A perspective on the concept of fragility

Gilles Tarjus

(LPTMC, CNRS/Univ. Paris 6)

Christiane Alba-Simionesco

(LLB, CNRS/CEA)

The concept of fragility....

(Kinetic) fragility -> how quickly transport coefficients and relaxation times increase as one cools a glass-forming system

- **Generic property**: In most glass-forming liquids and polymers the T-dependence is stronger than an Arrhenius one.

- **Specific measure**: The degree of super-Arrhenius behavior is a material property.

Usefulness of the concept of fragility

- A unifying classification scheme of all glass-forming systems.
- Taken as an intrinsic property of the dynamical slowdown, it has led to a variety of **empirical correlations** with other material-specific properties (associated with thermodynamics, slow or fast dynamics) => a key for understanding the glass transition?

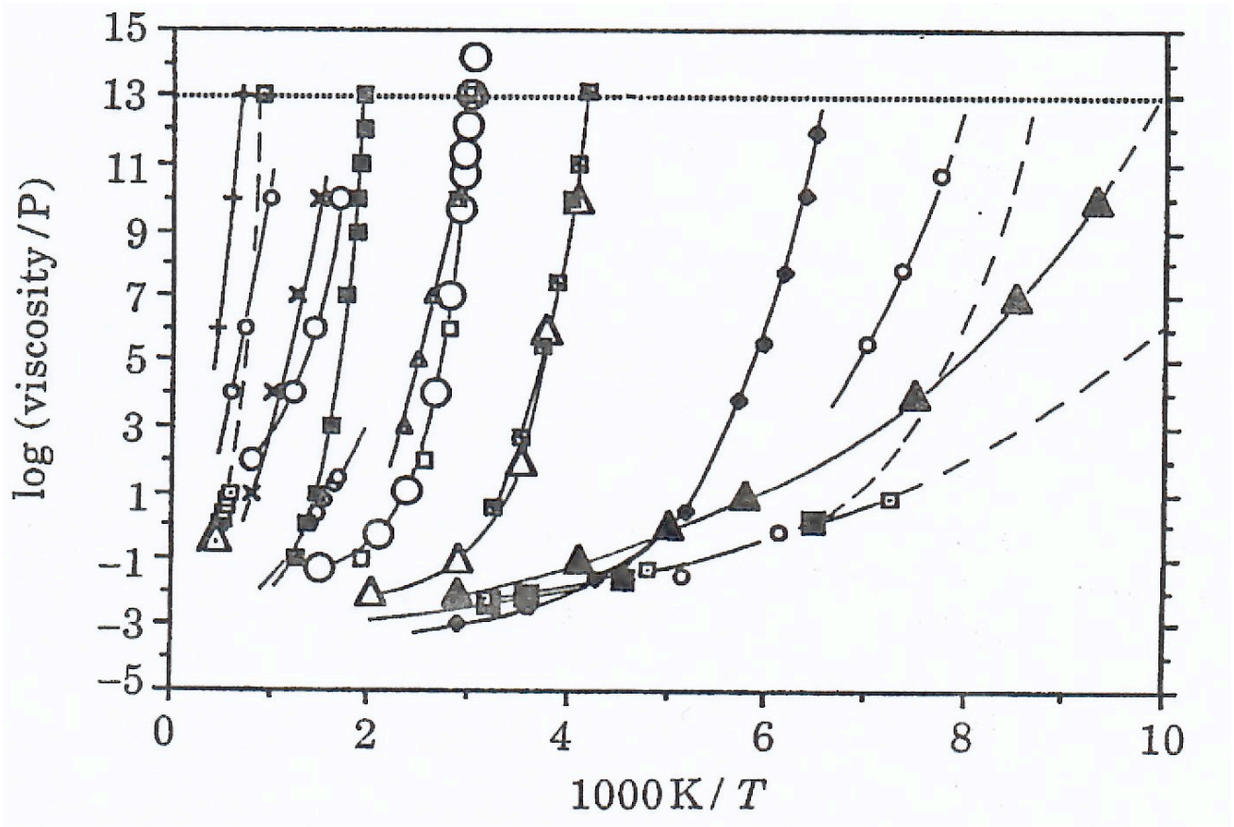
Assessing its operational and fundamental relevance: A selection of questions

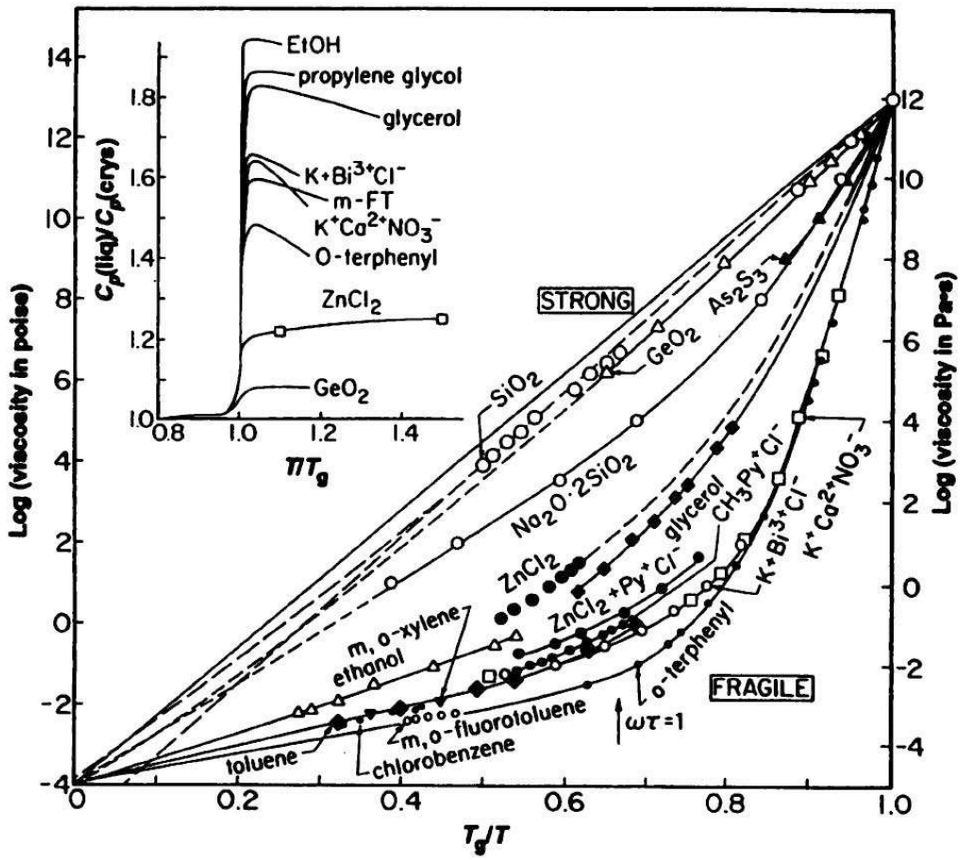
- How to best quantify fragility?
- How significant are the observed differences in fragility?
- Is fragility connected to "cooperativity"?

How to best quantify fragility?

Choice of a rescaling temperature
The conventional choice: T_g

Arrhenius plot without and with T scaled to T_g





Standard measure = Steepness index at T_g: $m = \left.\dfrac{\partial \log_{10}(\tau(T)/\tau_\infty}{\partial(T_g/T)}\right|_{T_g}$

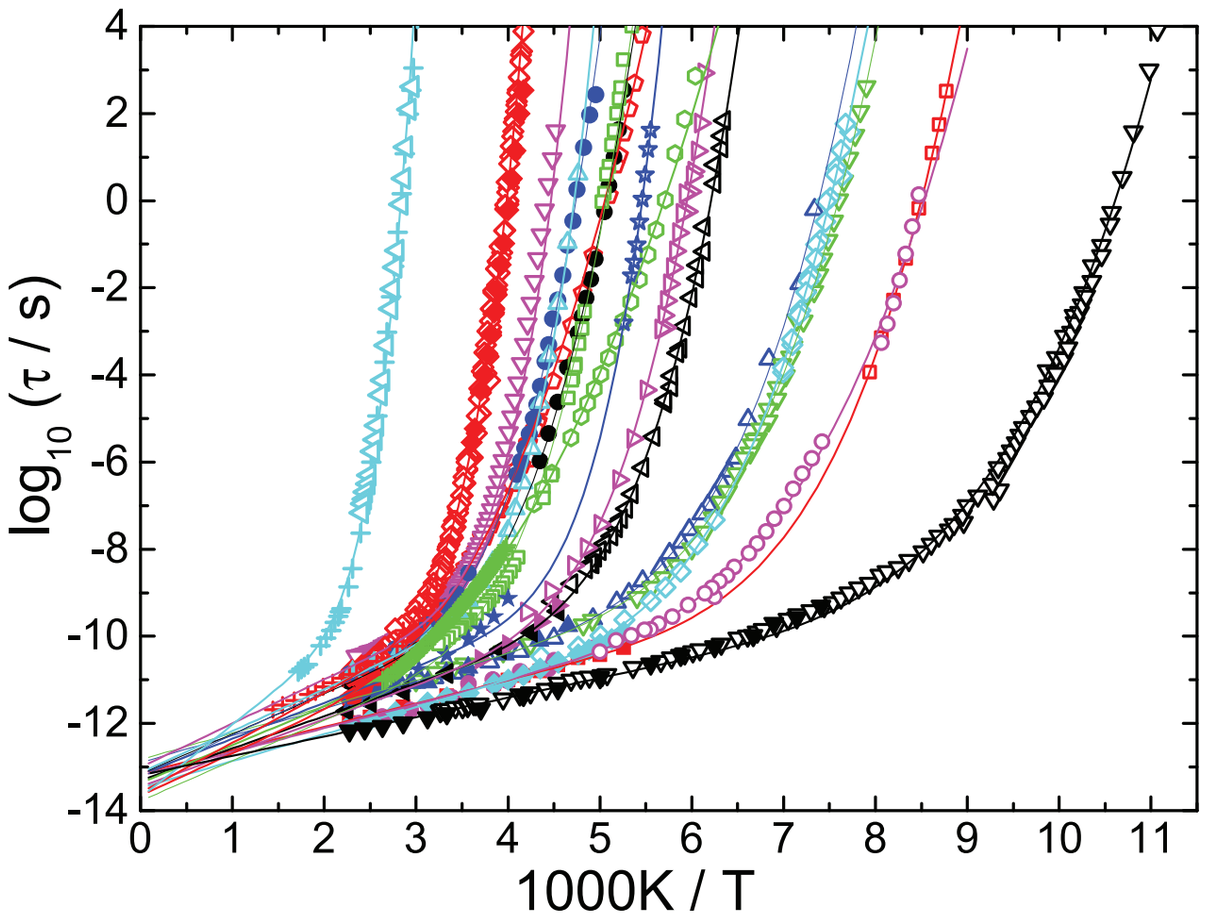
Shortcomings...

- Does not allow a comparison with liquid models studied by computer simulation,
- May include irrelevant effects, e.g. the contribution from the high-T dynamics,
- Depends on a time scale.

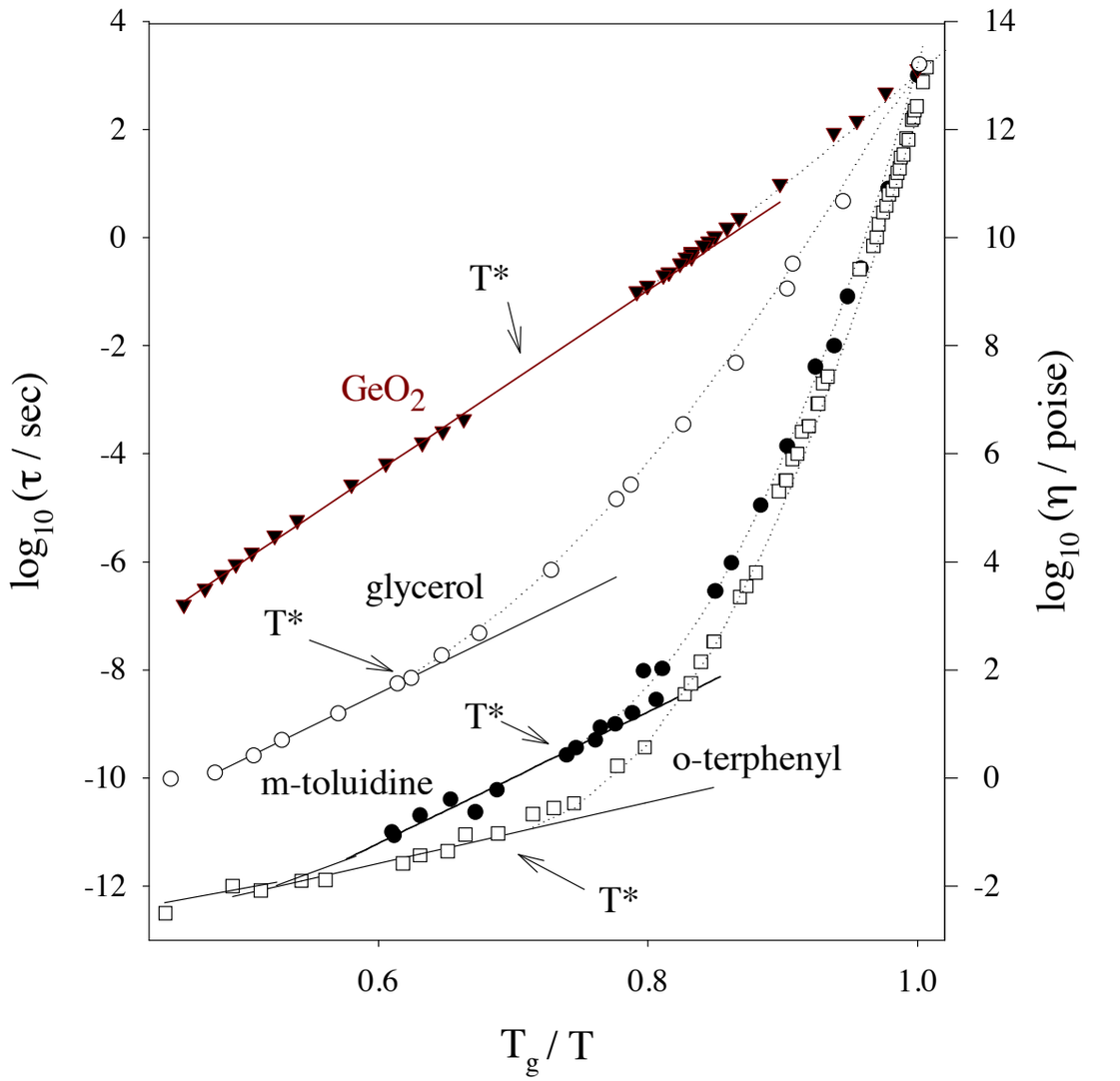
The high-T slowdown is intertwined with fragility: "strength" vs fragility

- At high T: $\tau(T)/\tau_\infty \simeq e^{\frac{E_\infty}{T}}$
- At low T: $\tau(T)/\tau_\infty \simeq e^{\frac{E(T)}{T}}$, with $E(T) = E_\infty + \Delta E(T)$

=> The steepness index at T_g depends on E_∞ [Ferrer et al., 1999]

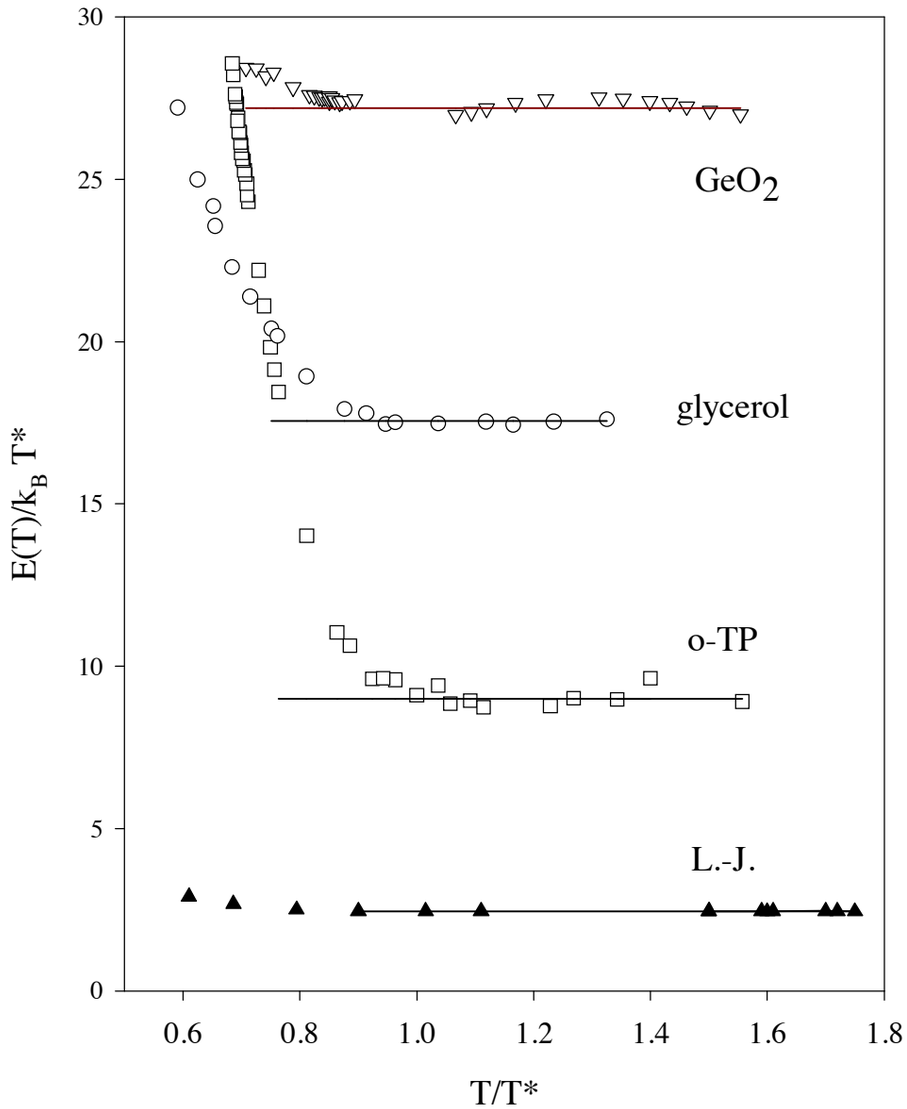


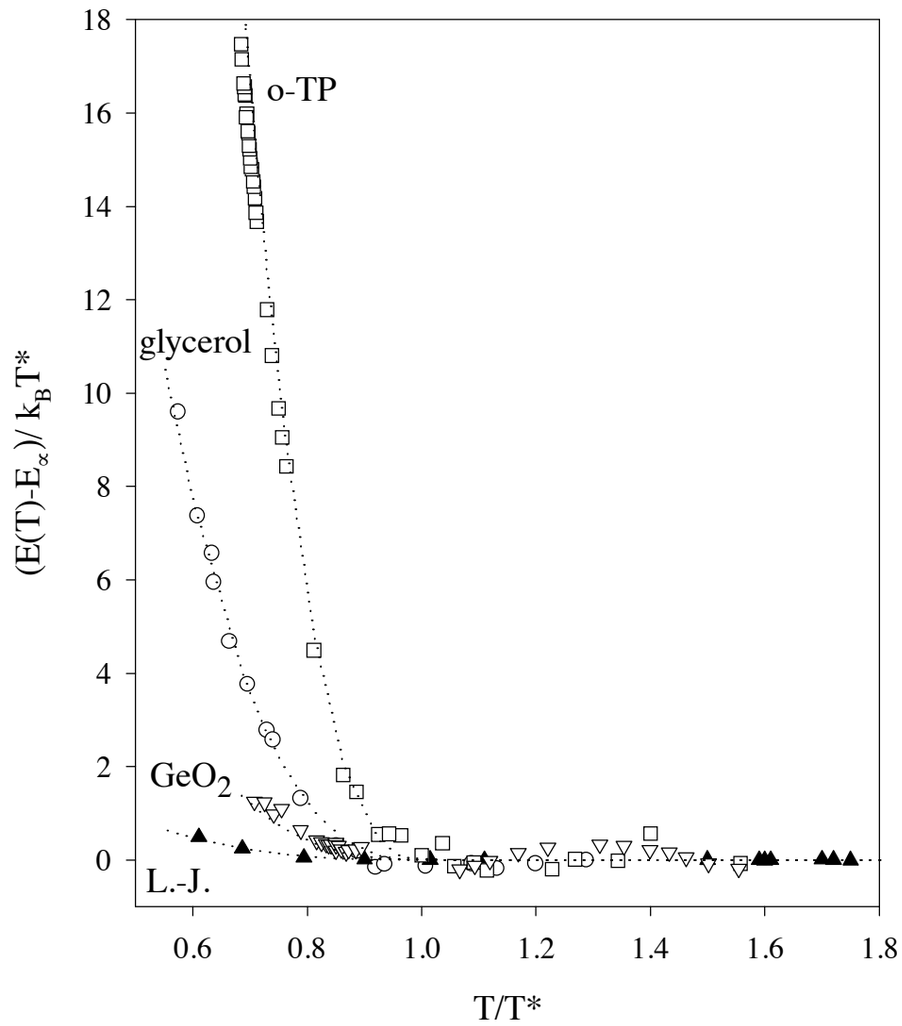
Arrhenius plot of the reorientational time of molecular liquids [Roessler et al., 2013]



A way out... but which requires additional manipulations

- Scale to a high (crossover, onset) temperature T*
- Define a cooperative contribution $E(T)-E_\infty$





[GT,Kivelson,Viot, 2000]

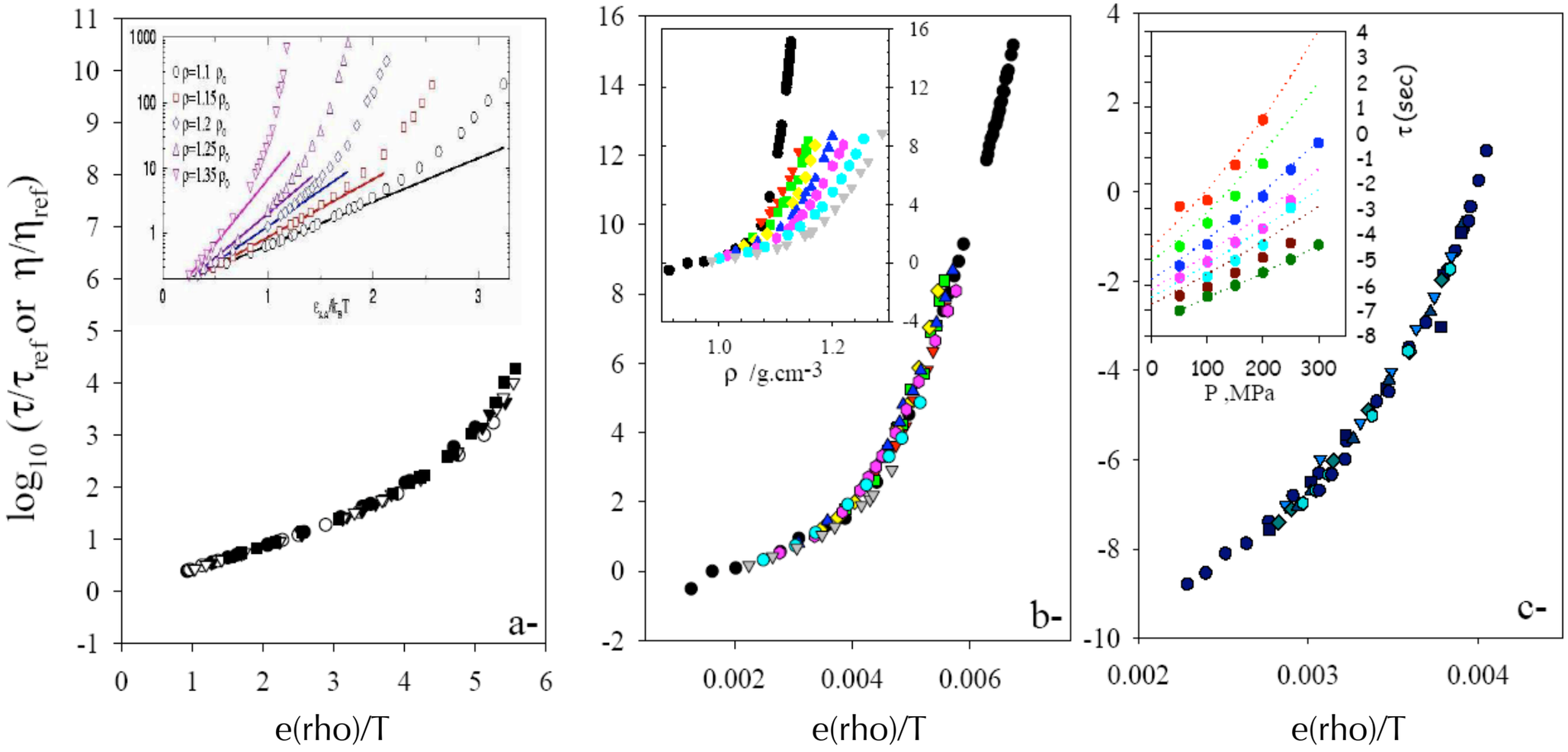
Fragility and thermodynamic path: isochoric vs isobaric fragility

At constant P, the slowdown of relaxation also depends on the increase of density.

=> A better **intrinsic** measure of the T dependence is then the isochoric fragility... but it is a priori harder to access experimentally.

Empirical (approximate) rescaling of density effect in glass-forming liquids and polymers

$$\log\left(\frac{\tau_\alpha(\rho,T)}{\tau_\infty}\right) = F\left(\frac{e(\rho)}{T}\right)$$



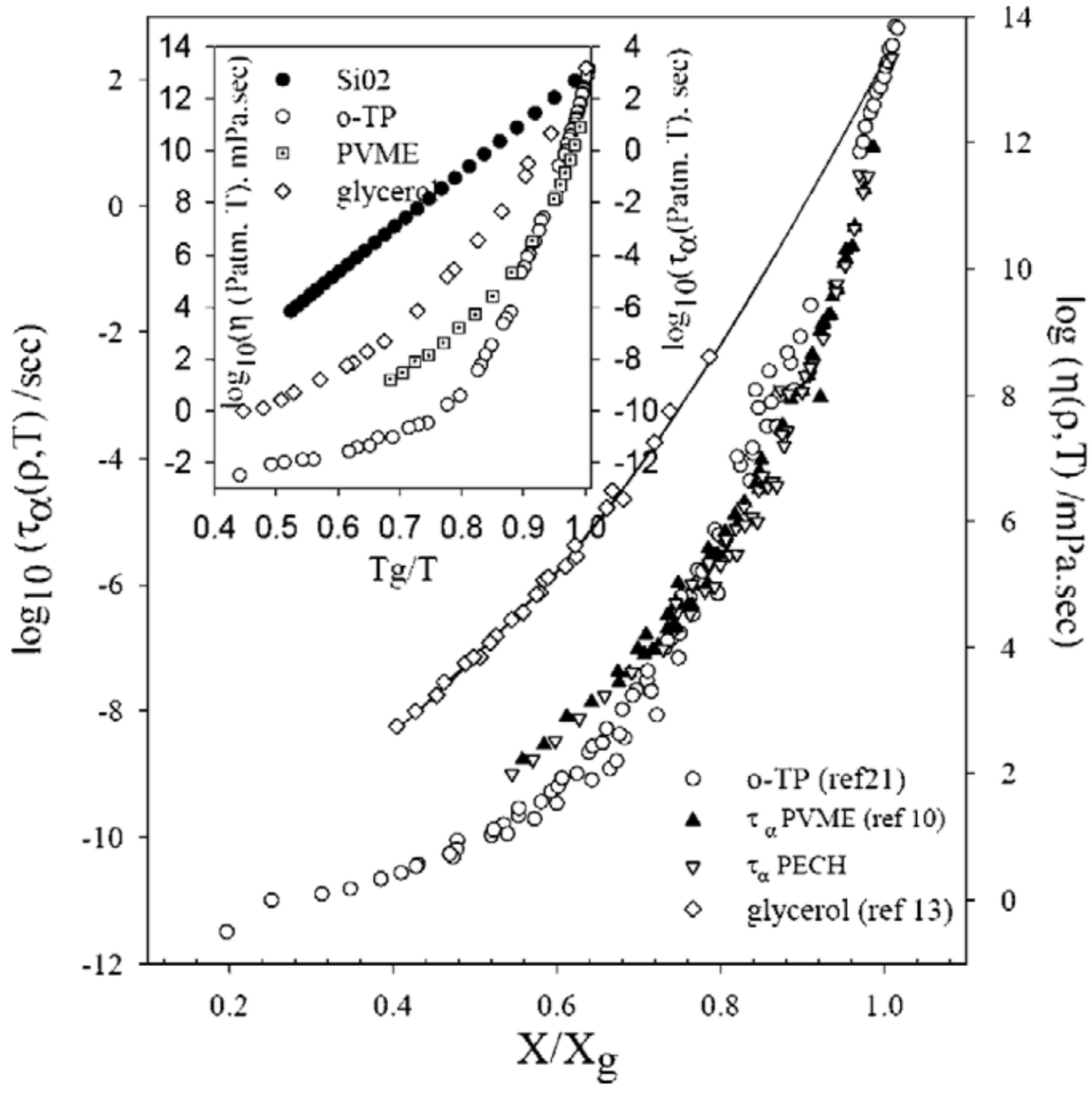
(a) Binary Lennard-Jones model; (b) Molecular liquid (o-TP); (c) Polymer (PVME)

[Alba-Simionesco et al., 2002-2005]

- Many more examples: see M. Roland et al. 2004-2005, and others...

Consequence of the density scaling: The isochoric fragility is independent of density!

Modified Angell plot: log(τ) vs X/Xg, with X=e(ρ)/T [CAS,GT,2004]



How significant are the observed differences in fragility?

In glass-forming liquids and polymers

The (isobaric) fragility index varies from 20 (silica) to 80-100 (fragile molecular liquids) and 150 or more (polymers).

However, one should account for possibly irrelevant or spurious effects,

- the role of the bare activation energy E_∞
- the role of density
- in polymers, the specific effects associated with the chain structure and the entropy of mixing

[Dalle-Ferrier et al, 2009, Novikov-Sokolov & coll.],

which may reduce the span of intrinsic fragilities.

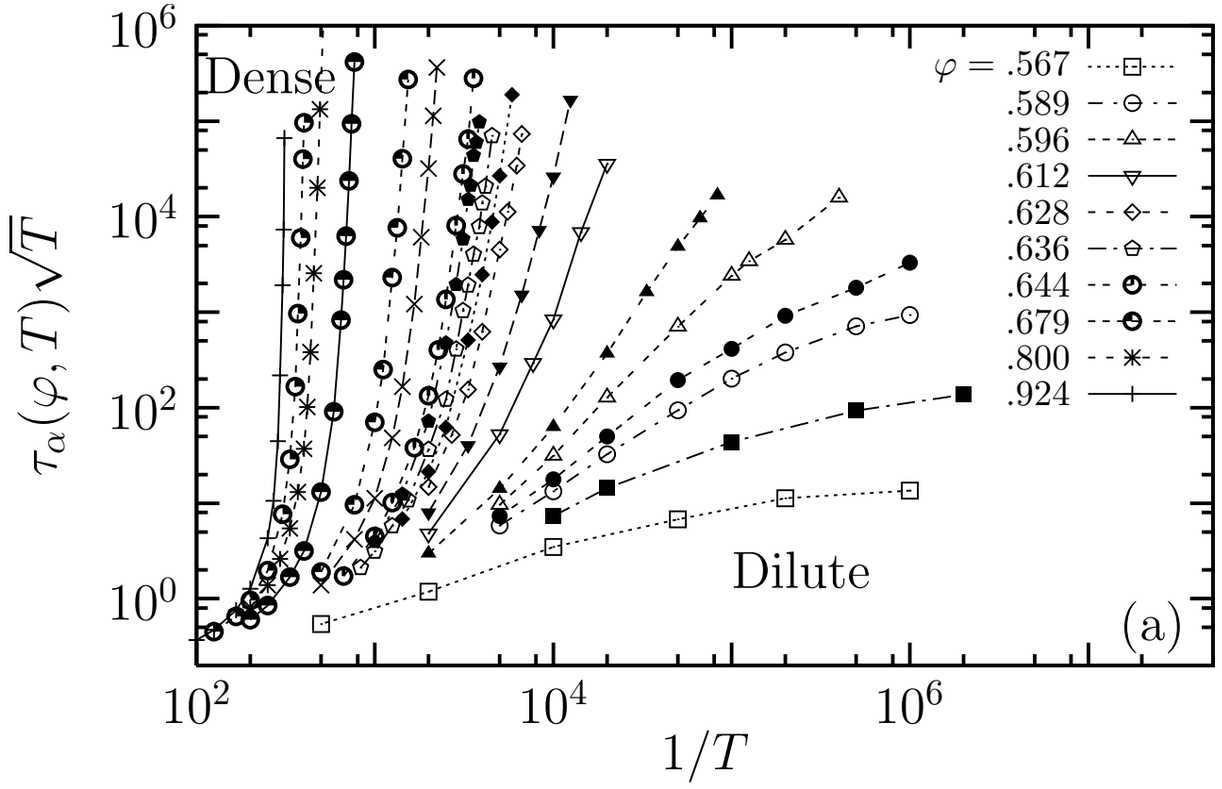
Quite a different behavior in soft-condensed (jamming) systems...

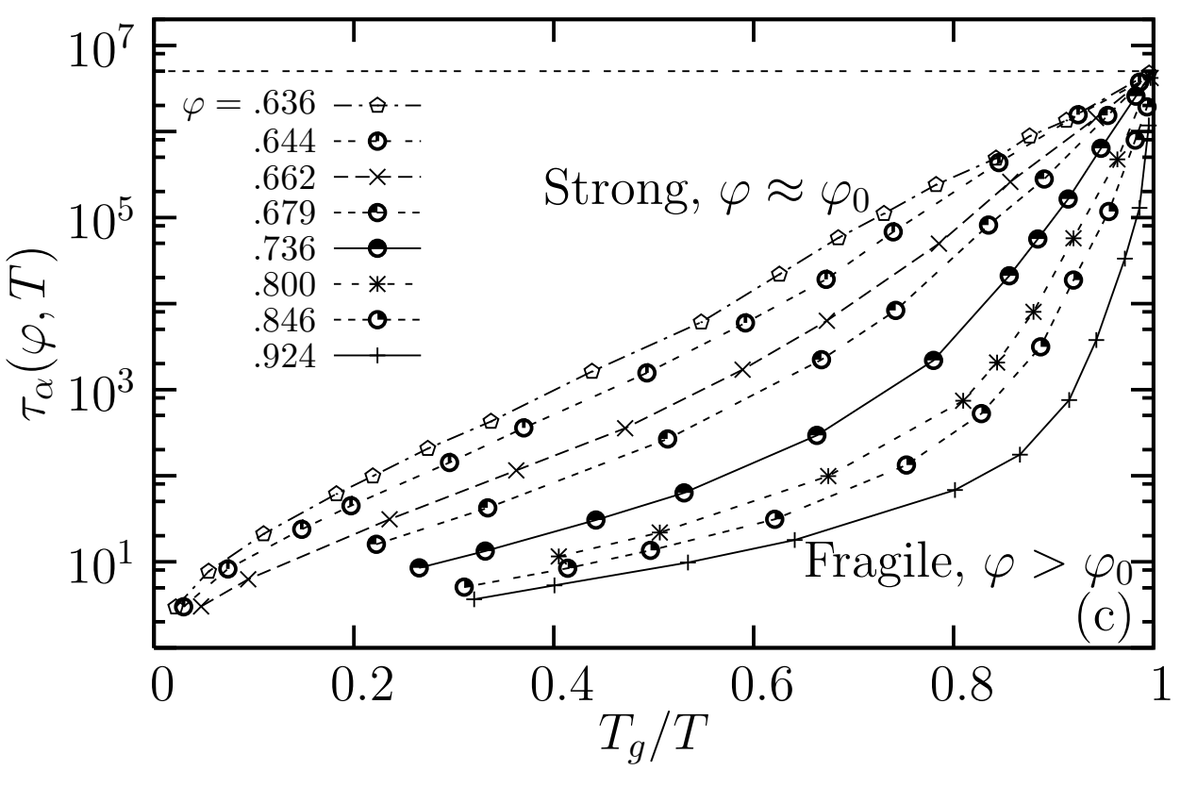
Fragility in models for foams and emulsions

- Simple models of spherical particles interacting via truncated repulsive potentials:

$$v(r) = \epsilon(1 - r/\sigma)^{\alpha} \text{ for } r < \sigma$$

- At low T, the isochoric fragility can vary by one order of magnitude or more. [Berthier,Witten, 2009]

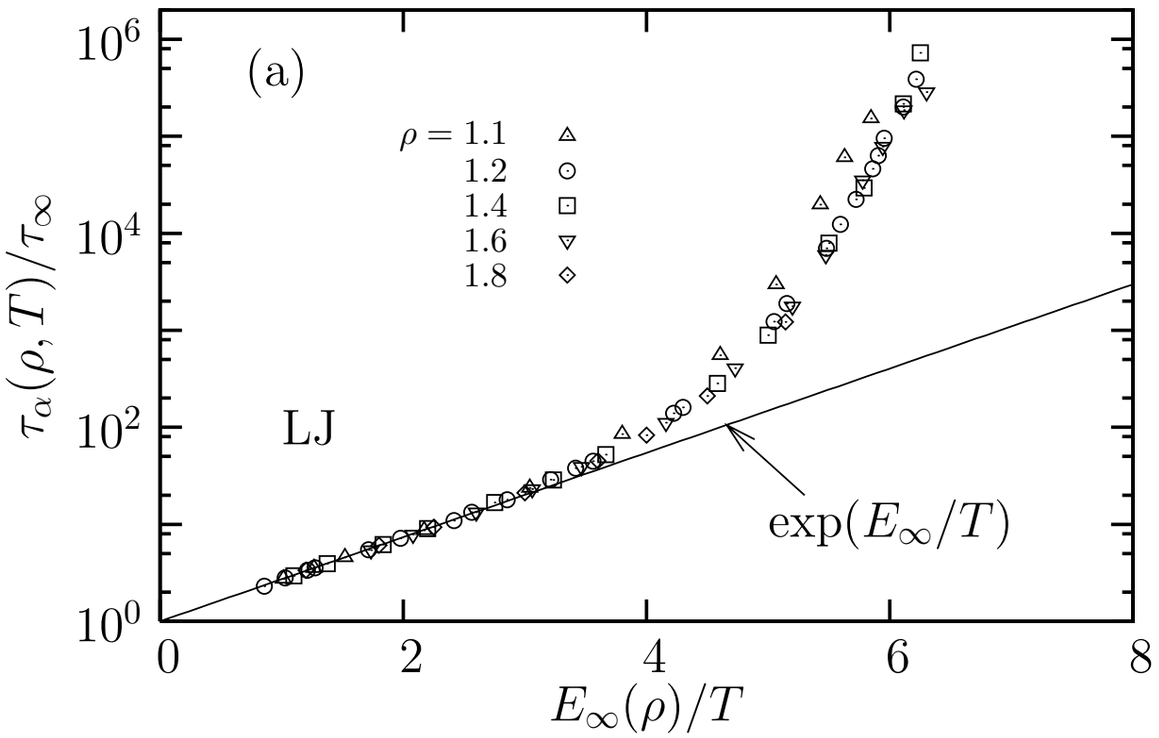




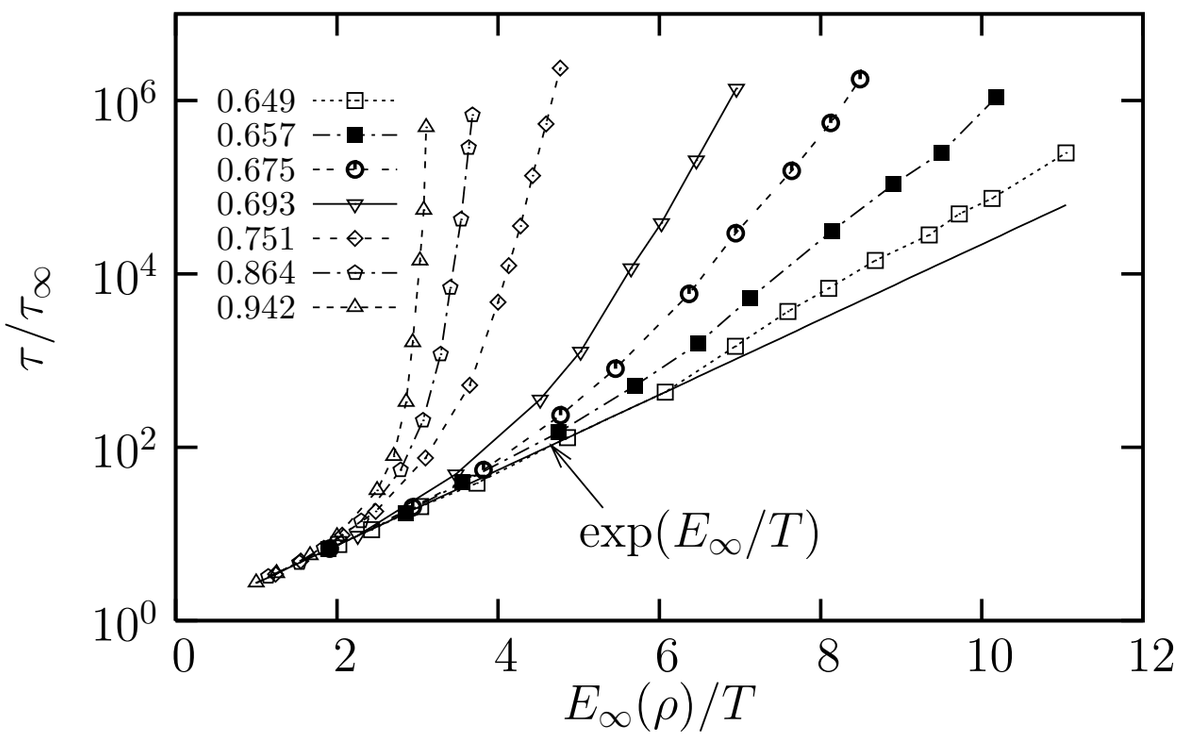
Jamming systems at low T behave differently from glass-forming liquids

- In glass-forming liquids and polymers, the density scaling implies a density independent isochoric fragility.
- In jamming systems, the low-T behavior is that of an effective hard-sphere model => strong dependence of the isochoric fragility.

Lennard-Jones model: density scaling

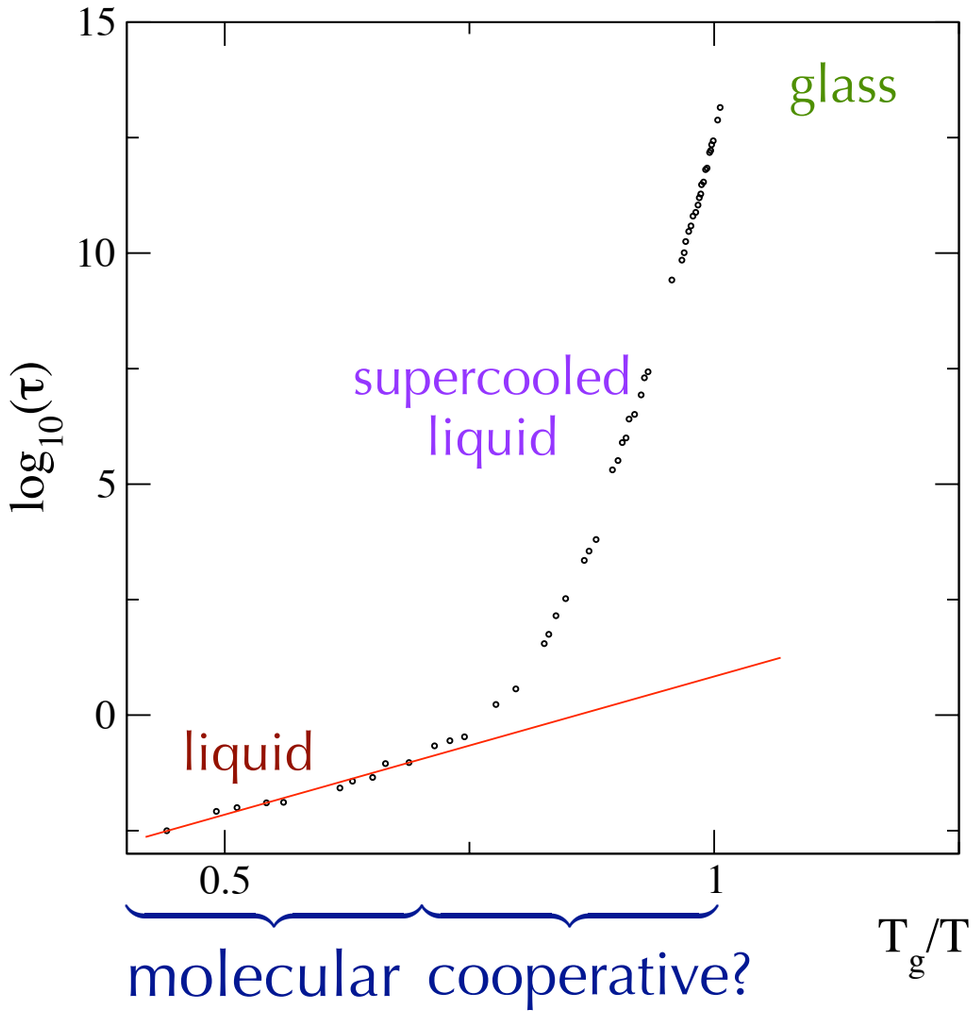


Truncated repulsive model: no scaling



Is fragility connected to "cooperativity"?

Generic fragile character of slowing down suggests cooperativity



- Fragility => quasi-universal super-Arrhenius T-dependence
- In the context of thermal activation: **Cooperativity** => many degrees of freedom and molecules conspire to make relaxation possible
  => barrier determined by the minimum number of cooperatively (collectively) involved molecules and varies with T.

Beyond Adam-Gibbs: looking for a growing length scale

Relation between the relaxation time and a (static) length:
From heuristic arguments,

$$\log(\tau(T)/\tau_\infty) \simeq \frac{A}{T}\xi(T)^\psi$$

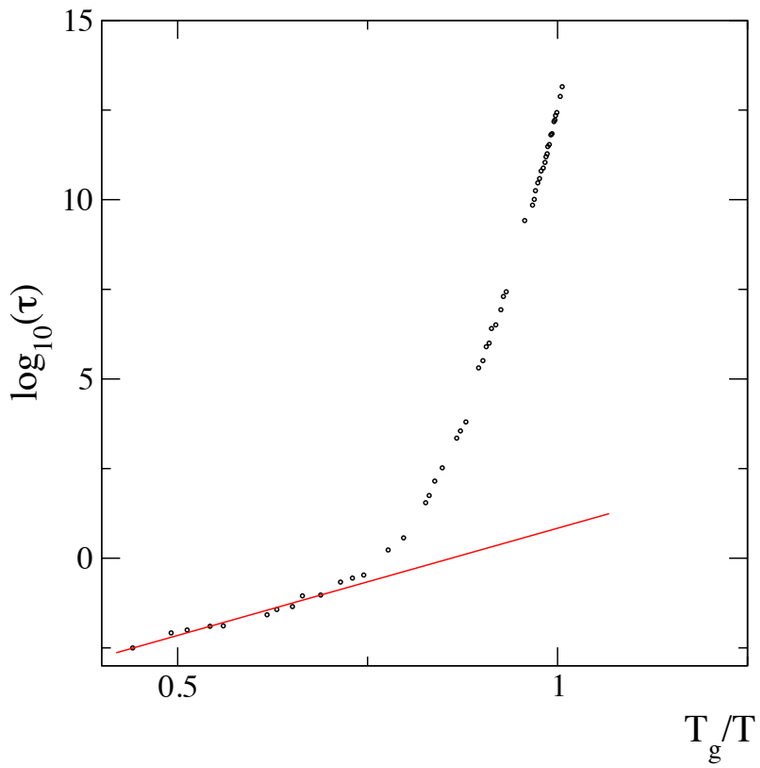
with $\psi \leq d$.

- Rigorous upper bound with $\psi = d$ [Montanari-Semerjian, 2006].
- At high T, $A(\xi_\infty)^\psi = E_\infty$.
- Involves static 'point-to-set' correlations, associated e.g. with the influence of amorphous boundary conditions.

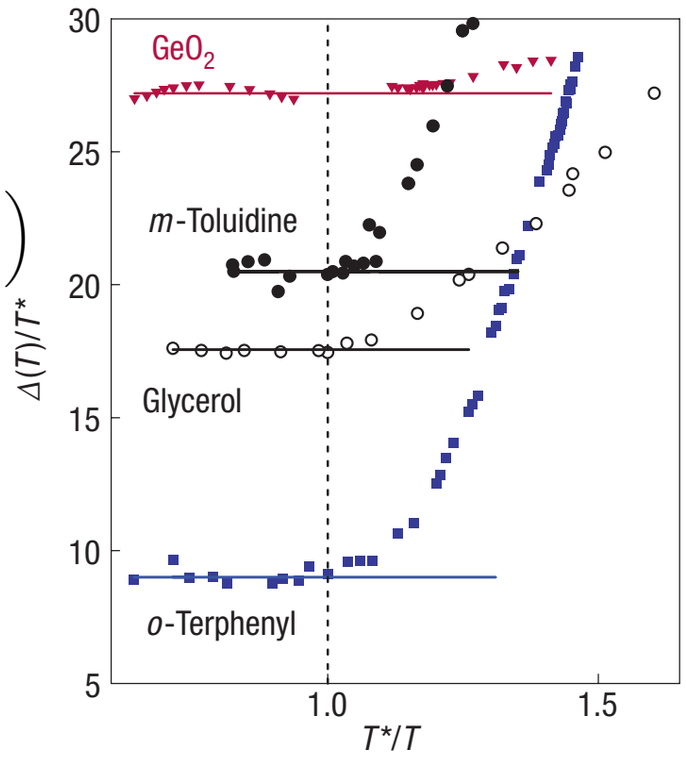
Fragility implies a growing length scale

$$\log(\tau(T)/\tau_\infty) \simeq \frac{E_\infty}{T}(\xi(T)/\xi_\infty)^\psi$$

Super-Arrhenius dependence of τ(T) => At some point, ξ(T) must grow when temperature T decreases => cooperativity!



$$\tau \simeq \tau_\infty \exp\left(\frac{E(T)}{T}\right)$$



A high fragility helps observing cooperative behavior but *per se* the magnitude does not tell us anything on its nature (theory dependent).

Conclusion

- The concept of fragility describes both a generic, universal, character of glass-formers (the super-Arrhenius T-dependence) and a material-specific property.

- Not easy to define an intrinsic measure of fragility, which would exclude as much as possible spurious and irrelevant effects and would allow more meaningful correlations with other characteristics of glass-formers.

- The fragility of glass-forming liquids and polymers appears of different nature than that of soft-condensed jamming systems.

- Fragility seems to implies cooperativity of the dynamics, but no obvious implication from the magnitude of the fragility.