What is there to be explained about glasses and glassformers ?

Facts, questions, views

Gilles Tarjus

(LPTMC, CNRS/Univ. Paris 6)

Diversity of views,
Diversity of questions

on glasses, glassformers,
and the glass transition

I

What is meant by a "glass", a "glassy" system ?

“Glass”

Wikipedia: “Strictly speaking, a glass is defined as an inorganic product of fusion which has been cooled through its glass transition to the solid state without crystallizing.”

However, the term is commonly used with a broader meaning.

“Glass”:

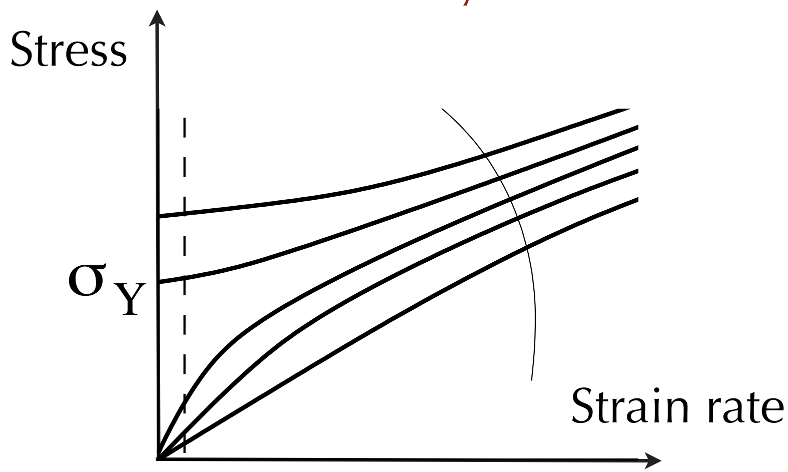
Jammed/frozen in a disordered state, generally out of equilibrium.

1) jammed/frozen
2) disordered
3) out-of-equilibrium

1) Jammed/frozen state

- (some) motions appear arrested,
- system appears as a solid that does not flow and resists to shear.

Nonzero yield stress σ_Y

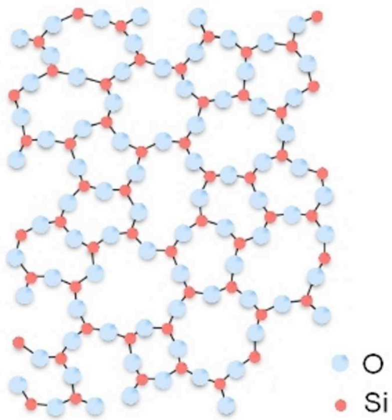


Schematic steady-state flow curves

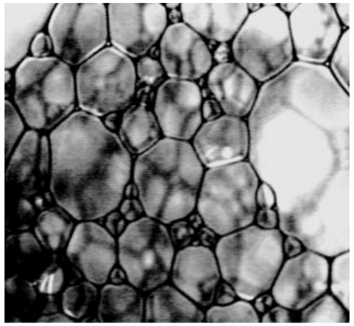
Different types of glasses

- "Hard" glasses:
  - ✳ Large elastic (e.g. shear) moduli (GPa and more)
  - ✳ Standard glasses: silica and inorganic, ionic mixtures, organic molecular (hydrogen-bonded and van der Waals) glasses; polymers (plastics); metallic glasses; glassy plastic crystals...
- "Soft" glasses:
  - ✳ Small elastic (e.g. shear) moduli (MPa down to a few Pa)
  - ✳ colloidal suspensions, foams, emulsions, granular media...
- Others: spin glasses, orientational glasses, vortex glasses, electron glasses, etc... + proteins ?

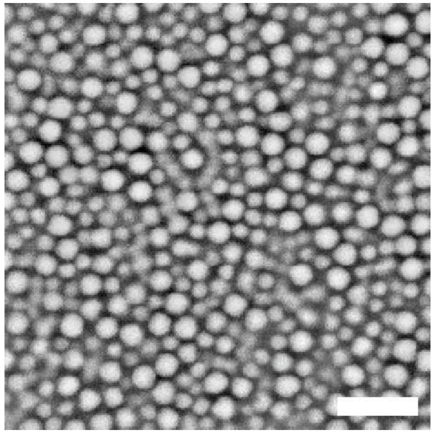
Different types of glasses



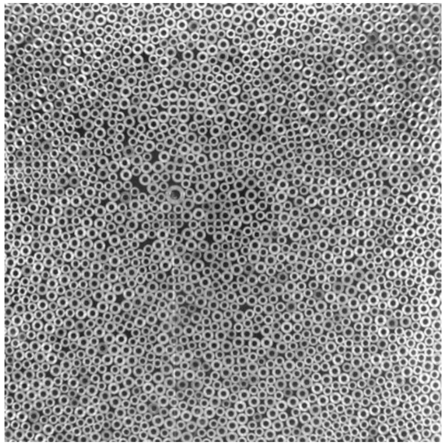
Schematic structure of glassy silica



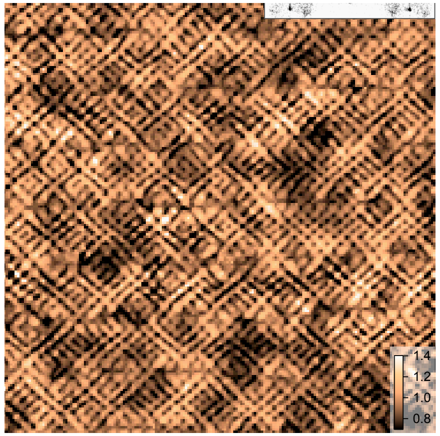
Foam



Colloidal glass (Weeks et al.,2009)



Granular material
(Candelier et al. 2009)

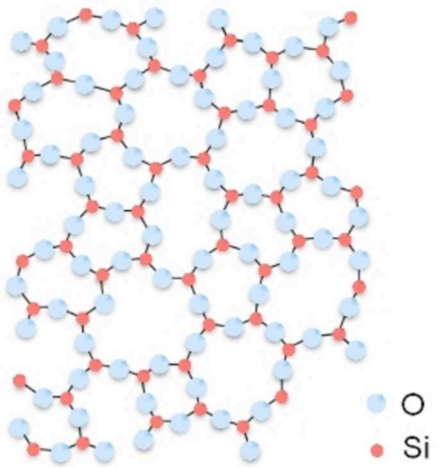


Electronic glass in underdoped cuprates
(Kohsaka et al., Science 2007)

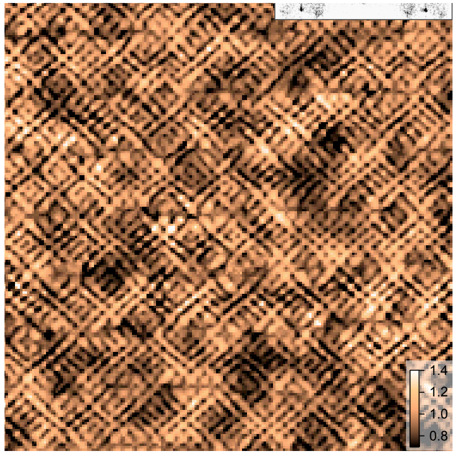
2) Disordered state

- No obvious long-range order, “amorphous” state.
- Do not confuse “quenched” disorder and “annealed” or “self-generated” disorder !!!
- Which degrees of freedom are disordered ?

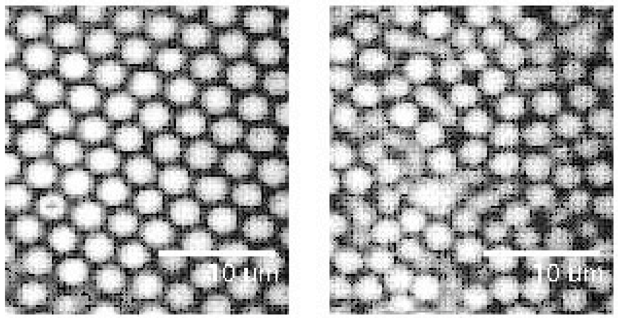
No long-range order



Schematic structure of glassy silica



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



Colloidal crystal (left) versus glass (Weeks et al., 2007)

Quenched versus annealed/self-generated disorder

- "Quenched" disorder: impurities or defects frozen for extremely long times; the system of interest equilibrates (or not) in the presence of impurities.

- Examples of systems with quenched disorder: spin glasses in magnetic materials, vortex and Bragg glasses in type-II superconductors, Coulomb electronic glasses in insulators.

- The glassiness of the system is due to the presence of the quenched disorder which acts as an external constraint.

Different from

- "Annealed", self-generated disorder in liquids, polymers, colloidal suspensions and granular media: disorder is intrinsic to the system.

Disordered state, however...

- Some glasses are associated with a true thermodynamic phase transition: systems in the presence of quenched disorder, such as spin glasses and vortex glasses, for example have true long-range order of an unusual type.

Amorphous long-range order ????

- In addition, some degrees of freedom may be ordered...

Disordered state, however...

Some degrees of freedom may be ordered:

- Glassy plastic crystals (cyanoadamantane, ethanol, etc...): the molecular orientational degrees of freedom are disordered but the molecular positions are ordered, forming a cubic crystal.

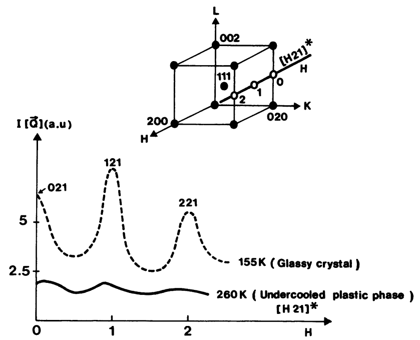


Fig. 3. — Diffuse X-ray scattering. Q scan along [H21]* in the glassy and undercooled plastic crystals of cyanoadamantane.

- Spin glasses, electron glasses: only the spin or the electronic degrees of freedom are concerned by glassiness and disorder.

3) Out-of-equilibrium state

Equilibration time is much longer than the observation time: on the time scale of the experiments, the system is out of equilibrium.

$$\tau_{micro} << \tau_{exp} << \tau_{equil}$$

Properties of the equilibrium state and of relaxation near and to equilibrium

- Properties are independent of preparation.

Stationary property/time-translation invariance:

For an observable A(t),

$$\langle A(t)\rangle = \langle A\rangle$$
$$\langle A(t')A(t'+t)\rangle = \langle A(0)A(t)\rangle$$
etc...

- Fluctuation dissipation theorem and linear response.

✳small perturbation applied to the system;
✳close to equilibrium, the response to a small perturbation can be expressed in terms of <u>correlation functions of the unperturbed system</u>.

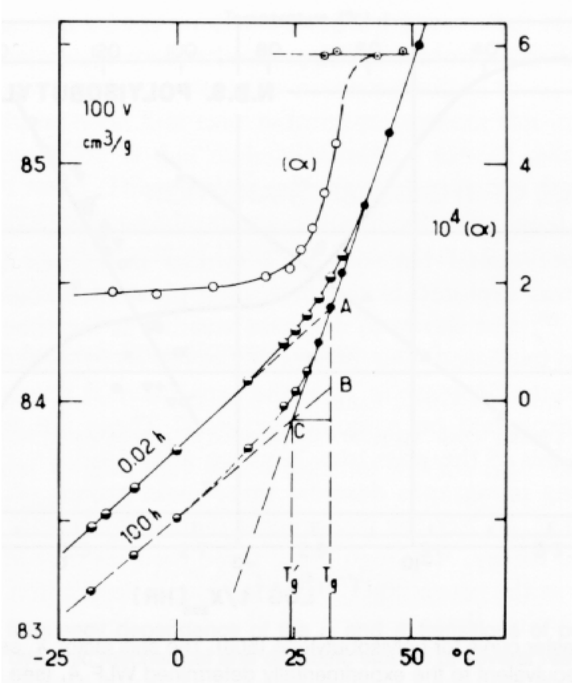
<u>Example</u>: Response of observable A at time t′+t to a perturbation that couples to A between t′ and t′+t:

$$\chi(t',t'+t) = \chi(0,t), \text{ with}$$
$$\chi(0,t) = T\,(\langle A(0)A(t)\rangle - \langle A(0)A(0)\rangle)$$

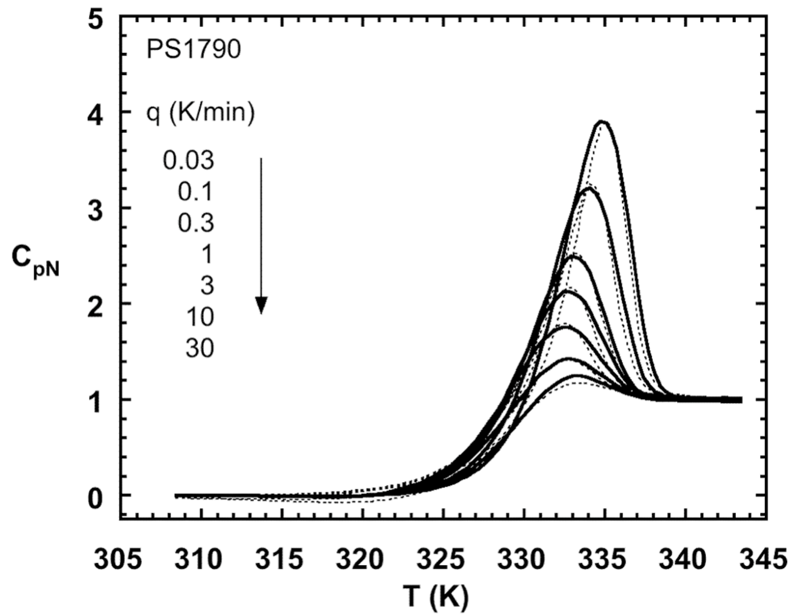
Manifestations of out-of-equilibrium character

- Dependence of properties on preparation history, *e. g.* on cooling rate.
- Hysteresis, memory effects.
- Aging (linear response regime).
- Violation of equilibrium relations (fluctuation-dissipation, time-translation invariance).

Dependence on cooling rate



Volume versus temperature for polyvinyl acetate at two different cooling rates (1K per 0.02 and 100 hr)

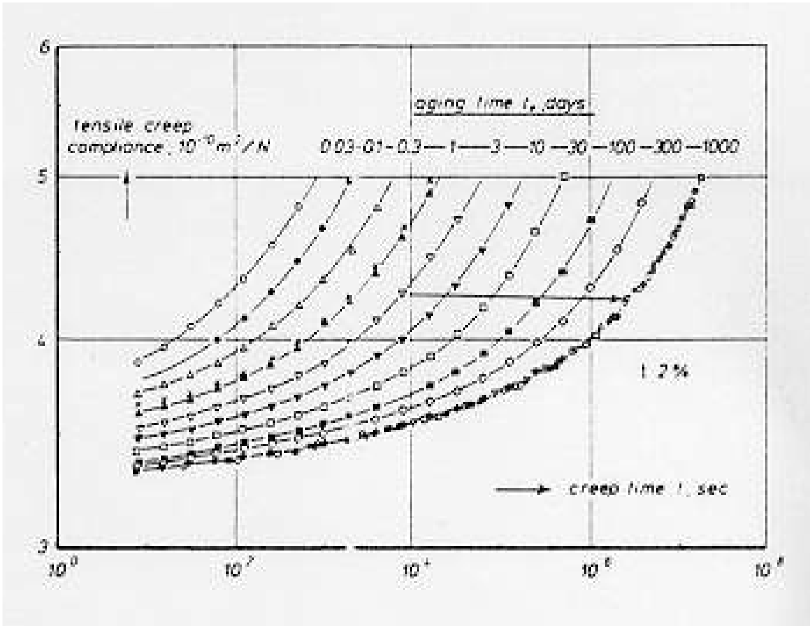


Normalized heat capacity versus temperature for polystyrene at different cooling rates q
(C. Alba-Simionesco et al.)

Aging

- The properties of a system depend on its "age", *i.e.* the time spent in the glassy state.
- More easily observed in two-time quantities: *e.g.*, the evolution with time t of the (linear) response of a system prepared for a "waiting time" (age) t_w.

$J(t,t_w)$



t

Aging in PVC glass: mechanical response (small-strain tensile creep) versus t for different (long) waiting times t_w (in days) at T=293K. (L.C.E. Struik, *Physical Aging in Amorphous Polymers and Other Materials*, Elsevier, 1978)

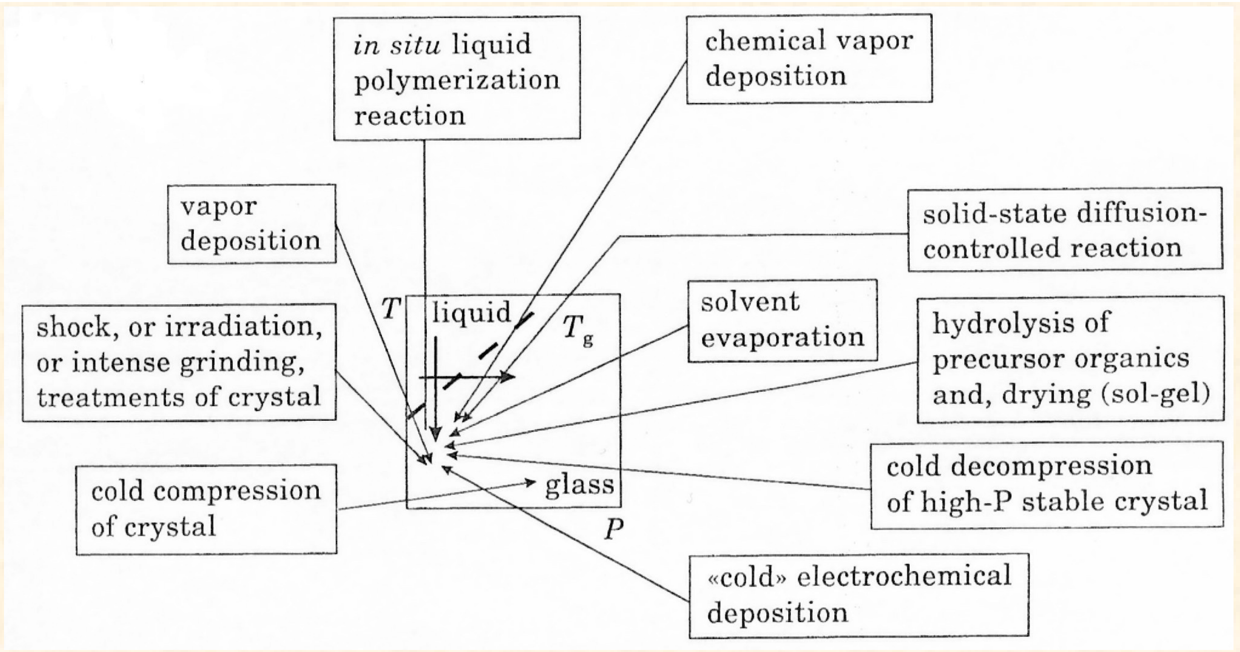
However...

- Some glasses are associated with a true thermodynamic phase transition: spin glasses and vortex glasses for example. Transition is then observable, but is the equilibrium glass phase observable ? Problem of infinite relaxation time (spin glass).

II

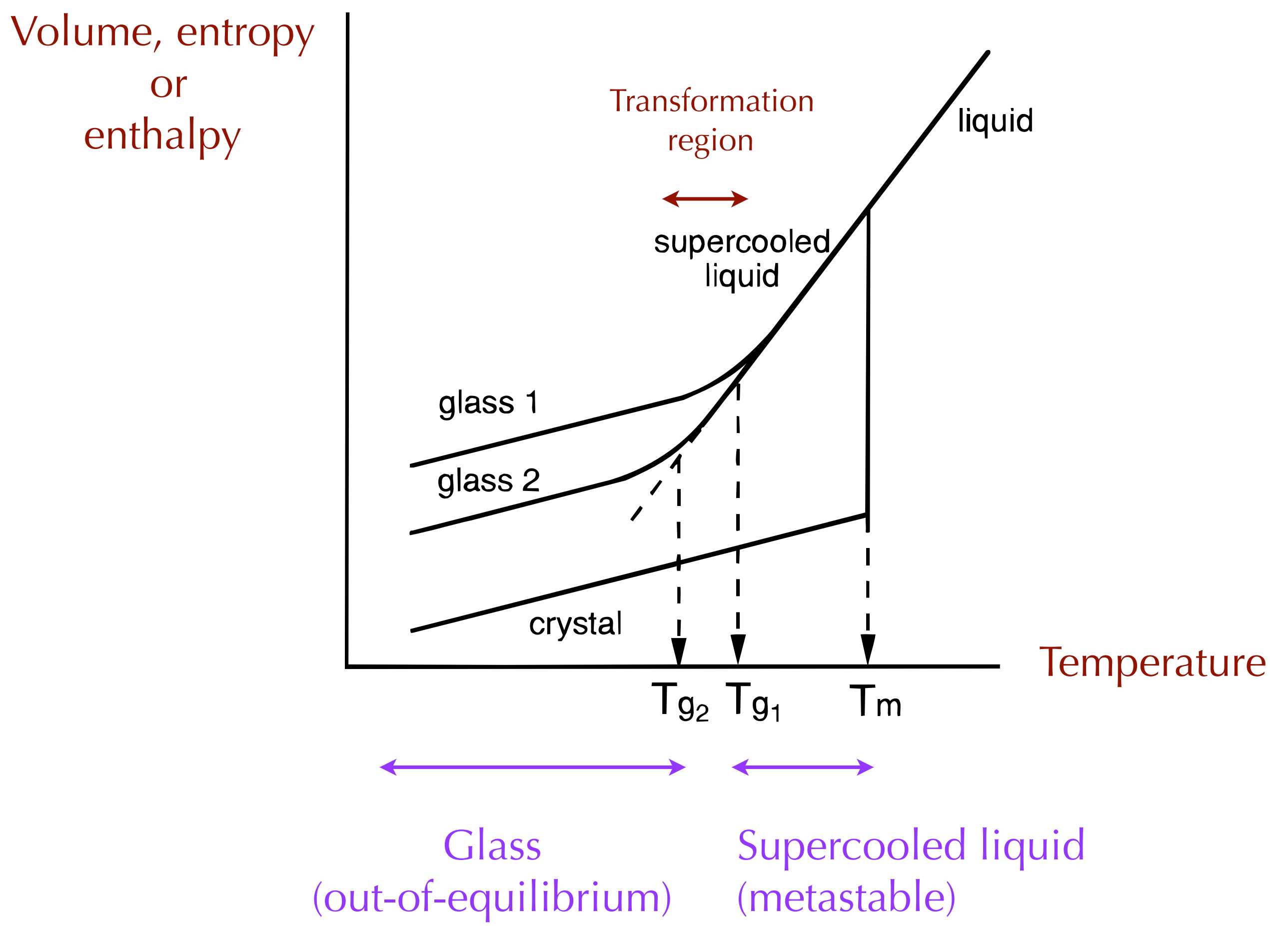
Glasses, glass formation

Different ways of forming an amorphous ("glassy") solid



Angell (Science, 1995)

Glass formation by cooling



Metastability versus out-of-equilibrium

- Liquid above T_m and crystal below T_m are the stable phases.
- Supercooled liquid below T_m is metastable.
- Glass below T_g is mechanically stable but out-of-equilibrium.

What does this mean ?

Variety of questions depending on temperature regime of interest

(1) In the glass:

* Low-T anomalies (below 1K; between a few K and a few tens of K): thermal, dielectric and acoustic properties.

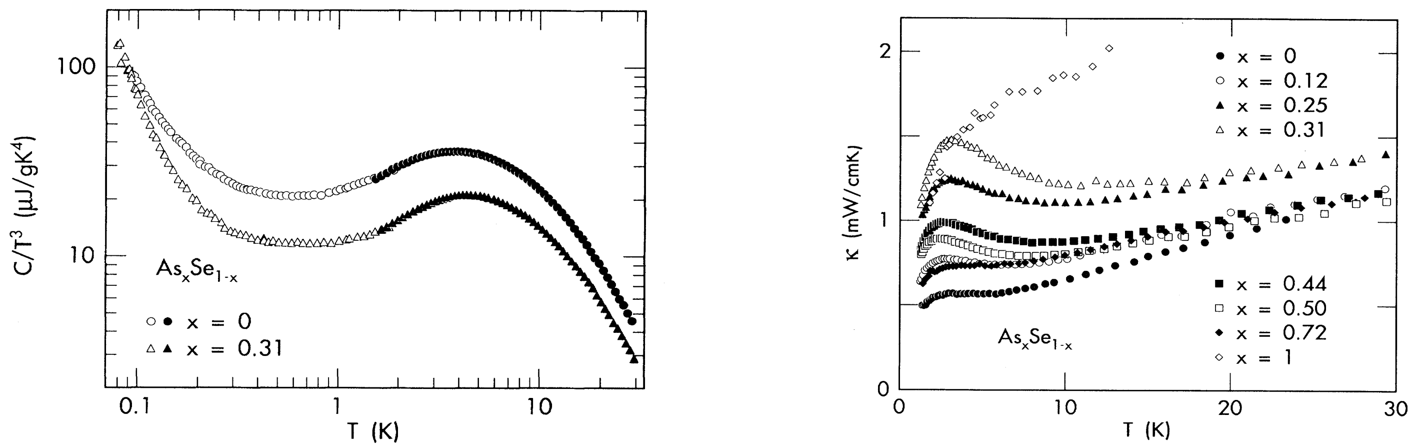
* At higher T: aging behavior + nonlinear rheology (*e.g.* under high enough shear stress).

* In the glass transformation region: nonlinear relaxation.

Low-temperature thermal anomalies in a glass

Anomalous behavior compared to the Debye behavior of perfect crystals:

Instead of T^3 dependence of heat capacity C and of thermal conductivity κ:
Roughly linear T dependence of C below 1K and excess peak around 5-30K;
T^2 dependence of κ below 1K and plateau around 5-30K.

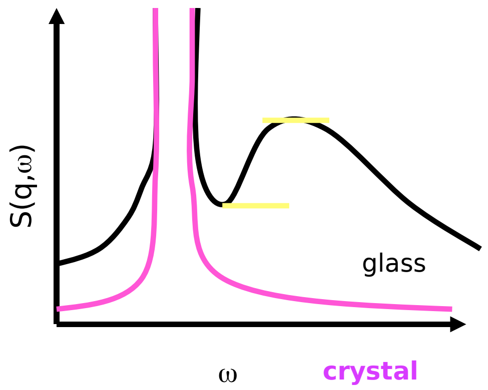


Heat capacity divided by T^3 (left) and thermal conductivity (right) of amorphous As_xSe_{1-x} (Liu et al., 1993)

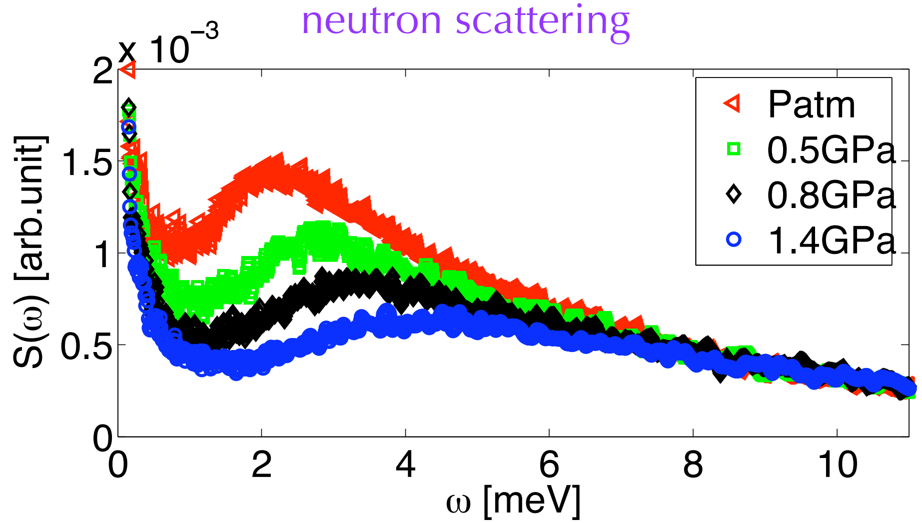
Boson peak

Anomalous behavior of heat capacity C around 5-30K possibly related to
an excess of vibrational modes compared to the Debye model ("Boson peak" in $g(\omega)/\omega^2$).

$$S(q,\omega) \sim q^2 \frac{g(\omega)}{\omega^2}$$



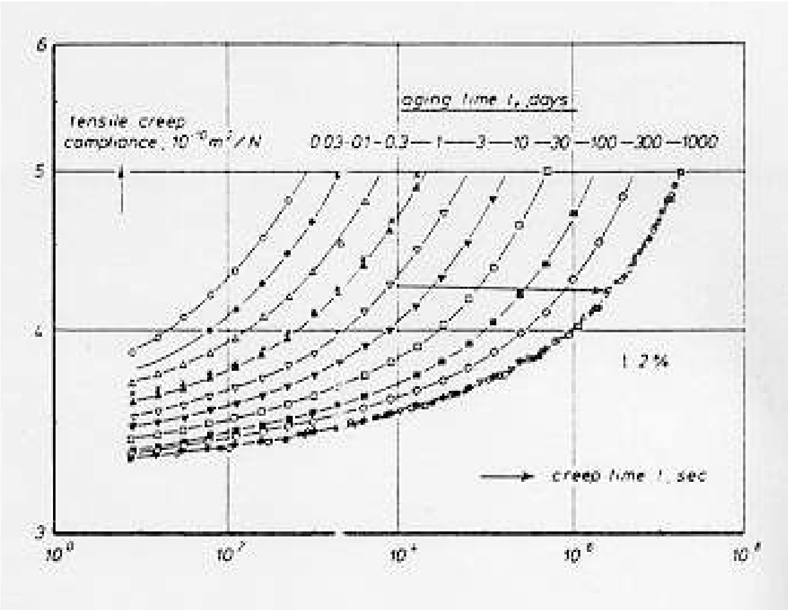
Incoherent inelastic neutron scattering



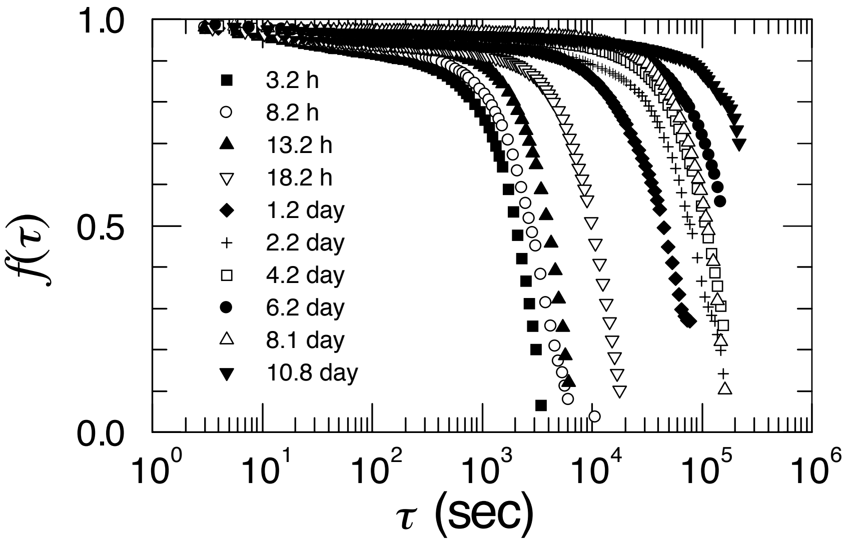
PIB glass at T_g (Niss, Alba-simionesco et al.)

1 meV ≃ 8 cm^{-1} ≃ 12K

"Universality" of physical aging in glasses (1)



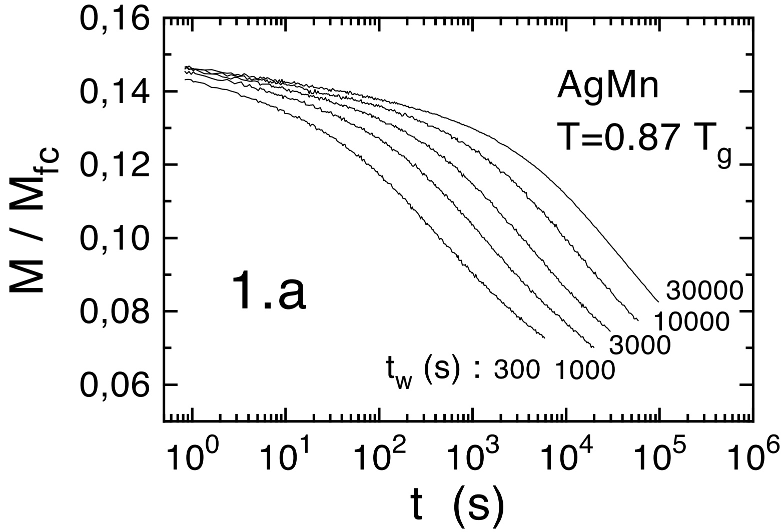
Aging in PVC glass: response (tensile creep) versus t for different waiting times t_w at T=293K. (Struik, 1978)



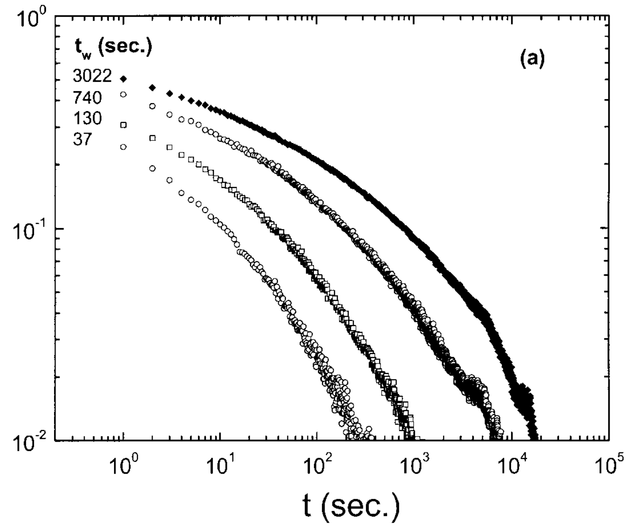
Aging in a colloidal gel: density correlation function versus t for different waiting times t_w at T=293K. (Cipelletti, 1978)

Characteristic "relaxation" time $\tau \sim \tau_0 \left(\frac{t_w}{\tau_0}\right)^{\mu}$ with $\mu \sim 1$

"Universality" of physical aging in glasses (2)



Aging in a spin glass: remanent magnetization versus t for different waiting times t_w (T=9K)
(Vincent et al., 1996)

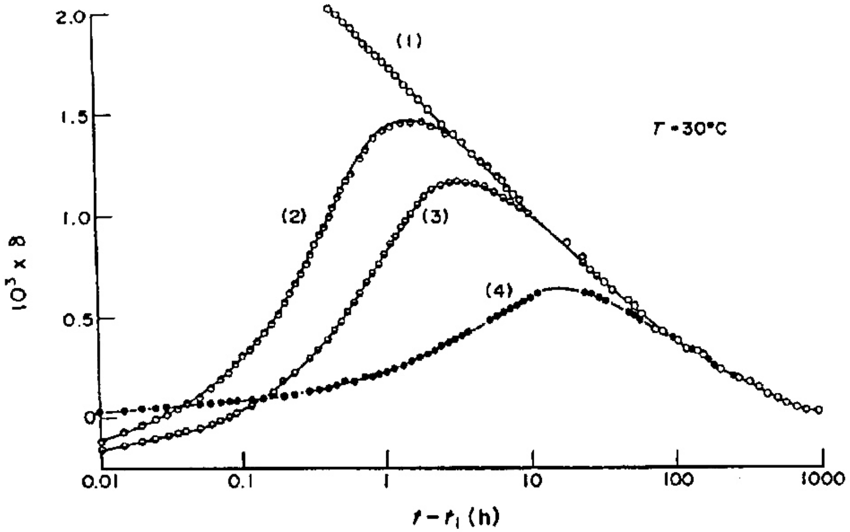


Aging in an electron glass: response (conductance) versus t for different waiting times t_w (T=4.11K)
(Vaknin et al., PRL 2000)

$$\tau \simeq \tau_0 \left(\frac{t_w}{\tau_0} \right)^{\mu}$$

How many parameters to characterize a glassy state ?

- P,V,T not enough...



Kovacs effect (1963):
Isothermal evolution with time (in hours) of the relative volume variation of polyvinyl acetate at T_2=30°C,
after a direct quench from T_0=40°C
and
after quenches at T_1 lower than T_2 (until the volume equals the equilibrium volume at T_2) followed by reheating to T_2.

- But, whole history untractable!

→ Quest for effective/fictive temperatures

Nonlinear relaxation in the glass transformation region (near T_g)

Out-of-equilibrium relaxation within a slowly relaxing structure -> nonlinearity.

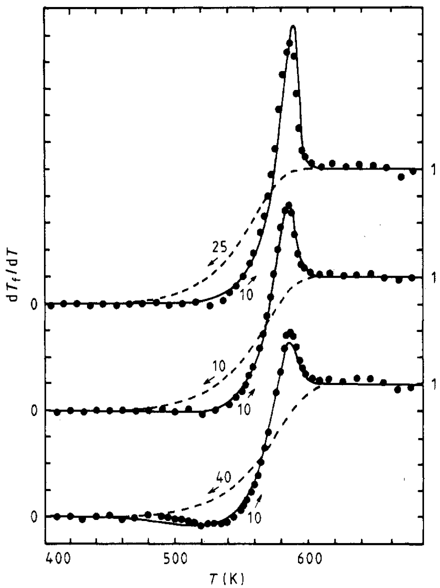


Figure 14. Plot of dT_f/dT against ambient temperature T for B_2O_3 at a heating rate of 10 K min^{-1} following cooling through the transition region at rates shown on figure (in K min^{-1}). Points are experimental heating curves. Solid lines are calculated for best-fit parameter values $\tau_0 = 1.5 \times 10^{-33}$ s, $A = 3.9$ eV, $x = 0.4$, $\beta = 0.65$ (from De Bolt *et al* 1976).

Phenomenological modeling: "fictive temperature"

(Tool-Narayanaswami-Moynihan, Hodge, ...)

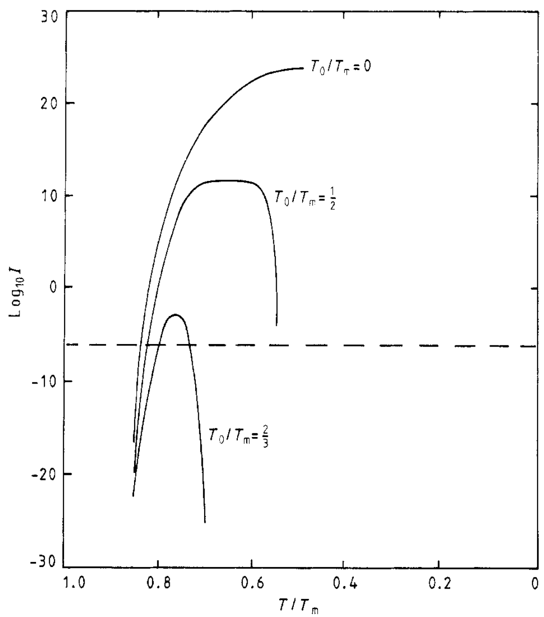
Variety of questions depending on temperature regime of interest

(2) In the liquid:

- ✳ How is cristallization avoided ?
- ✳ Properties of the slowing down of relaxation/ viscous slowdown. How does one get to the glass "transition" ?
- ✳ Glass transition from above and from below.

Avoidance of crystallization, glass-forming ability

Strong first-order transition -> nucleation and growth

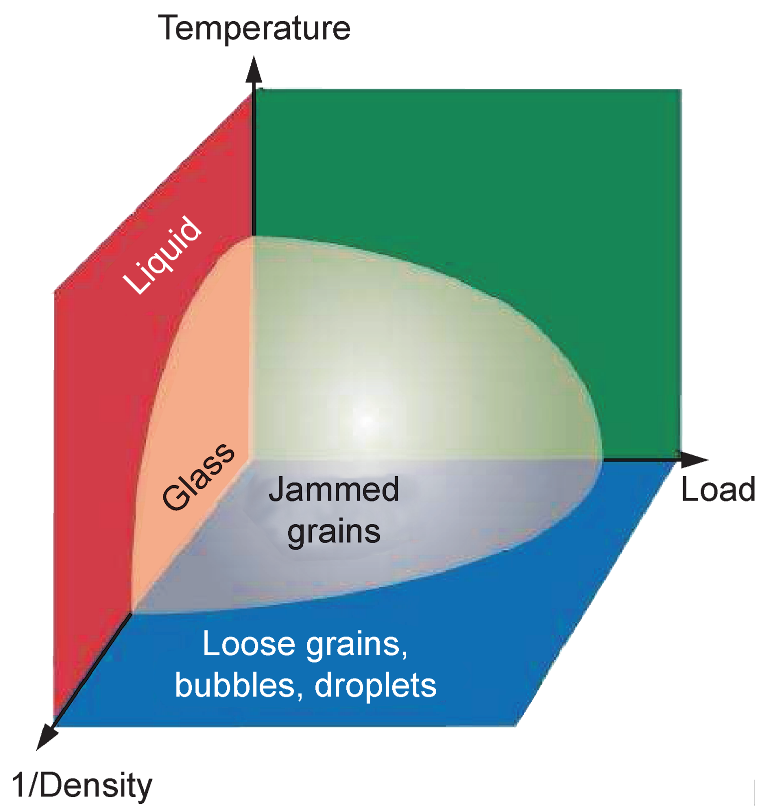


Rate of homogeneous crystal nucleation I versus T/T_m for different liquid behavior.
Below the dashed line, crystallization cannot be detected (Turnbull, 1968)

Role of frustration (Frank, 60's) ??

Different control parameters:

"Jamming diagram"

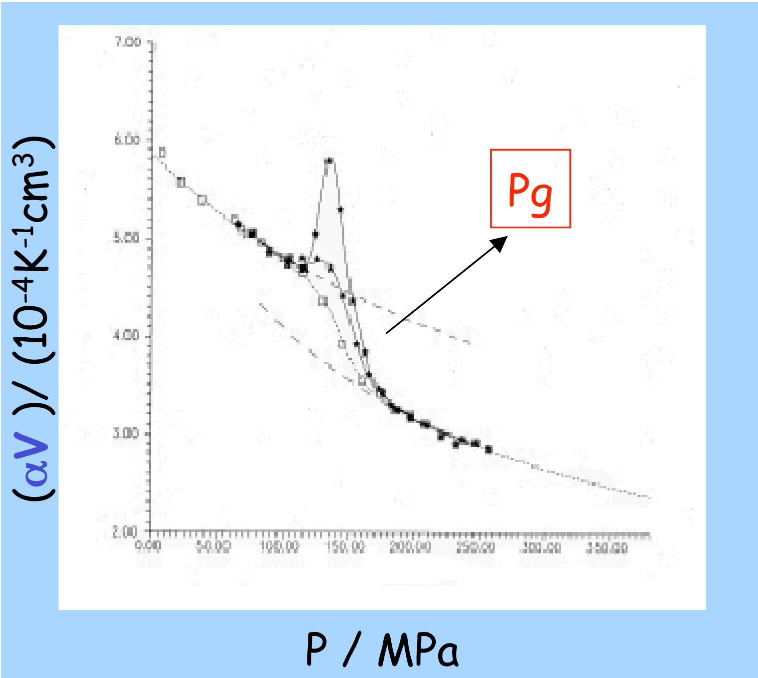


[Liu-Nagel, 1998]

Molecular liquids: temperature, pressure/density, driving force
Polymers: temperature, pressure/density, molecular weight, driving force
Grains, colloids: density/concentration, driving force, interaction strength

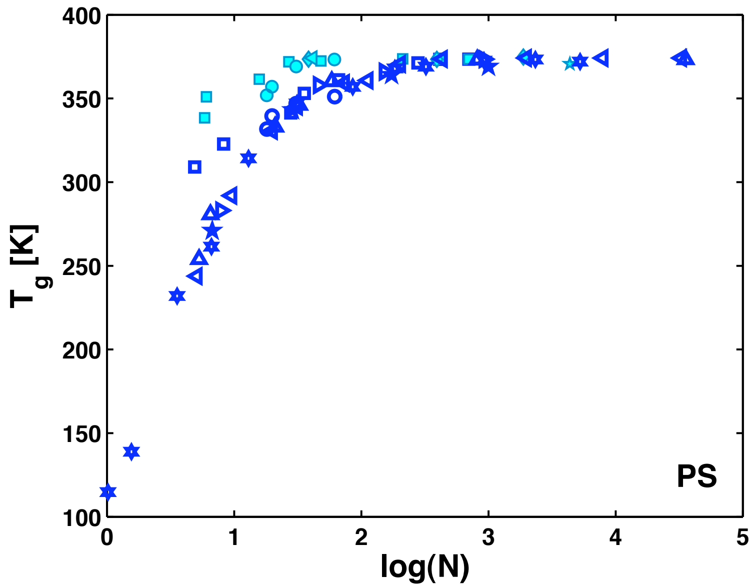
Different control parameters: examples

Pressure



Isothermal glass formation: jump in expansivity at constant T=182.4K for liquid m-fluoroaniline (Alba-Simionesco, 1994)

Molecular weight



Glass transition temperature vs log of monomers for linear polystyrene (dark blue) from DSC and dielectric measurements