An overview of the theories of the glass transition

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Outline

- Diversity of views and questions on glasses and glass formation.
- What is there to be explained about the glass transition ?
- Diversity of theoretical approaches.
- What experimental evidence for growing collective behavior in glass-forming liquids ?

Diversity of views, Diversity of questions

on glasses, glassformers, and the glass transition

With a broad meaning:

“Glass” = Jammed/frozen system in a disordered state, generally out of equilibrium.

Includes among others

- “soft glasses”: colloidal suspensions, foams, emulsions, granular media,
- spin glasses, orientational glasses, vortex glasses, electron glasses, etc...
- proteins...

Here, I focus on

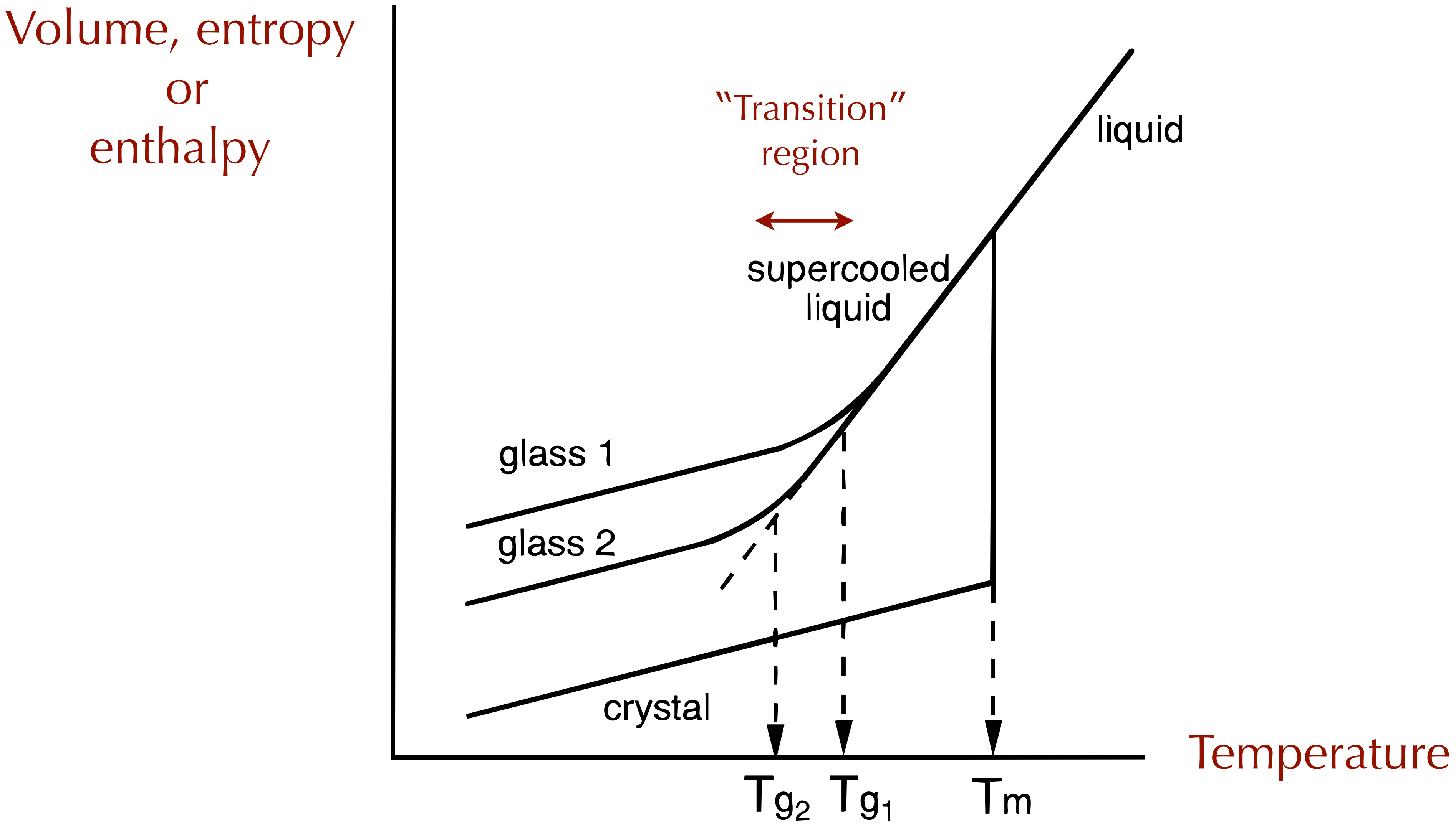
Glasses formed by cooling a liquid

This includes

- ✴ silica and inorganic glasses, ionic mixtures, organic molecular (hydrogen-bonded and van der Waals) glasses,
- ✴ polymers (plastics),
- ✴ metallic glasses.

However, one could envisage a broader scope (“jamming”)

Glass formation by cooling



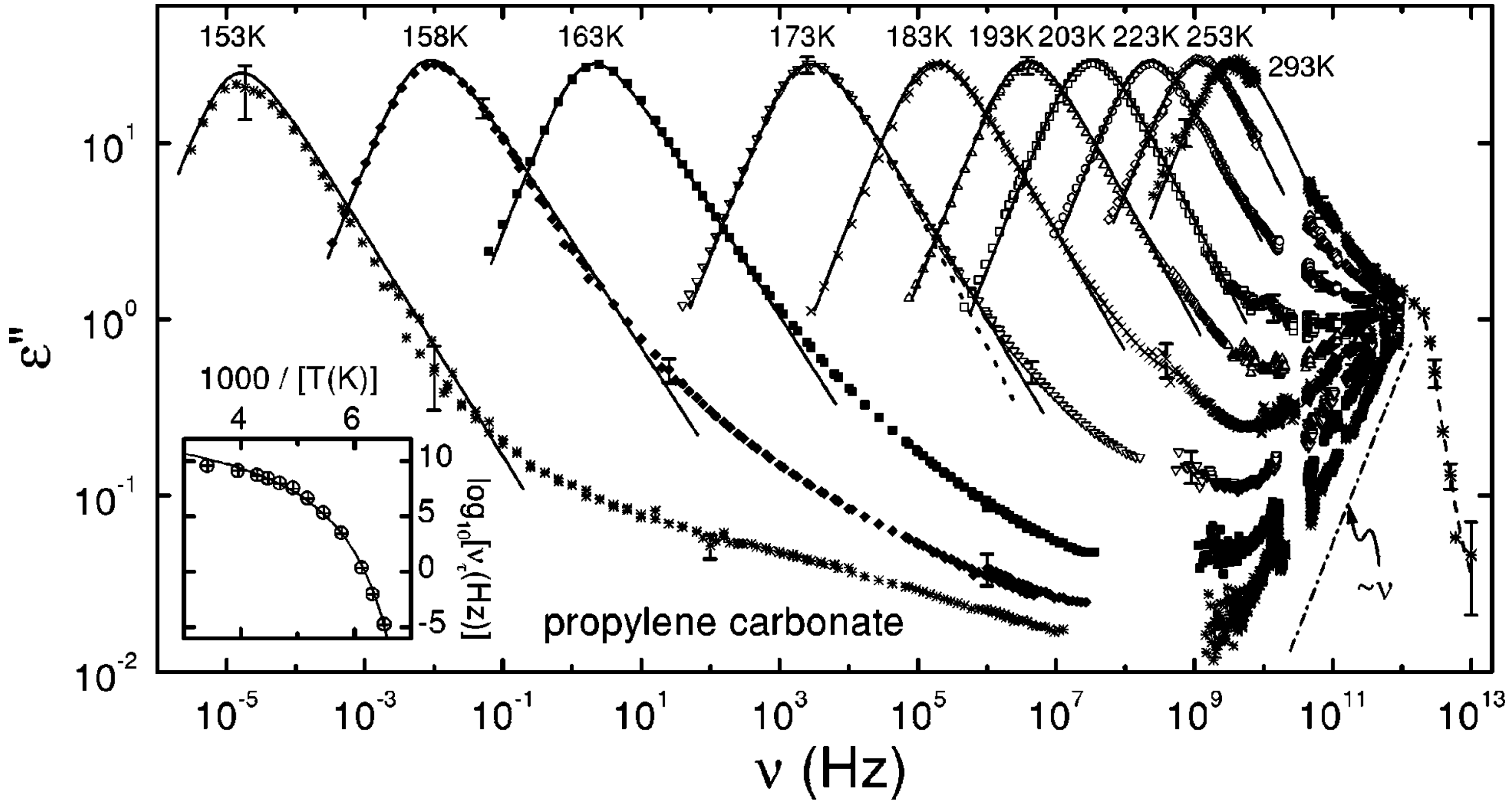
Glass
(out-of-equilibrium)

Supercooled liquid
(metastable)

Variety of questions depending on the temperature regime of interest

What is there to be explained about the glass “transition” ?

One of the most spectacular phenomena in all of physics in terms of dynamical range

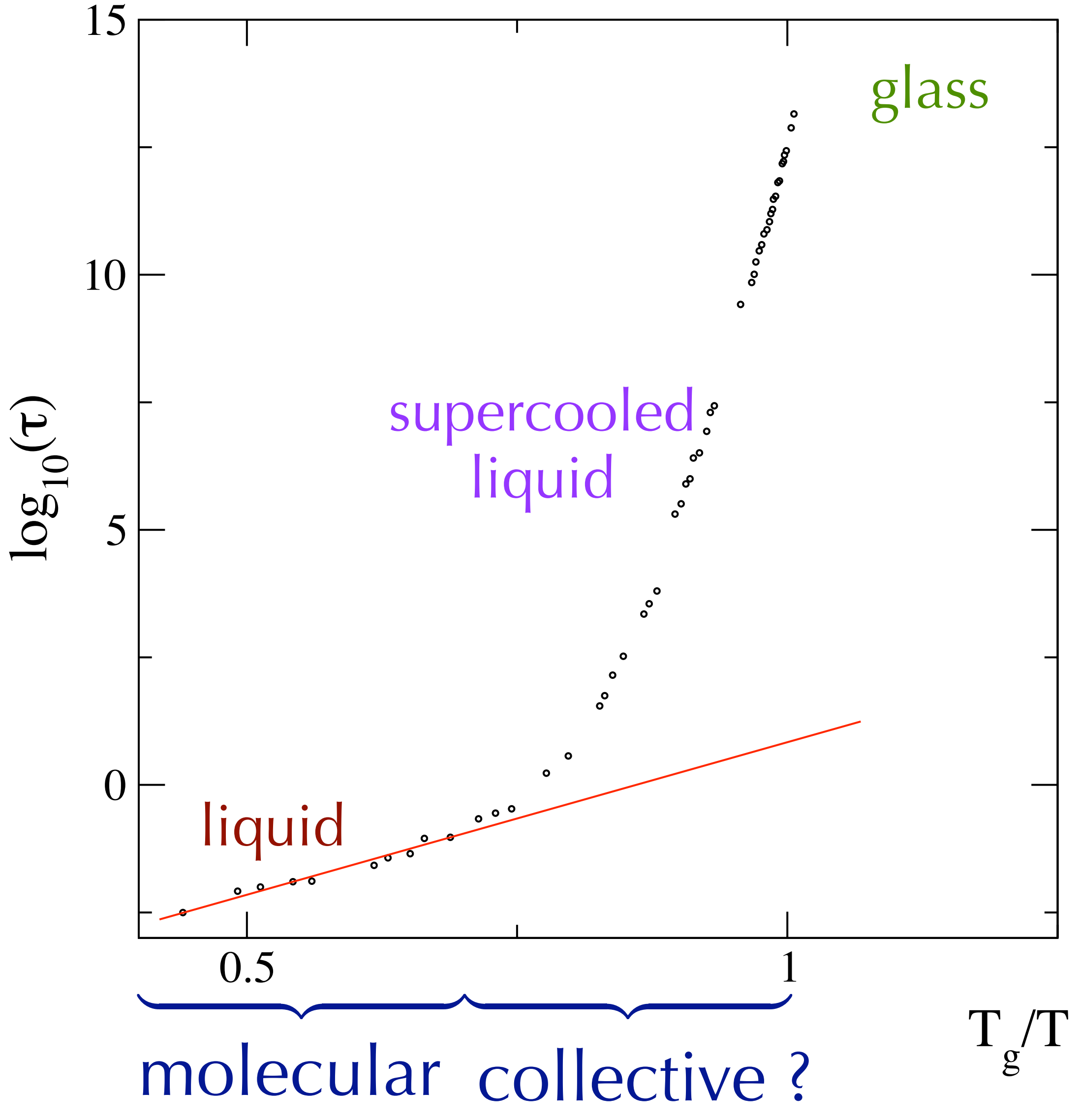


$$\omega_{peak} \sim \frac{1}{\tau_{relax}}$$

Frequency-dependent dielectric susceptibility (imaginary part) for liquid propylene carbonate (Lunkenheimer et al., JCP 2001)

Dramatic temperature dependence of relaxation time and viscosity

Arrhenius plot of the relaxation time of liquid ortho-terphenyl

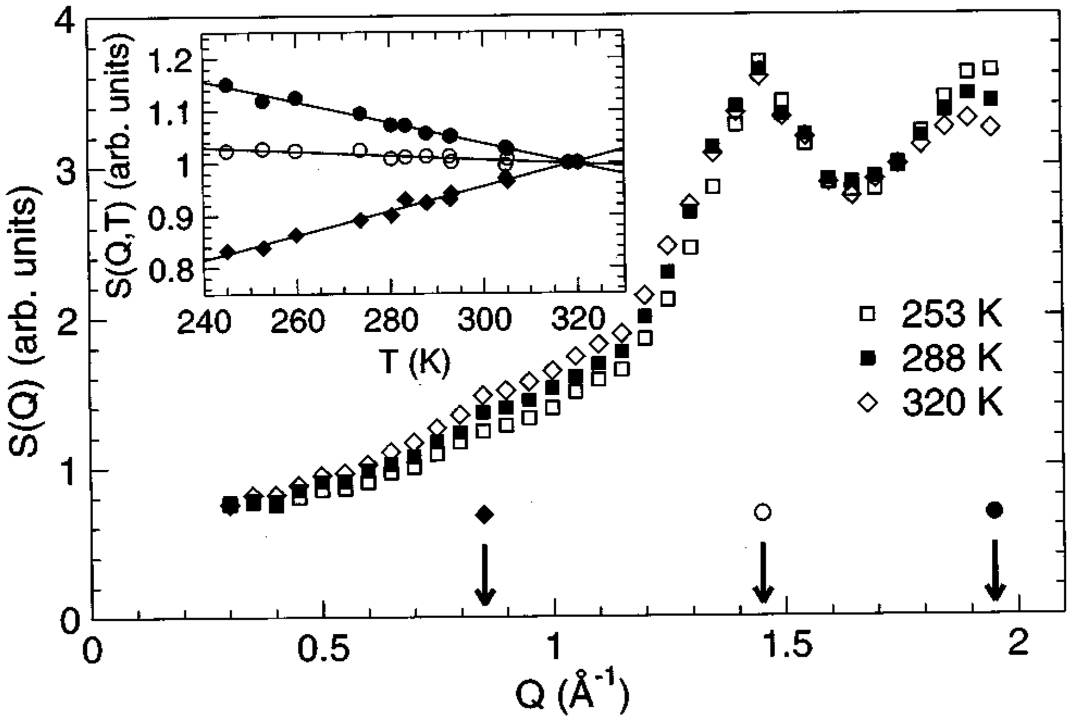


- Phenomenon is universal and spectacular
- Slowing down faster than anticipated from high-T behavior

Tempting to look for a detail-independent collective explanation!

Expected collective behavior, but....

- No observed, nor nearby, singularity in the dynamics and the thermodynamics.
- Correlation length obtained from the pair density correlation function (structure factor) is small and does not vary with temperature.



Static structure factor $S(Q)$ of liquid o-TP at several temperatures from just below melting (T_m=329K) to just above the glass transition (T_g=243K).

(Tölle et al.,1997)

Diversity of theoretical approaches

What makes the problem interesting ?
What would it take to declare it solved ?

Atomic-level description & local relaxation mechanisms

versus

Coarse-graining, scaling & underlying critical points

- If the collective glass-forming behavior assigned to a **critical point**, still variety of theories: the critical point may be either

Dynamic or **static**

Unreachable or **avoided**

Theories based on an underlying dynamic transition

- **Mode-coupling theory**: an avoided transition at $T_c > T_g$

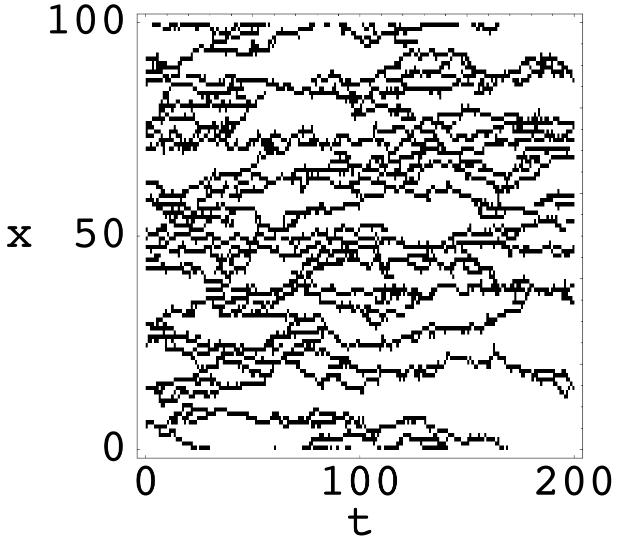
[Gotze and coll (80's to now)]

Self-consistent kinetic freezing: relaxation channel for density fluctuations via product of density modes.

- **Dynamical facilitation and kinetic constraints**: an unreachable critical point at $T = 0$.

[Fredrickson-Andersen (80's)... Garrahan-Chandler]

Sparse mobility defects in an essentially frozen background;
mobility triggers mobility.

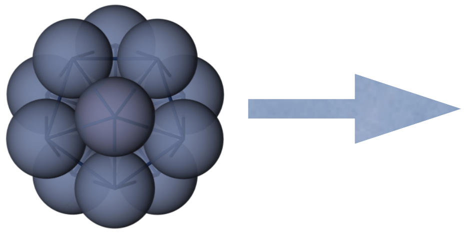


Theories based on an underlying thermodynamic transition

- **Frustration-based approach**: an avoided transition at $T^* > T_g$

[Nelson, Sadoc-Mosseri (80‘s)... Kivelson, GT and coll.]

Frustration = incompatibility between extension of the local order preferred in a liquid and tiling of the whole space

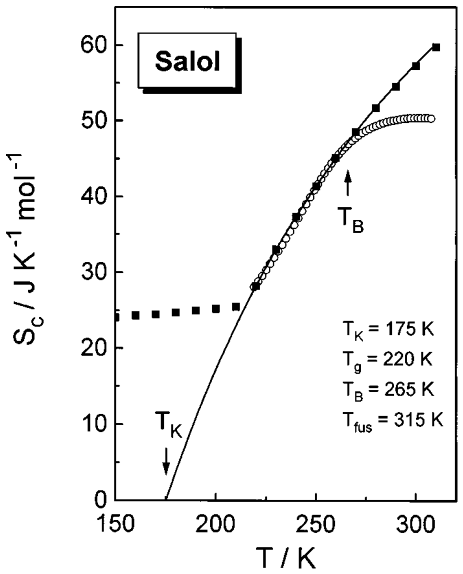


No icosahedral xtal

- **Random first-order transition theory**: an unreachable transition at $T_K < T_g$

[Wolynes and coll. (80‘s to now) + many...]

Exponentially large number of metastable states that trap the liquid (configurational entropy) between T_c and T_K



Different theoretical descriptions of the same physics!

No consensus on the most relevant characteristic temperature

Experimental: T_m, T_g

Unreachable (extrapolated):

$T_0 \simeq T_K$ (RFOT),

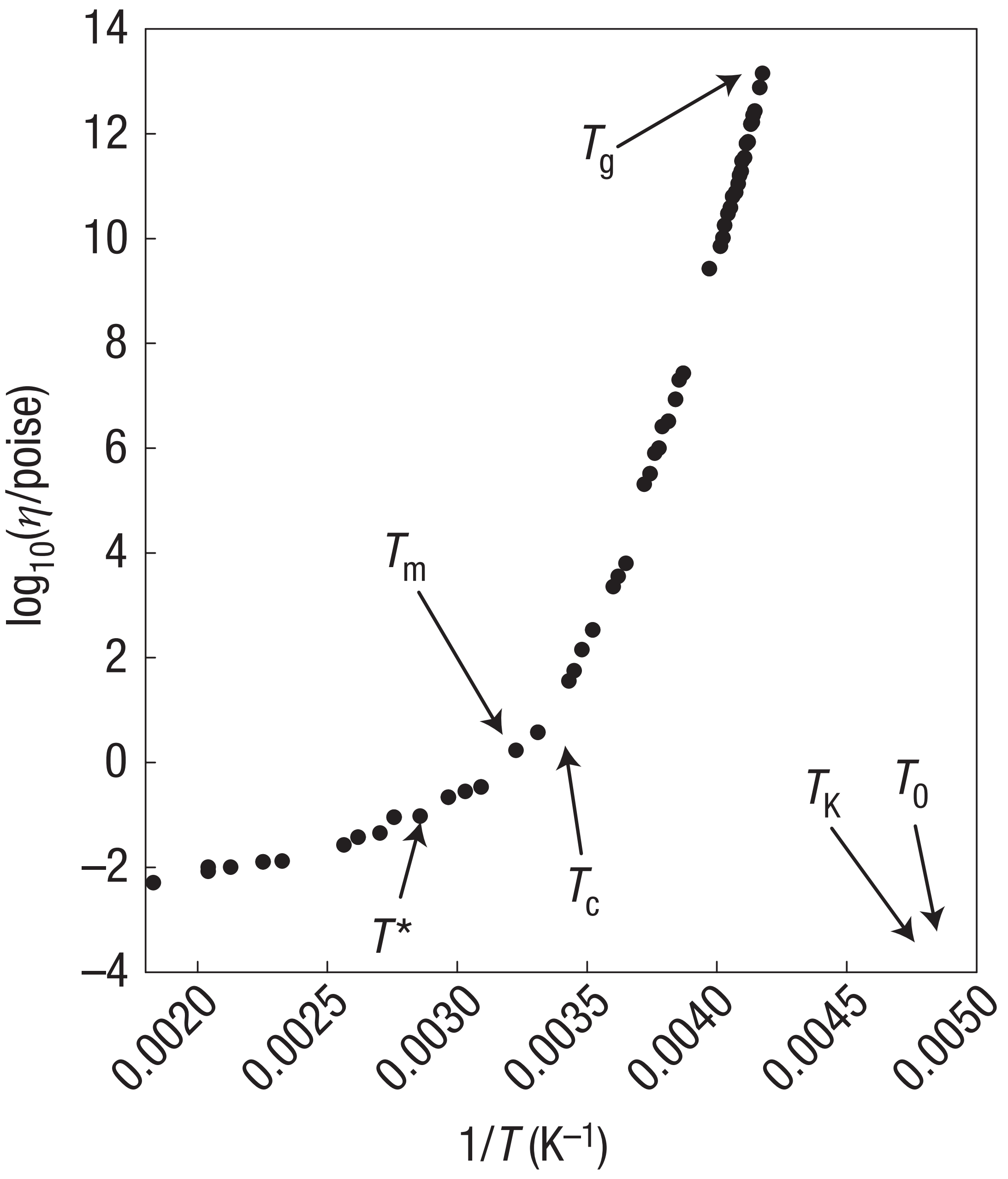
T = 0 (facilitation).

Avoided (crossover):

T* (frustration),

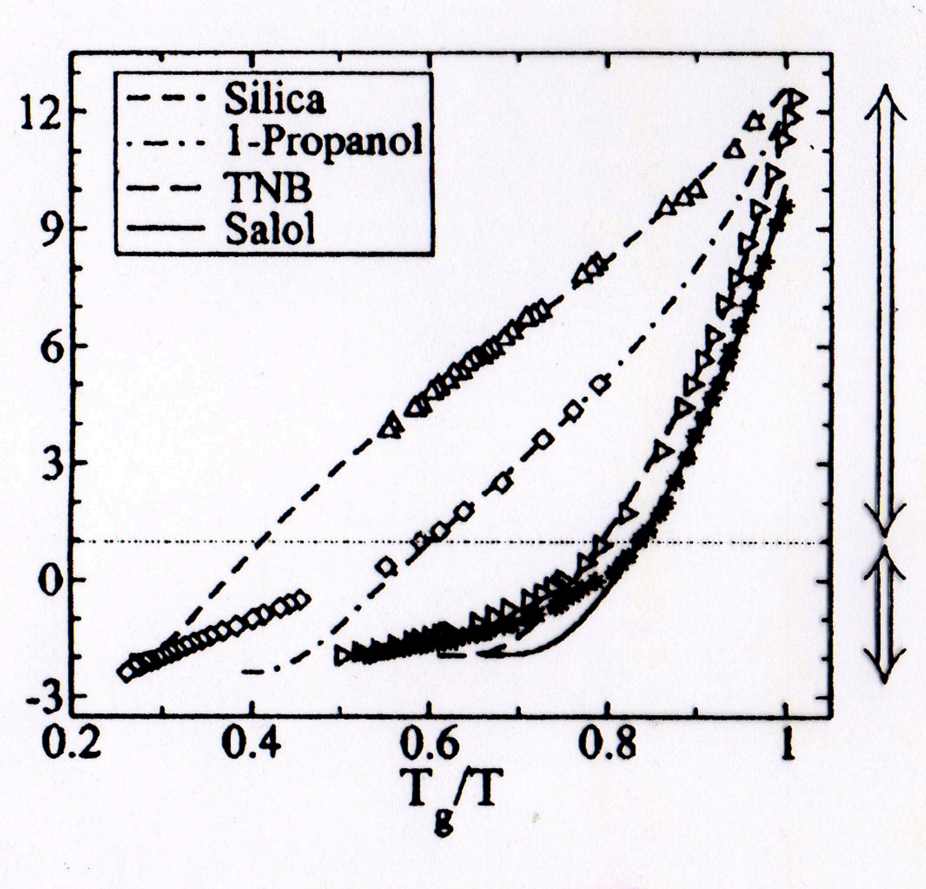
T_c (MCT).

(T-dependent viscosity of o-TP)

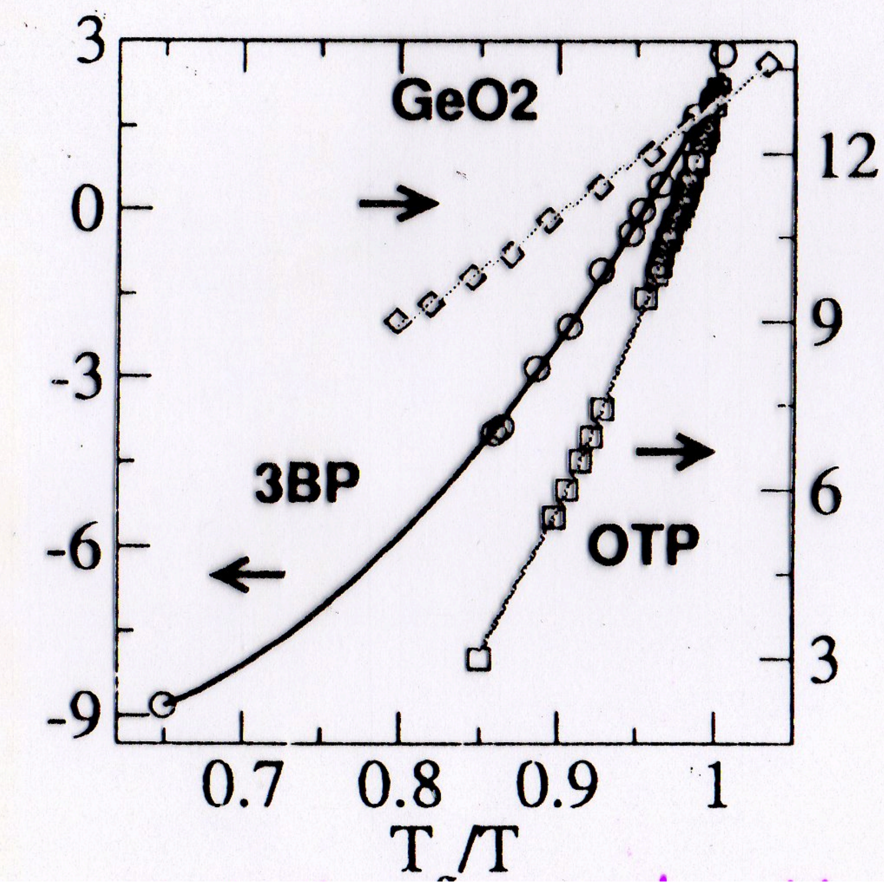


Weak constraints from comparison to experimental data...

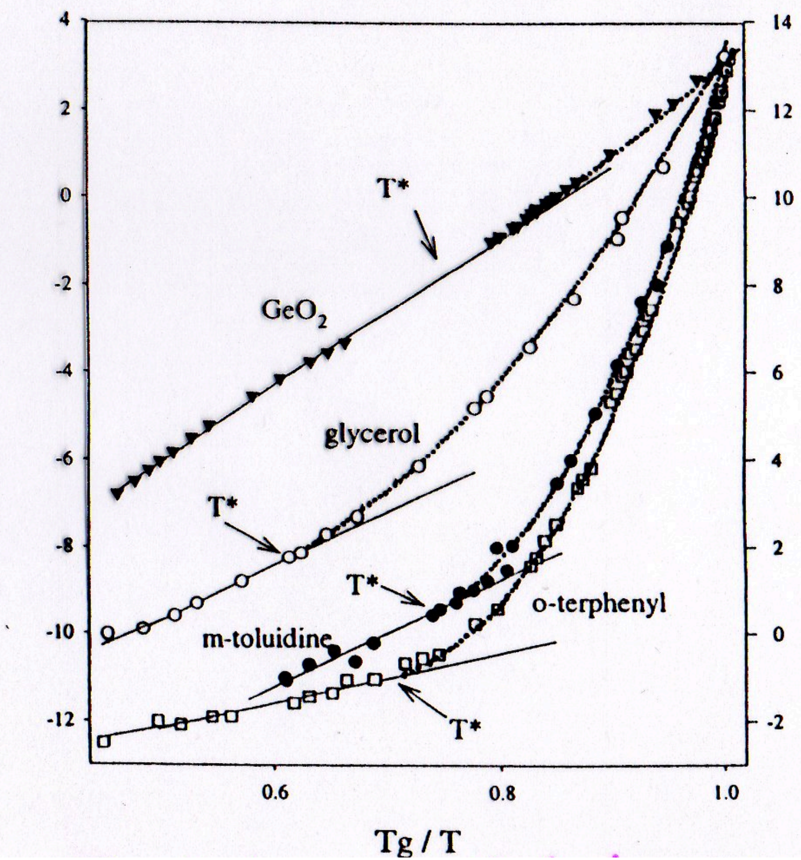
With the help of (unavoidable ?) adjustable parameters, several theories fit the same data equally well



RFOT (Wolynes et al.)



Facilitation (Garrahan-Chandler)



Frustration (Kivelson-GT)

log(viscosity or time) vs T_g/T

What experimental evidence for growing collective behavior in glass-forming liquids ?

In search of a supermolecular length characterizing collective behavior

No relevant info from the **average** dynamics or structure

=> need for ways to study fluctuations around the average and detect (at least) multi-point space or space-time correlations:

- nonlinear responses (cf. Ladieu-L'hôte)
- hybrid diffraction-imaging techniques (FEM, XCCA,???)
- specially tailored perturbations (pinned particles and "weak" confinement, ???)

Chemistry: can one find "extremely fragile" glass-formers dominated by collective effects ?

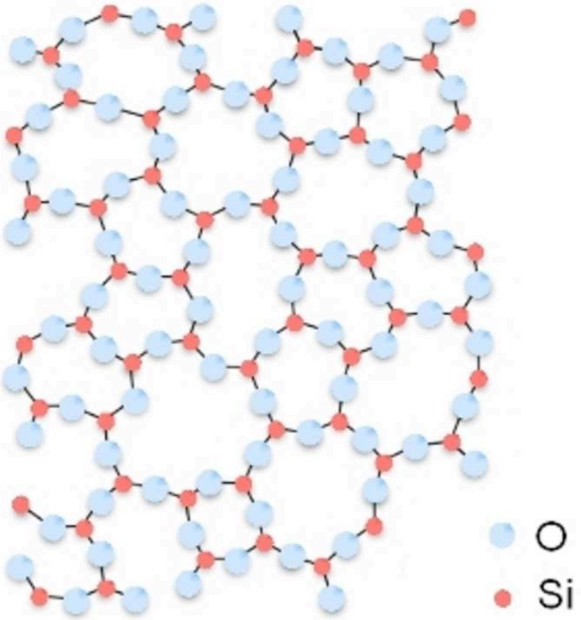
Conclusion

- Diversity of views and of approaches on glasses and glass formation.

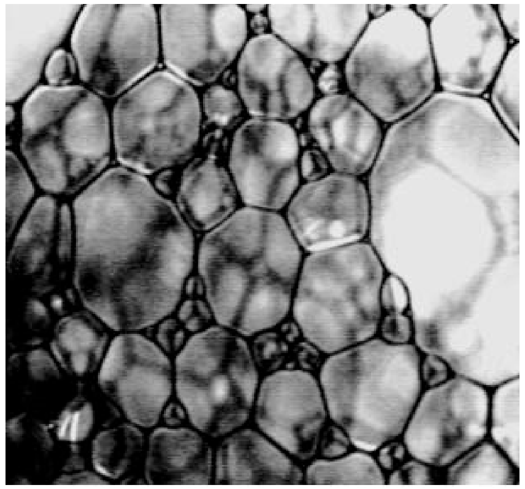
- No consensus on the theory of the glass transition. Several candidates not necessarily at odds with each other.
  No consensus on a minimal model (≠ spin glasses).

- Existence and nature of growing lengthscales = crucial issue for understanding the glass transition.
  Need progress in this direction!!!

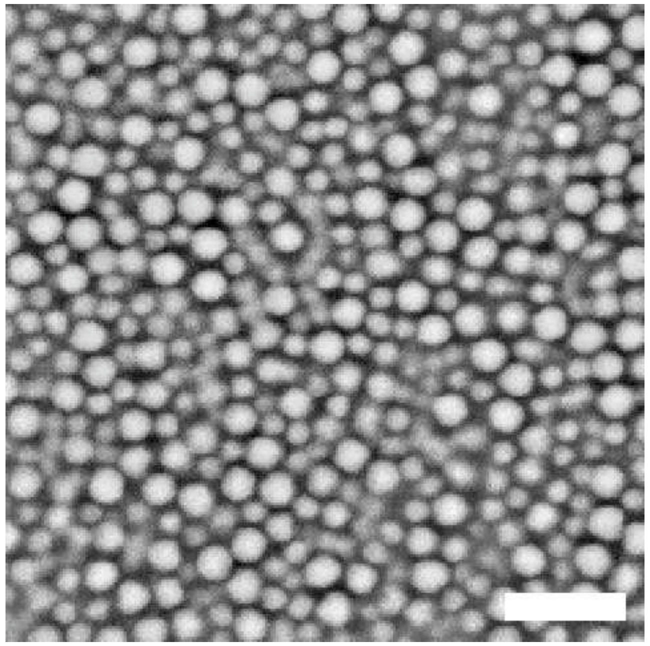
Different types of glasses



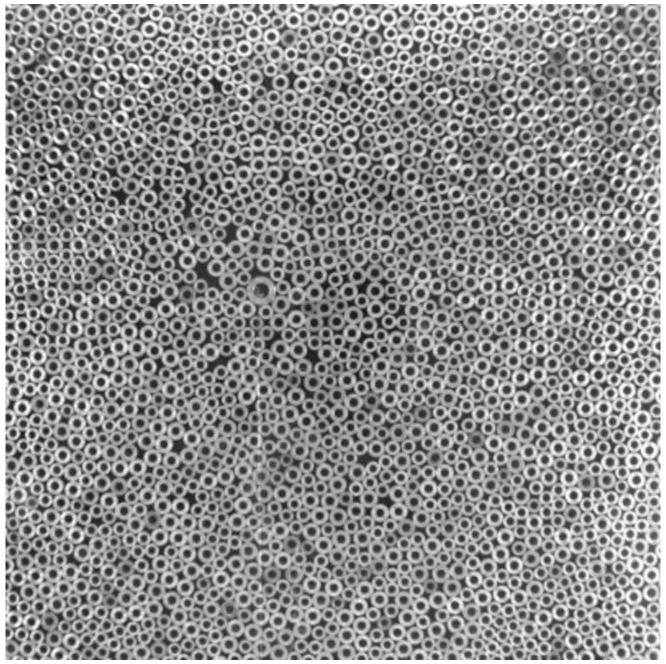
Schematic structure of glassy silica



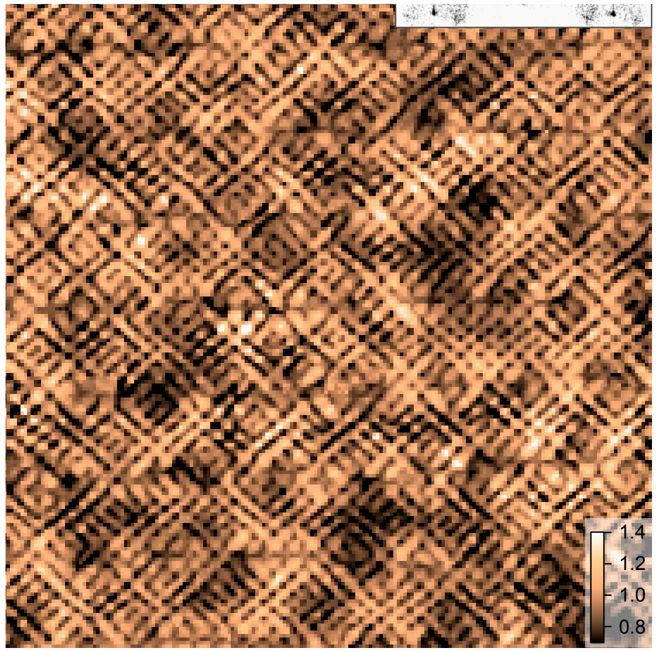
Foam



Colloidal glass (Weeks et al.,2009)



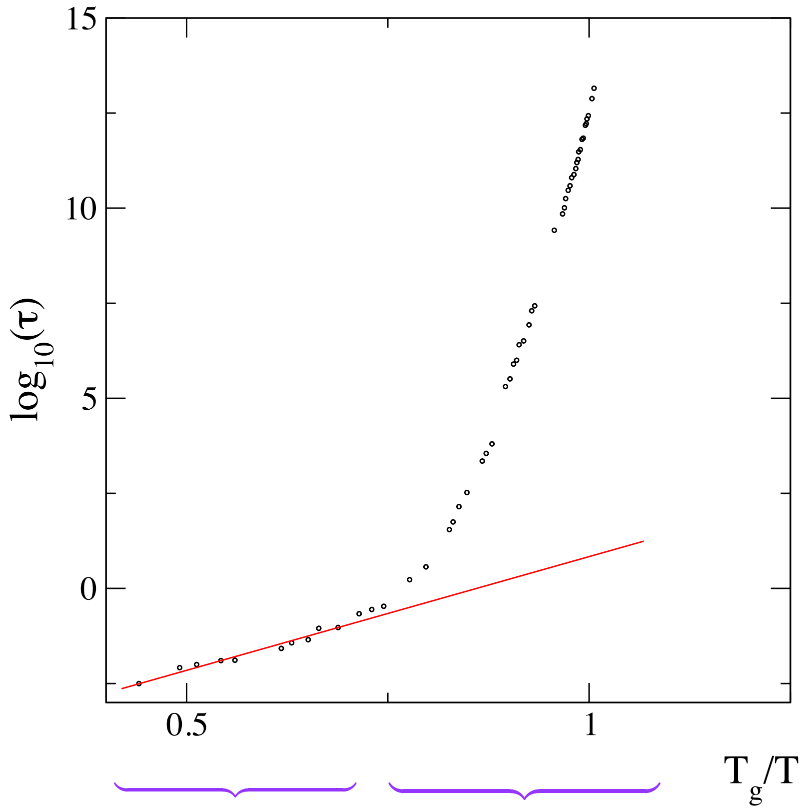
Granular material
(Candelier et al. 2009)



Electronic glass in underdoped cuprates
(Kohsaka et al., Science 2007)

However...

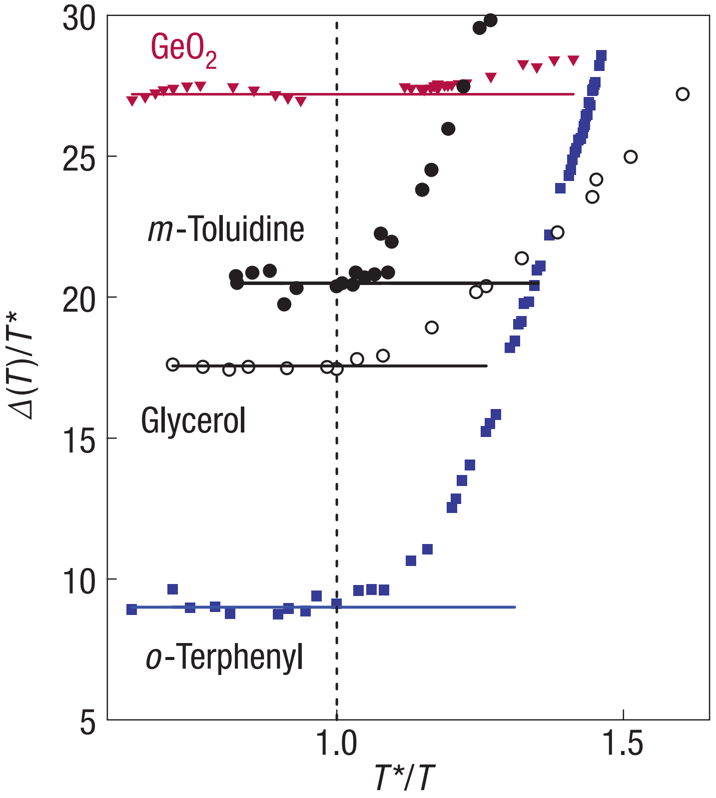
- the viscous slowdown of relaxation seems of cooperative (or collective) nature...



molecular ? collective ?

$$\tau \sim \exp\left(\frac{E(T)}{T}\right)$$

T-dependent effective activation energy



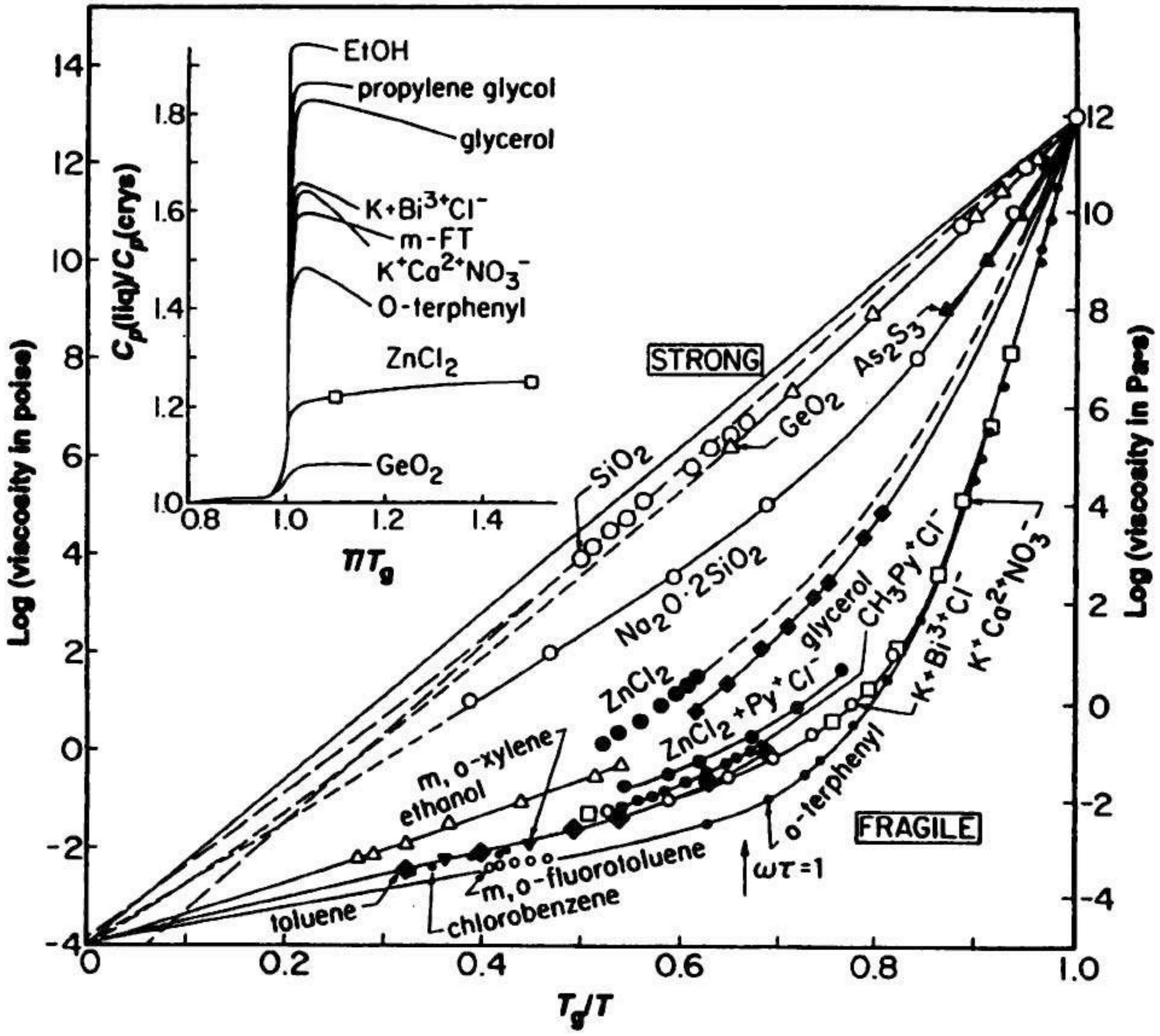
- ... Yet with an activated T-dependence:

e.g., empirical fit to VTF formula $\tau \sim \tau_0 \exp\left(\frac{C}{T-T_0}\right)$

Collective behavior, but... large differences among glass-formers: "Fragility"

Arrhenius plot with T scaled to T_g

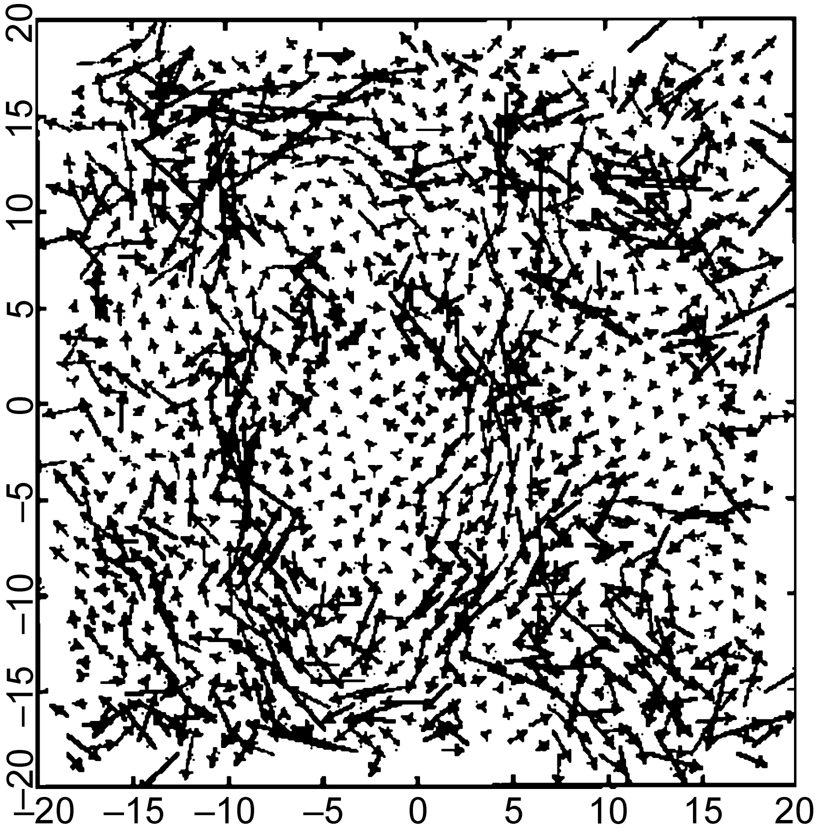
(Angell, 1993)



Spatially heterogeneous dynamics

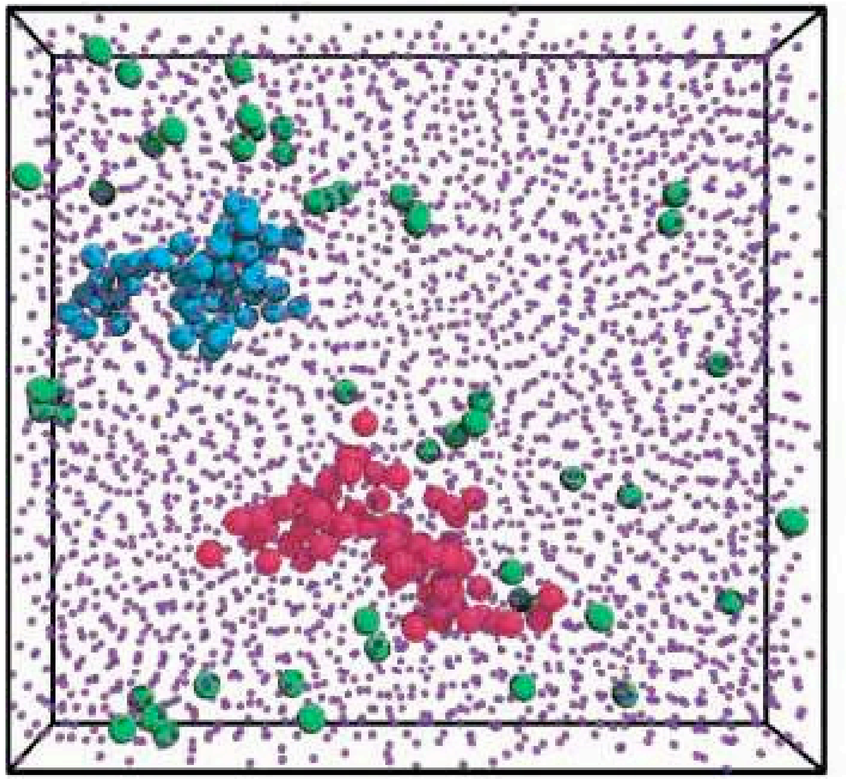
When approaching glass formation:
fast and slow moving regions over an increasing time

Computer simulation



Particle displacements in the MD simulation of a 2-D binary soft-sphere liquid (during roughly 10 τ_α).
(Hurley-Harrowell, 1995)

Experiment on colloids



3-D visualization (confocal microscopy) of a concentrated colloidal suspension close to the glass transition. Large spheres: fast moving particles (0.5 diam. during τ_α). (Weeks et al., 2000)

Dynamic heterogeneity and multi-point space-time correlations

Local probe for atom *j*, e.g.: $f_j(\mathbf{k},t) = \Re\{e^{i\mathbf{k}[\mathbf{r}_j(t)-\mathbf{r}_j(0)]}\}$

with *k* of the order of inverse of interatomic distance

- Average dynamics: self intemediate scattering function

$$F_s(k,t) = \frac{1}{N}\sum_{j=1}^{N} < f_j(\mathbf{k},t) >$$

- Fluctuations in the dynamics: $\delta f_j(\mathbf{k},t) = f_j(\mathbf{k},t) - < f_j(\mathbf{k},t) >$

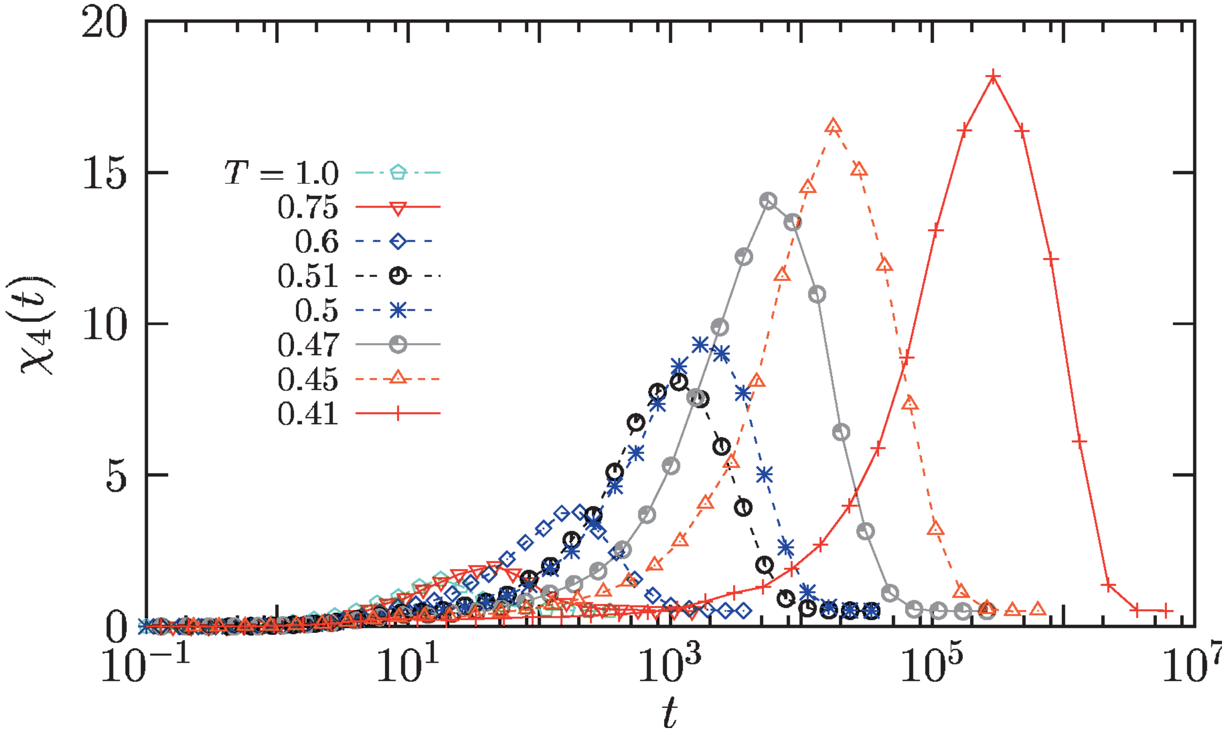
$$G_4(r,t) = \frac{1}{N}\sum_{i,j=1}^{N} \delta(\mathbf{r}_{ij} - \mathbf{r}) < [\delta f_i(\mathbf{k},t)][\delta f_j(\mathbf{k},t)] >$$

From which: correlation length $\xi_4(t)$ and susceptibility $\chi_4(t)$

$$\chi_4(t) = \int d^3 r G_4(r,t) = \frac{1}{N} < [\sum_{j=1}^{N} \delta f_j(\mathbf{k},t)]^2 >$$

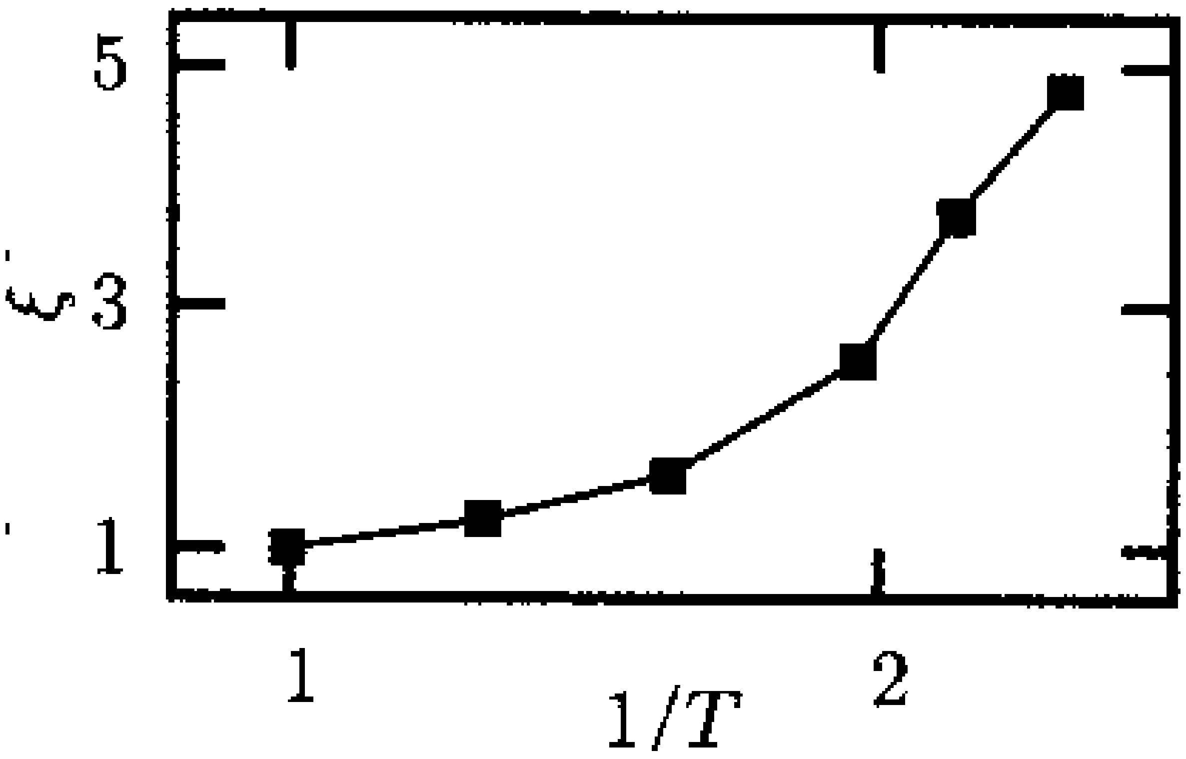
Spatial correlations in the dynamics and associated length scale

Computer simulation of a binary Lennard-Jones model



Time dependence of the 4-point susceptibility. The maximum shifts in time with τ_α and its amplitude increases with decreasing T

(Berthier-Biroli, 2009)



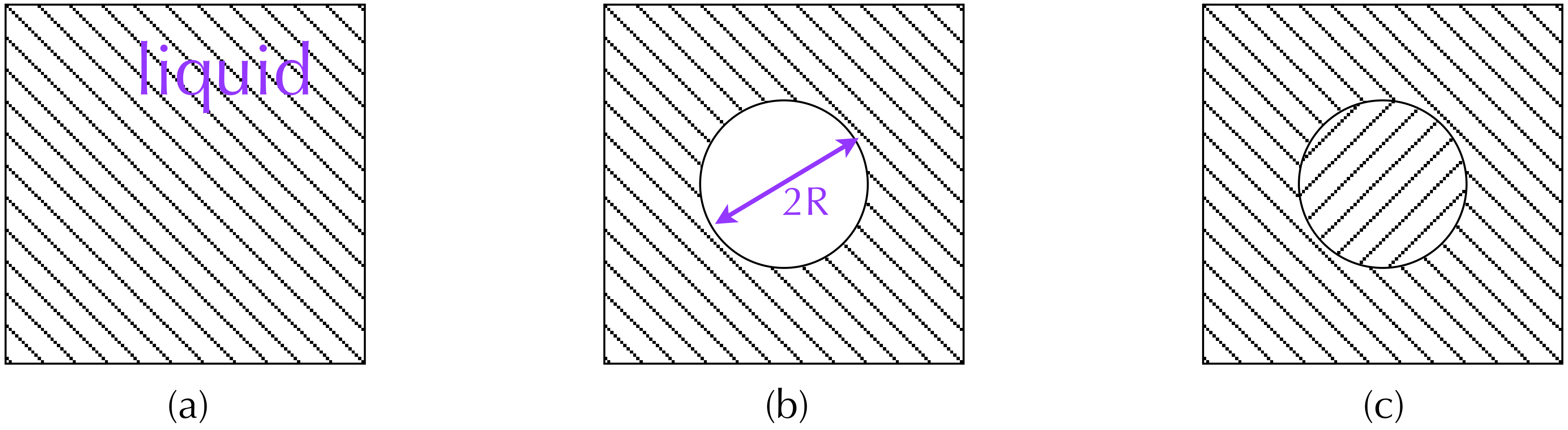
Estimate of the dynamic length ξ_4(t_max)

(Berthier et al., 2007)

Supported by experimental results. Length never grows bigger than 10 molecular diameters (optimistic estimate)

Static "point-to-set" correlations and associated length scale

Thought experiment (Biroli-Bouchaud, 2004)



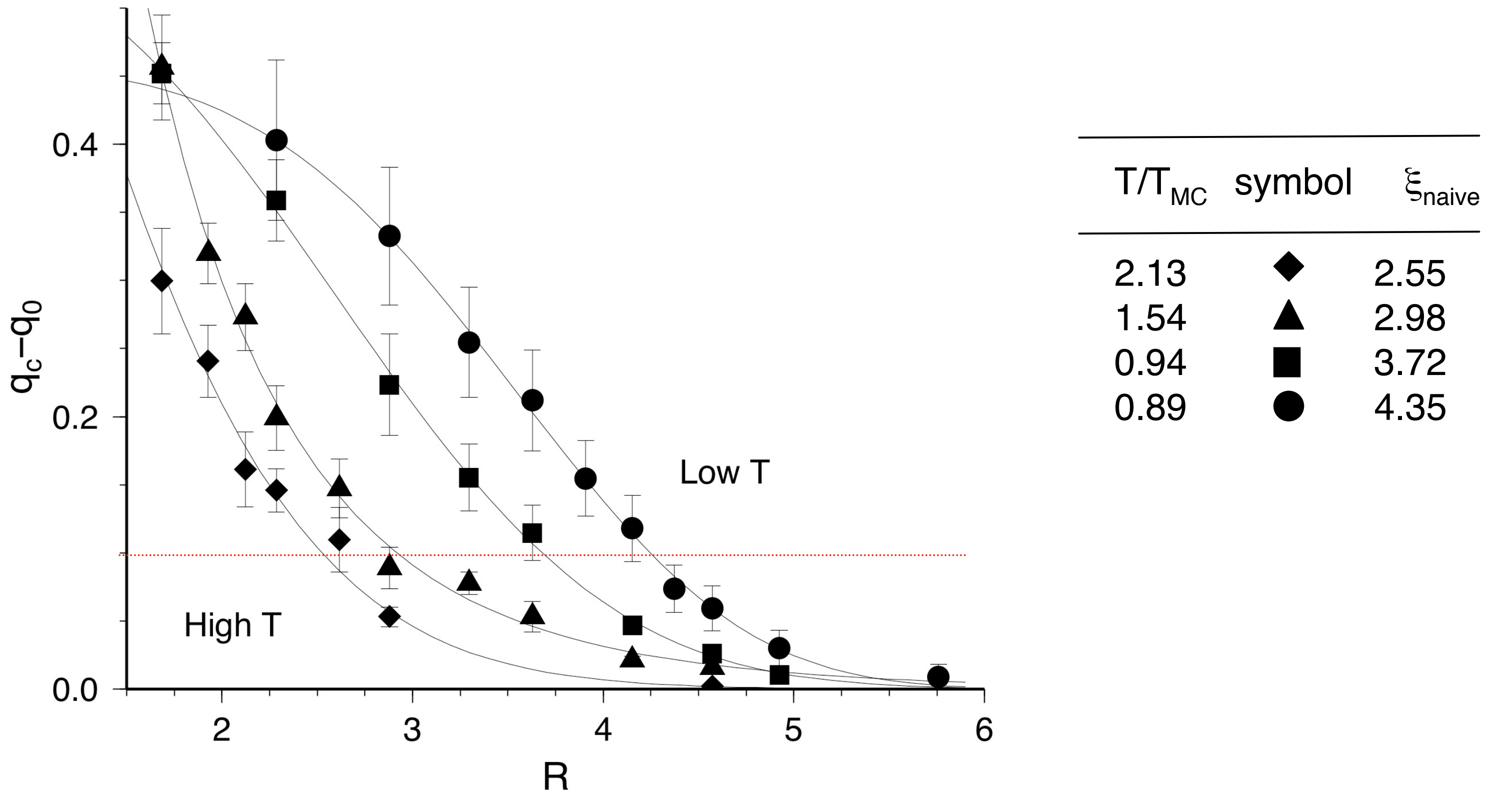
Consider an equilibrium liquid configuration (a). Freeze it outside a cavity of radius R (b). Then let the liquid equilibrate inside the cavity (c) and measure the similarity with the original configuration around the cavity center.

- ➡ Defines a point (the center) to set (the cavity boundary) correlation function depdt on R
- ➡ Defines a point-to-set correlation length ξ_{PS}

Relation between the relaxation time $\boldsymbol{\tau}$(T) and the point-to-set static correlation length

$$\tau(T) \lesssim \tau_0 \exp[\frac{C}{T}\xi_{PS}(T)^3]$$

Some evidence for a growing point-to-set correlation length from computer simulation of a binary soft-sphere liquid model (Cavagna and coll.,2008)



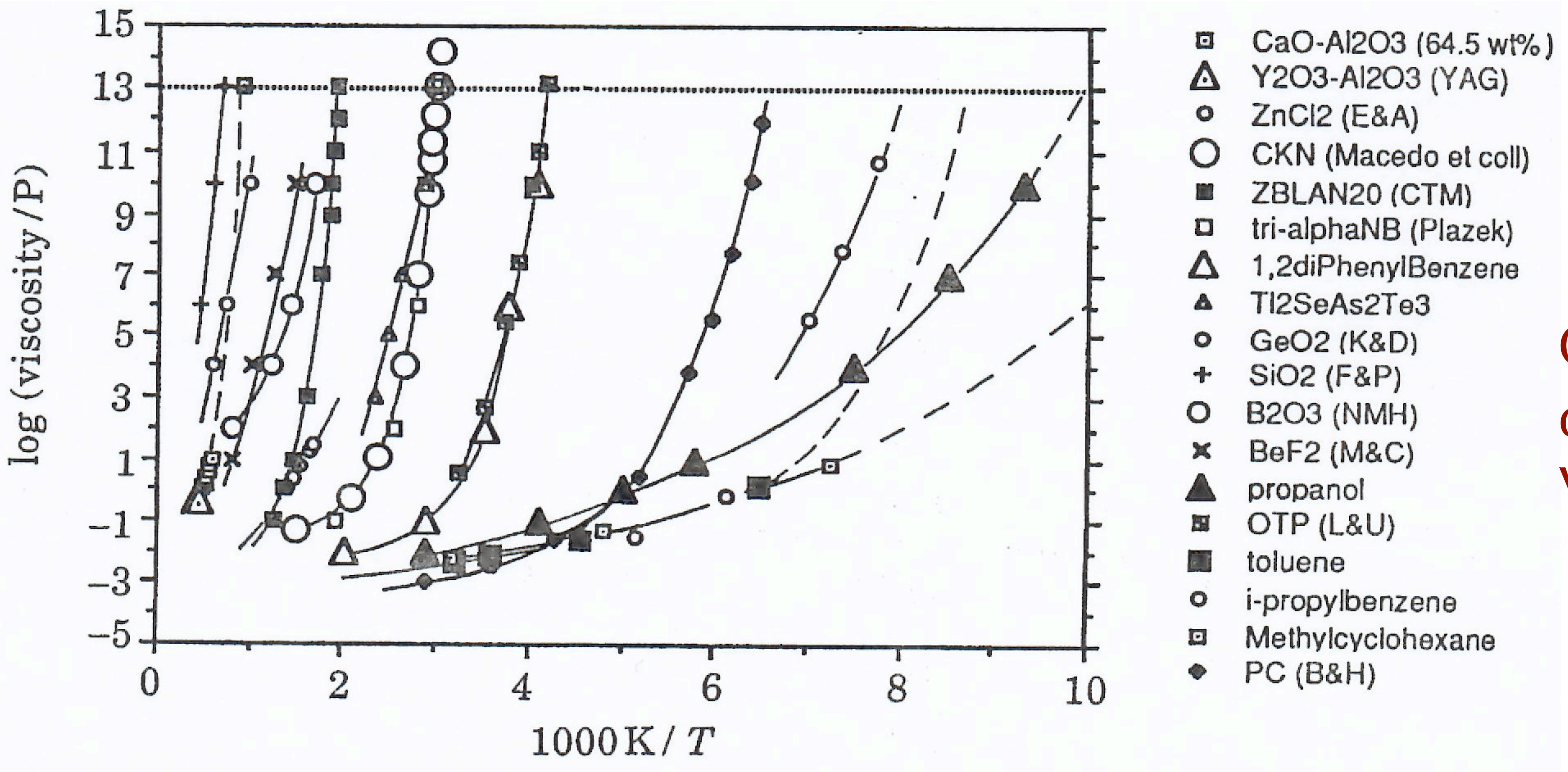
T/T_{MC}	symbol	ξ_{naive}
2.13	◆	2.55
1.54	▲	2.98
0.94	■	3.72
0.89	●	4.35

Point-to set correlation function versus cavity radius for various temperatures. (Inset: estimate of the point-to-set length.)

One of the most spectacular phenomena in all of physics in terms of dynamical range

Arrhenius plot of the viscosity: Log(viscosity/poise) versus 1/T.

(Angell, 1995)

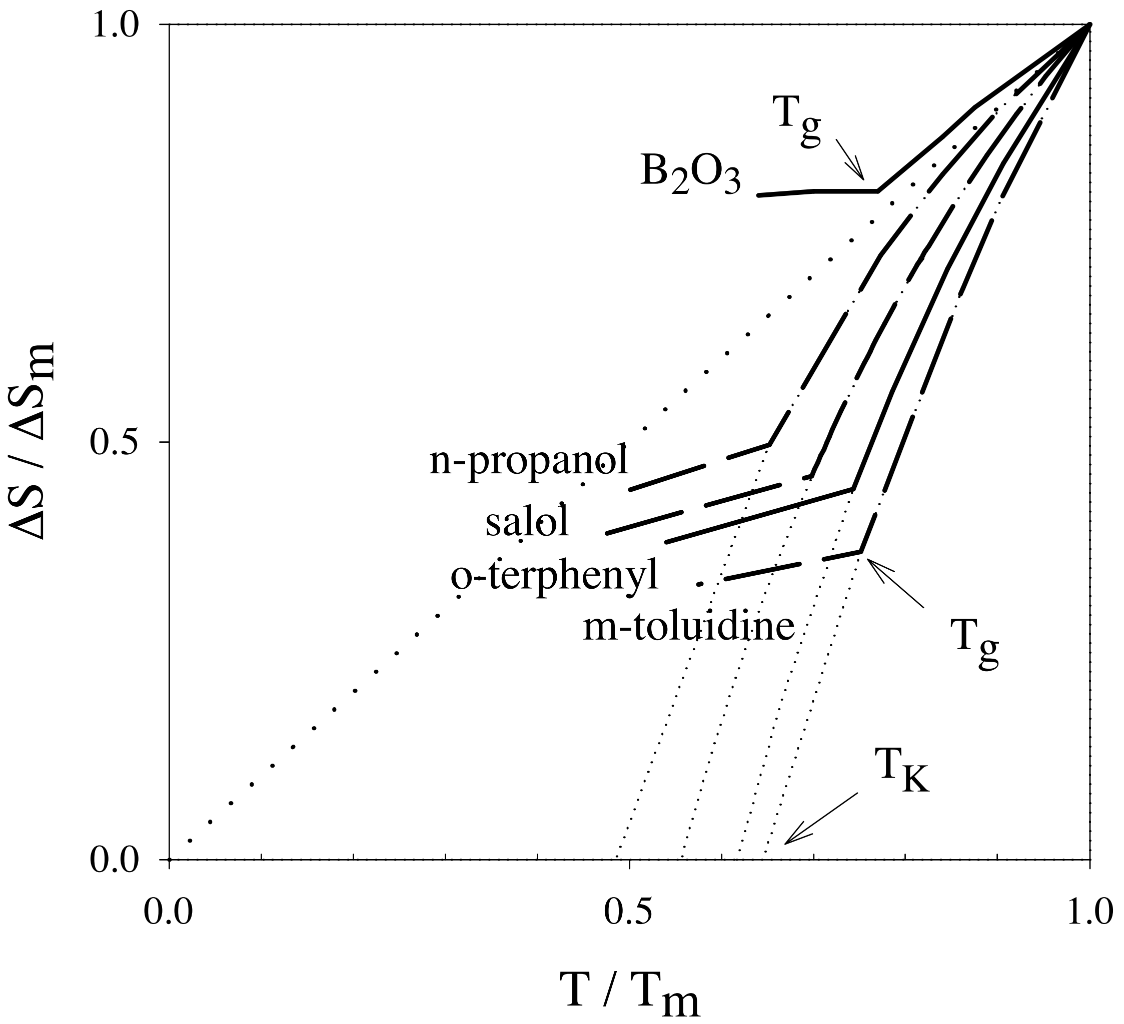


Conventional (arbitrary) definition of T_g: Viscosity = 10^3 Poise

Similar results for relaxation time τ measured by various techniques.

Rapid decrease of the entropy

Kauzmann "entropy paradox"

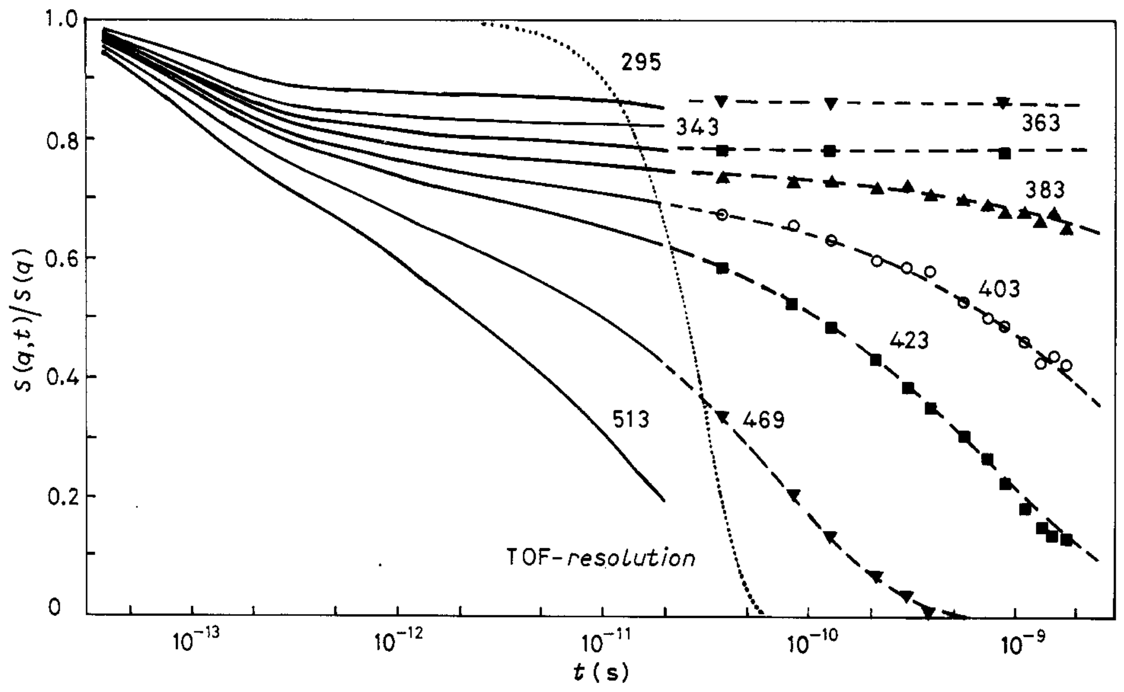


"Configurational" entropy, normalized by its value at melting versus T/T_m.

$$\Delta S = S_{liquid} - S_{xtal}$$

Nonexponential and multi-step relaxation

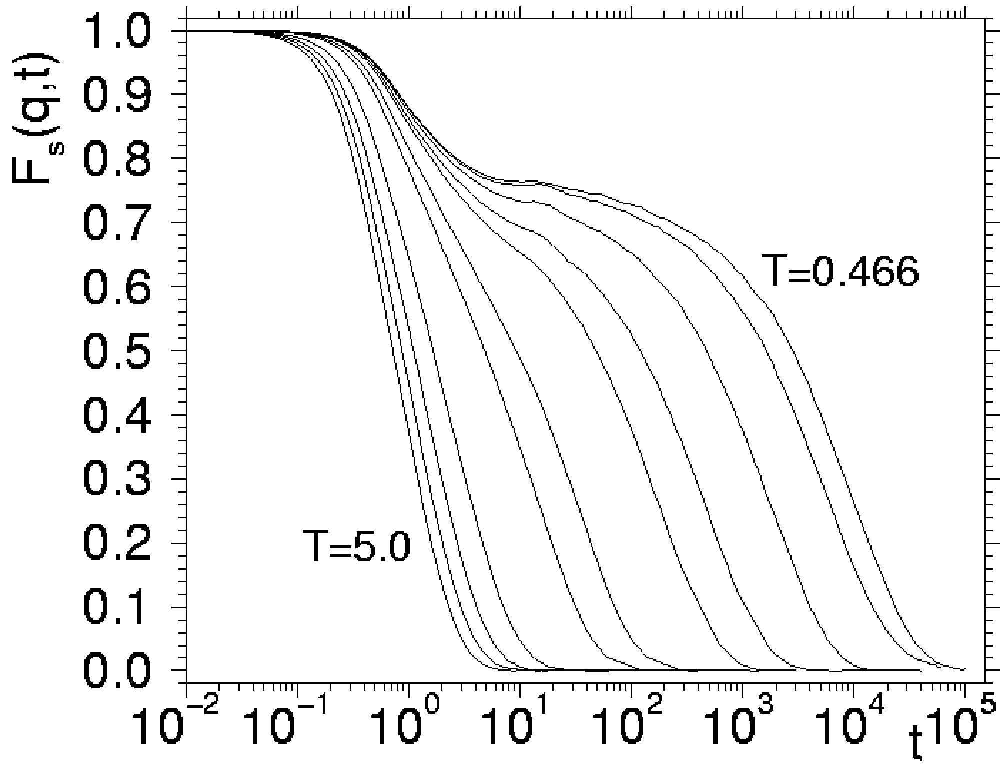
Neutron experiments



Time dependence of the (normalized) dynamic structure factor $S(Q,t)/S(Q)$ for liquid CKN at various temperatures as obtained from neutron time-of-flight and neutron spin-echo experiments.

(Knaak et al., 1988)

Computer simulations



Time dependence of the self-intermediate scattering function $F_s(Q,t)$ at various temperatures for a binary Lennard-Jones model.

(Kob-Andersen, 1995)

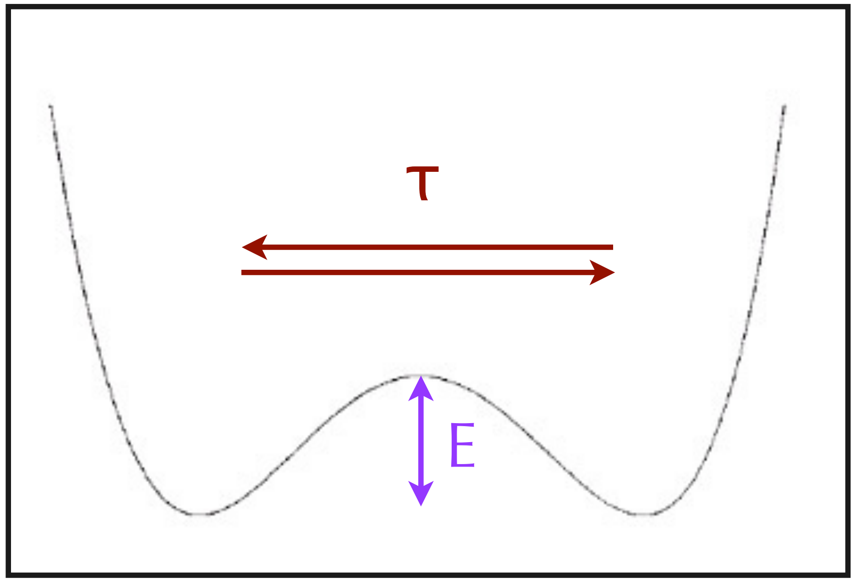
Interlude 1: Explanations of slow dynamics

- Non-cooperative:

  Arrhenius T-dependence for chemical relaxation time

  $$\tau \sim \exp\left(\frac{E}{T}\right)$$

  with a roughly constant activation energy E.



- Cooperative:

  Critical slowing down of relaxation (approaching a critical point at T_c)

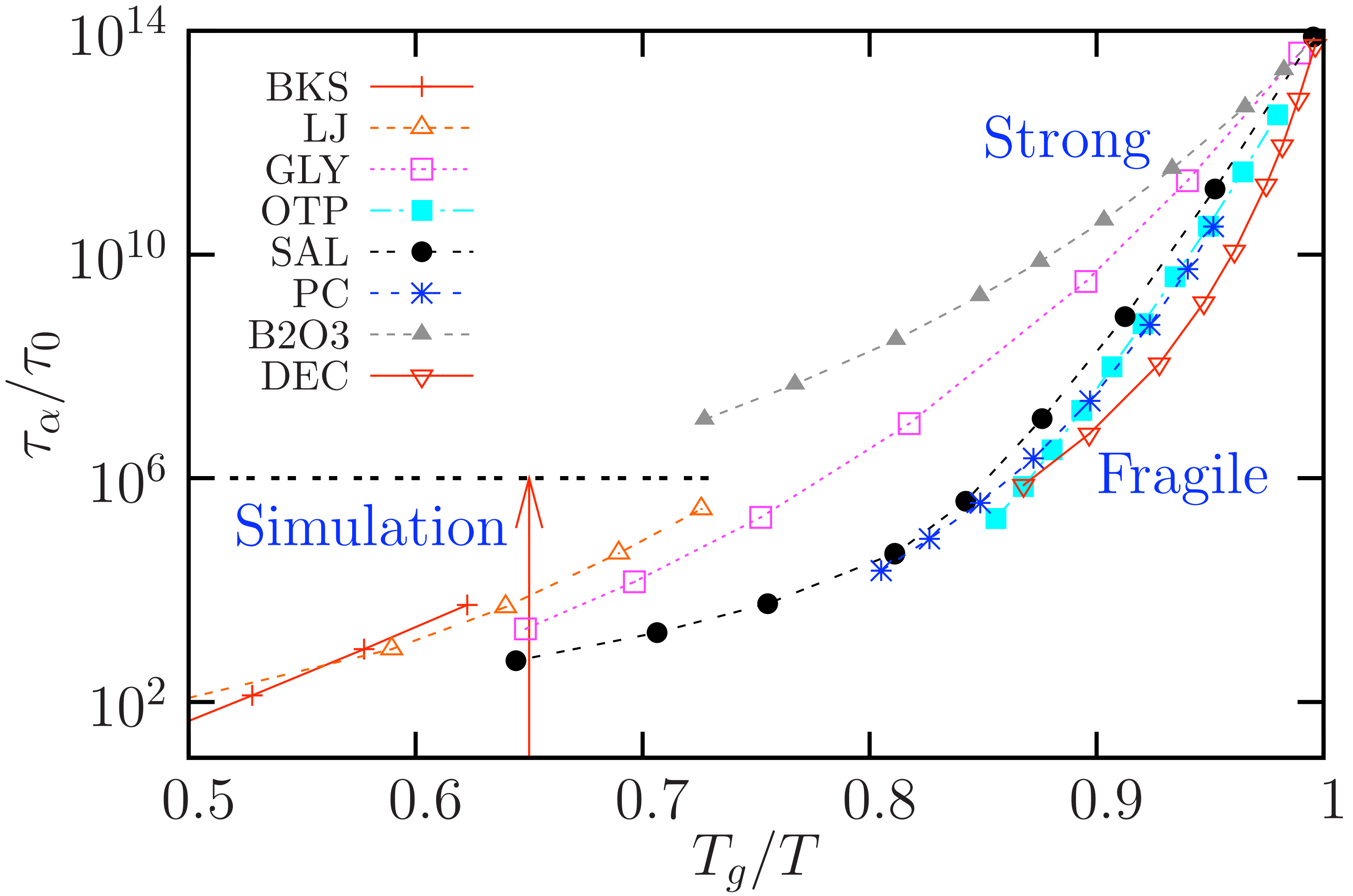
  - ✳ Diverging correlation length: $\xi \sim |T - T_c|^{-\nu}$
  - ✳ Diverging relaxation time: $\tau \sim \xi^z \sim |T - T_c|^{-z\nu}$

Interlude 2: Modeling and simulations

Number of atomic liquid models that resist crystallization and form a (computer) glass,

but

Strong limitation on accessible time scale!



Arrhenius plot with T scaled to T_g from expts and simulations (Berthier-Biroli, 2010)