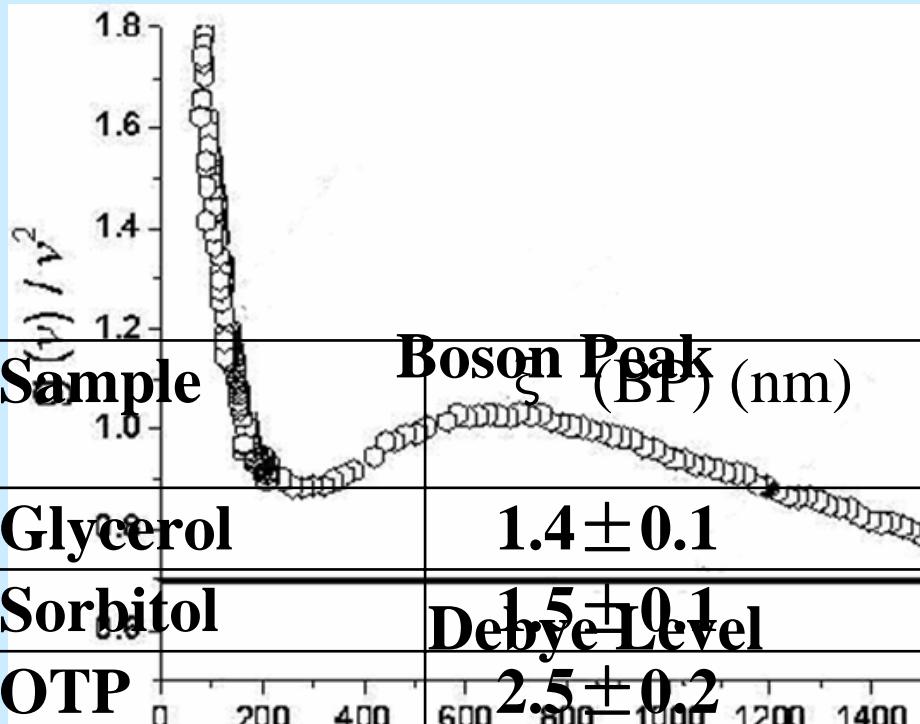
Comparison of the Boson Peak and NMR data [Qiu, Ediger, **J. Phys. Chem. B 107,** 459 (2003)] reveals a good agreement, supporting the proposed idea.

L. Hong, et al., **J. Chem. Phys. 131**, 194511 (2009).

No clear correlation between ξ and fragility.
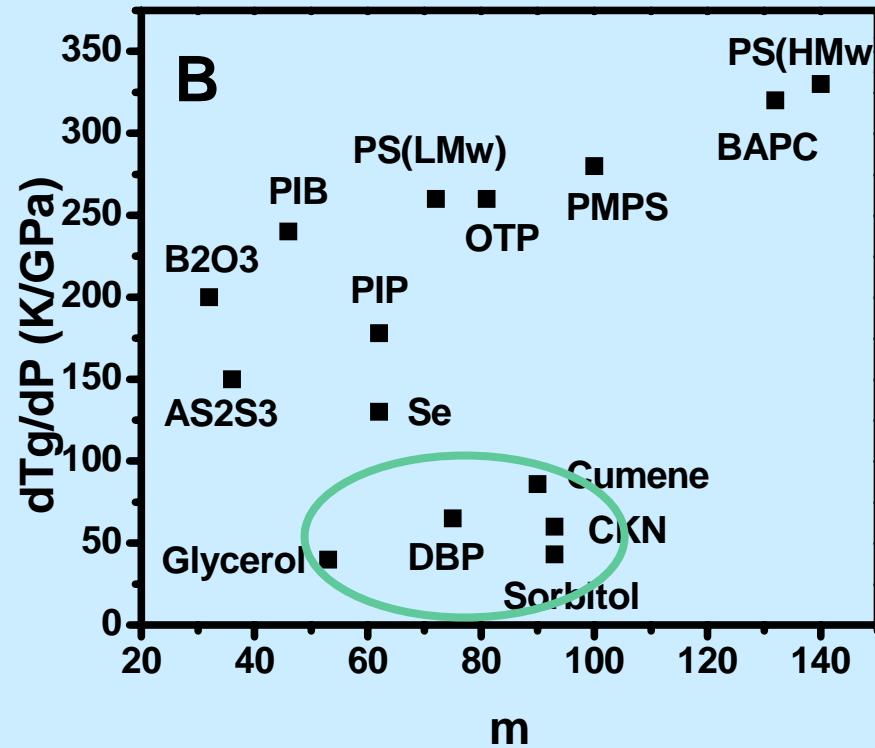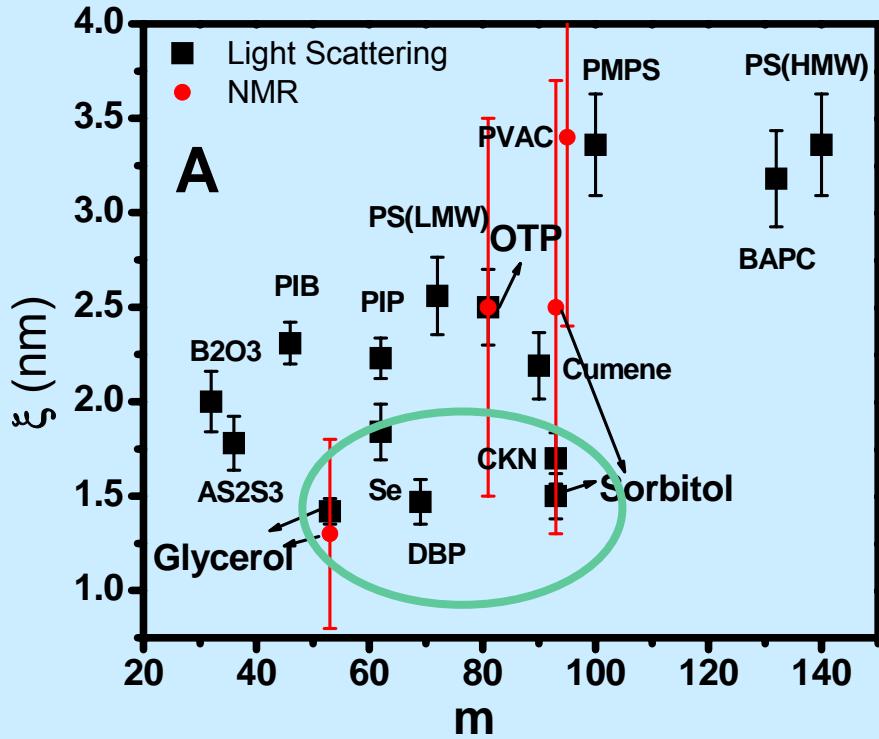
Systems that deviates from a general trend have weak variation of Tg under pressure

L. Hong, et al., **J. Chem. Phys. 131**, 194511 (2009).

$$\tau_\alpha(T,P) = \tau_\alpha(T,0) * \exp(\frac{P*\Delta V^{\#}}{RT})$$

$$\Delta V^{\#} = \ln 10 * m * \frac{dTg}{dP} * k_B$$

slope:0.31+-0.02

ξ (nm) vs ΔV# (nm³)
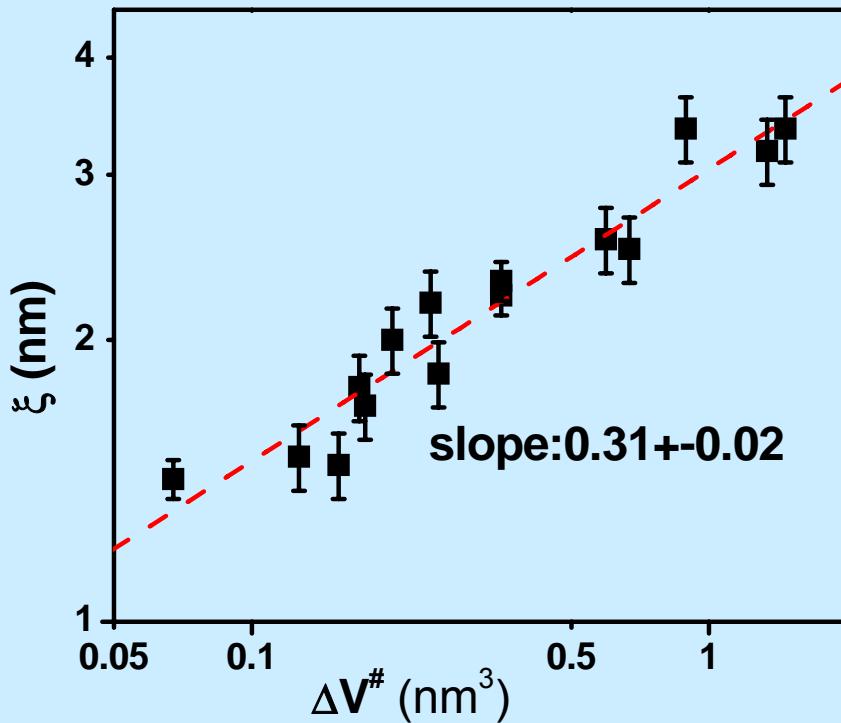
systems	$\Delta V^{\#}/\xi^3$
CKN	0.036
B2O3	0.025
As2S3	0.031
glycerol	0.024
BAPC	0.042
Cumene	0.023
PS(Mn=550)	0.035
PIB (Mn=20000)	0.028
PIP	0.032
PS(Mn=200600)	0.039
OTP	0.043
Sorbitol	0.038
PMPS	0.023
Se	0.041
DBP	0.049

$$\xi^\beta \propto \Delta V^{\#}$$

$$\beta = \frac{1}{slope} = 3.2 \pm 0.2 \approx 3$$

$$\frac{\Delta V^{\#}}{\xi^3} \approx 2 \sim 5\%$$

$$\xi^3 \propto \Delta V^{\#}$$

L. Hong, et al., **J. Chem. Phys. 131**, 194511 (2009).

Two contributions to fragility

A

PMPS   PS

Salol   OTP

PIB   PIP   Cumene

Glycerol DPG   Sorbitol

DBP

ξ (nm)

B

PIP

PIB OTP PMPS PS

DBP

Salol Glycerol

$\xi/a = \xi * Q/2\pi$

m_V
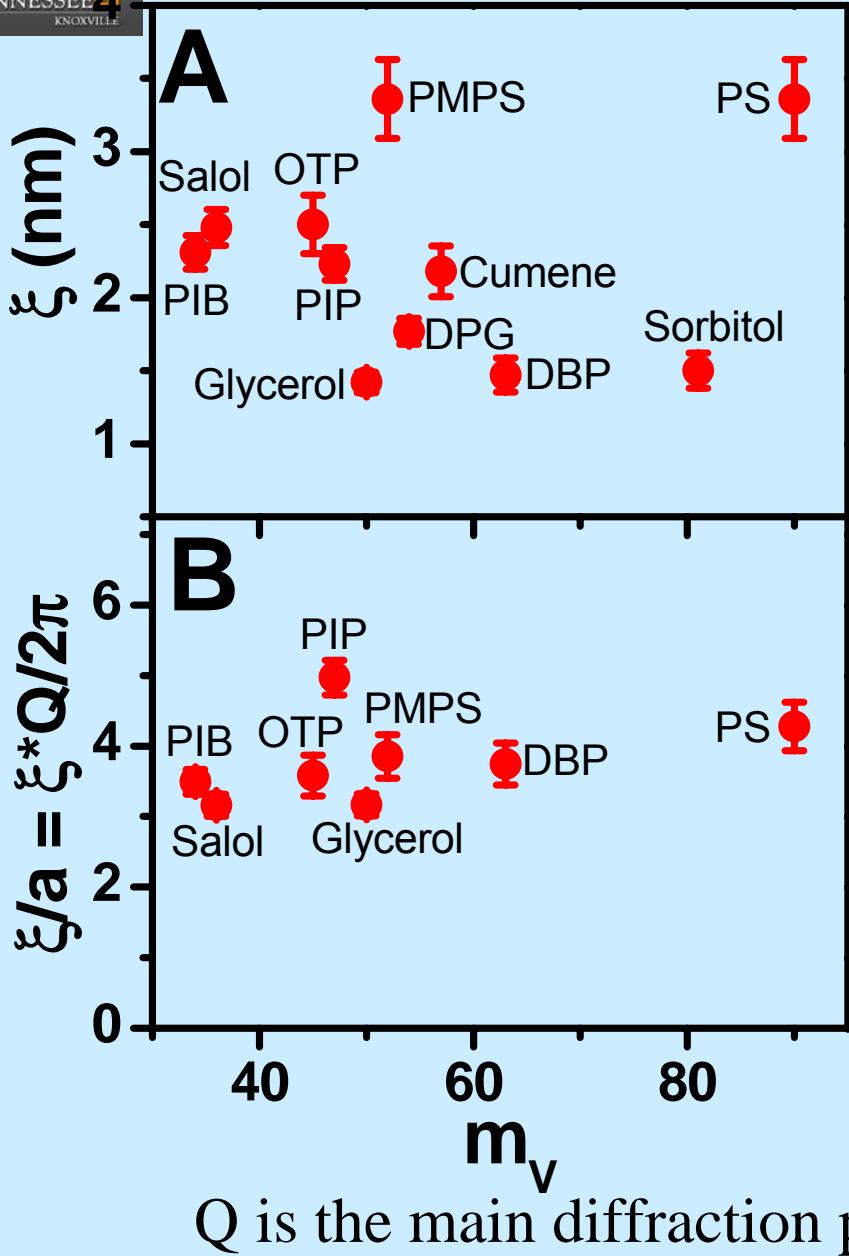
$$m = \left.\frac{\partial \lg \tau_\alpha}{\partial \frac{Tg}{T}}\right|_{T=Tg,V} + \left.\frac{\partial \lg \tau_\alpha}{\partial P}\right|_{T=Tg,T} * \left.\frac{\partial P}{\partial \frac{Tg}{T}}\right|_{T=Tg,V}$$

$$= m_V + \frac{\Delta V^{\#}}{\ln 10 * k_B} * \frac{\alpha_T}{\kappa}$$

Pure thermal   **Volume contribution**

Only volume contribution correlates to the cooperativity length scale.
Pure thermal contribution exhibits no connection to ξ.

Clear separation of these two contributions is critical for understanding of the temperature variations of τ_α

Q is the main diffraction peak

$$m - m_V = \frac{\Delta V^{\#}}{\ln 10 * k_B} * \boxed{\frac{\alpha_T}{\kappa}}$$

$$m - m_V \propto \Delta V^{\#}$$

$$\Delta V^{\#} \propto \xi^3$$

$$m - m_V \propto \xi^3$$

slope: 0.32 ± 0.05

ξ (nm)

m-m$_V$
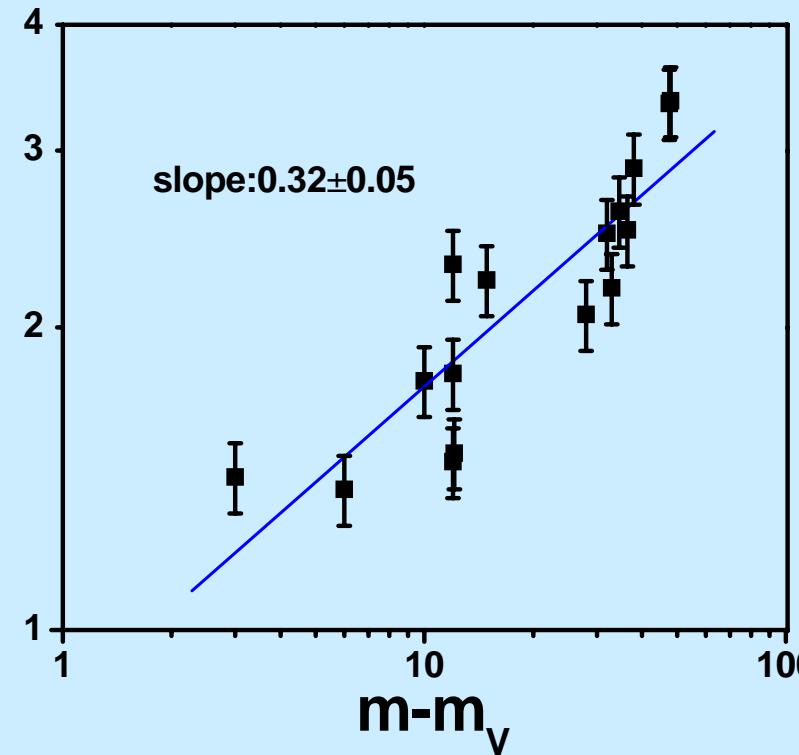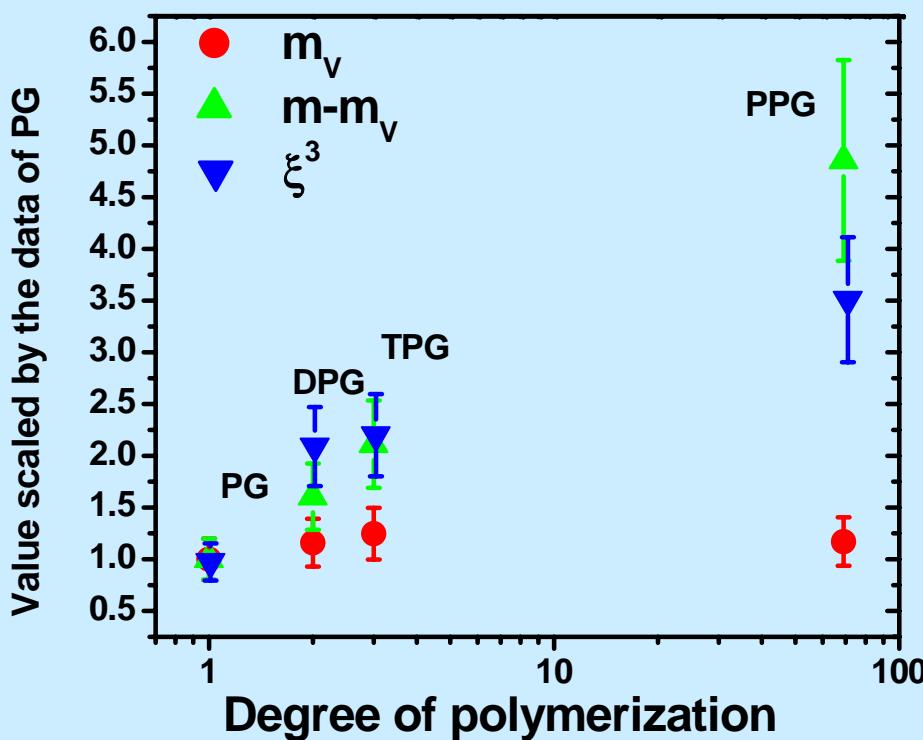
Thorough test with poly(propylene glycol)

Propylene glycol (PG)

HO - CH$_2$ - CH- OH
|
CH$_3$

Poly (propylene glycol) (PPG)

HO - (CH$_2$ - CH- O)$_n$-H
|
CH$_3$

Value scaled by the data of PG

- ● m$_V$
- ▲ m-m$_V$
- ▼ ξ^3

PPG

TPG

DPG

PG

Degree of polymerization
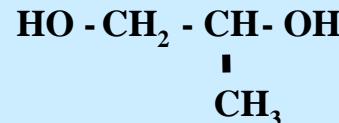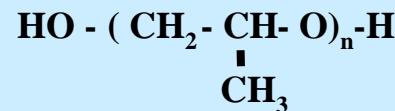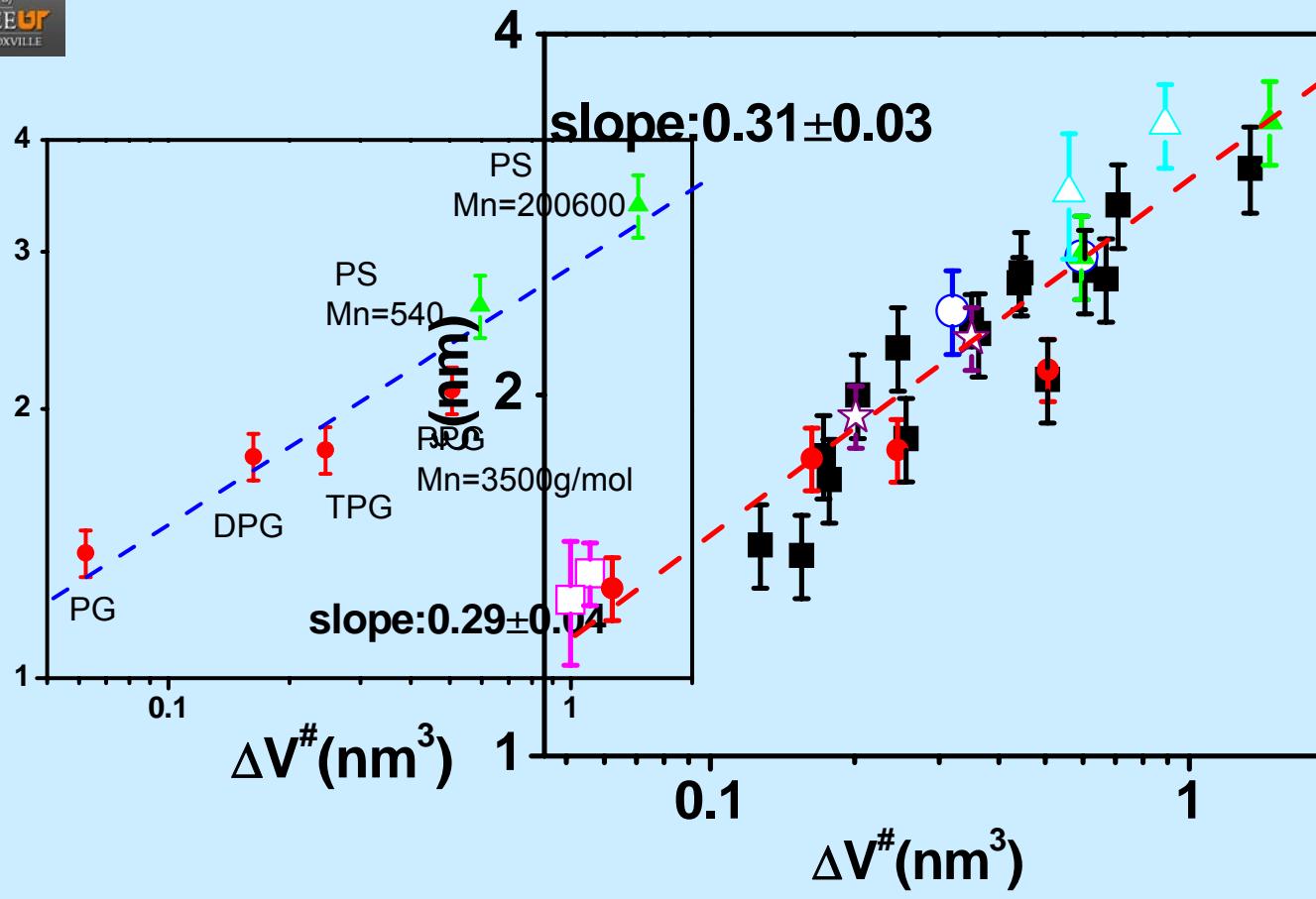
Different species at ambient pressure: ■

Changing molecular weight at ambient pressure: ● **PPG**; ▲ **PS**

Changing pressure : □**Glycerol**; ○**PS oligomer**; △ **PMPS**; ☆ **PIP**

Cooperativity and Fragility
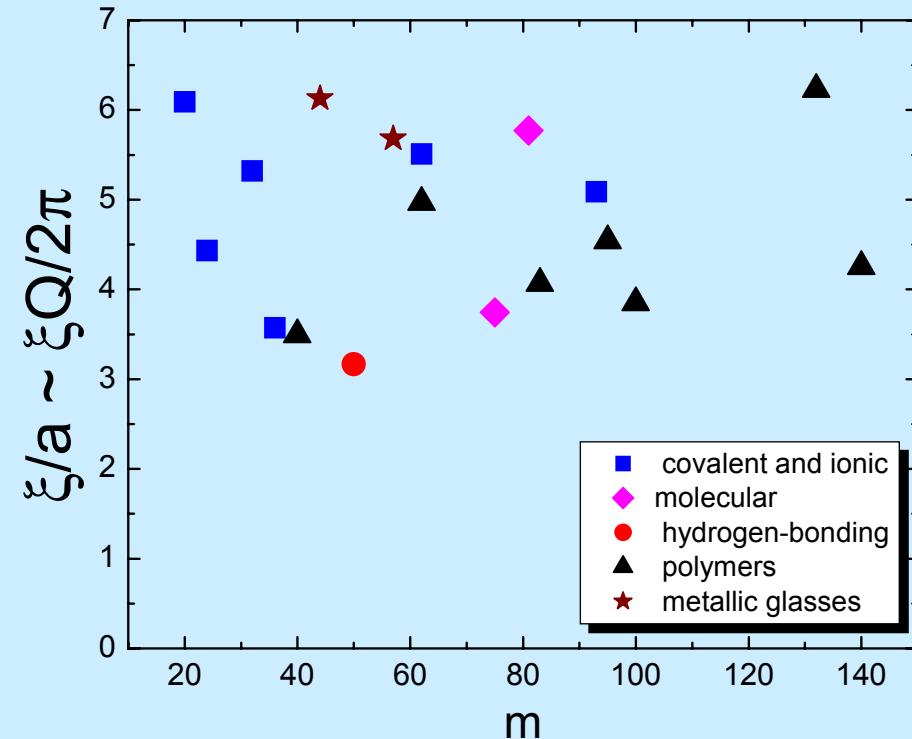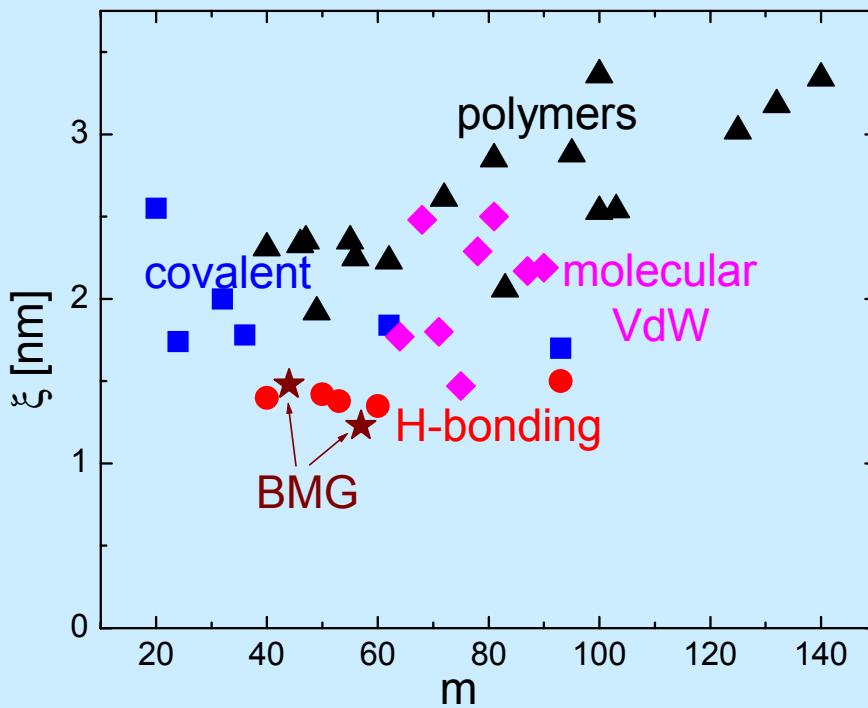
> ξ depends on type of the system (smallest in H-bonding and BMG, highest in polymers);

> It does not correlate to fragility

$$\frac{\xi}{a} \approx \frac{\xi Q}{2\pi} \sim 3.5 - 6$$

Independent of fragility
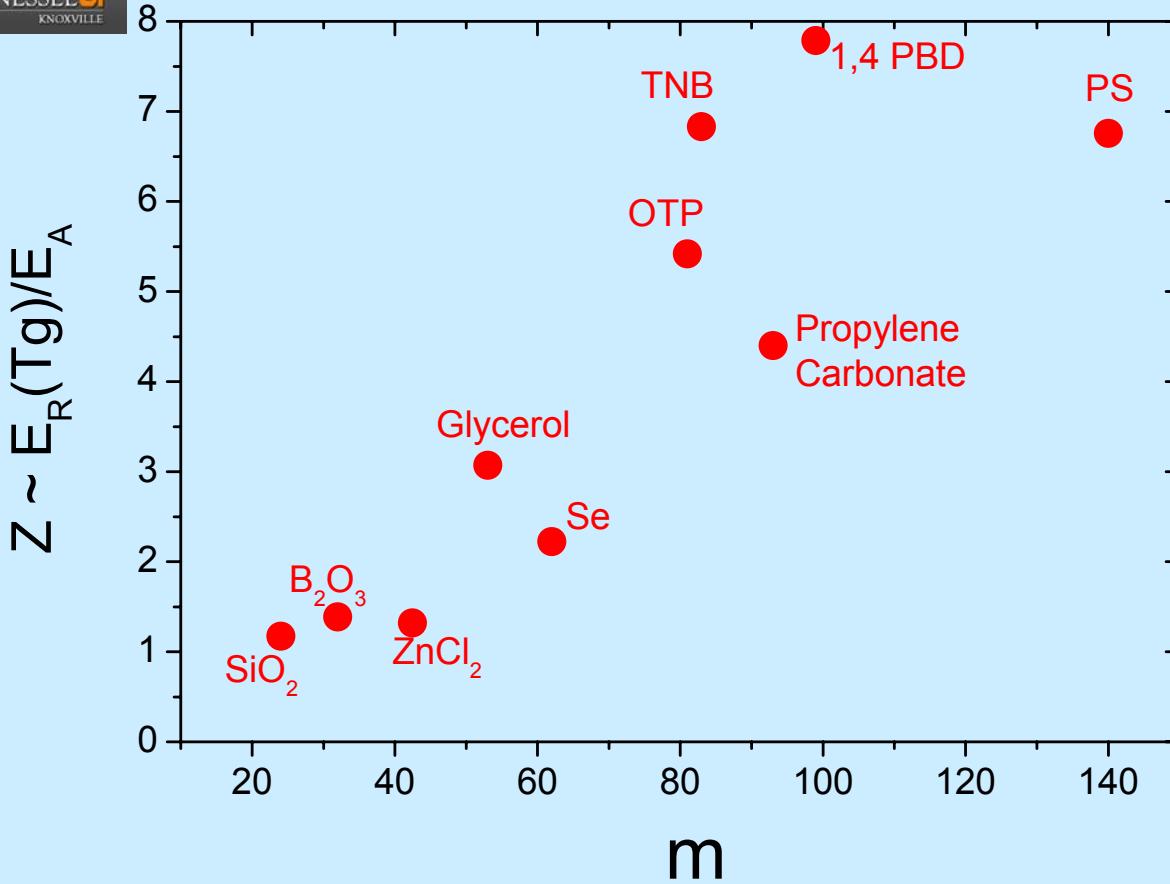
AG cooperativity parameter Z estimated from the change in activation energy.

E_A – high temperature limit (Arrhenius regime)

$E_R(Tg)$ - activation energy at Tg estimated from VFT.

➢The parameter Z (as expected) has clear correlation to fragility and differs significantly between strong and fragile systems.
➢It is inconsistent with rather universal ξ/a at Tg reported in many papers.

➢Despite their importance, *dynamic heterogeneity and cooperativity remain ill-defined quantities*.

➢There is no correlation between fragility and dynamic heterogeneity length scale. ξ seems to be dependent on the type of the system (e.g. H-bonding, polymers).

➢One should always separate volume and energetic contributions to fragility. Only activation volume at Tg correlates to the heterogeneity volume.

➢*Does the Adam-Gibbs approach provide the right picture?*