

LECTURE 1 : FROM LIQUIDS TO GLASSES

What is a glass ?

Thermodynamic properties

Models



The glass problem (transition+properties), a modern Oklahoma Land Run ?

« The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition. The solution of the (...) important and puzzling glass problem may also have a substantial intellectual spin-off. Whether or not it will help make better glass is questionable. »

P.W. Anderson, Science (1995)



Oklahoma Land Run, April, 22nd 1889

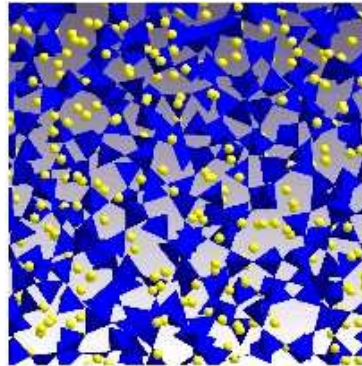
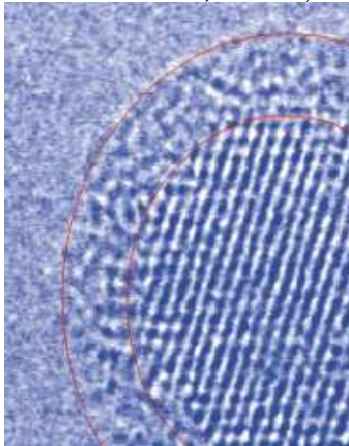
A) WHAT IS A GLASS ?

1) A glass is an amorphous (disordered) material

No long-range translational order (periodicity) as in crystals

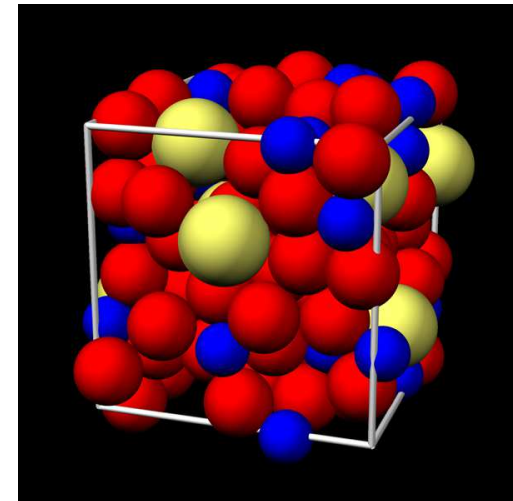
Iono-covalent glasses

a-Si, SiO₂



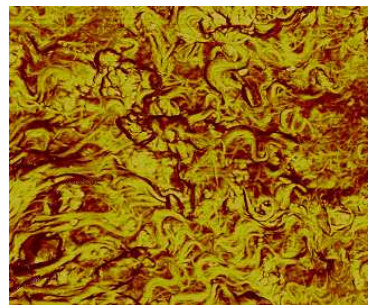
Metallic glasses

Zr-Ti-Cu-Ni-Be, Mg-Cu, Fe-B



Polymeric glasses

PMMA, PS



C nanotube glass

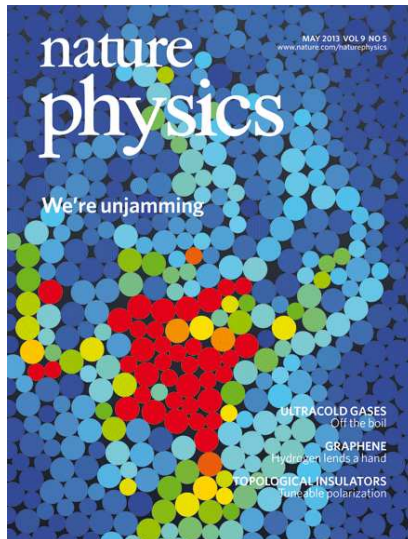
« *A glass is an amorphous disordered material* »

Much larger definition. The word « Glass » applies also to

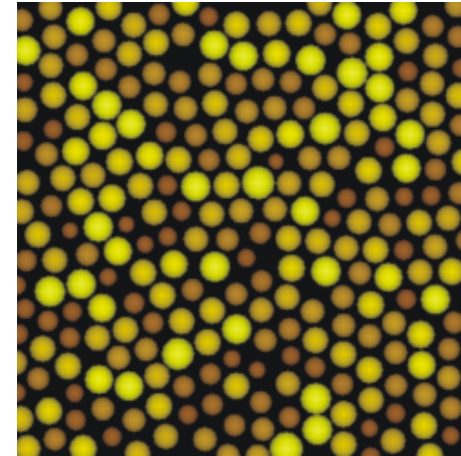
❑ Dense assemblies (foams, cells)



❑ Granular media (jamming)

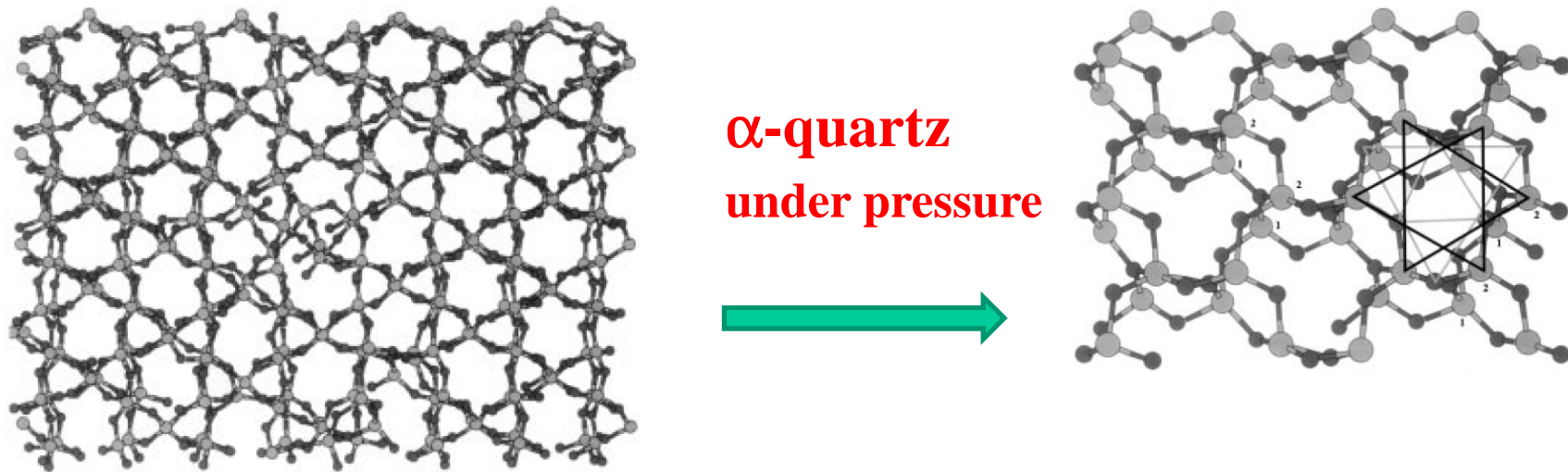


❑ Colloids



« *A glass is an amorphous disordered material* »

An amorphous system can be obtained from a crystal under pressure/irradiation

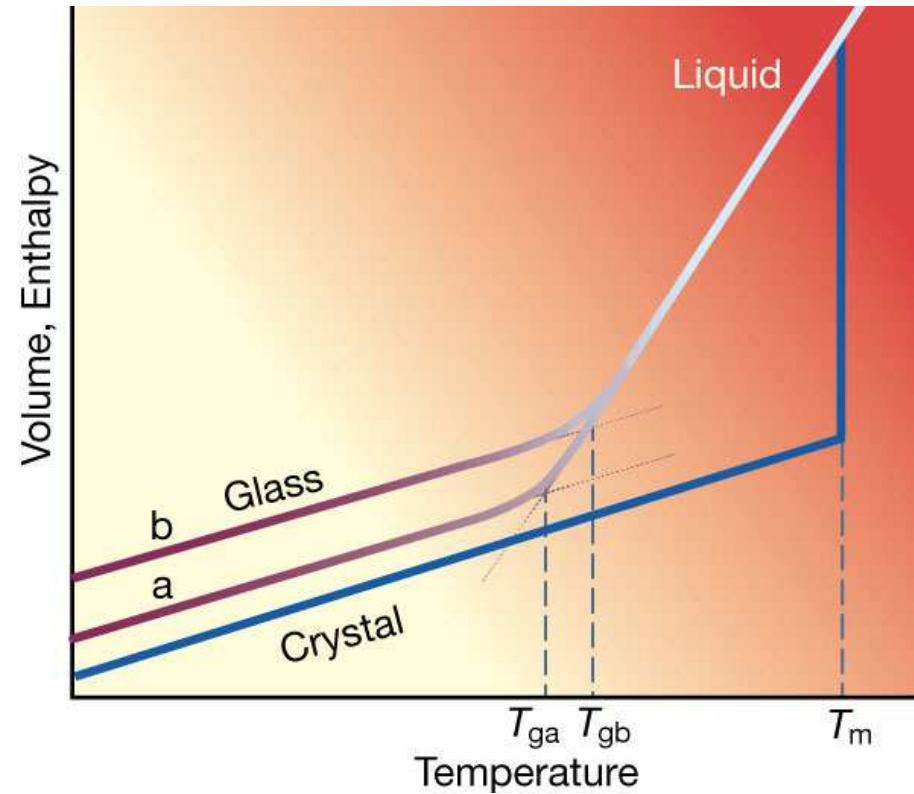
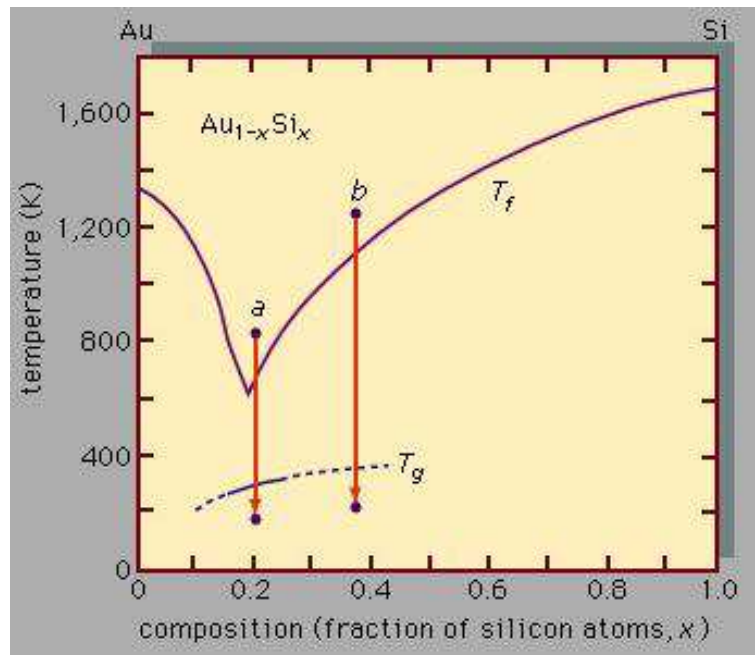


J. Badro et al. PRL 1996

A glass is an amorphous solid that has been quenched from the liquid state.

« A glass is an amorphous solid that has been quenched from the liquid state ».

$T > T_m$ -normal liquid
 $T_m < T < T_g$ -supercooled liquid
 $T < T_g$ -glass



Okamoto, Bulletin of Ph. Diagr. 1983

- ❑ Glass-forming liquids are those that are able to bypass the melting point.
- ❑ As the temperature is lowered, viscosity increases. Liquids will have increasing difficulties to diffuse in order to rearrange into the crystalline structure

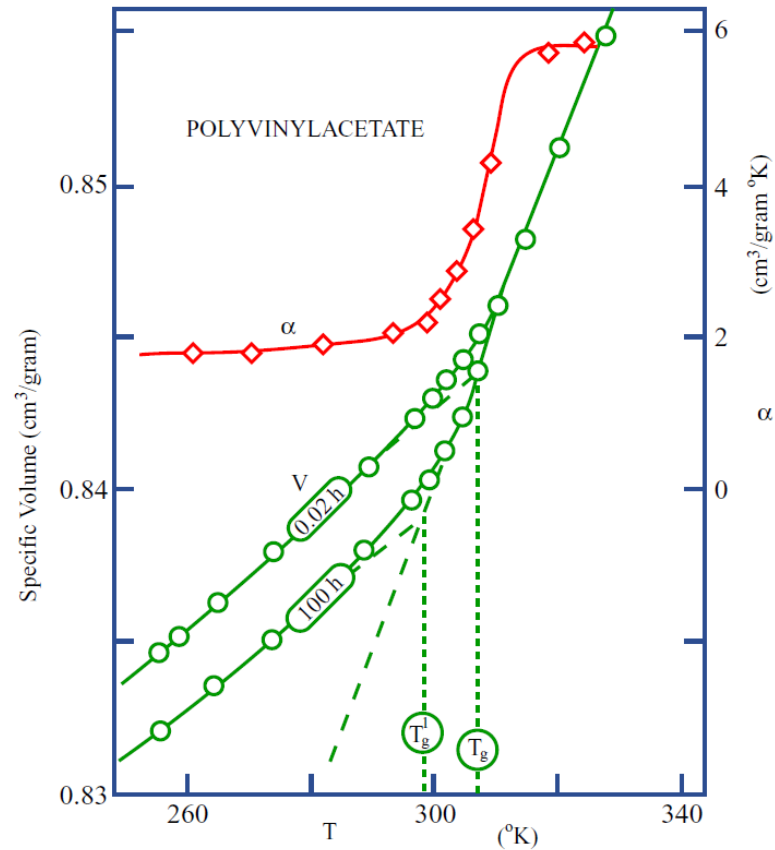
❑ Importance of timescales:

- **Quench rate**: liquid may be cooled so fast that there is no time for crystallize
- Internal timescale (viscosity, bonding) τ allowing the reach equilibrium
- External timescale (cooling/quench rate)
- **Measurement or observation timescale t_{obs}**

Liquid : $t_{\text{obs}} \gg \tau$

Glass : $t_{\text{obs}} \ll \tau$

- T_g is cooling/heating rate dependent.



Volume-versus-temperature cooling curves for an organic material in the neighborhood of the glass transition. $V(T)$ is shown for two greatly different cooling rates, as is the coefficient of thermal expansion $\alpha(T)$ is shown for the fast-cooling curve (0.02 hr). The break in $V(T)$, and the corresponding step in $\alpha(T)$, signal the occurrence of the liquid \rightarrow glass transition.

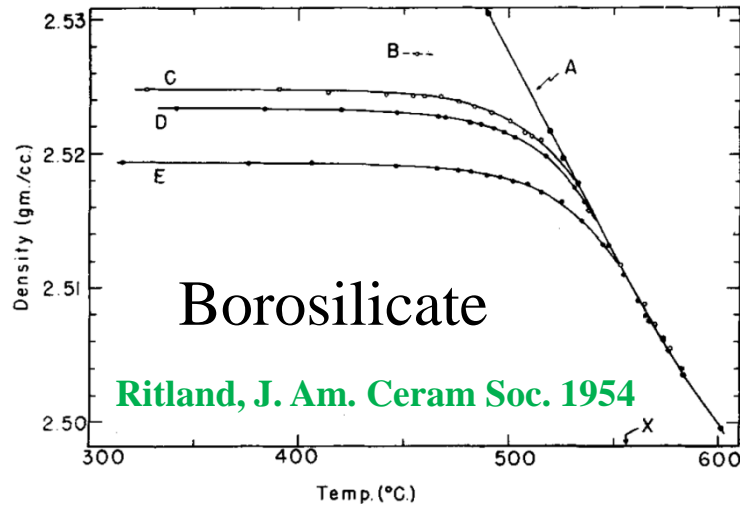
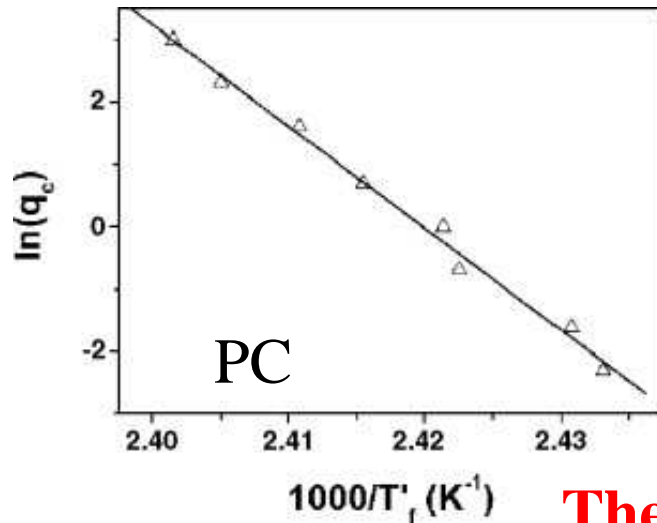


Fig. 8. Room-temperature density and fictive temperature during cooling from 575°C. at constant rate. The equilibrium density curve (A) is that shown in Fig. 4; (B) cooling rate, 0.32°C. per hour; (C) cooling rate, 1.00°C. per hour; (D) cooling rate, 1.86°C. per hour; (E) cooling rate, 9.87°C. per hour; and (F) 360°C. per hour. Point X indicates the annealing point of the No. 8370 glass.



Debreuilh et al, Mat. Lett. 2005

- T_g is cooling/heating rate dependent.

- With fast cooling, the system fails to equilibrate at higher temperatures

High $q = dT/dt \Rightarrow$ higher T_g

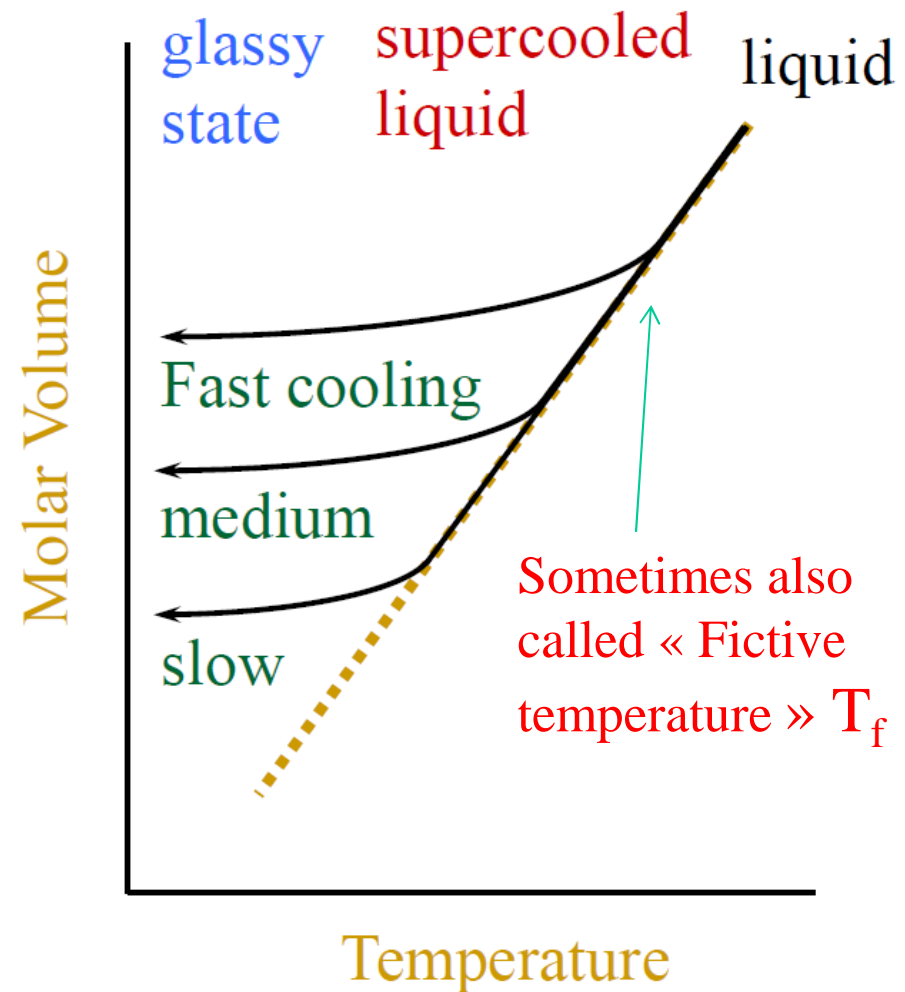
$$\frac{d \ln q}{d \frac{1}{T_g}} = -\frac{H}{R}$$

The glass transition is a kinetic phenomenon

Glass: a kinetic phenomenon

- ❑ Faster (slower) cooling freezes glass in at higher (lower) temperature
- ❑ Low cooling allows the system to relax more and will lead to structure/properties which may be different.
- ❑ Properties of glasses may differ depending on their cooling rate
- ❑ Given that $t_{\text{obs}} \ll \tau$, properties will depend on ageing

Glass is an out of equilibrium material



B) THERMODYNAMIC PROPERTIES

Entropy and entropy crisis

- ❑ Entropy measures the disorder in the system ($S = k_B \ln \Omega > 0$).
- ❑ For a perfect crystal, one has $S = 0$ @ $T = 0$ K.
- ❑ Glass forming liquids exhibit continuously changing $S(T)$ that shows no discontinuities.
- ❑ At T_g , continuously changes from liquid-like values to solid like values

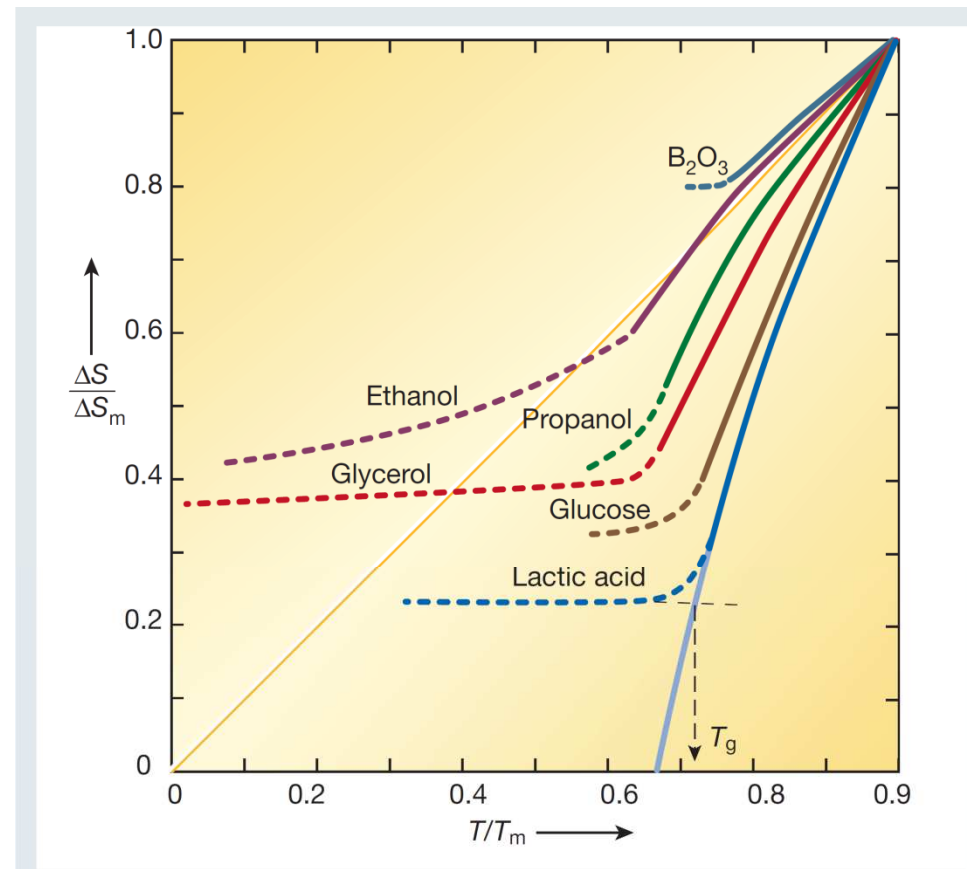


Figure 4 Temperature dependence of the entropy difference between several supercooled liquids and their stable crystals at atmospheric pressure. ΔS_m is the melting entropy and T_m is the melting temperature. The glass transition always intervenes before the vanishing of the entropy surplus. For fragile liquids such as lactic acid, however, an entropy crisis is imminent. (Adapted from ref. 45.)

B) THERMODYNAMIC PROPERTIES

Entropy and entropy crisis

- ❑ If $S(T)$ curve continues along the supercooled liquid line, at some temperature $T_K < T_g$, one would have $\Delta S < 0$.
- ❑ Below, the liquid entropy would appear to be less than that of a crystal (**Entropy crisis**).
- ❑ T_K is termed the Kauzmann temperature, defined by:

$$\Delta S_m = \int_{T_K}^{T_m} \frac{\Delta C_p}{T} dT$$

- ❑ Glass at this temperature is often called an “*ideal glass*”, i.e. a unique configuration exists at T_K (thermodynamics view of the T_g)

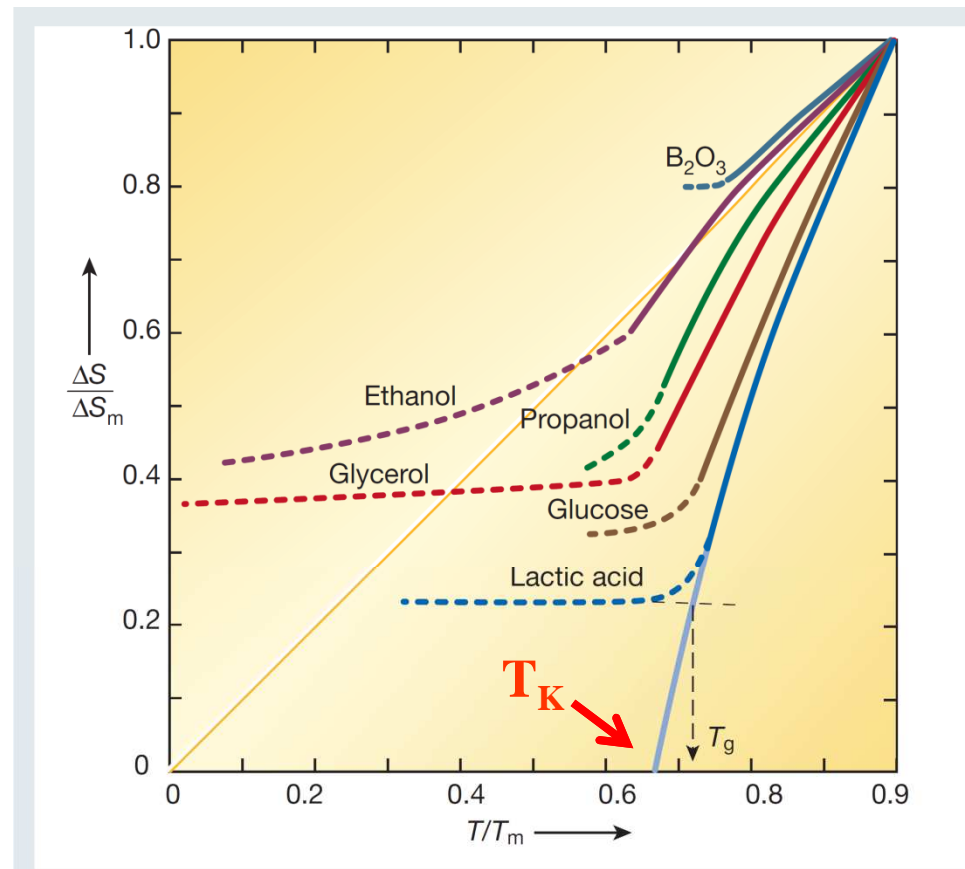


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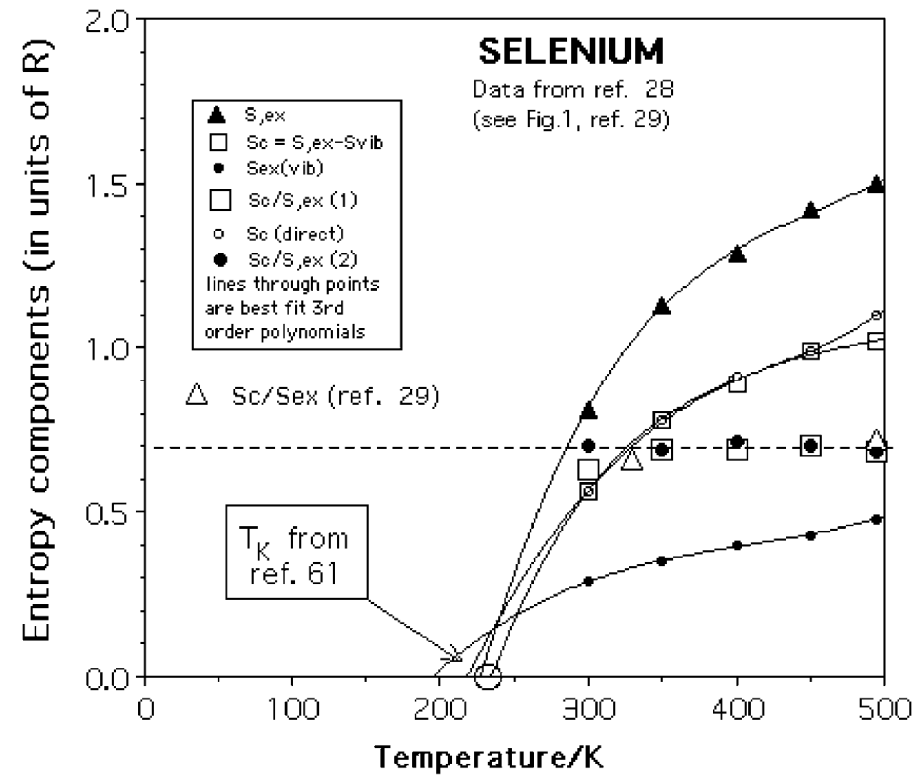
B) THERMODYNAMIC PROPERTIES

Entropy crisis and Kauzmann paradox

- ❑ The Kauzmann temperature T_K is hidden by the huge increase of the relaxation time of the liquid towards its equilibrium line.
- ❑ Equilibrium liquids for $T > T_m$ have no excess entropy. Supercooled liquids have excess entropy because they have avoided the melting point.
- ❑ Excess entropy is lost during further cooling at a rate

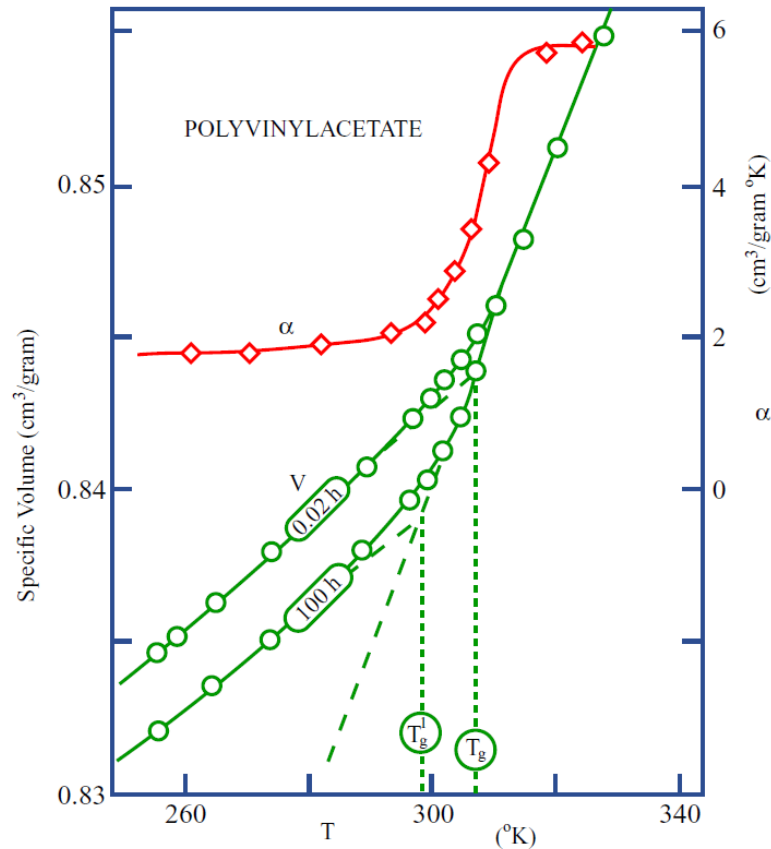
$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$

- ❑ Highly controversial



Angell et al. JNCS 2002

C) THERMAL PROPERTIES



Volume-versus-temperature cooling curves for an organic material in the neighborhood of the glass transition. $V(T)$ is shown for two greatly different cooling rates, as is the coefficient of thermal expansion $\alpha(T)$ is shown for the fast-cooling curve (0.02 hr). The break in $V(T)$, and the corresponding step in $\alpha(T)$, signal the occurrence of the liquid→glass transition.

$V(T)$, $E(T)$ continuous at T_g
 T_g found at the kink of the $E, V(T)$ curve

$\alpha(T)$ discontinuous at T_g

$C_p(T)$ discontinuous at T_g

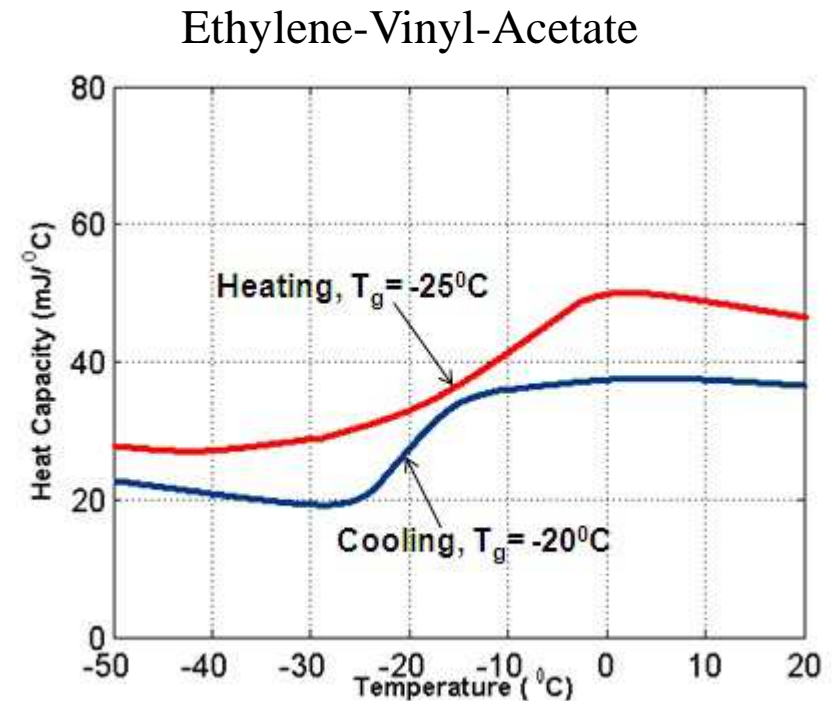
- most common way to measure T_g in a heating experiment

- Calorimetric determination of T_g
Differential scanning calorimetry
(DSC or mDSC)

C) THERMAL PROPERTIES

Heat Capacity upon cooling

- ❑ The change in slope in $H(T)$ at T_g is a measure of the difference between $C_p(T)$ of the liquid and the glass.
- ❑ C_p in liquids arise from three contributions: rotational, translational, and vibrational.
- ❑ In glasses, only vibrational contributions are left as rotational and translational degrees of freedom have been “frozen” out.
- ❑ Measuring C_p in a cooling and heating experiment is different.
➡ **Enthalpic relaxation**

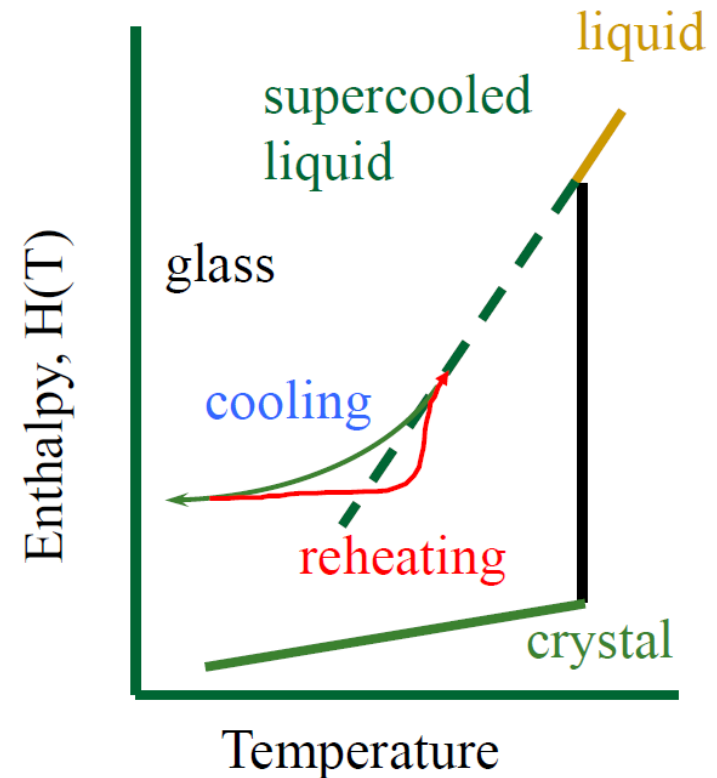


Dahiya et al., Azo J. Mater. 2012

C) THERMAL PROPERTIES

Heat Capacity upon heating

- ❑ With heating, a hysteresis loop appears, causing a heat capacity “overshoot” at the glass transition, creating a peak.
- ❑ The overshoot in the heat capacity curve is a direct manifestation of the relaxation taking place between room temperature and T_g when the glass is reheated.

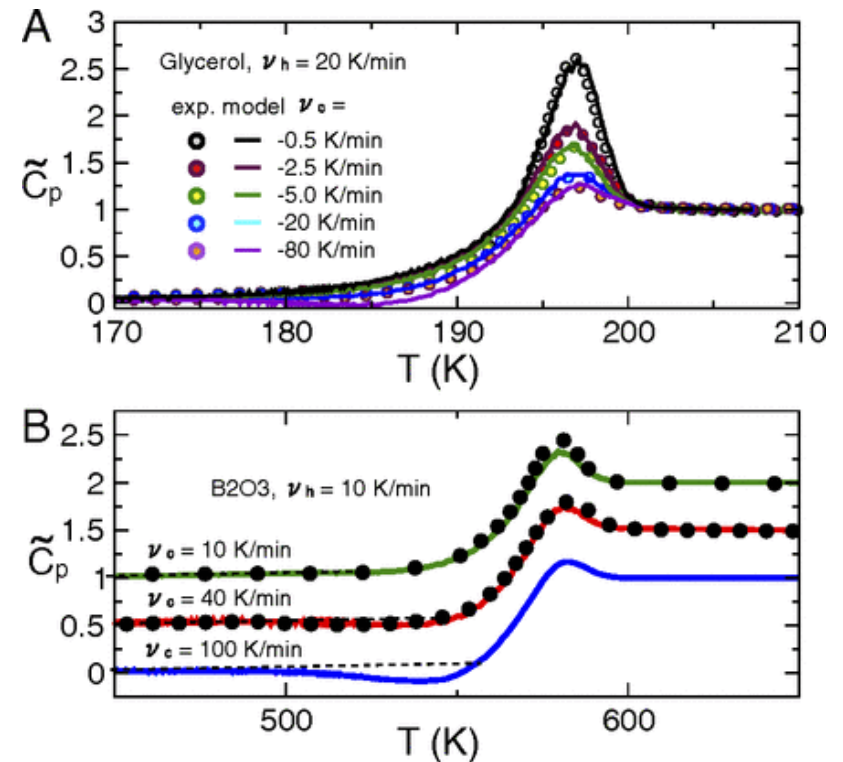


C) THERMAL PROPERTIES

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- ❑ The overshoot in the heat capacity curve is a direct manifestation of the relaxation taking place between room temperature and T_g when the glass is reheated.
- ❑ The enthalpic (or C_p) overshoot is directly linked with the heating rate
 - slow heating=more relaxation
- ❑ In a DSC experiment, the heat capacity jump ΔC_p at the transition is directly linked to the nature of the chemical bonding
 - Van de Waals liquids=important relaxational changes=large ΔC_p
 - Iono-covalent=weak relaxational changes=small ΔC_p

S. Keys et al. PNAS 2013



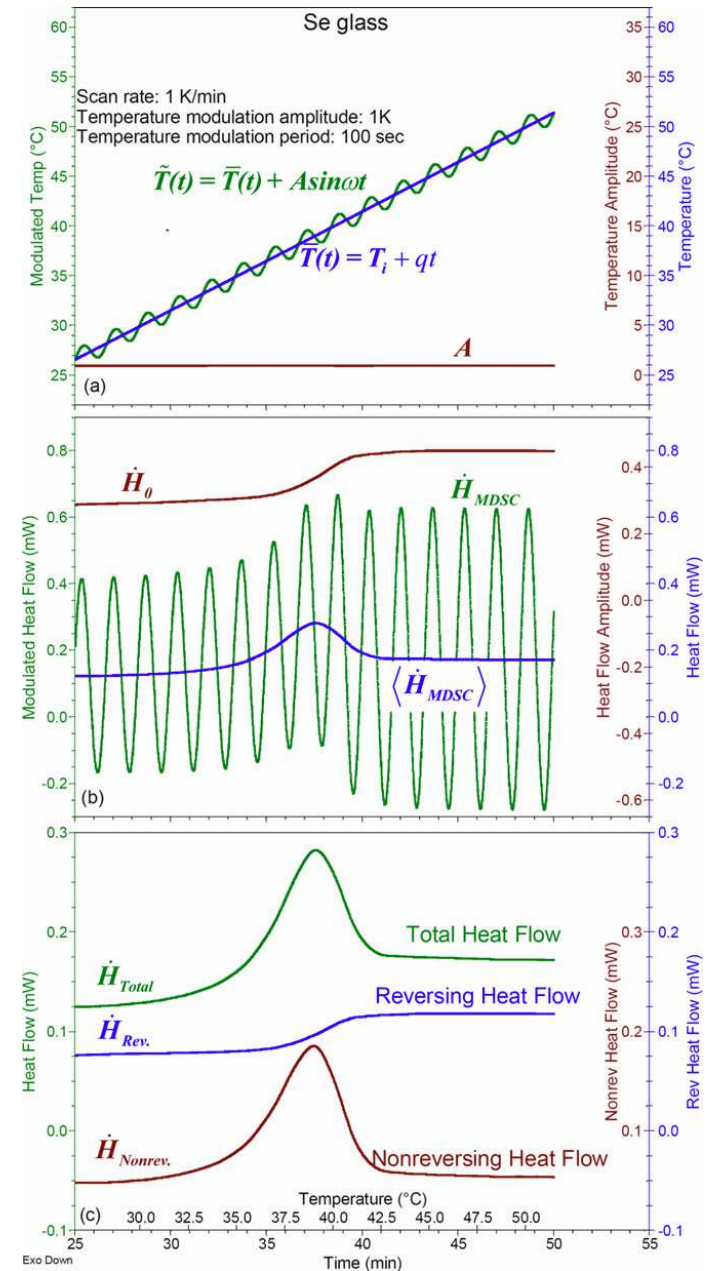
C) THERMAL PROPERTIES

Reversing and non-reversing heat flow

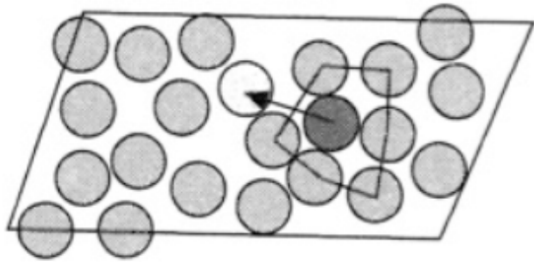
Linear ramp + sinusoidal T oscillations

Allows separating thermal exchange (C_p) from relaxation/kinetics event at T_g

- ❑ Average of the modulated heat flow is the total heat flow (as in DSC).
- ❑ Amplitude of the modulated heat flow = reversing heat flow.
- ❑ The Difference signal between the total and the reversing heat flow is the non-reversing heat flow.
- ❑ Once frequency-corrected, the non-reversing heat flow contains most of the relaxational events of the glass transition.



D) MORE ON RELAXATION



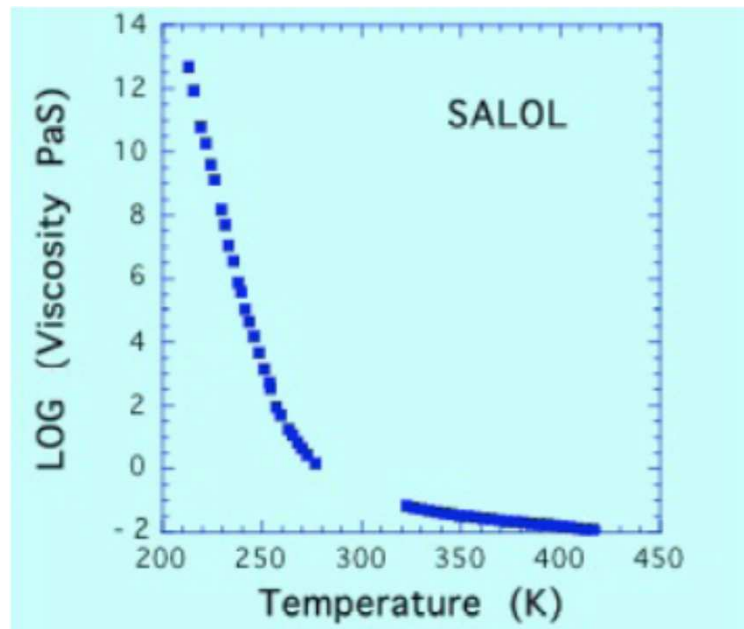
Relaxation in a simple liquid

Potential to escape from local neighbourhood $-E$

Thermally activated process – Boltzmann distribution

ν attempt frequency
 G shear modulus

$$\tau = \nu^{-1} e^{E/k_B T} \quad \eta = G_{\infty} \tau$$



Central quantities:

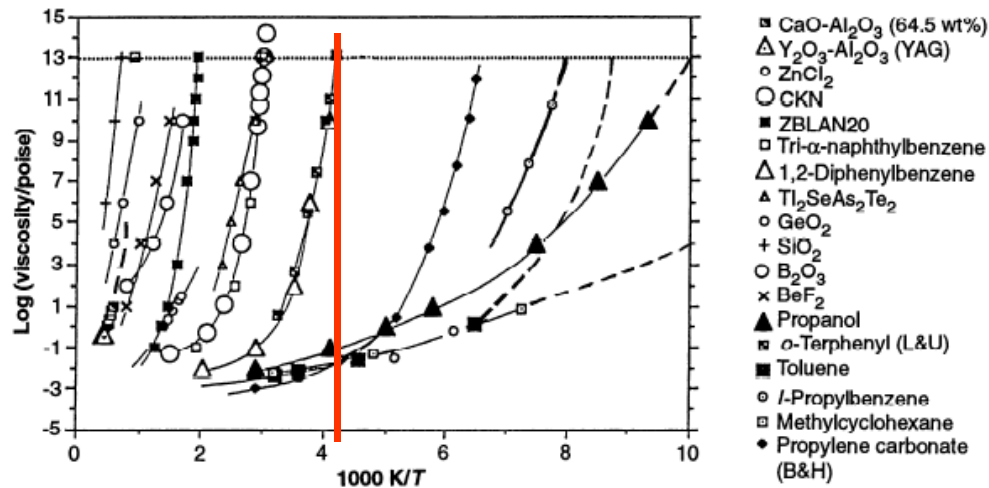
Viscosity, relaxation time

Usual temperature-dependence:

- Arrhenius (why not with $E_A(T)$?)
- Vogel-Fulcher-Tamman

$$\tau = \tau_0 \exp \left[\frac{D}{T - T_0} \right]$$

Fragile versus strong liquids ...



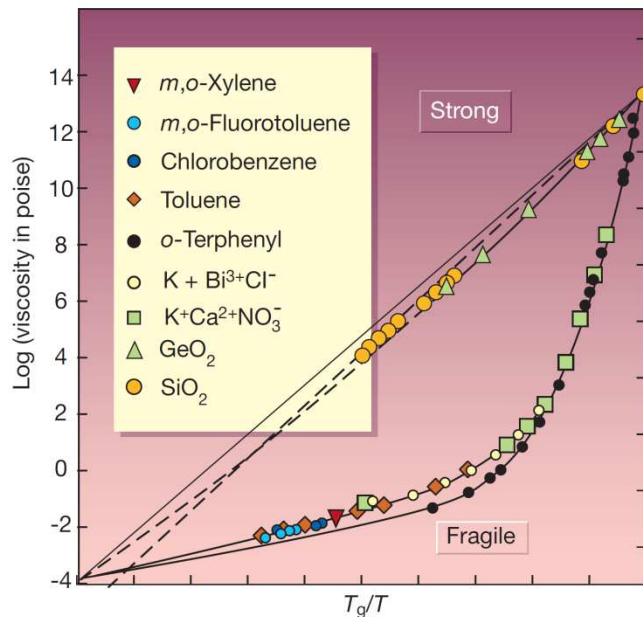
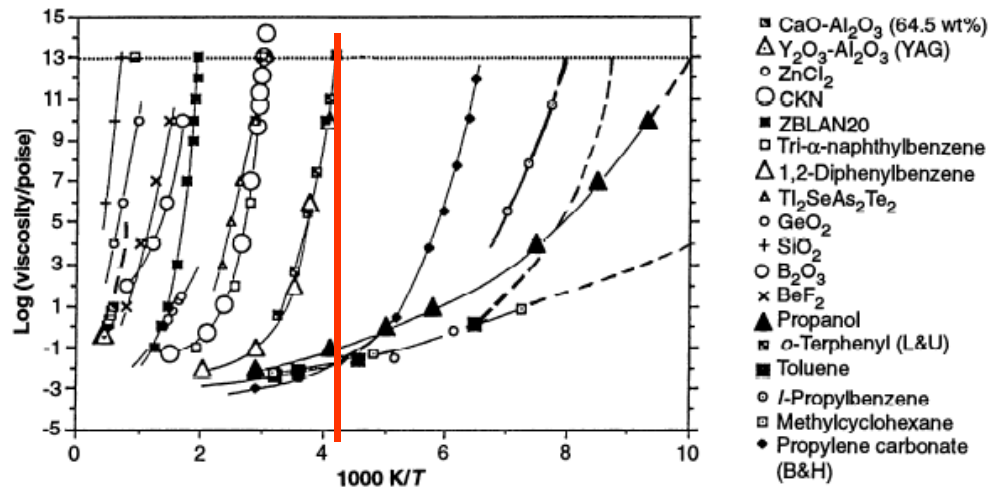
Dramatic temperature behaviour

Viscous slowing down with temperature decrease

- Structure frozen in
- Relaxation time to equilibrium diverges
- System falls out of equilibrium

T_g practically defined as
 $\tau = 10^2 - 10^3$ s, $\eta = 10^{13}$ poise

Fragile versus strong liquids ...



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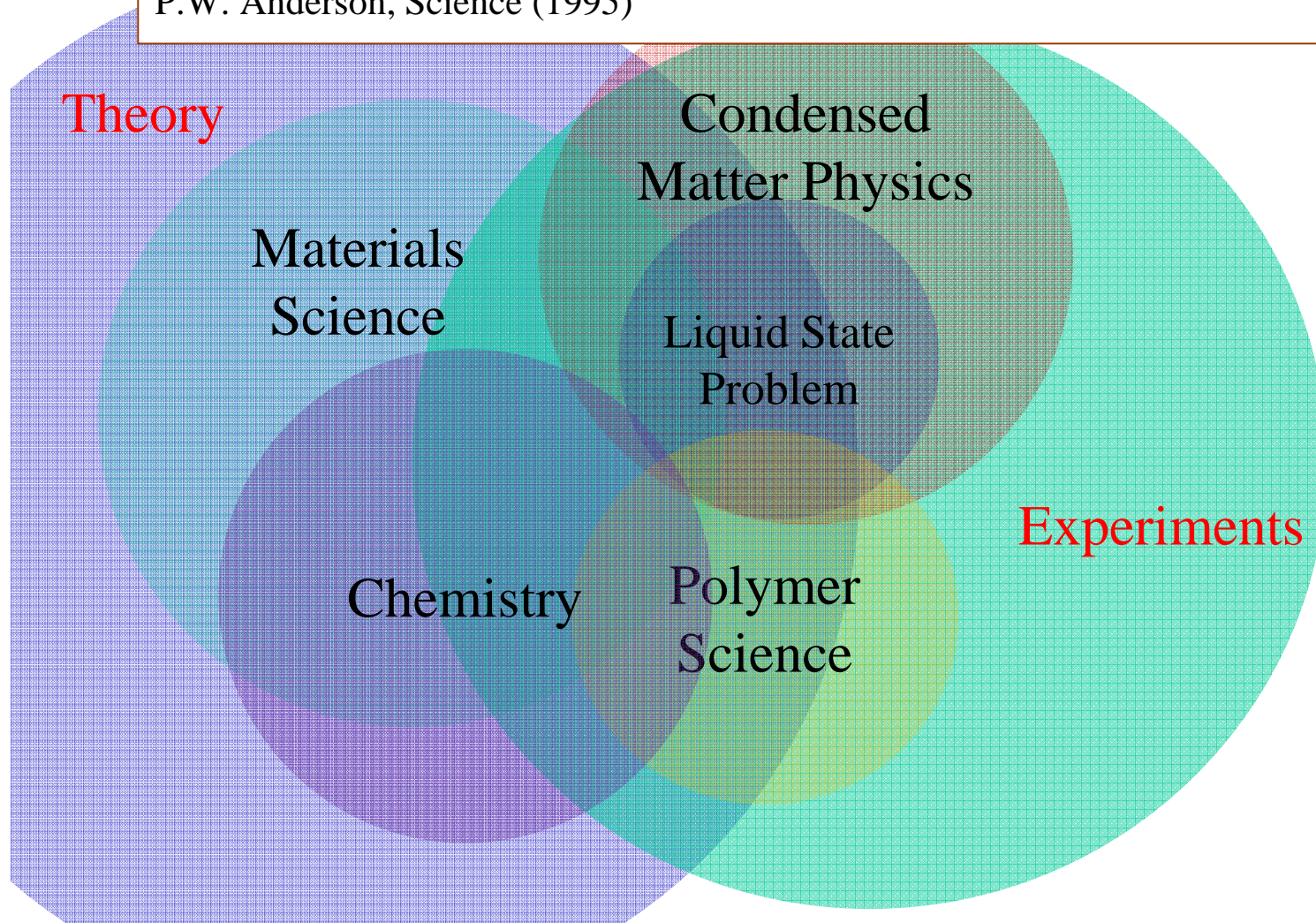
T_g practically defined as $\tau=10^2-10^3s, \eta=10^{13}$ poise

Fragility index (Angell plot)

$$M = \left[\frac{d \log_{10} \eta}{d \left(\frac{T_g}{T} \right)} \right]_{T=T_g}$$

« The deepest and most interesting unsolved problem in solid state theory is probably the theory of the nature of glass and the glass transition... etc etc »

P.W. Anderson, Science (1995)



What can be (or has been) done in terms of modelling ?

- ❑ **Seminal models** ... still useful and referenced.
- ❑ **Kinetic constrained models** (Community of Statistical Physics of liquids): Trivial thermodynamics, complicated dynamics.
- ❑ **Classical thermodynamics models** (usually trivial dynamics).

Next lectures

E) SEMINAL MODELS FOR THE GLASS TRANSITION

Adam-Gibbs theory (1965)

Basic idea: Relaxation dynamics of a glass is due to individual events involving sub-regions (cooperative rearranging regions, CRR) of the liquid which relax to a new local configuration.

Assumptions:

- ❑ The CRRs are independent of each other
- ❑ The CRRs contain sufficiently many particles to allow to apply the formalism of statistical mechanics

- ❑ Consider a CRR with z particles. Its partition function is:

$$\Delta(z, P, T) = \sum_{E, V} W(z, E, V) \exp[-\beta H]$$

where $w(z, E, V)$ is the number of states of the CRR with energy E , and volume V , and H is the enthalpy of the system.

E) SEMINAL MODELS FOR THE GLASS TRANSITION

- Suppose a CRR has z particles. The fraction $f(z,T)$ that can undergo rearrangements involves a similar partition function containing the states associated with a rearrangement, so that one has:

$$\tau(z, T) = \frac{\Delta'}{\Delta} = \exp[-\beta(G - G')] = \exp[-\beta z \delta\mu]$$

with Gibbs energies $G = -k_B T \ln \Delta$ and $\delta\mu$ is the difference in chemical potential per particle.

- The probability that the system makes a CR is proportional to $f(z,T)$:

$$W(z, T) = A \exp[-\beta z \delta\mu]$$

- Suppose one has a density $n(y,T)$ of regions having y particles. On average, the probability that a particle makes a rearrangement is:

$$W^*(T) = \frac{1}{N} \sum_{z=z^*}^N z n(z, T) W(z, T)$$

with z^* the smallest CR cluster

E) SEMINAL MODELS FOR THE GLASS TRANSITION

$$W^*(T) = \frac{1}{N} \sum_{z=z^*}^N zn(z, T)W(z, T)$$

Or :

$$W^*(T) = \frac{1}{N} z^* n(z^*, T) \exp[-\beta z^* \delta\mu] \sum_{z=z^*}^N \frac{zn(z, T)}{z^* n(z^*, T)} A \exp[-\beta(z - z^*) \delta\mu]$$

□ For $\beta\delta\mu \gg 1$ (relaxation mostly involve small cluster sizes z^* , at the lowest order), one has :

$$W^*(T) = A' \exp[-\beta z^* \delta\mu]$$

□ **Can we say something about z^* ?** At LT, the dynamics of the particles is mostly made of vibrations around local minima (bonds) and transitions between these minima (bond rearrangements).

□ The number of CRRs in a system with N particles is $n(z^*, T) = N/z^*$.

E) SEMINAL MODELS FOR THE GLASS TRANSITION

□ The configurational entropy of each CRR is : $s_{conf} = S_{conf}/n(z^*, T)$

□ Since we also have $n(z^*, T) = N/z^*$, we can write:

$$z^* = N/n(z^*, T) = Ns_{conf}/S_{conf}$$

□ We remind that : $W^*(T) = A' \exp[-\beta z^* \delta\mu]$

So that we obtain: $W^*(T) = A' \exp\left[-\frac{\beta N s_{conf} \delta\mu}{S_{conf}}\right]$

or : $W^*(T) = A' \exp\left[-\frac{C}{T S_{conf}}\right]$

□ If one assumes that the relaxation time of the system is inversely proportional to the probability of a CRR event [$\tau(T) \sim 1/W^*(T)$], we obtain:

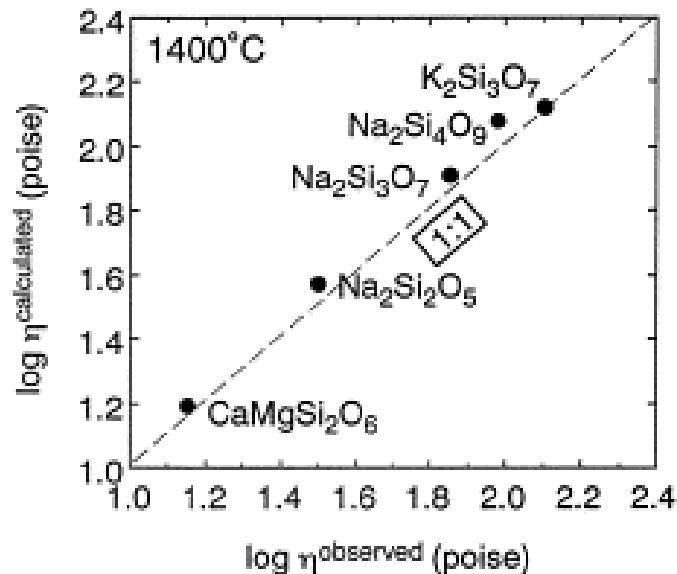
$$\tau(T) \propto \exp\left[\frac{C}{T S_{conf}}\right]$$

E) SEMINAL MODELS FOR THE GLASS TRANSITION

Adam-Gibbs theory : consequences

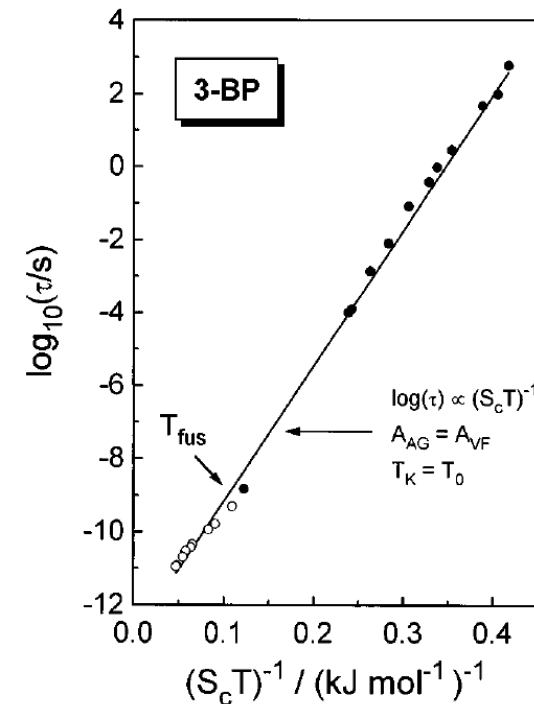
$$\tau(T) \propto \exp \left[\frac{C}{TS_{conf}} \right]$$

- ❑ Since one has $\tau \sim \eta$, viscosity also obeys the Adam-Gibbs relation.
- ❑ Verified experimentally (Richet): - Calorimetric measure of C_p and calculation of S_{conf} by thermodynamic integration+ measure of viscosity.



Richet, GCA 1984

Richert and Angell, JCP 199



E) SEMINAL MODELS FOR THE GLASS TRANSITION

Adam-Gibbs theory : consequences

□ In several glass-forming liquids, the excess specific heat behaves as

$$C_p(T) = C_p^{\text{glass}} - C_p^{\text{crystal}} = K/T.$$

where K is a constant. Integration leads to :

$$S(T) = \int_{T_K}^T C_p \frac{dT}{T} = K \left(\frac{1}{T_K} - \frac{1}{T} \right)$$

Identification of the entropy $S(T)$ with $S_{\text{conf}}(T)$, and using the Adam-Gibbs relation leads to the Vogel-Fulcher law:

$$\tau = \tau_0 \exp \left[\frac{D}{T - T_0} \right]$$

Where the reference temperature T_0 becomes the Vogel-Fulcher law.

Drawbacks:

- Origin of these CRR.
- No energy penalty for CRR rearrangements
- Single prediction (relaxation time)

E) SEMINAL MODELS FOR THE GLASS TRANSITION

Free volume (Cohen-Turnbull (1959))

Basic idea: Statistical redistribution of the free volume occasionally opens up voids large enough for diffusive displacement.

Central quantity in a hard sphere model: free volume v_f per particle given by:

$$V_f = V - V_0$$

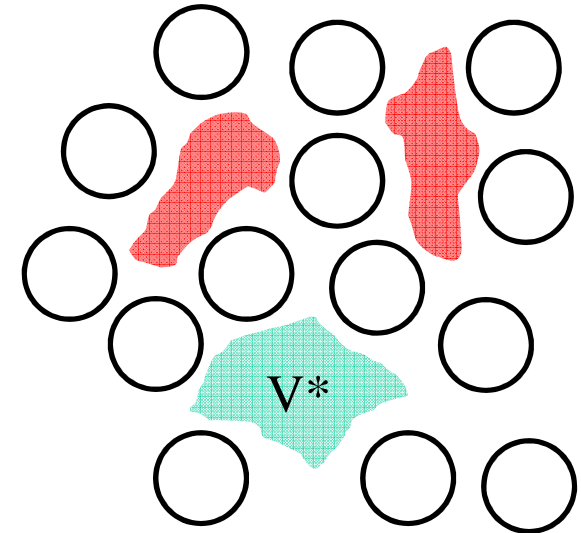
with v_0 the volume per particle accessible only to one particle at a time (= volume of hard sphere).

□ The average diffusion is given by :

$$D = \int_{v^*}^{\infty} D(v) p(v) dv$$

where $p(v)$ is the probability of finding free volume between v and $v+dv$, v^* is a critical volume just large enough to permit another molecule to jump in after displacement.

□ Probability of finding free volume is given by: $p(v) = (\gamma/v_f) \exp(-\gamma v/v_f)$



E) SEMINAL MODELS FOR THE GLASS TRANSITION

Free volume : results and consequences

□ We have
$$p(v) = (\gamma/v_f) \exp(-\gamma v/v_f)$$

γ being a geometrical factor. CT assume that as $v^* < 10 v_f$ one can assume that $D(v)$ is slowly varying so that one can write $D = D(v^*)P(v^*)$ and :

$$D = D(v^*)P(v^*) = D(v^*) \int_{v^*}^{\infty} p(v) dv \propto A \exp(-\gamma v^*/v_f)$$

Consequences:

□ One has $D=0$ if $v_f=0$.

□ Assuming a linear expansion for the free volume of the liquid,

one recovers a Vogel-Fulcher law.
$$v_f = v_f^{glass} + V_g \Delta\alpha (T - T_g)$$

F) KINETIC CONSTRAINED MODELS

+ many other models

The Famous Glassotron (Berthier & Kurchan, 2002)

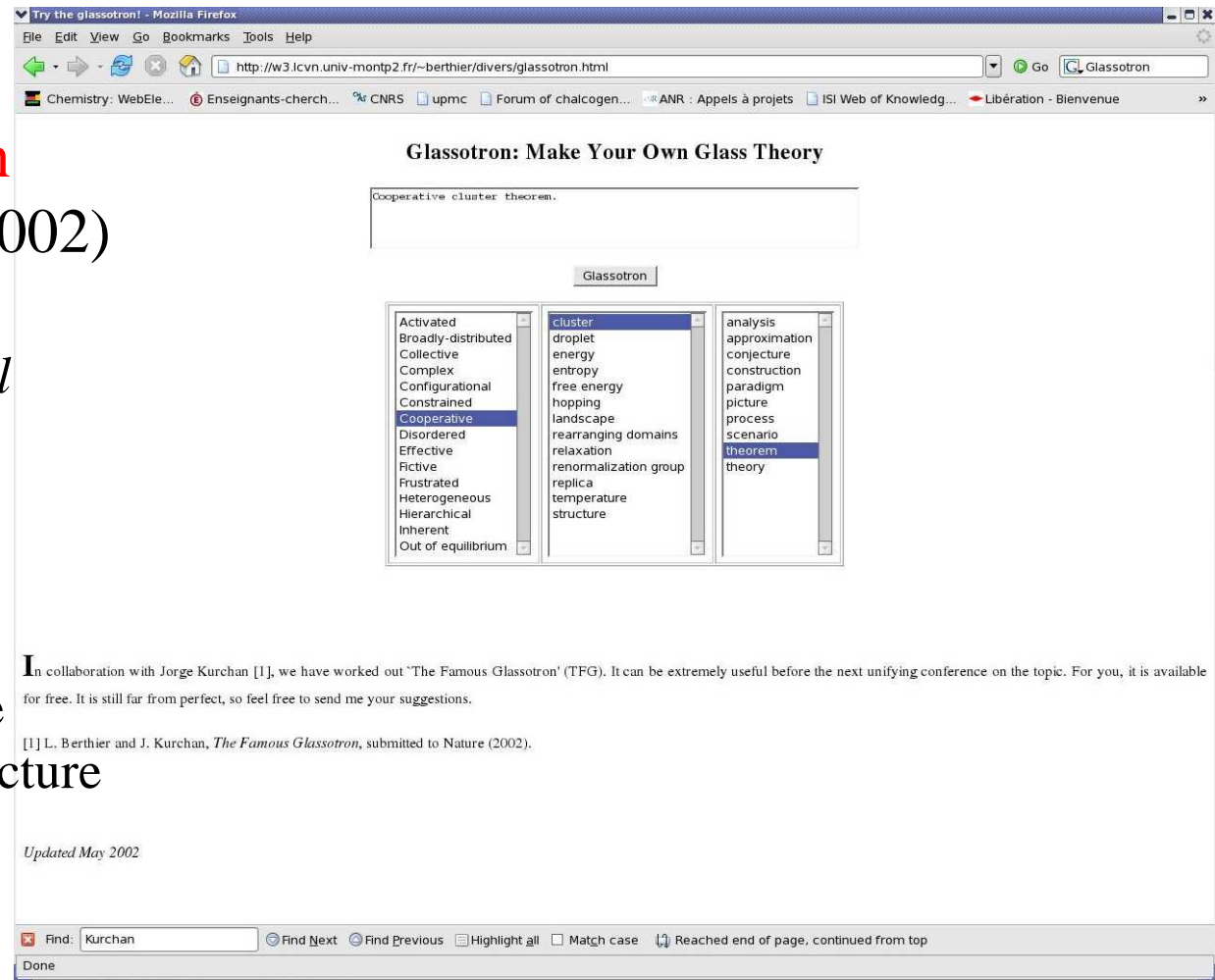
*« It can be extremely useful
before the next unifying
conference on the topic »*

Examples:

Frustrated droplet scenario

Effective entropy conjecture

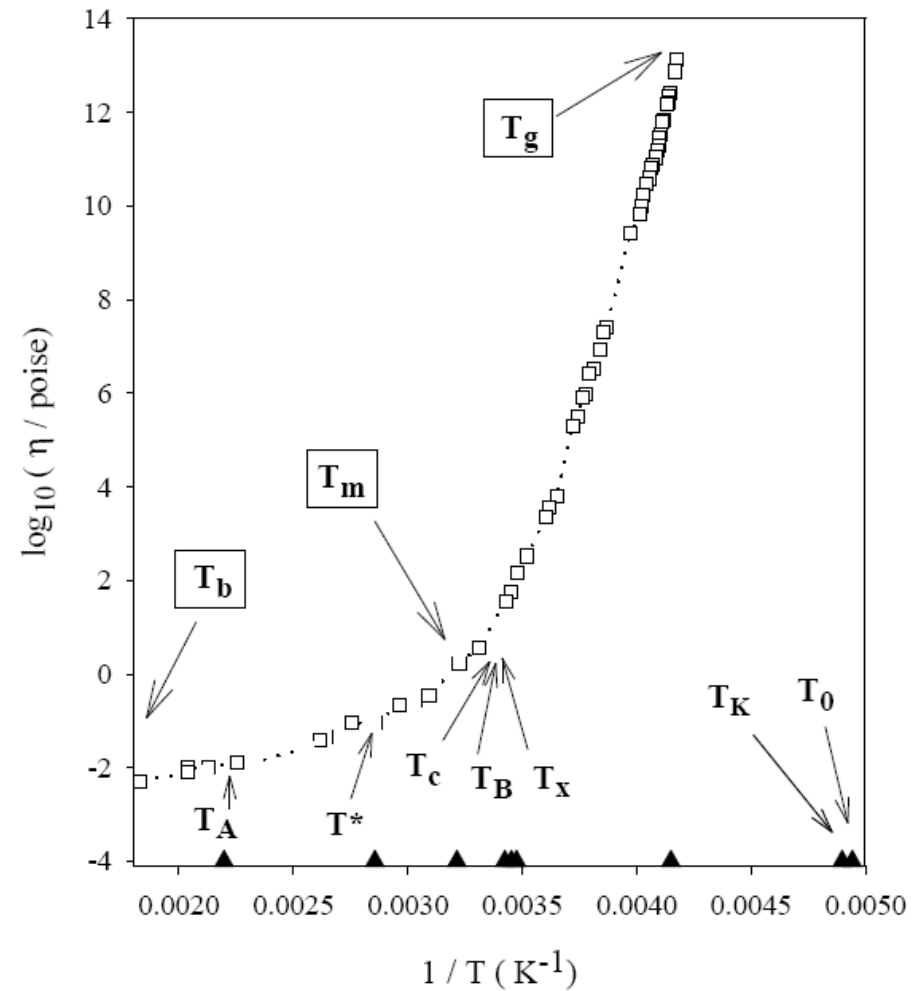
Heterogeneous landscape picture



F) KINETIC CONSTRAINED MODELS

+ many other models

« The temperature disease »:
Introduce a hidden temperature



Kivelson-Tarjus, 1999

F) KINETIC CONSTRAINED MODELS

Ritort oscillator model (1995)

Properties:

- Set of non-interacting oscillators each described by a continuous variable x_i and the energy function:

$$E = \sum_{i=1}^N V(x_i)$$

- $V(x)$ real valued potential energy and leads to finite Z at finite temperatures

$$Z = \int_{-\infty}^{\infty} \exp[-\beta V(x)] dx$$

$T=1/\beta$, temperature of the bath with which the system is put in contact

F) KINETIC CONSTRAINED MODELS

Properties (continued):

- Stochastic dynamics where all oscillators are updated in parallel, according to the rule:

$$x_i \rightarrow x_i + \frac{r_i}{\sqrt{N}}$$

with r_i uncorrelated Gaussian variables having

$$\langle r_i \rangle = 0 \quad \langle r_i r_j \rangle = \Delta^2 \delta_{ij}$$

- Move accepted according to the Metropolis rule
- Trivial statics $Z_N = Z^N$, complicated dynamics (Kinetically Constrained Models) **Random bond model: $T=0, X=1$
 $T=\infty, X=0$**

F) KINETIC CONSTRAINED MODELS

Construction:

Change in energy in an elementary move:

$$\Delta E = \sum_{i=1}^N V\left(x_i + \frac{r_i}{\sqrt{N}}\right) - V(x_i) = \sum_{i=1}^N \sum_{k=1}^{\infty} \frac{1}{k! N^{k/2}} V^{(k)}(x_i) r_i^k$$

Probability distribution of energy changes:

$$P(\Delta E) = \int_{-\infty}^{\infty} \delta\left(\Delta E - \sum_{i=1}^N \sum_{k=1}^{\infty} \frac{1}{k! N^{k/2}} V^{(k)}(x_i) r_i^k\right) \prod_i \frac{dr_i}{\sqrt{2\pi\Delta^2}} e^{-r_i^2/2\Delta^2}$$

Dirac function in Fourier space + ΔE being a random variable, $P(\Delta E)$ can be reconstructed from the moments $\underline{\Delta E^k}$

$$P(\Delta E) = \int_{-\infty}^{\infty} \frac{dq}{2\pi} e^{iq\Delta E} \sum_{k=0}^{\infty} \frac{(-iq)^k}{k!} \underline{\Delta E^k}$$

F) KINETIC CONSTRAINED MODELS

Gaussian distribution for $P(\Delta E)$ in the thermodynamic limit

$$P(\Delta E) = \frac{1}{\sqrt{2\pi\sigma_{\Delta E}^2}} \exp\left[-\frac{(\Delta E - M_{\Delta E})^2}{2\sigma_{\Delta E}^2}\right]$$

With mean $M_{\Delta E}$ and variance $\sigma_{\Delta E}$ given by:

$$M_{\Delta E} = \underline{\Delta E} = \frac{\Delta^2}{2} \langle V'' \rangle = \frac{\Delta^2}{2} \frac{1}{N} \sum_{i=1}^N V''(x_i)$$

$$\sigma_{\Delta E}^2 = \underline{\Delta E^2} - \underline{\Delta E}^2 = \Delta^2 \langle V'^2 \rangle$$

Evolution for the energy (Metropolis):

Accepted (1) of $\Delta E < 0$, otherwise accepted with probability $\exp[-\beta\Delta E]$

$$\tau_0 \frac{\partial e}{\partial t} = \int_{-\infty}^0 x P(x) dx + \int_0^{\infty} x P(x) e^{-\beta x} dx$$

F) KINETIC CONSTRAINED MODELS

Evolution for the energy:

$$\tau_0 \frac{\partial e}{\partial t} = \frac{M_{\Delta E}}{2} \operatorname{erfc} \left[\frac{M_{\Delta E}}{\sqrt{2\sigma_{\Delta E}^2}} \right] - \frac{1}{2} (\beta\sigma_{\Delta E}^2 - M_{\Delta E}) e^{\frac{\beta}{2}(\beta\sigma_{\Delta E}^2 - 2M_{\Delta E})} \operatorname{erfc} \left[\frac{\beta\sigma_{\Delta E}^2 - M_{\Delta E}}{\sqrt{2\sigma_{\Delta E}^2}} \right]$$

With erfc the complementary error function $\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} \exp(-u^2) du$

Relaxation towards equilibrium:

Linearisation of energy equation.

$$\text{Relaxation time: } \tau = \tau_0 \frac{\sqrt{\beta M_{\Delta E}^3}}{\sqrt{\pi} \left[\frac{2}{\sigma_{\Delta E}} \left(\frac{d\sigma_{\Delta E}}{de} \right) - \frac{1}{M_{\Delta E}} \left(\frac{dM_{\Delta E}}{de} \right) \right]_{e=e_{eq}}} \exp \left[\frac{\beta M_{\Delta E}}{4} \right]$$

- Arrhenius divergence of the relaxation time with decreasing temperature, of activated type.

- Activation energy:
$$E_A = \frac{M_{\Delta E}}{4} = \frac{\Delta^2}{8} \langle V'' \rangle$$

F) KINETIC CONSTRAINED MODELS

□ Suppose the interacting potential is harmonic: $E = \sum_{i=1}^N \frac{k}{2} x_i^2$

□ Mean and variance of the energy change are given by:

$$\sigma_{\Delta E}^2 = k^2 \Delta^2 E \quad M_{\Delta E} = \frac{k\Delta^2}{2}$$

□ Probability distribution of the energy change

$$P(\Delta E) = \frac{1}{\sqrt{4\pi k E \Delta^2}} \exp \left[-\frac{\left(\Delta E - \frac{k\Delta^2}{2} \right)^2}{4kE\Delta^2} \right]$$

□ Evolution for the energy:

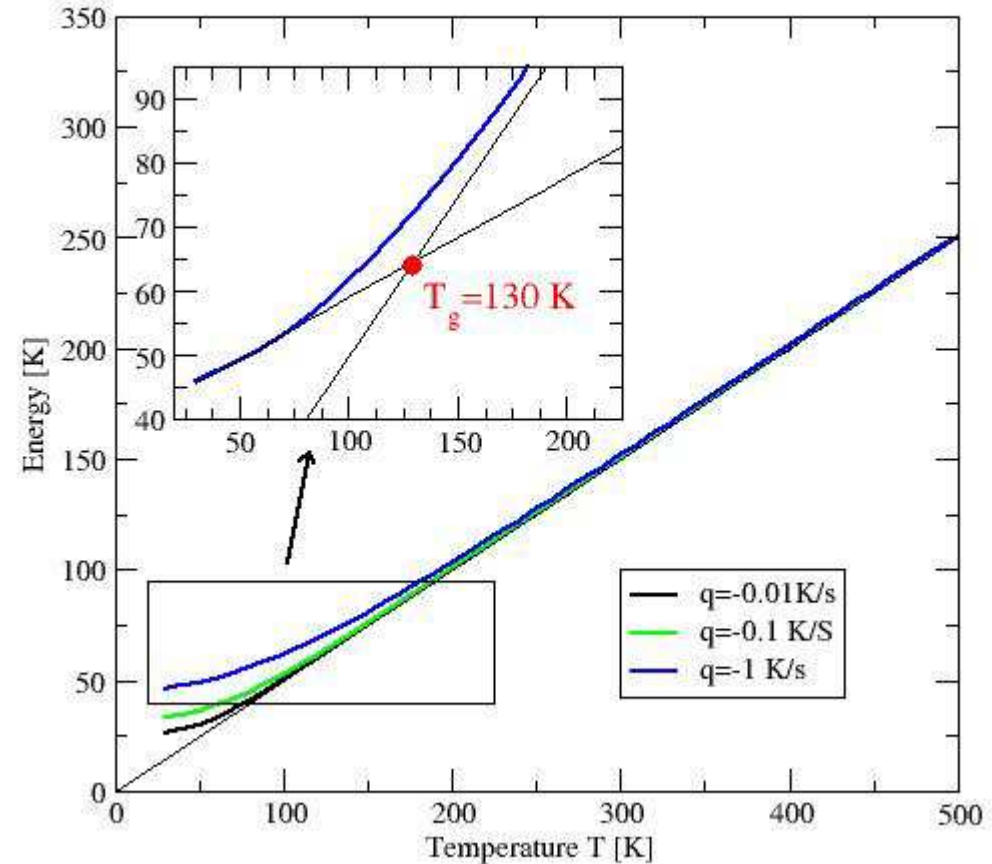
$$\frac{\partial E}{\partial t} = \frac{k\Delta^2}{2} \left((1 - 4E\beta) e^{-\beta k\Delta^2 / 2(1-2E\beta)} \operatorname{erfc} \left(\sqrt{\frac{k\Delta^2}{16E}} \right) (4E\beta - 1) \right)$$

Cooling/heating solution: $q = dT/dt$ for various strengths k

F) KINETIC CONSTRAINED MODELS

Out of equilibrium behaviour at low temperature

- ❑ T_g increases with the cooling rate q . Reproduction of glass transition phenomenology
- ❑ At $T=0$: activated jumps ($\Delta E > 0$) are rejected.
- ❑ At high T , all moves are accepted. Faster relaxation to equilibrium

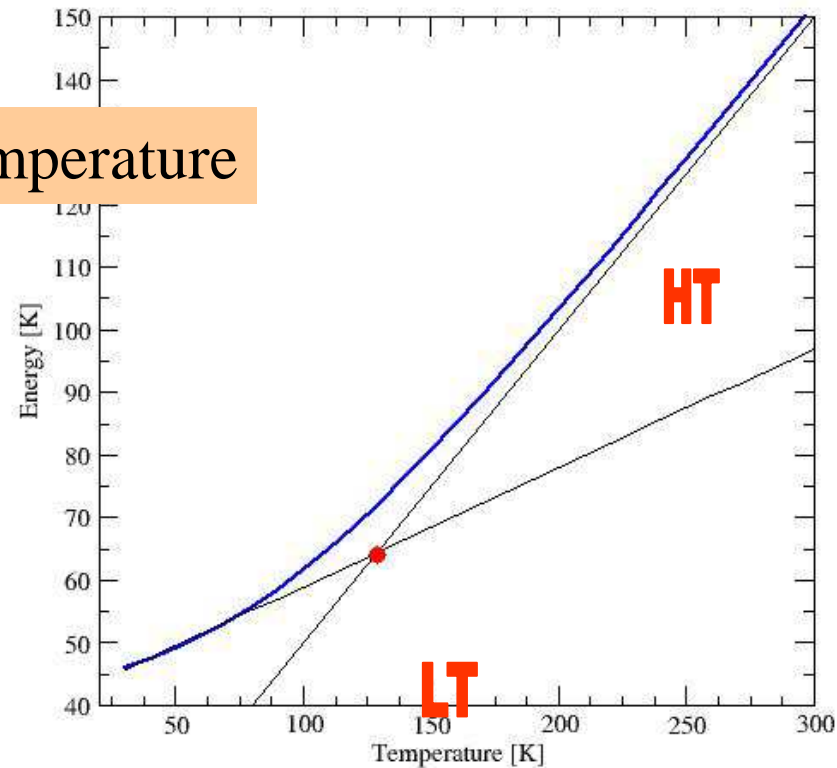


F) KINETIC CONSTRAINED MODELS

Defining a glass transition temperature

Cross point between the HT and LT behaviour for the energy.

$$E_{HT} = \frac{T}{2}$$



$$\tau_0 \frac{\partial E_{LT}}{\partial t} = - \sqrt{\frac{8}{MT_g \pi \ln 10}} E_{LT}^{3/2} \exp[-8MT_g \ln 10 / 16E_{LT}]$$

Low T expansion of the equation for the evolution of the energy.

F) KINETIC CONSTRAINED MODELS

Heating curve

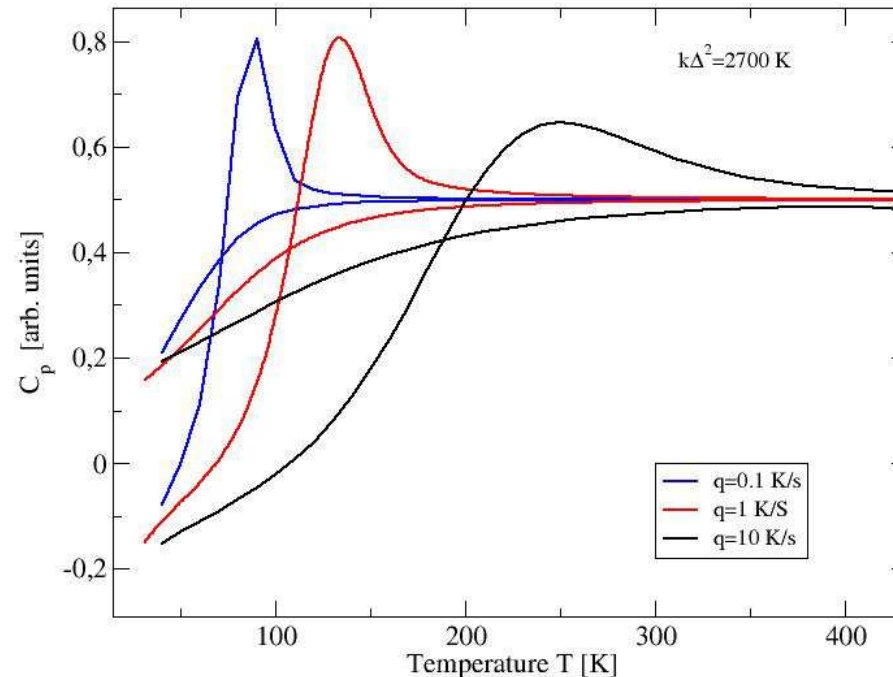
- For a given potential ($k\Delta^2$)

Enthalpic overshoot/ Heat capacity jump ΔC_p decreases with heating rate

T_g increases with cooling rate

- For a given heating rate (q)

Enthalpic overshoot/ Heat capacity jump ΔC_p increases with potential stiffness



Conclusion:

- ❑ Glasses are out-of-equilibrium liquids
(increase of the relaxation time, kinetic phenomenon)
- ❑ Thermodynamics involved
- ❑ Basic questions. Glass transition is still poorly understood
(theory+exp.)
- ❑ Small-world communities are working on glasses

Home reading: The glass transition, P. Debenedetti, F. Stillinger, Nature 410, 259 (2001), available from the lecture website or:
http://www.lptl.jussieu.fr/user/mmi/IMI_lecture/lecture_1/OPEN_add_reading_lecture1_glass_transition.pdf

Next lecture: Structure of glasses