Transition vitreuse et relaxation dans les liquides surfondus :
Un aperçu théorique

Gilles Tarjus

(LPTMC, CNRS/Univ. Paris 6)

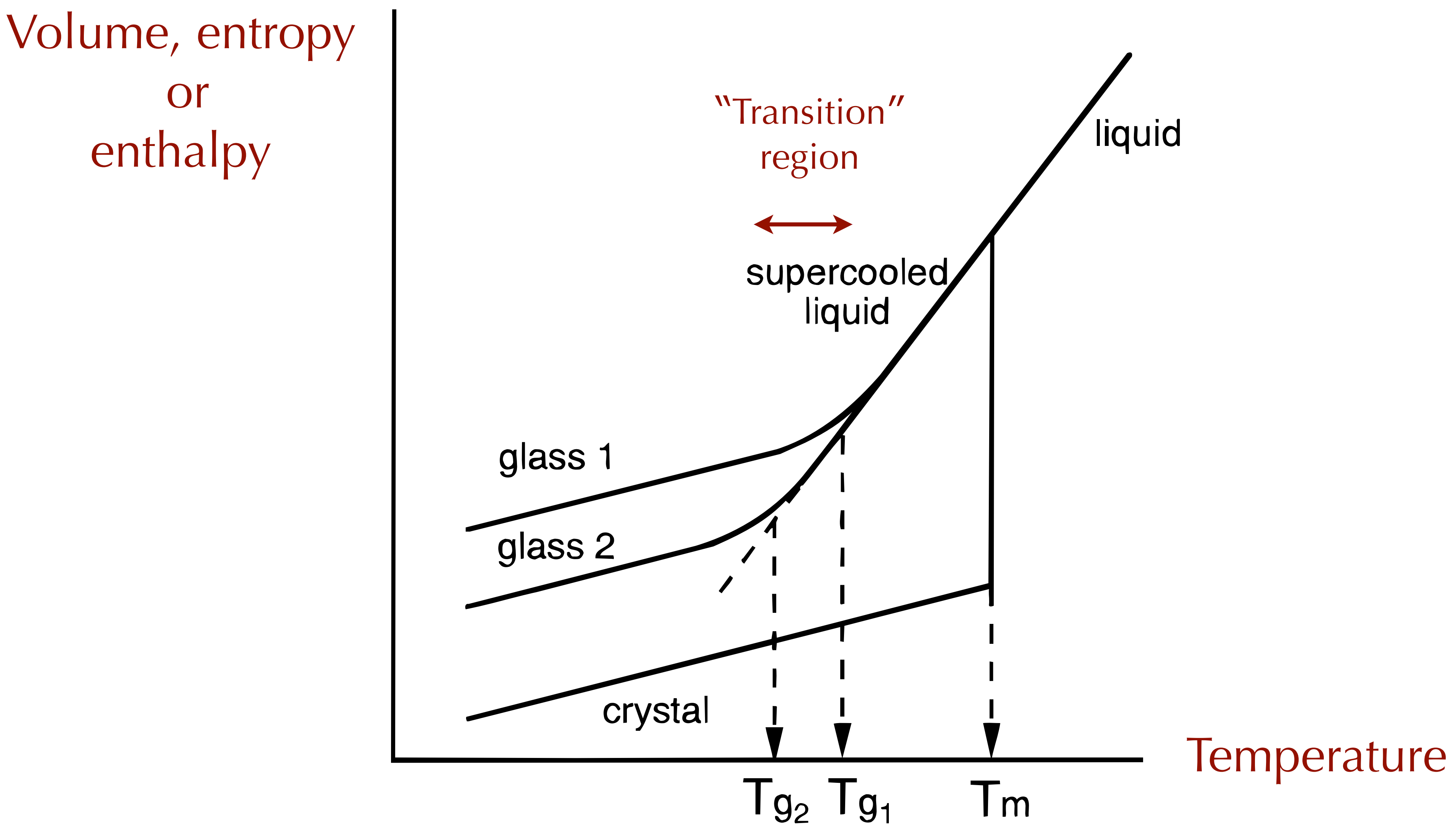
Fréjus GDR Verres 2015

Outline

- What is there to be explained about the glass transition and the viscous slowing down of relaxation?
- Are there growing characteristic lengths associated with glass-forming behavior?
- Theoretical approaches: in search of an effective theory and an appropriate order parameter.

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

Glass formation by cooling a liquid (or a polymer)

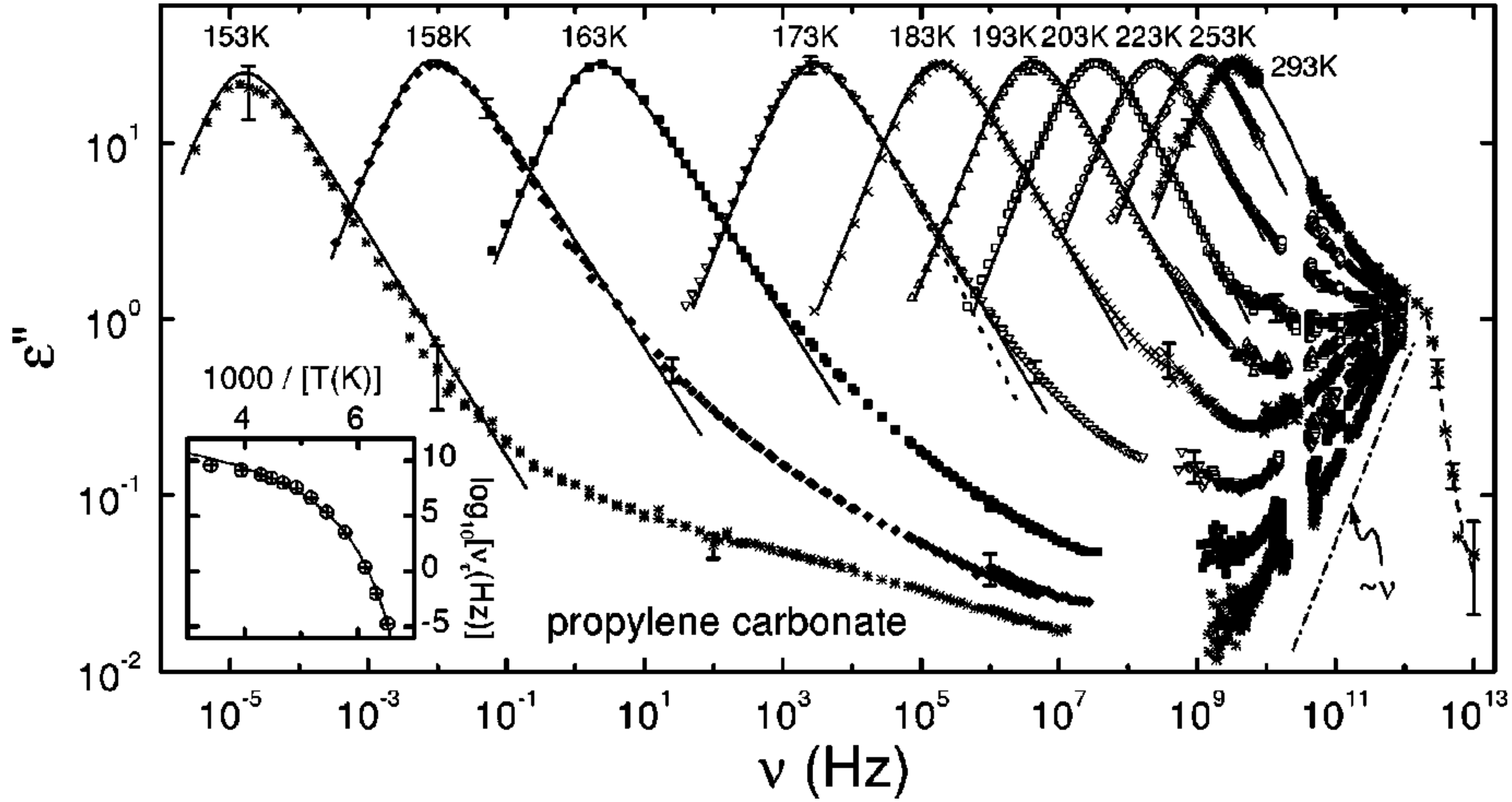


Glass (out-of-equilibrium)

Supercooled liquid (metastable)

Observed glass "transition" = kinetic crossover

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

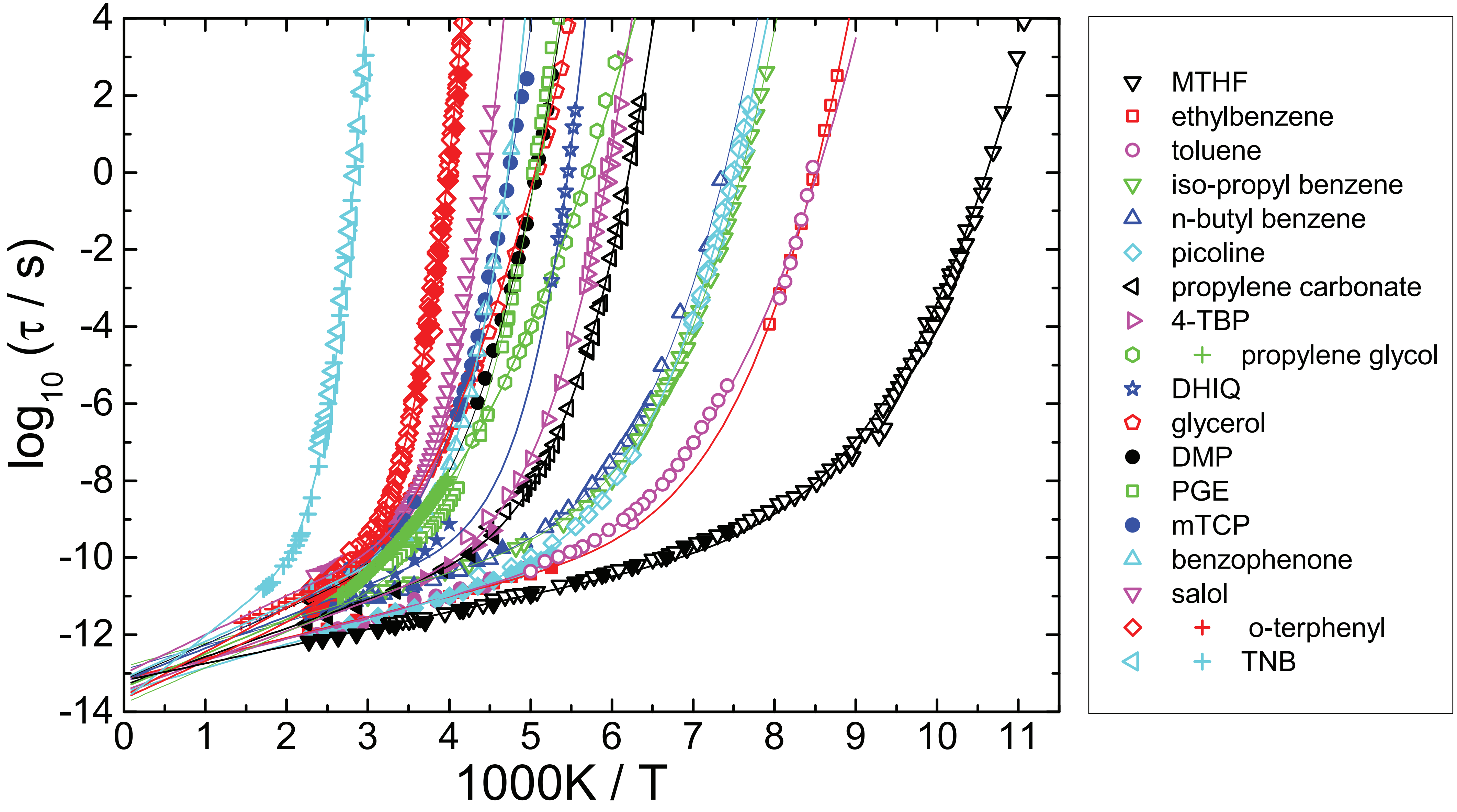


$$\omega_{peak} \sim \frac{1}{\tau_{relax}}$$

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

Dramatic super-Arrhenius temperature dependence of relaxation times (and viscosity)

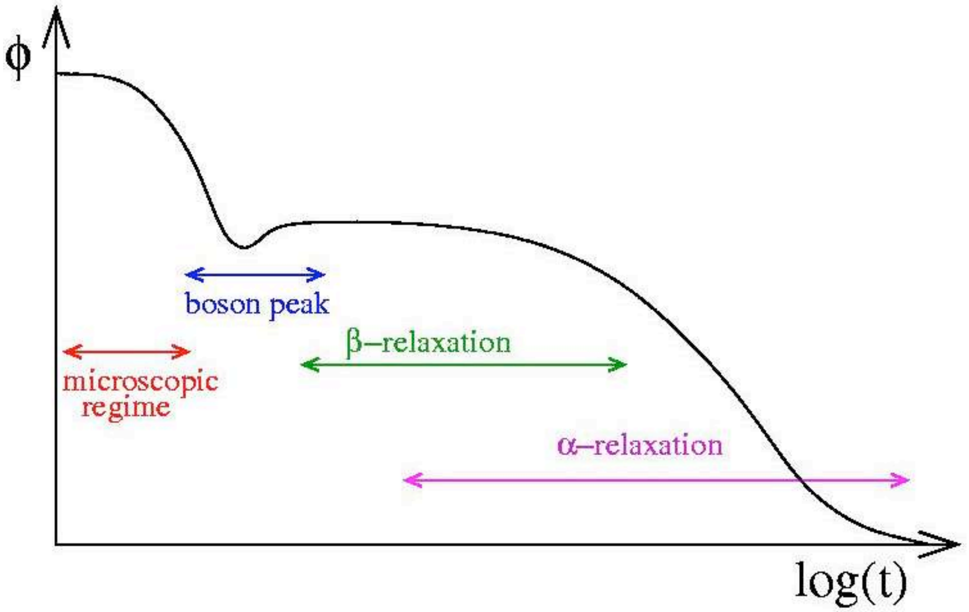
Arrhenius plot of the reorientational time of molecular liquids [Roessler et al., 2013]



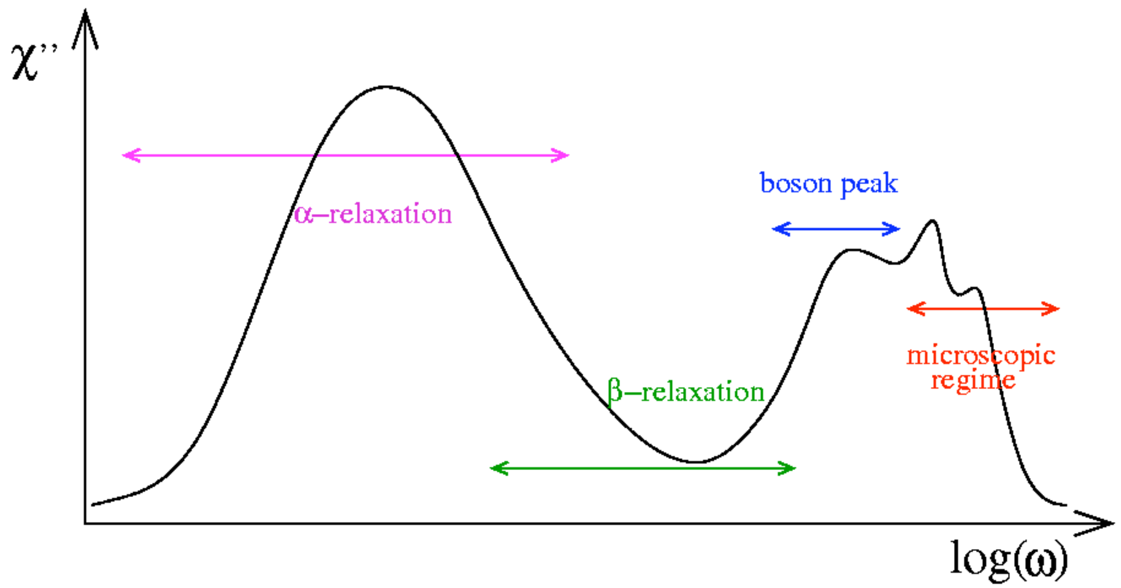
Nonexponential and multi-step relaxation

Time versus frequency domain:

$$\chi''(\omega) \propto \omega \int_{-\infty}^{+\infty} dt e^{i\omega t} \phi(t)$$



Time-dependent response/correlation function



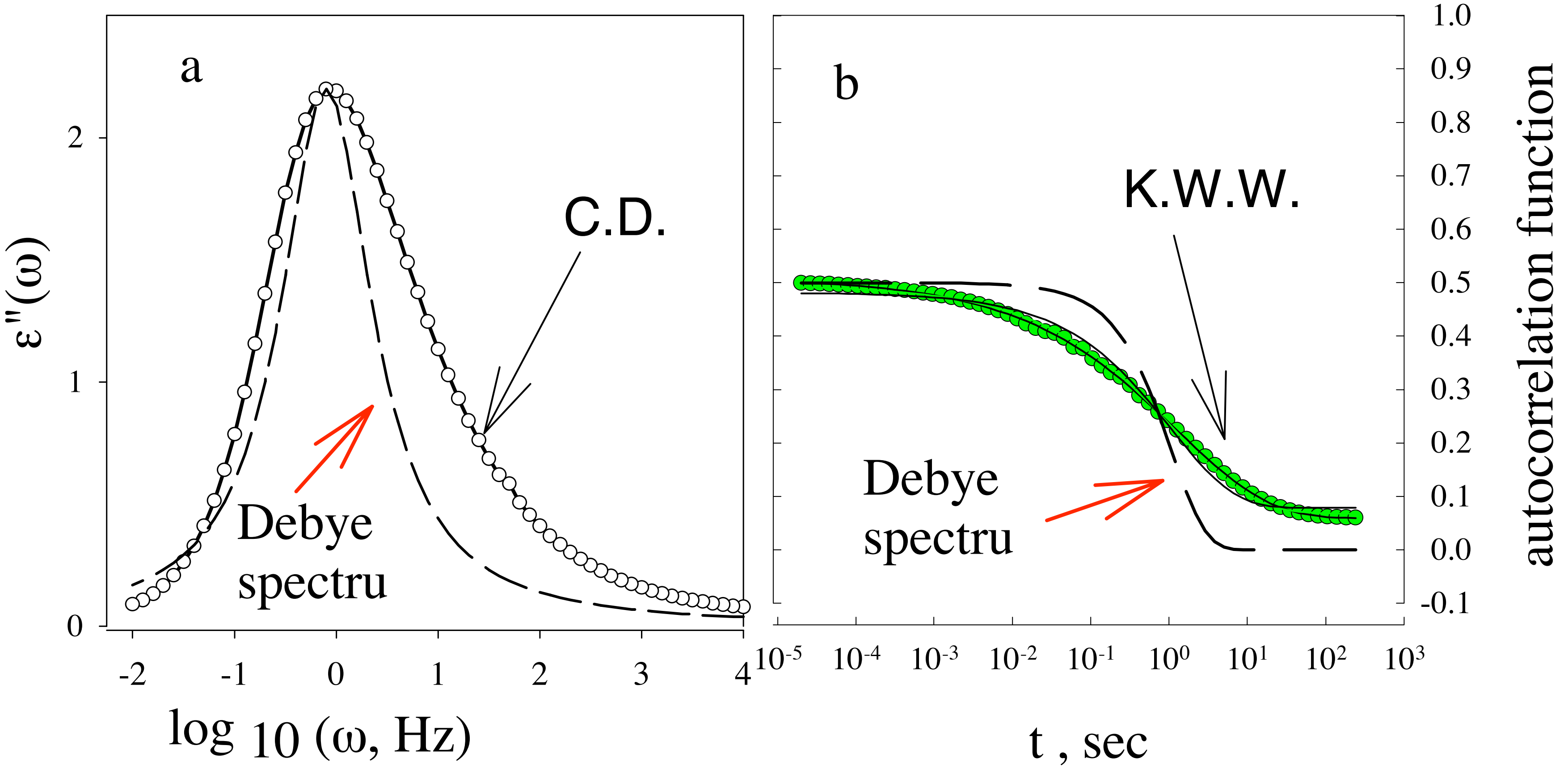
Frequency-dependent dynamic susceptibility

Nonexponential relaxation (contd)

"Stretched" α-relaxation: $\phi(t) \simeq e^{-\left(\frac{t}{\tau}\right)^{\beta}}$ (K.W.W.)

$$\chi(\omega) = \chi_\infty + \frac{(\chi_0 - \chi_\infty)}{(1 - i\omega\tau_{cd})^{\beta_{cd}}}$$

Stretched relaxation of liquid m-toluidine (C. Alba-Simionesco, 2001)

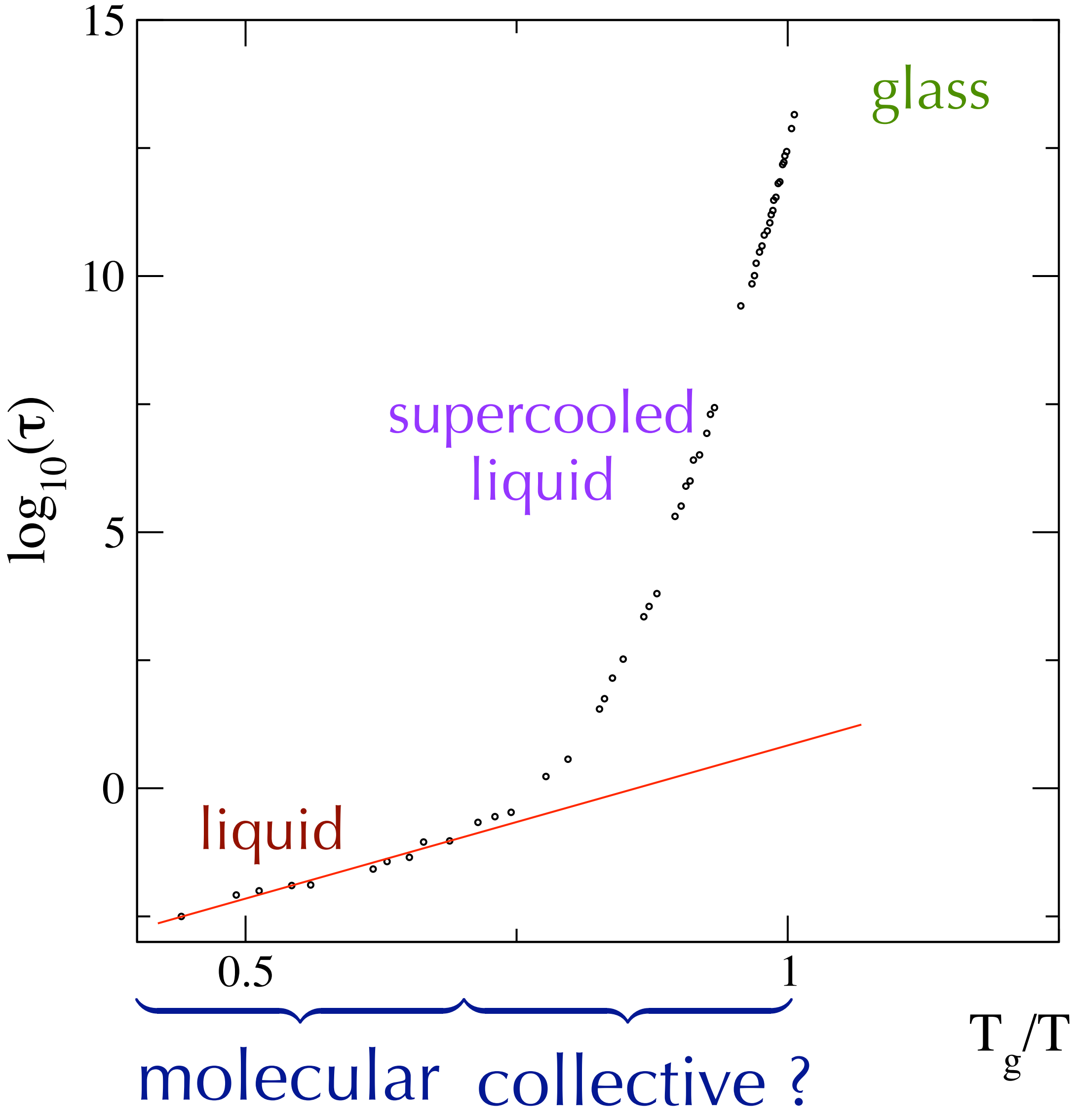


Left, dielectric spectrum. Right, photon correlation spectroscopy.

Signature of a distribution of local relaxation times?

Dramatic temperature dependence of relaxation time and viscosity

Arrhenius plot of the viscosity 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!

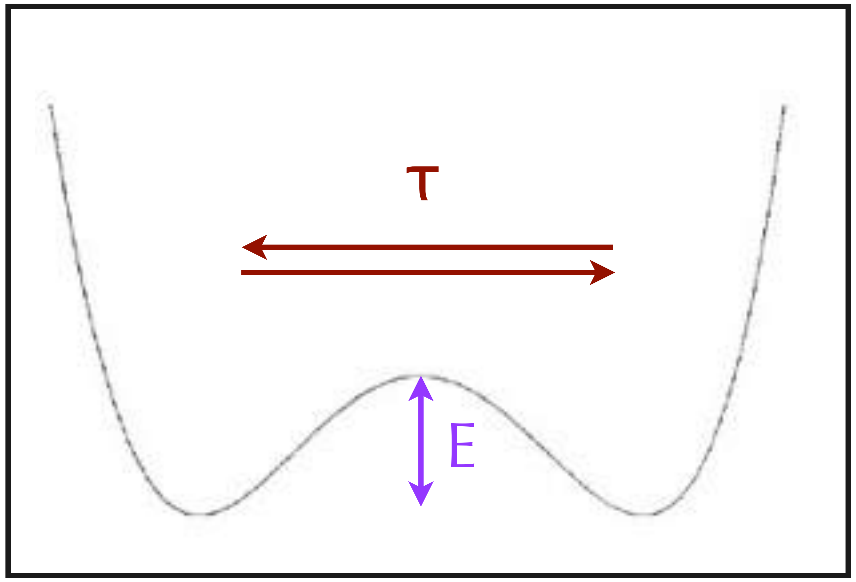
Interlude: Explanations of slow dynamics

- "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)

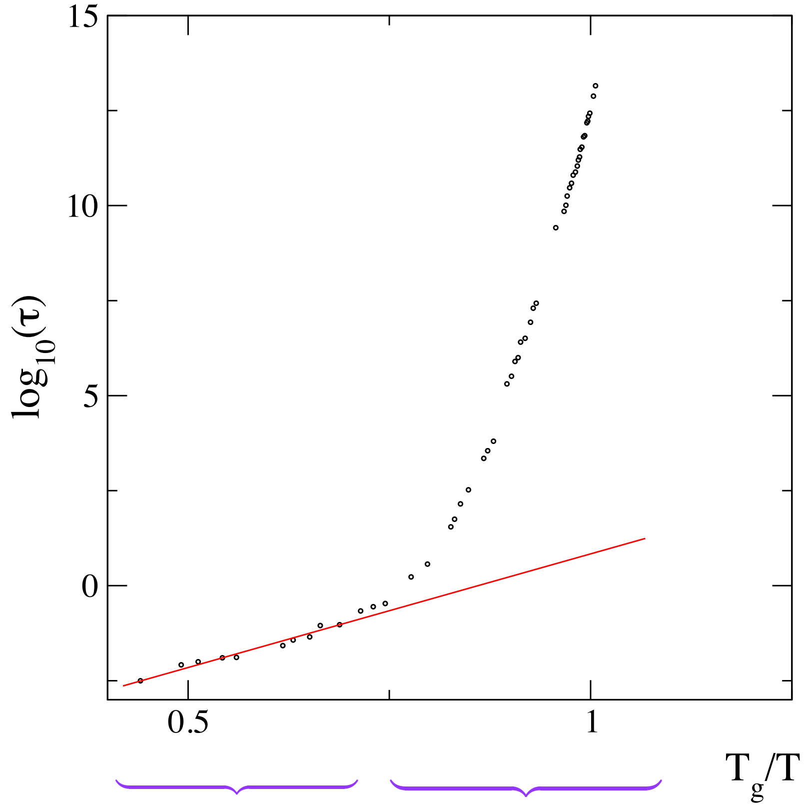
  - ✳ Diverging correlation length: $\xi \sim |T - T_c|^{-\nu}$
  - ✳ Diverging relaxation time: $\tau \sim \xi^z \sim |T - T_c|^{-z\nu}$

Interlude (contd.)

However...

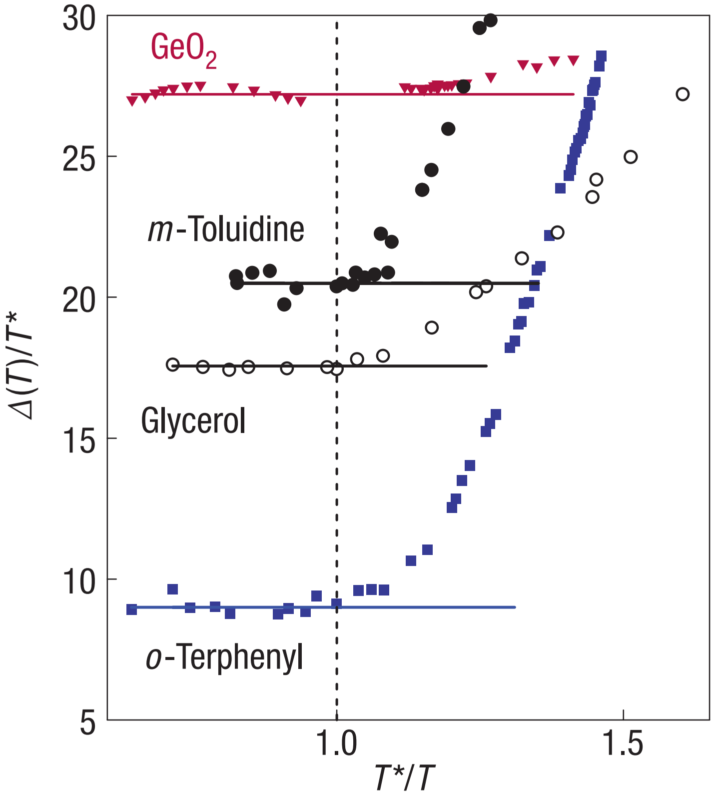
- Viscous slowing down of relaxation seems of cooperative (or collective) nature...

T-dependent effective activation energy



molecular ?　collective ?

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



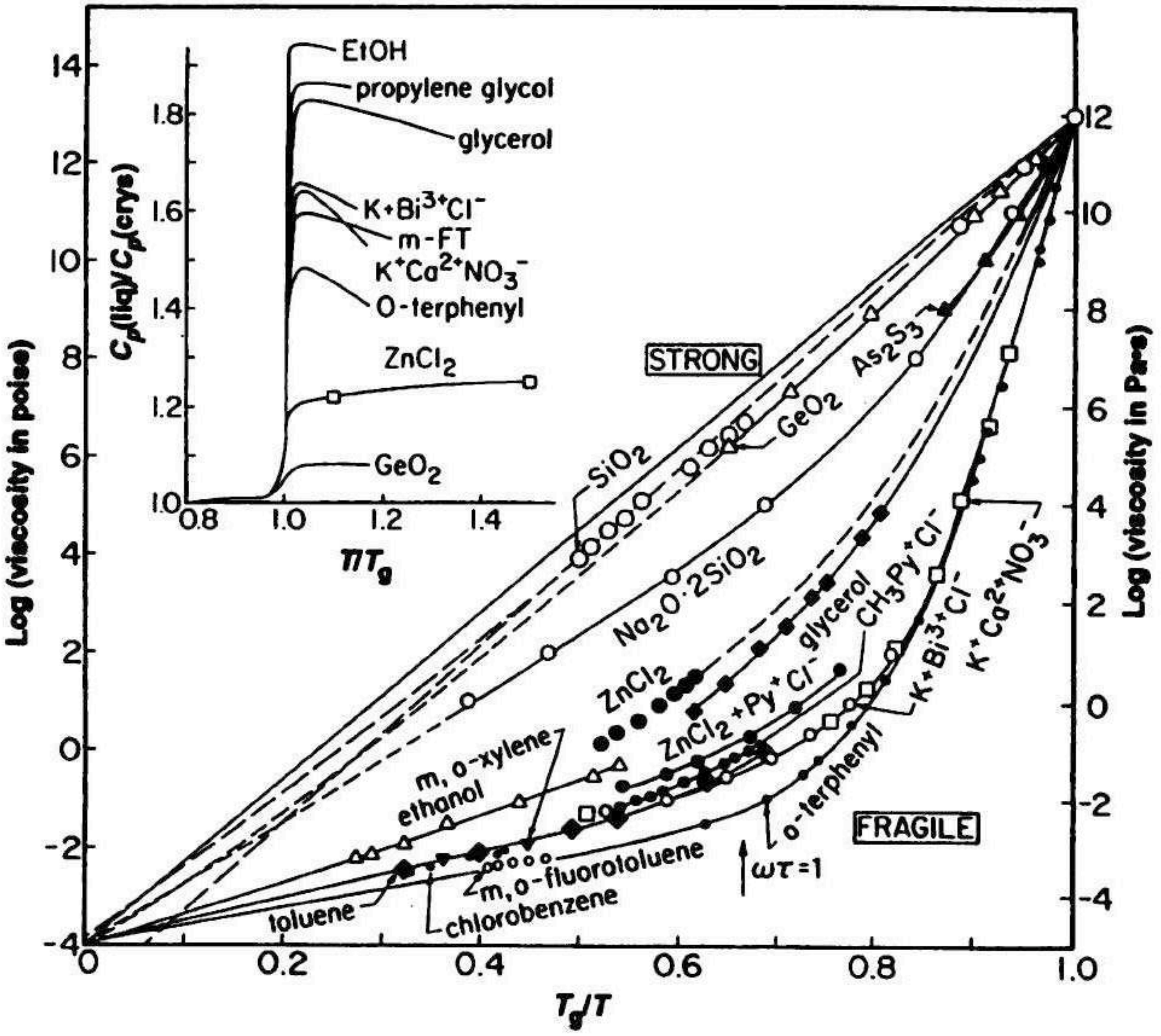
- ... But with an activated T-dependence:

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

Expected collective behavior, but... large differences among glass-formers: “Fragility”

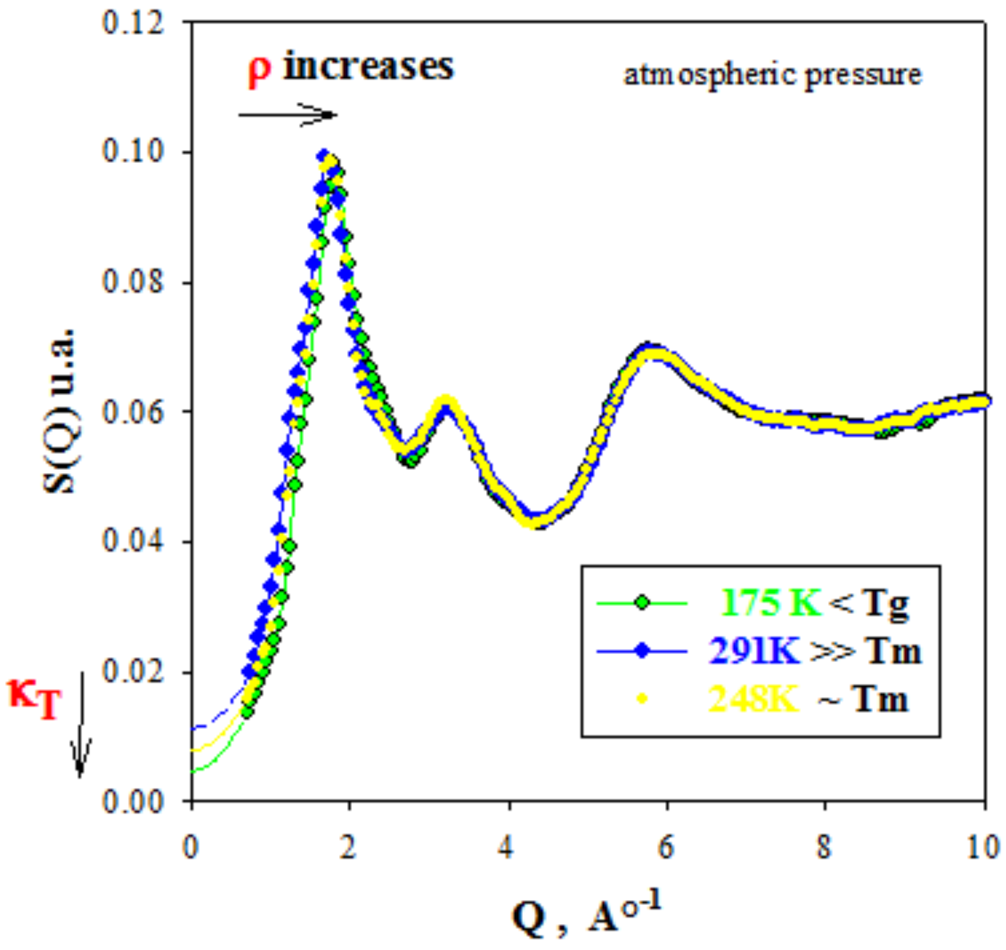
Arrhenius plot with T scaled to T_g

(Angell, 1993)



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.

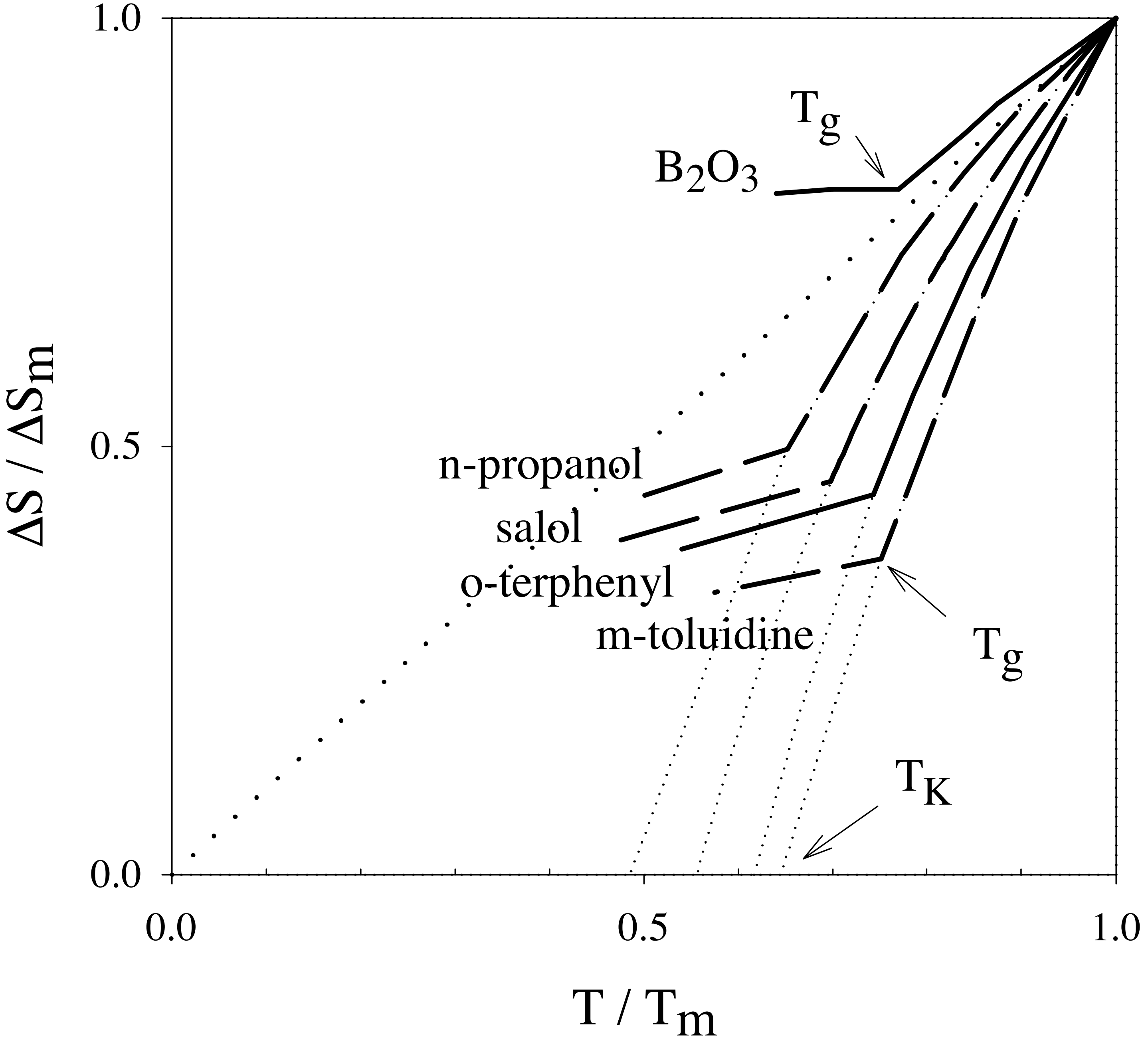


Static structure factor S(Q) of liquid m-toluidine at several temperatures from just above melting (T_m) to below the glass transition (T_g).

[C. Alba-Simionesco et al.]

Only significant change in thermodynamic data:

Rapid decrease of the entropy



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

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

What makes the problem interesting...

There are hints that glass formation involves

- ✴some form of universality
- ✴some form of collective/cooperative behavior

Yet, of an unusual kind...

- If dynamics in the viscous regime is dominated by a unique **mechanism**, what is its nature?
- What are the characteristic (growing?) **length scales**?
- If the collective glass-forming behavior is assigned to an **underlying phase transition** (critical point), where is it located, what are its properties, what is the **local order parameter**?

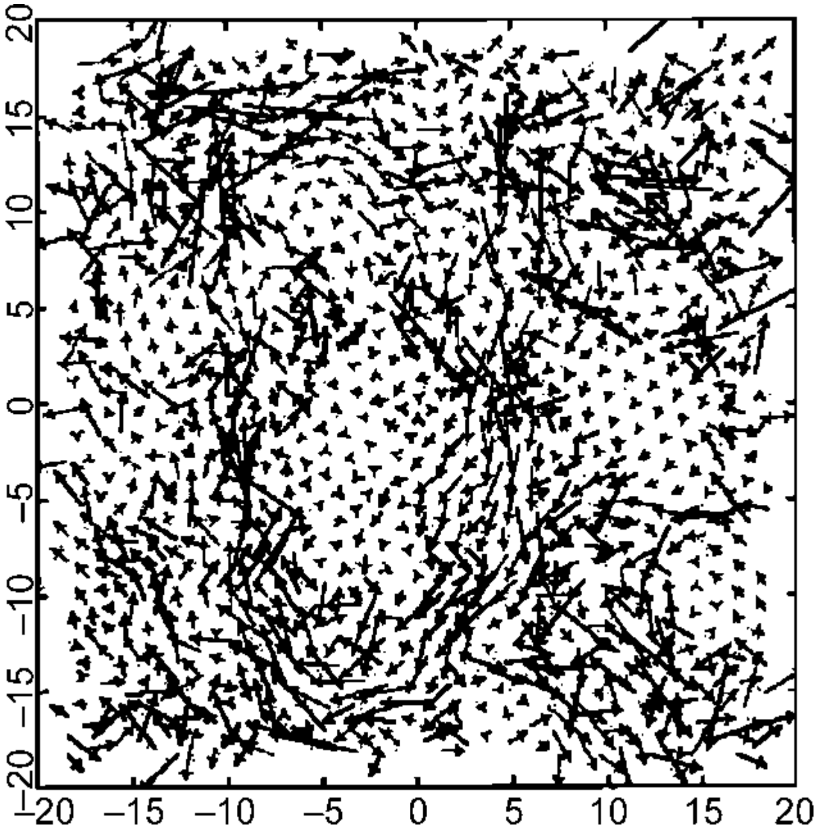
Recent advances:
Are there growing characteristic lengths associated with collective behavior in glass-forming liquids?

[No relevant info from the dynamics or the structure at a **2-body** level]

Spatially heterogeneous dynamics

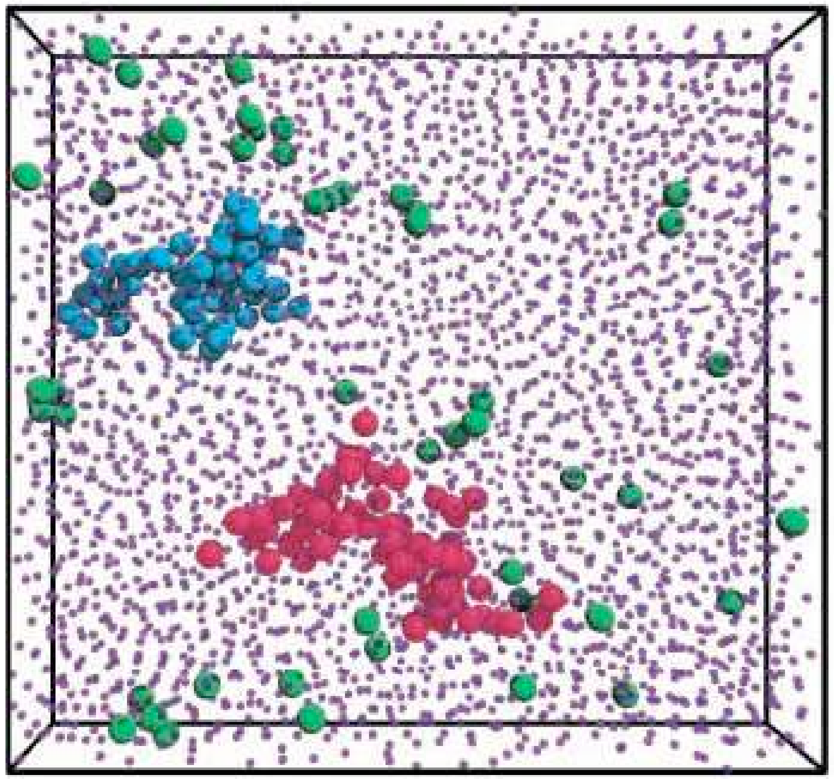
When approaching glass formation:
Presence of fast and slow moving regions over an increasing time scale

Computer simulation



Particle displacements (during roughly 10 τ_α)
[Hurley-Harrowell, 1995]

Experiment on colloids



Confocal microscopy of a colloidal suspension. Large spheres: fast moving particles (0.5 diam. during τ_α).
[Weeks et al., 2000]

The info is embodied in multi-point space-time correlation functions

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 $\chi_4(t)$

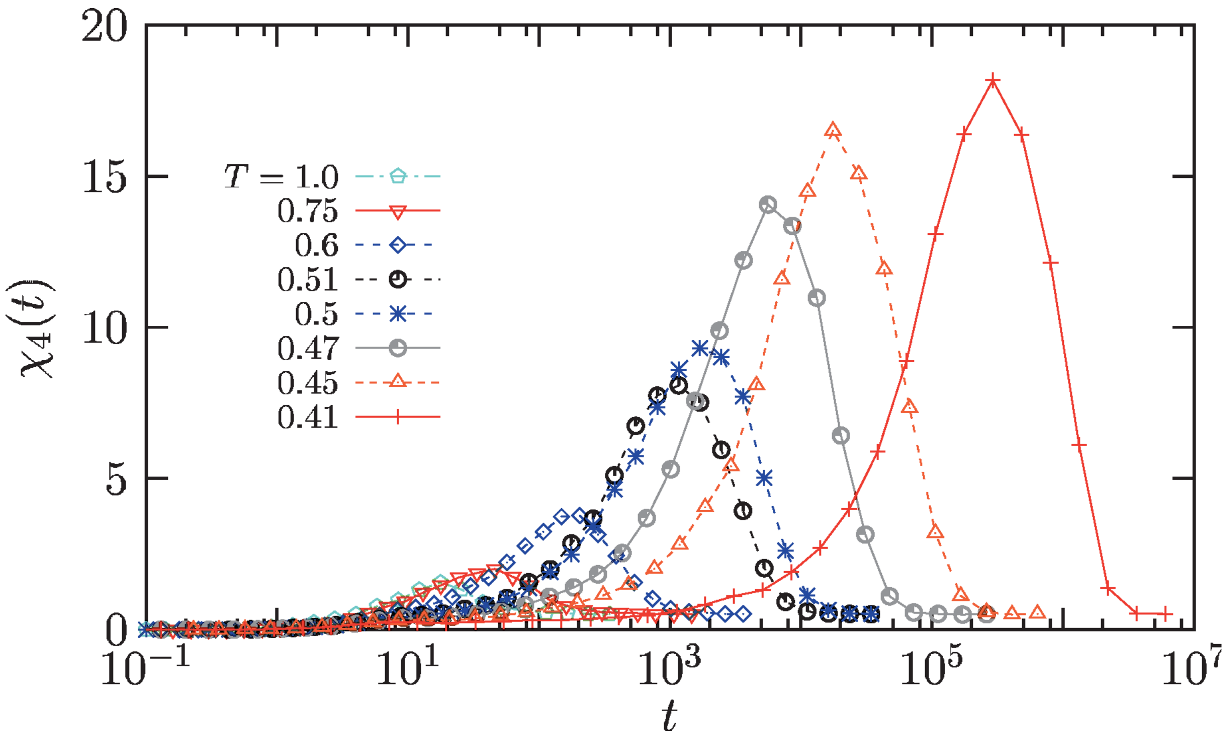
$$\chi_4(t) = \int d^3r G_4(r,t) = \frac{1}{N} < [\sum_{j=1}^{N} \delta f_j(\mathbf{k},t)]^2 >$$

Spatial correlations in the dynamics and associated length scale

Need multi-point space-time correlation/response functions

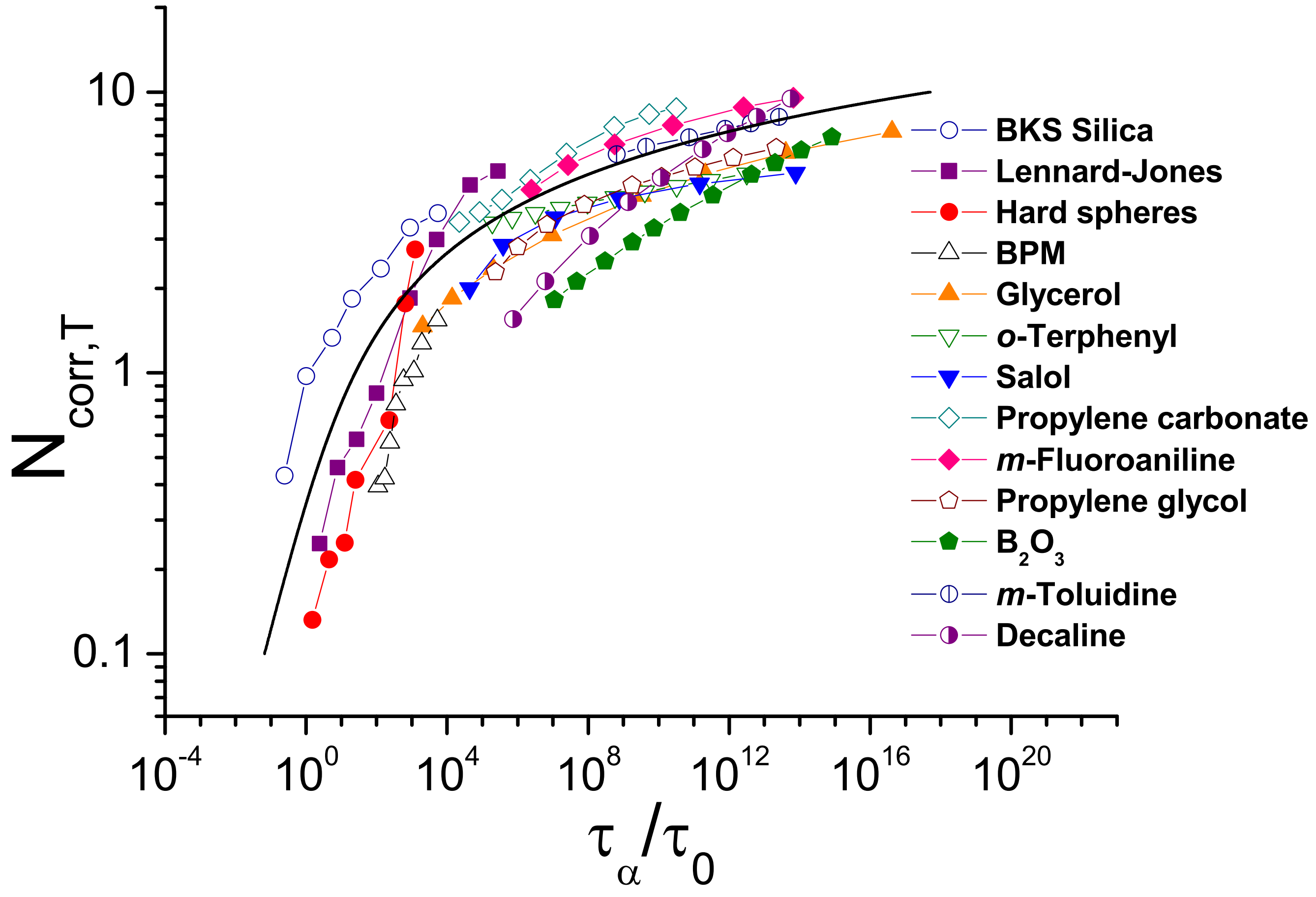
(Simulation, Imaging techniques, nonlinear dielectric spectroscopy, solid-state NMR)

Computer simulation of 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]

Experimental results for the maximum of χ_4 from a lower bound



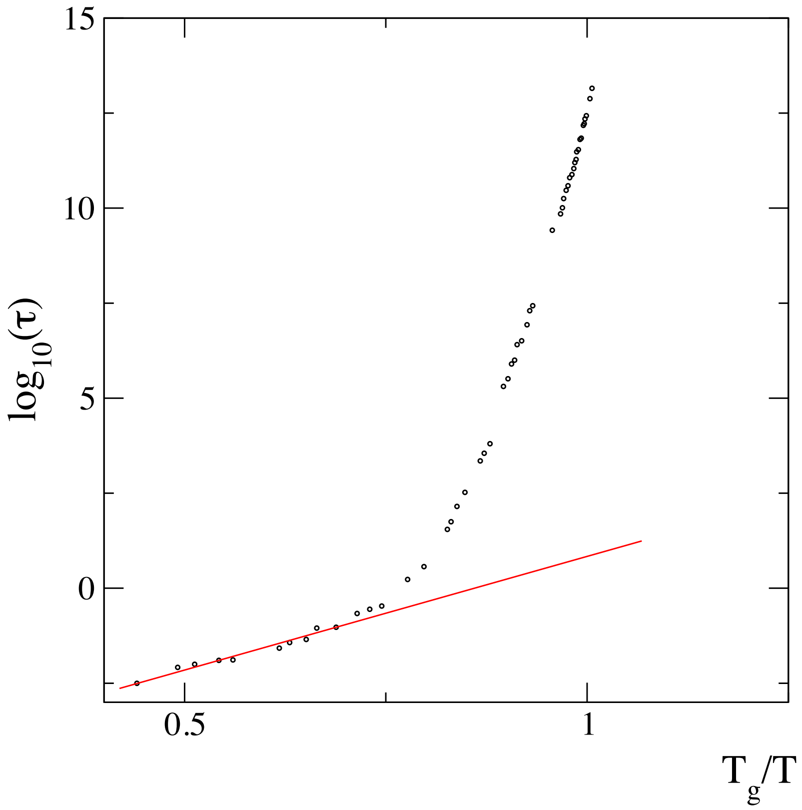
Correlation length never grows bigger than 5-10 molecular diameters

How about a growing **static** length scale ?

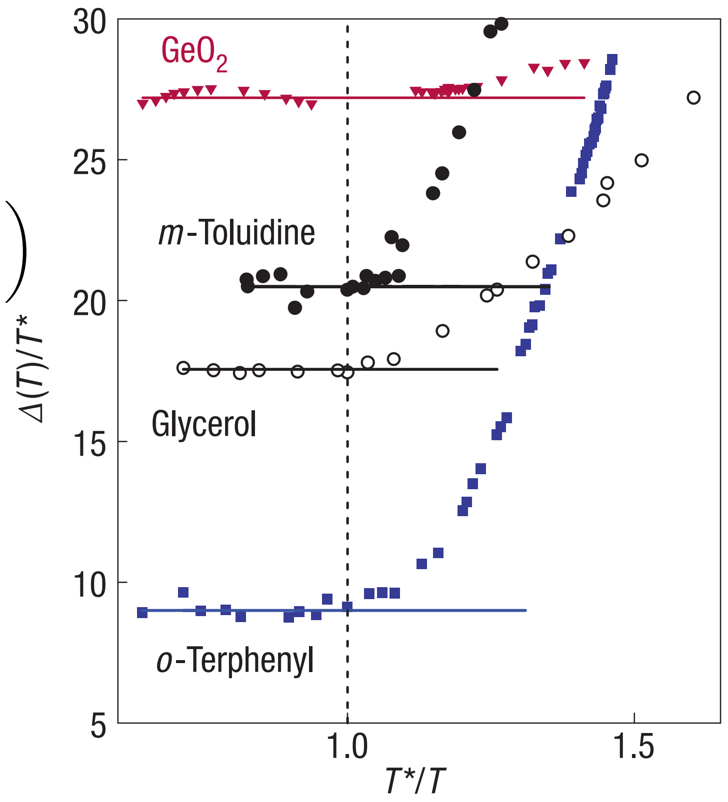
Relation between the relaxation time and a static correlation length:

$$\tau(T) \leq \tau_\infty \exp[\frac{C}{T}\xi_{PS}(T)^3]$$ [Montanari-semerjian, 2006]

=> If super-Arrhenius dependence of τ(T):
at some point, $\xi_{PS}(T)$ must grow when T↓.



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



How about a growing **static** length scale ?

General idea: Try to measure the length associated with the bound on the relaxation time

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

=> **Point-to-set correlation** function and associated length, extracted *e.g.* from the influence of amorphous boundary conditions.

- Evidence for some (limited) growth with decreasing temperature in computer simulations.
- Hard to access experimentally. No progress thus far.

Theoretical approach(es): in search of an effective theory of glass-forming liquids

What is the appropriate local order parameter?
A thermodynamic/structural or a purely kinetic approach?

Different strategies for determining a local order parameter

- **Based on physical intuition on 3-D glass-forming liquids**:

  => **Structural view**: a complex local arrangement in liquids that is incompatible with crystallization (frustration).

  => **Dynamical view**: a mobility field with constraints (dynamical facilitation).

- **A more generic route:**

  Derive the proper **mean-field theory** and the **order parameter** (*à la* Landau) + include **spatial fluctuations** of this order parameter.

  Then: Renormalization group & nucleation theory

  [Compare with the well-known case of the gas-liquid transition]

Some theoretical ingredients

- **Frustration**: The energy of a system cannot be minimized by simultaneously minimizing all the local interactions.

  => Multiplicity of low-energy ("metastable") states.

  => Thwarts crystallization.

- **Thermal activation in a rugged (free) energy landscape**: Presence of an exponentially large number of metastable states that may trap the system.

  => Relaxation slowdown is associated with thermally activated escape from metastable states.

- **Dynamical facilitation**: Mobility triggers mobility in nearby regions.

  => Spatial correlations in the dynamics.

Different ways to incorporate the ingredients in a general theory!

Putative local order parameter(s)

- **Local structural order**: Observables characterizing the locally preferred molecular arrangement in the liquid, if present (e.g., related to bond-orientational order).

  => Such a local order (*e.g.*, poly-tetrahedral in metallic glasses) can be detected by multi-point, not simply pair, static correlation functions.

- **Similarity or "overlap" between configurations:** Measures of the similarity between two equilibrium configurations of the liquid.

  High overlap => in the same state ("localized")
  Low overlap => in different states ("delocalized")

- **Local mobility field**: Mobility or activity defined by following the dynamics in small volumes of space over short periods of time.

  => Easier at low T where mobility is localized and scarce.

Theories based on an underlying dynamic transition

- **Mode-coupling theory** [Götze & coll (80‘s to now)]

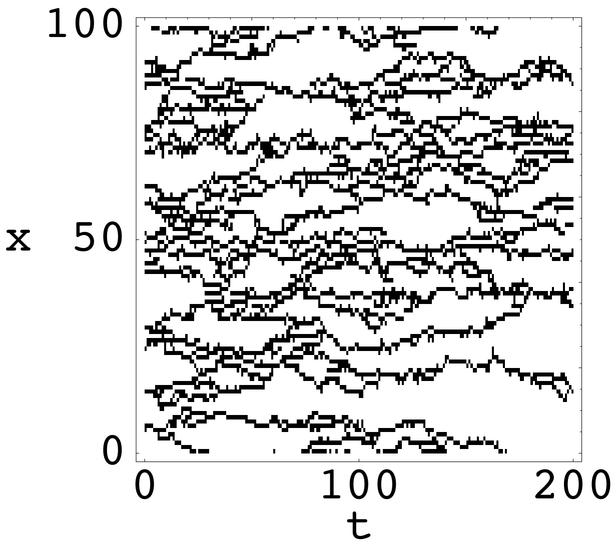
  Self-consistent kinetic freezing: relaxation channel for density fluctuations via product of density modes.

  => an avoided transition at $T_c > T_g$

- **Dynamical facilitation and kinetic constraints** [Fredrickson-Andersen (80‘s)... Garrahan-Chandler]

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

  => an unreachable critical point at T=0

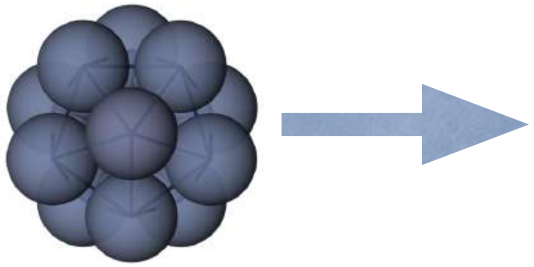


Theories based on an underlying thermodynamic transition

- **Frustration-based approach** [Nelson, Sadoc et al (80‘s), Kivelson + GT, Tanaka et al]

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

  => competition
  => an avoided transition at $T^* > T_g$



No icosahedral xtal

- **Random first-order transition theory**: [Wolynes & coll (80‘s to now), Parisi & coll + Many...]

  Dynamic slowdown driven by the decrease of the configurational entropy

  => an unreachable transition at $T_K < T_g$

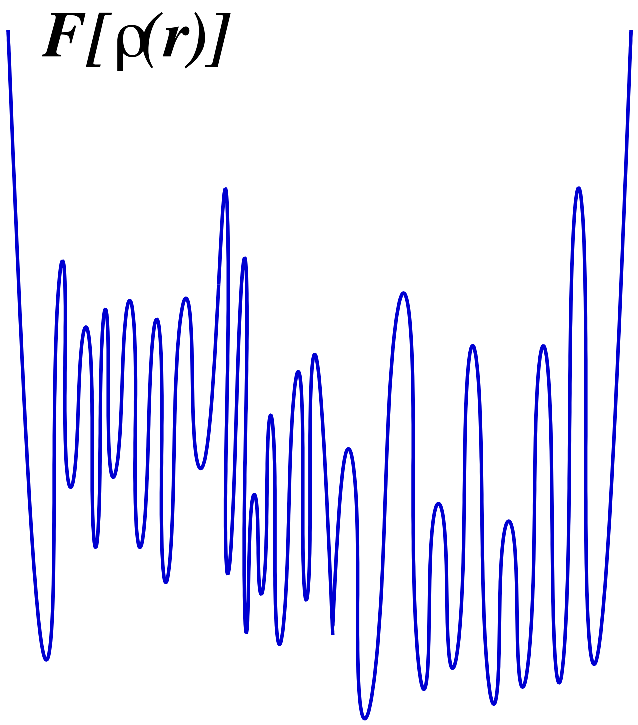
The free-energy landscape/RFOT scenario as the mean-field theory of glass-forming liquids

Analog of the van der Waals theory for the gas-liquid transition

[Wolynes, Kirkpatrick, Thirumalai, 80's + Parisi-Mezard-Franz-Zamponi + many]

- **An intricate mean-field theory** (exact for the D->∞ hard-sphere fluid) with **two critical temperatures.**

- **An exponentially large number of metastable states** that may trap the liquid (configurational entropy) between a **dynamical transition at T_d** and a **"random first-order transition" (RFOT)** at a lower temperature **T_K**.



cut in $\rho(\boldsymbol{r})$ *space*

Summary of the characteristic (theoretical) temperatures

Unreachable (extrapolated):

$T_0 \simeq T_K$ (RFOT),

T = 0 (facilitation).

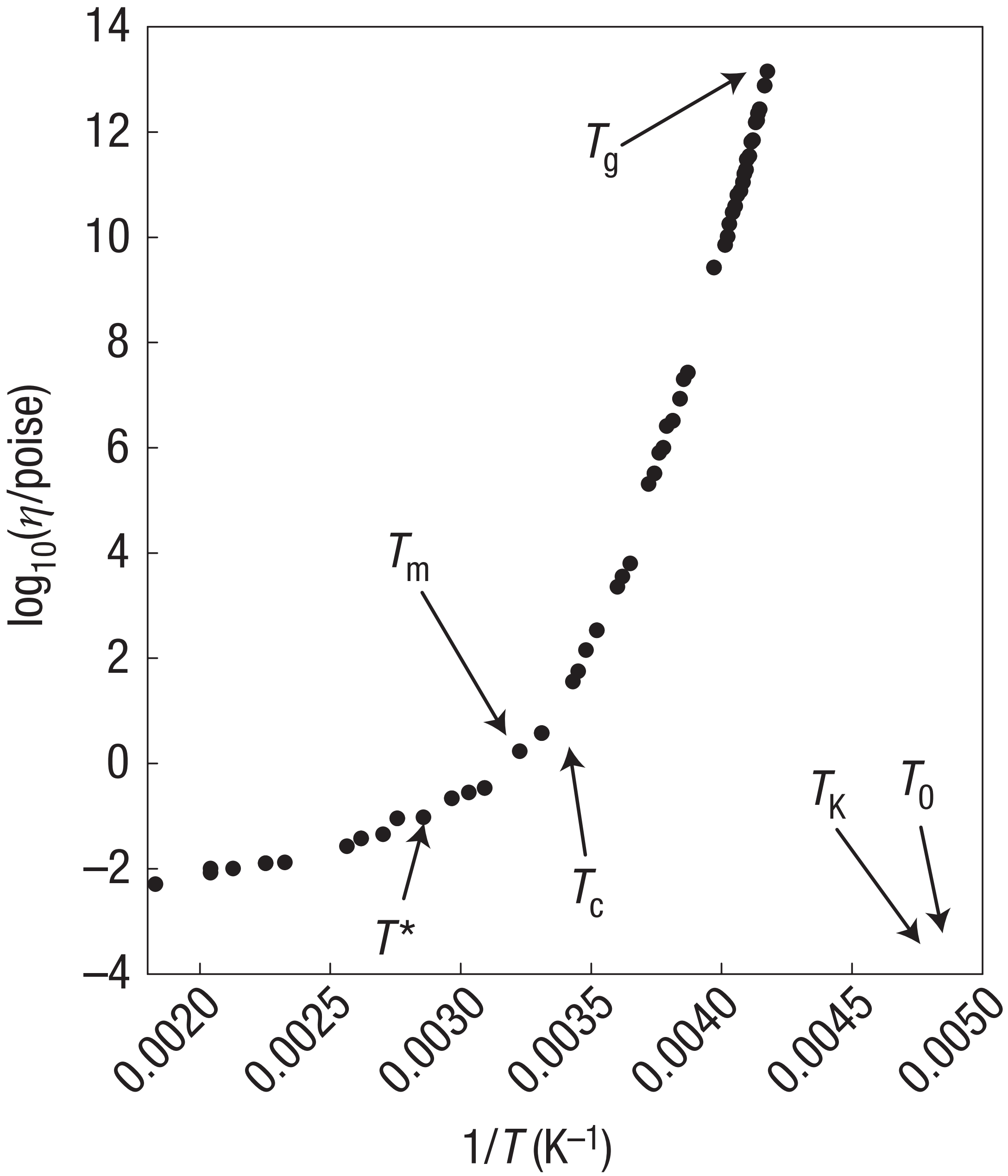
Avoided (crossover):

T* (frustration),

$T_c = T_d$ (MCT & RFOT).

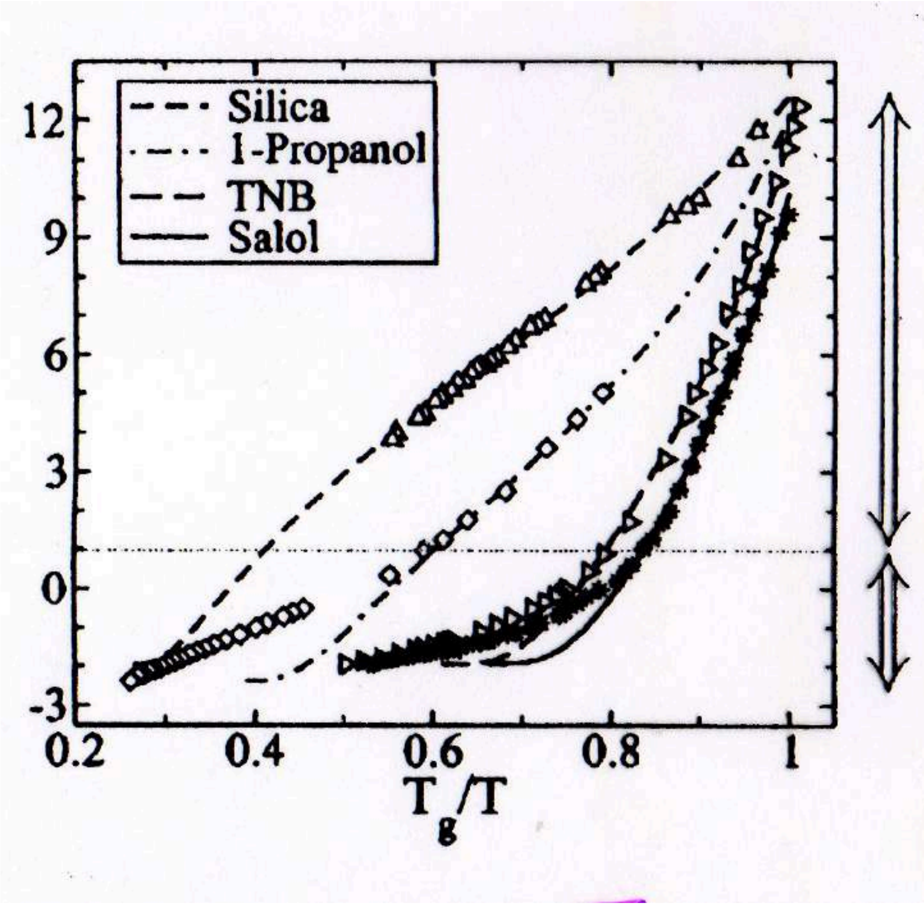
Experimental: T_m, T_g

(T-dependent viscosity of o-TP)

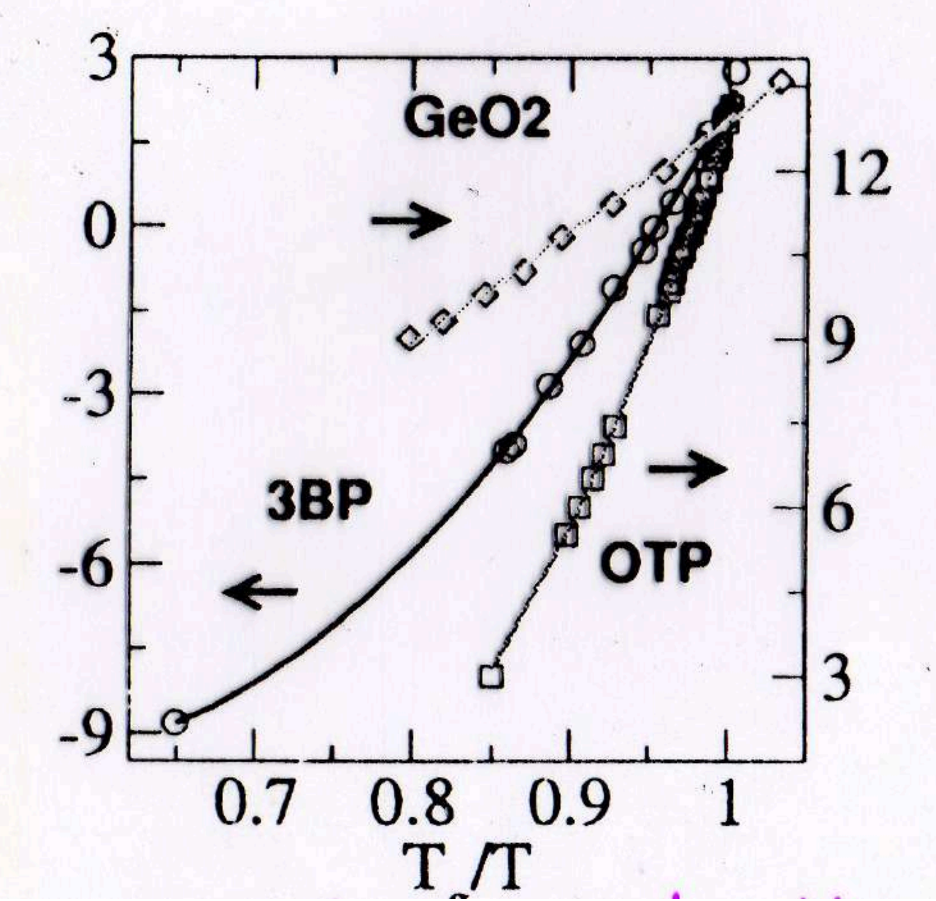


Weak constraints from comparison to experimental data...

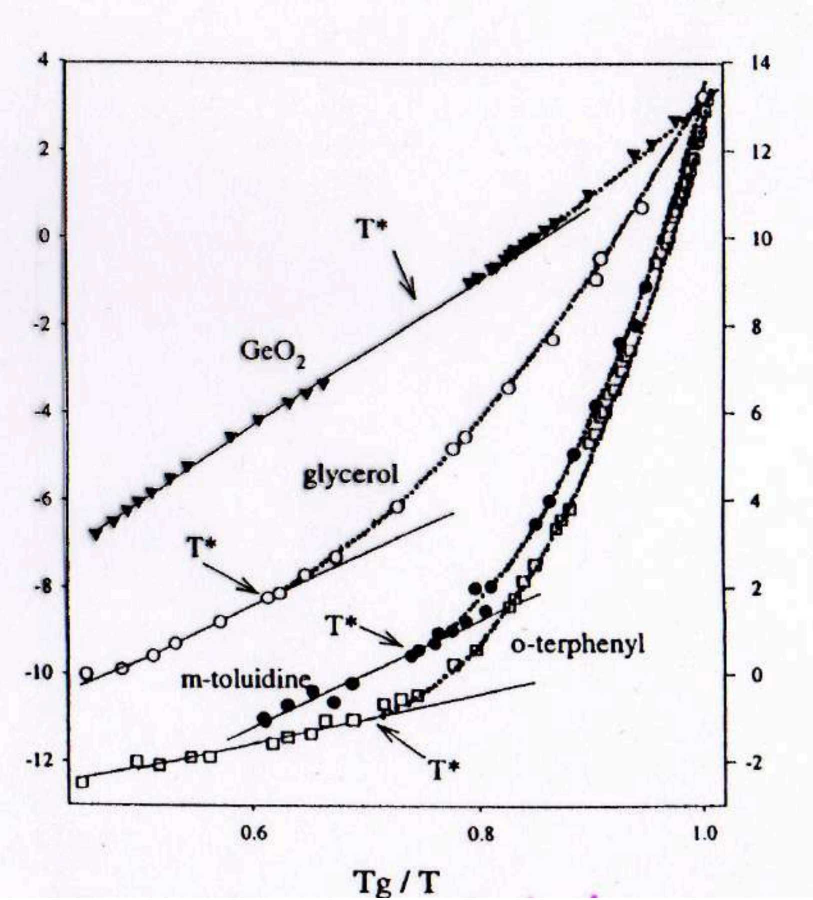
With the help of (unavoidable ?) adjustable parameters, several theories fit the same data equally well



RFOT (Wolynes et al.)



Facilitation (Garrahan-Chandler)



Frustration (Kivelson-GT)

log(viscosity or time) vs T_g/T

Conclusion

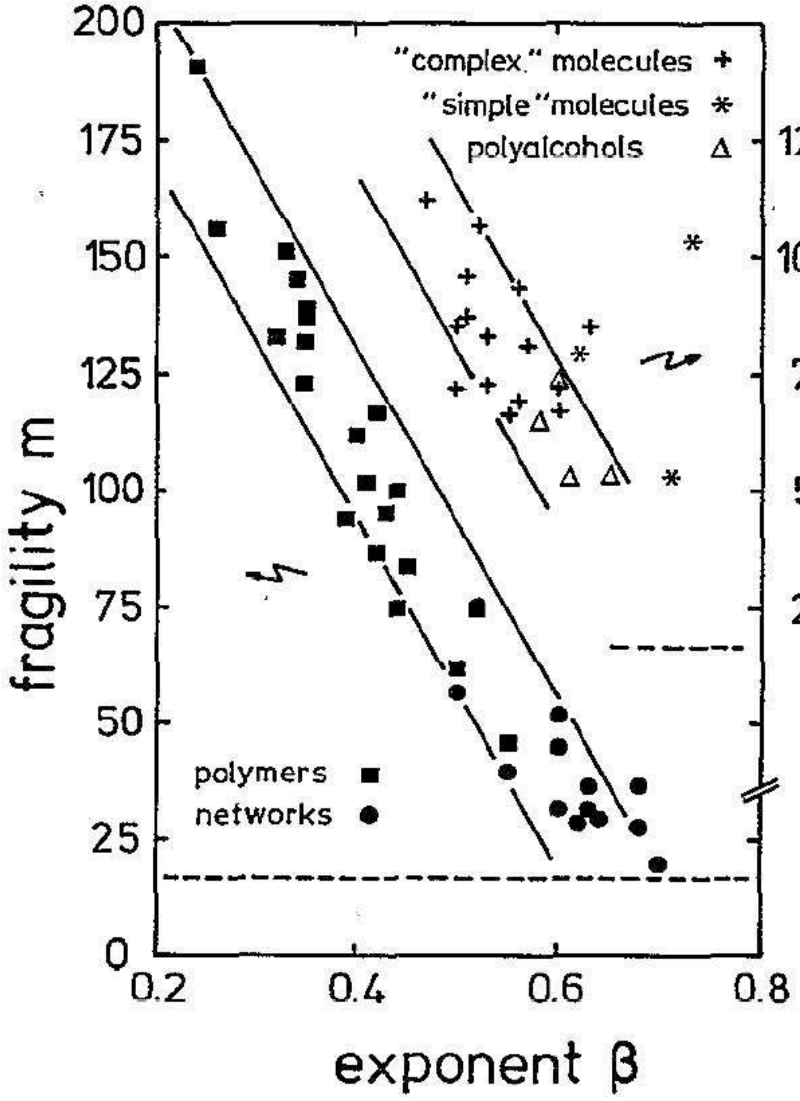
- No consensus on theory of glass transition. Still a challenging problem!
- Existence and nature of growing length scales = key issue for understanding the glass transition.
- New developments in theories of the glass transition that may allow more stringent internal consistency checks and more rigorous treatments... but weak constraints from experiments.

A few references

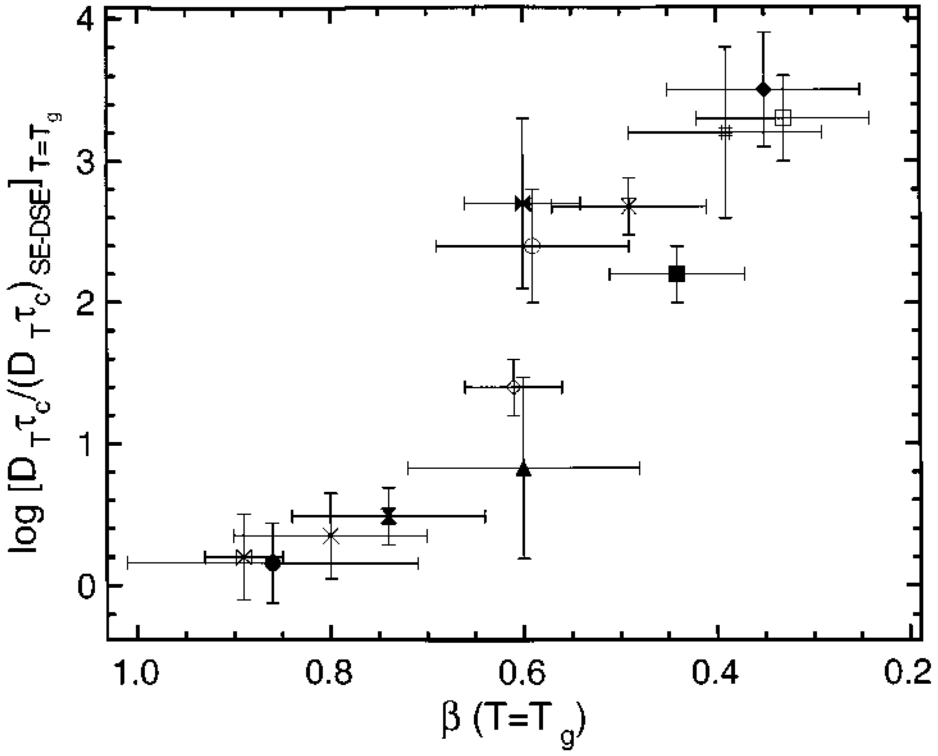
- S. Kivelson and G. Tarjus, “In search of a theory of supercooled liquids”, Nature Mat. **7**, 831 (2008); ArXiv:0804.1718.
- G. Tarjus, “An overview of the theories of the glass transition”, (in *Dynamical Heterogeneities in Glasses...,* L. Berthier et al. Eds. (Oxford Univ. Press, 2011); ArXiv:1010.2938.
- L.Berthier and G. Biroli, “Theoretical perspective on the glass transition and amorphous materials”, Rev. Mod. Phys. **83**, 587 (2011).
- M. D. Ediger and P. Harrowell, “Perspective: Supercooled liquids and glasses”, J. Chem. Phys. **137**, 080901 (2012).

Empirical correlations

Correlations among characteristics of the slow dynamics



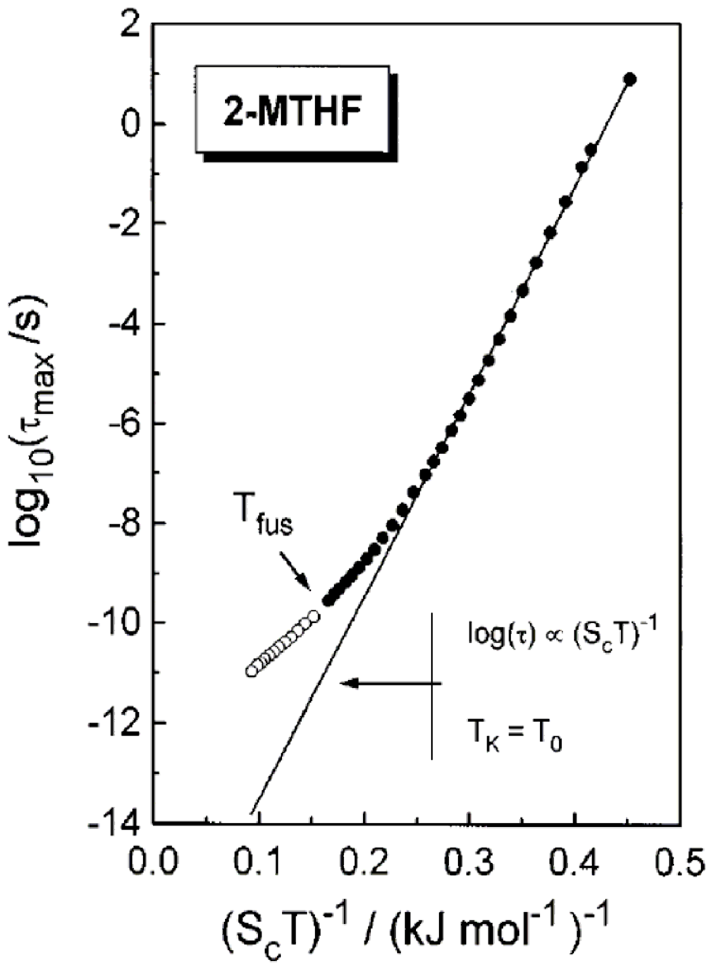
Correlation between fragility and stretching exponent
(Bohmer et al., 1993)



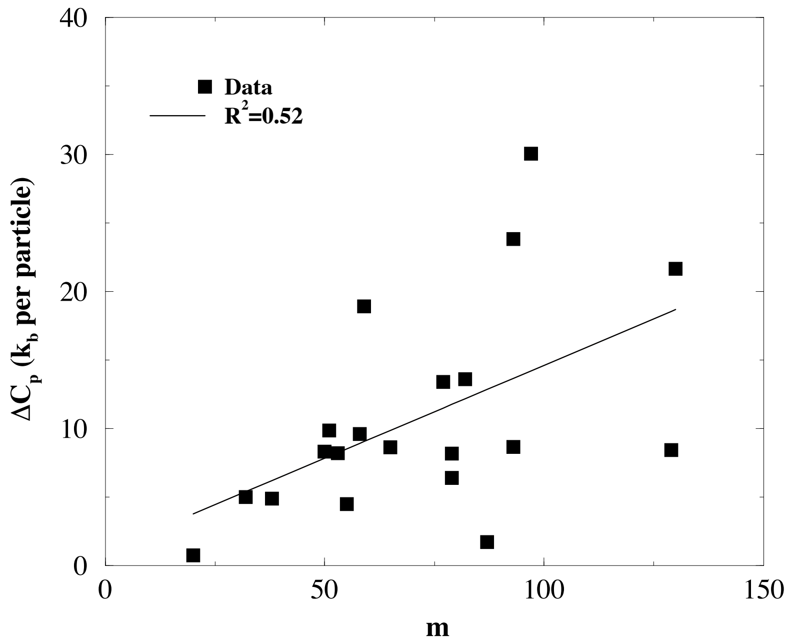
Correlation between translation-rotation decoupling and stretching at T_g for liquids and polymers
(Ediger, 2000)

+ Correlation fragility & nonlinear relaxation
+ Universality of alpha relaxation
+ Density/temperature scaling
+ etc...

Correlations between slow dynamics and thermodynamics



Log(τ/τ_0) versus the inverse of T times the configurational entropy S_c for liquid 2-MTF (Richert-Angell, 1998)



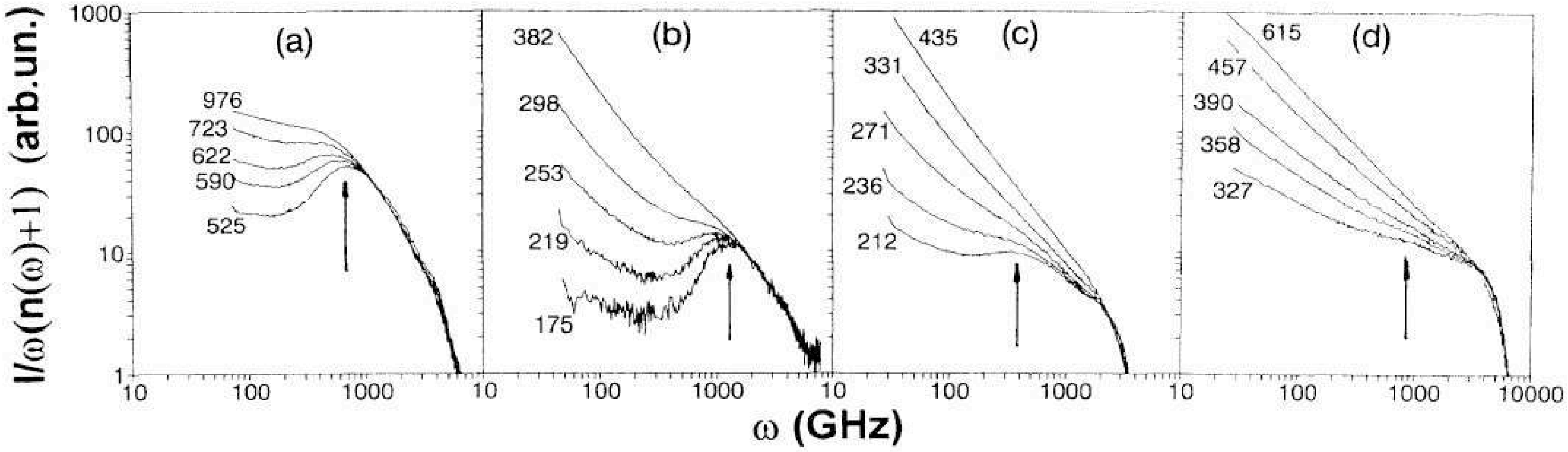
Correlation between heat capacity jump at Tg and fragility for molecular liquids
(Stevenson-Wolynes, 2005)

\+ Correlation between dynamic and thermodynamic fragilities (Ito et al.,1999)
\+ Correlation between VTF T_0 and Kauzmann T_K
\+ etc...

Correlations between slow dynamics and fast dynamics (in liquid or glass)

Example:

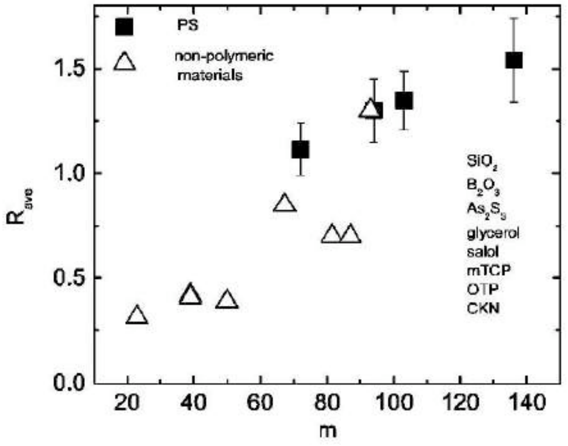
Large intensity of boson peak small fragility



Sokolov *et al.* 1993

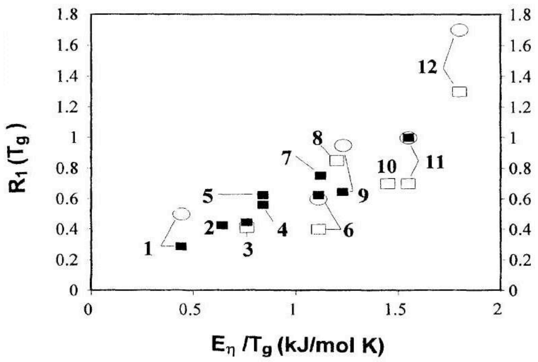
$$\frac{g_{DB}(\omega)}{g(\omega)}$$

$$R = \frac{I_{quasi}}{I_{BP}}(T = T_g)$$

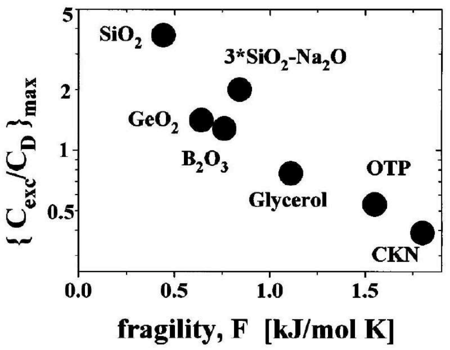


Correlations between slow dynamics and fast dynamics (in liquid or glass)

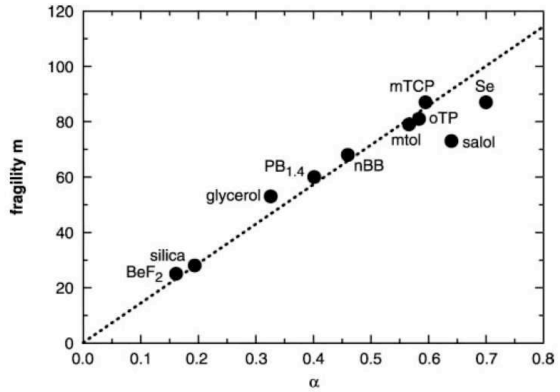
Correlations between fragility and: Poisson ratio of elastic moduli, relative amplitude of Boson peak, mean-square displacement, ergodicity parameter at T_g, etc...



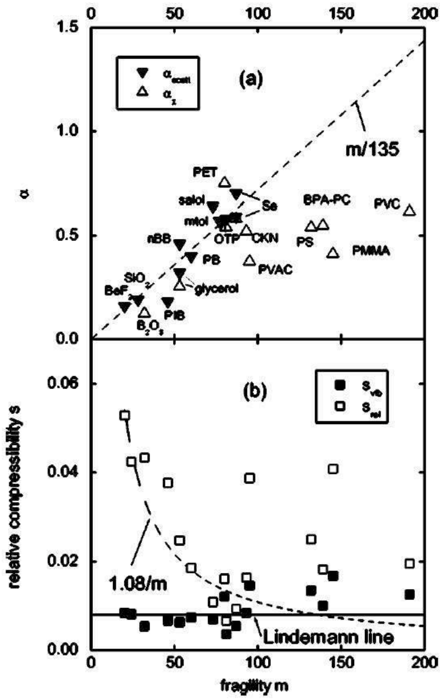
Sokolov et *al.* 1993



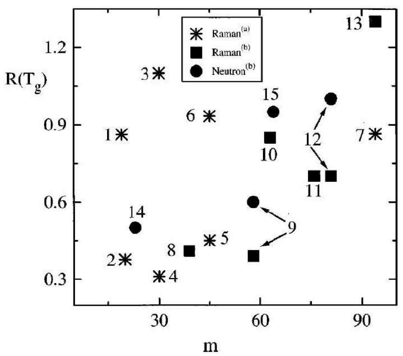
Sokolov et *al.* 1997



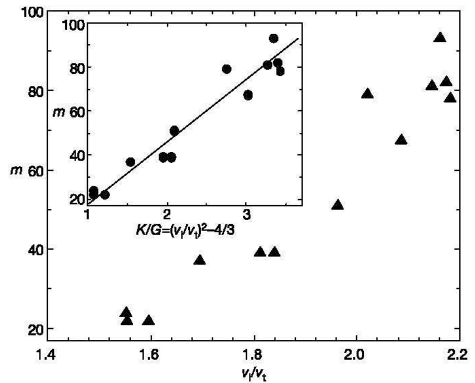
Scopigno et *al.* 2003



Buchenau et *al.* 2004

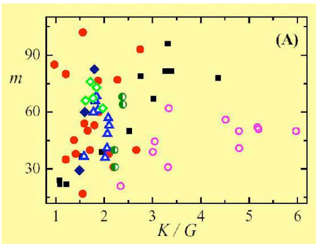


Yannopoulos et *al.* 2000



Novikov et *al.* 2004

+ Correlation between alpha relaxation time and shear modulus or mean-square displacement (Dyre), etc...



Yannopoulos et *al.* 2000

Caution!!!

- Correlation does not mean causality

- Large body of data and systems are required to ascertain correlation

- Large error bars

- Correlations may not be robust when studying effect of additional control parameters (pressure, molecular weight,...)