03/07/2017 GILLES TARJUS : AN OVERVIEW OF THE GLASS TRANSITION.

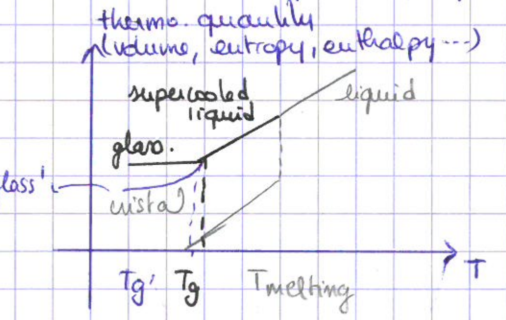
I WHAT IS A GLASS ?

System frozen in a disordered system.
This lecture will be restricted to structural glasses (formed by liquids).
e.g. polymers, colloidal suspension.
high vs small elastic constants.

Glasses are solid : - doesn't flow
- resist to small shear.

amorphous : homogeneous material (optical propeties, windows..)

Glass formation = cooling a liquid.



But cristal formation can be by-passed (1^{st} order transition) if cooling in a smart way.

* Instead we'll form a <u>supercooled liquid</u> (metastable).

The equilibrium metastable phase : its free energy is higher than that of the cristal, nevertheless it is said to be at equilibrium because there is not experimental measurement that would allow to see that it is not.
The system forgets the initial preparation
→ propeties independent of preparation
time translational invariance. $A(t) : \begin{cases} \langle A(t)\rangle = \langle A\rangle \\ \langle A(t)A(t')\rangle = \langle A(0)A(t-t')\rangle \end{cases}$

→ fluctuation-dissipation relations (near equilibrium in linear response regime) $\chi_A(t,t') = -\Theta(t-t')\frac{1}{T}\partial_t\langle (A(0)-\langle A\rangle)(A(t-t')-\langle A\rangle)\rangle$

causal indicator

temperature

spontaneous fluctuation at equilibrium

* The glass further down in temperature is out of equilibrium.

→ dependence on preparation and history. (glass / glass', depending on preparation)

→ hysteresis, memory effect : if heating the system, will not be following exactly the same curve until reaching back to the equilibrium supercooled structure.

→ Aging $\langle A(t)\rangle$ evolving very slowly with time

$\langle A(t)A(t')\rangle$ does depend on age t and $t'-t = \Delta t$. (no more translat. invariance)

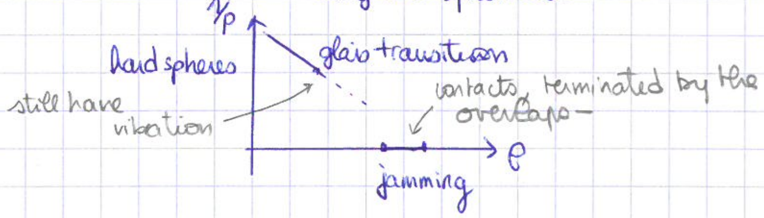
At the glass transition, it is actually an observed "transition" corresponding to a <u>kinetic crossover</u>. So that it depends on the scale at which you look at the relaxation time of your system. (no discontinuity)

Rk: The question is what is the time scale to reach the metastable state
e.g. diamonds are metastable states, nevertheless we don't only have graphite.

Rk: You cannot always avoid the first order transition e.g. noble glass, will always cristallize no matter how fast you cool them.

DIVERSITY OF QUESTIONS ABOUT GLASSES:

- nature and properties of the glass phase. (low temperature anomalies,
  aging behavior,
  non linear rheology / plasticity
- relation between glass and jamming (jamming = zero temp, out of equilibrium, infinite pressure

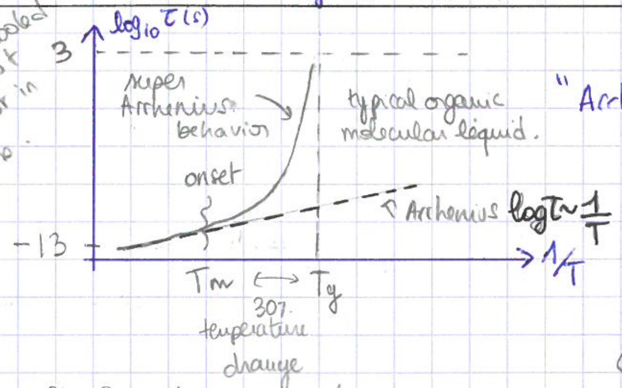


- how to avoid xtallization?
  metallic glasses would need 10^6 K/s speed of cooling, which is huge!
- properties of the "glass transition" from the supercooled liquid.

II What is there to be explained about the glass transition?

II 1 Dramatic slow down of relaxation when T ↘ in the supercooled liquid.

for the supercooled liquids, cannot follow the plot in the glass.



"Arrhenius plot"

where τ characterizes the time for the system to relax to equilibrium probes: $A(t) = \frac{1}{\sqrt{N}} \sum_{i=1} Y(\Omega_i(t))$
spherical harmonics for molecular liquids

$\langle A(t) - \langle A \rangle \rangle$ $\downarrow$ $= \frac{1}{\sqrt{N}} \sum_{i=1}^{n} e^{i q \cdot r_i(t)}$ displacement

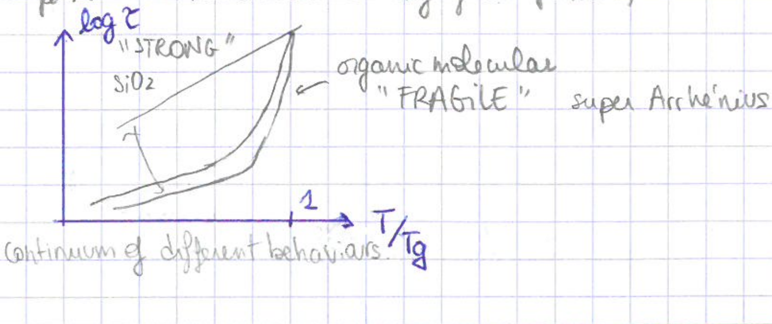
$\hookrightarrow \langle \delta A(0) \delta A(t) \rangle \rightarrow \tau_{relax}$.

Rk: SiO_2 has very weak super Arrhenius behavior

Super Arrhenius behavior must arise from collective behavior.
Interactions between organic molecules is mere weak VdW → so build this impressive Arrhenius activation energy everybody must be conspiring!

Rk: SiO_2 has very weak super Arrhenius behaviour (strong glass former)

Angell classification (1984)



continuum of different behaviours

How can we describe in formula the rise of the relaxation time?

$k_B = 1$.

Arrhénius $\tau \sim \tau_0 e^{E/T}$ E = apparent activation (free) energy.

Super-Arrhénius $\tau \sim \tau_0 e^{E(T)/T}$ with $E(T)$ increasing as T decreases.

Phenomenological formula were introduced:

→ Vogel-Fulcher-Tamman $\tau \sim \tau_0 e^{\frac{A}{T-T_0}}$ → diverges at T_0 that has to $T_0 < T_g$ to fit the data.

→ Bässler $\tau \sim \tau_0 e^{B/T^2}$ → diverges only at T=0.

→ Mauro et al (2010 ich) $\tau \sim \tau_0 e^{\frac{C}{T} e^{D/T}}$

→ others that also fit all the data... some theoretical insights only could constrain one whether the other formula.

Another observation here:

The viscous slow down = relaxation slow down, although a priori two different properties.
(↳ stops flowing)

↳ relation between elasticity / viscosity and visco elasticity theory by Maxwell.

The system at short time looks like a solid (elastic) $t \ll \tau_{relax}$
at long time looks like a liquid (viscous) $t \gg \tau_{relax}$

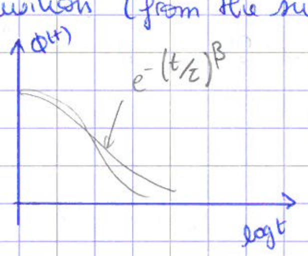
High frequency relation: $\underset{\text{viscosity}}{\eta} = \underset{\text{shear modulus}}{G_\infty}\ \tau_{Relax}$ ↳ relaxation time

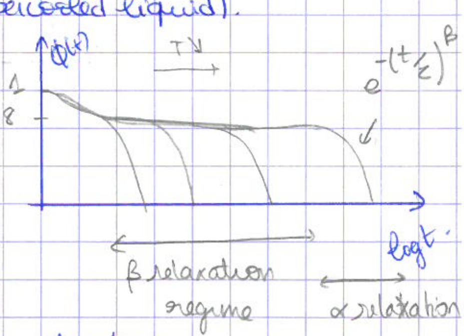
↳ increases 2-5 times when T↗.

05/07/2017

What is there to be explained about the glass transition (from the supercooled liquid).

- A(t) $\Phi(t) = \langle (A(0) - \langle A \rangle)(A(t) - \langle A \rangle) \rangle$
$\simeq e^{-(t/\tau)^\beta}$ → stretched expo.
$0{,}3, 0{,}4 < \beta < 1$



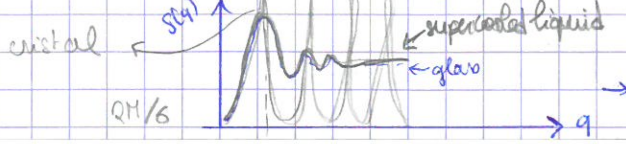


→ slow relaxation, yet plateau is not necessary to all slow relaxation.
What is explaining it here is the landscape picture with local minima blocking the relaxation. One has a separation of the time scales:
- at small times, particles in a "cage" vibrating (pictural view).
- at large time, will escape to equilibrium.

↳ Mode coupling theory

II 2 About the static observables this time: There is very little changes in the observed static.

→ structure measured by $S(q) = \langle \delta\rho_{-q} \delta\rho_q \rangle$ where $\delta\rho_q$ = density fluctuation at coordinate q.



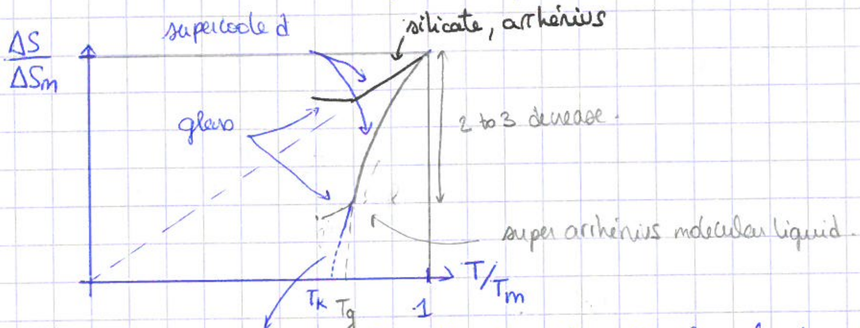
QM/6

→ almost identical, $\xi_2 \sim$ few % change from T_m to T_g

→ The only significant variation is for the <u>entropy</u> (of the supercooled)

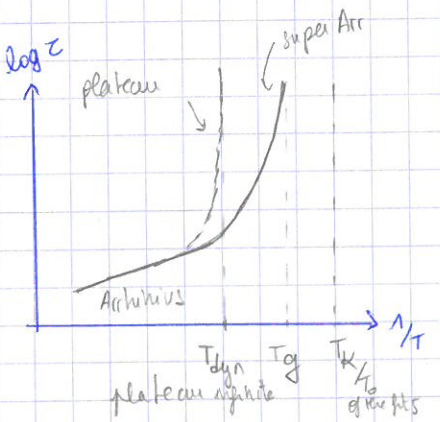
considering the configurational entropy = $S_{liquid} - S_{xtal} = \Delta S$

Kauzmann 1948



extrapolation: imagine cooling the liquid infinitely slowly. Imagine a state for which the entropy of the xtal = entropy liquid → <u>entropy crisis</u>
<u>Kauzmann temp</u>.
$\Delta S = 0$ at $T = T_K$.

Rk: The mean-field description of the REM or the p-spin, is a point of connection as they are descriptions idealized of low temperature regime.

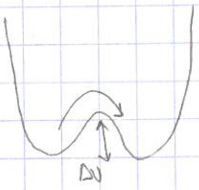


III THE SLOWING DOWN OF RELAXATION: WHAT IS UNIQUE ABOUT THE GLASS TRANSITION?

simple well understood models

- <u>Non collective / non cooperative</u> → Arrhénius law

classical reaction
chemical



ΔU = energy barrier
$\Delta U \gg T$
$\tau \sim \tau_0 e^{\Delta U / T}$

nothing collective about forming the barrier, it is there and pretty unchanged by state

- <u>Collective</u> → critical slowing down. (conventional, eg Curie-Weiss para → ferro).

For temperatures just above $T_c > 0$: $T \to T_c^+ \begin{cases} \xi \sim |T - T_c|^{\nu} \\ \tau \sim \xi^{z} \end{cases}$ z = dynamical exponent $= o(1)$.

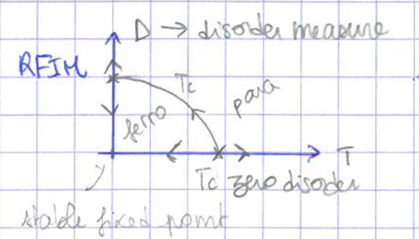
so that here the slowing down is in a powerlaw and not exponential!
so nothing comparable in simple model to supercooled liquids.

- <u>Activated dynamic scaling</u> $\tau \sim e^{\xi^{\psi}/T}$ with $\xi \sim |T - T_c|^{\nu}$.

1. Models with quenched disorder: RFIM, random elastic manifolds, (P. Le Doussal)
C.P controlled by a zero-temperature fixed point (RG)

"critical point"

e.g. RFIM



study in renormalisation formalism of C.P.

$T_e \sim e^{-\Theta} T$
↳ $l \to \infty$ for fixed point
↳ $T=0$ fixed point $\Rightarrow \Theta > 0$.
↳ non trivial

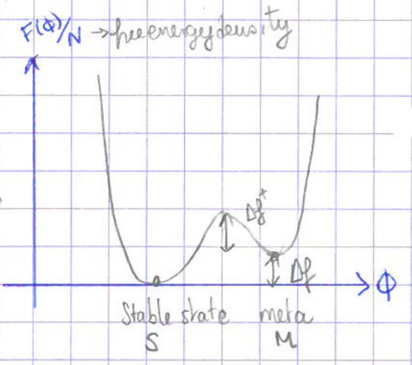
and $\tau_e \sim e^{U/T_e} \sim e^{U e^{\Theta}/T}$ $\Psi = \Theta$ (functional RG).

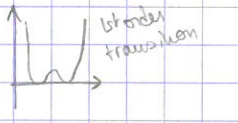
• Nucleation and metastability:

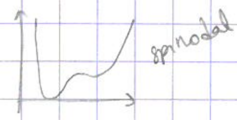
(i) Landau formalism
↳ escape of M: $\tau \sim e^{\frac{\Delta f^{+} N}{T}} \xrightarrow[N \to +\infty]{} +\infty$

so M has in <u>mean-field</u> an <u>infinite life time!</u>

mean field because Φ is supposed to be homogeneous



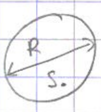




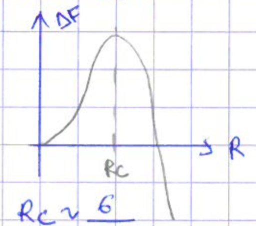
(ii) Finite range, finite d-system: $\Phi(x)$ allowed to be inhomogeneous
$\Phi(x) \to$ barrier state = localized excitation
- classical theory of nucleation
- field theory (instanton) ↳ J. Langer (68)

What if I have a droplet of size R of the stable state inside my metastable state?

M.



free energy change: $\Delta F(R) = -\Delta f R^{d} + \underset{\substack{\uparrow \\ \text{interfacial cost}}}{\sigma} R^{d-1}$

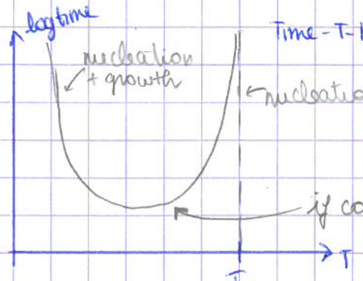


↳ As soon as $R > R_c$ → system will prefer to turn to S. $R_c \sim \frac{\sigma}{\Delta f}$.
↳ Consequently the time of relaxation for nucleation $\tau \sim e^{\Delta F_c/T}$
$\sim e^{c\sigma R^{d-1}/T}$ → activated dynamic.
(finite this time).

Rk: At melting $R_c \to +\infty$ has $\Delta f = 0$ and the relaxation is infinite.

Cristallization

$\tau_{\substack{\text{relax} \\ \text{liquid}}} \ll \tau_{obs} \ll \tau_{xtal}$



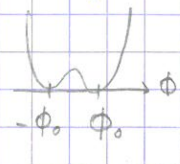
Time-T-transformation

if cooling faster than this can avoid xtallization.

ref: A. Cavagna "Supercooled liquids for pedestrians"

↳ ϕ^4-theory; instanton calculation: localized / inhomogeneous solution of effective Hamiltonian

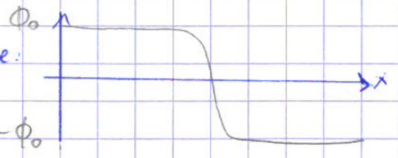
still using effective yet more powerful than Landau!



Φ^4-theory: $V(\phi) = -\frac{|\tau|}{2}\Phi^2 + \frac{g}{4!}\Phi^4$

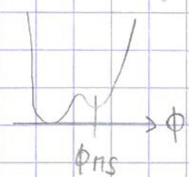
$$S[\phi] = \int_x \frac{1}{2}\left(\partial_x \Phi(x)\right)^2 + V(\Phi(x))$$

Consider the case:

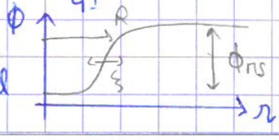


$\Delta F \sim \sigma L^{d-1}$ ← typical

slightly more complicated:



$V(\phi) = \frac{\tau}{2}\Phi^2 - \frac{w}{3}\Phi^3 + \frac{g}{4!}\Phi^4$
↳ spherical droplet R
$\xi/R \ll 1 \equiv$ thin wall



→ maximum of action recovers Nucleation theory

05/07/2017 II

IV COLLECTIVE BEHAVIOR IN GLASS FORMATION: CHARACTERISTIC LENGTH SCALE.

IV 1 Spatially heterogeneous character of the dynamics

$D \sim \frac{T}{\eta}$ decoupling between translational diffusion and $\begin{cases} \text{viscosity} \\ \tau_\alpha . \end{cases}$ ≡ DYNAMICAL HETEROGENEITIES

→ fast and slow regions in the system
→ characteristic sizes of these regions depend on the temperature.

Can we be more quantitative about that?

define $f_j(t';t'+t) = \mathrm{Re}\left\{ e^{iq[\underline{r}_j(t'+t) - r_j(t')]} \right\}$ intermediate scattering function
measure of the displacement.

↳ mobility field: $f(r,t',t'+t) = \frac{1}{\rho} \sum_{i=1}^{N} f_j(t';t'+t)\,\delta(\underline{r} - r_i(t'))$

⇒ average dynamics: $\phi(t) = \frac{1}{V} \int d^d r \langle f(r;t',t'+t) \rangle = \frac{1}{N} \sum_j \langle f_j(t',t'+t) \rangle$

$= \langle f_1(0,t) \rangle$ self averaging

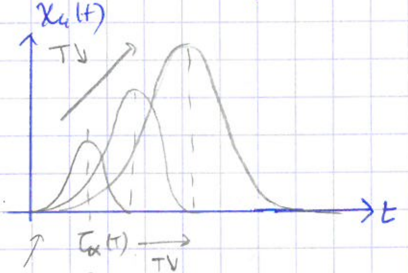
⇒ fluctuations in dynamics: $f - \langle f \rangle = \delta f$
↘ 4pt correlation function: $G_4(r,t) = \rho \left\langle \frac{1}{V} \int d^d r' \delta f(r';t',t'+t)\, \delta f(r'+r,t',t'+t) \right\rangle$

dynamical correlation length $\xi_4(t)$

yet would be easier to compute a susceptibility: $\chi_4(t) = \int d^d r\, G_4(r,t)$

$= N \left\langle \left[\frac{1}{N} \sum_{j=1}^{N} \delta f_j(t',t'+t) \right]^2 \right\rangle$

variance.

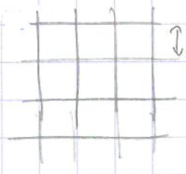


small and large time = homogeneous

↳ correlation length $\xi_4^4(t)^d$ ← naive dimensional analysis.

experimental estimates: At Tg $\xi_4 \leq$ 5-10 molecules

If there is a relevant static correlation length ξ:



$\updownarrow \xi$ independent sub systems → $\tau_{relax} \sim \tau_{relax}(\text{sub system})$.

in the case of activated dynamics: what is the biggest possible barrier in a finite size system? (worst-case scenario)
→ $\Delta E \sim \xi^d$.

which implies $\tau_{relax} \sim \tau_{relax}(\text{subsystem}) < \tau_0 e^{c\,\xi^d / T}$ rigorously Guillhem/Andrea 2006

Recall super-arrhenius $\tau_{relax} \sim \tau_0 e^{A/T^2}$ $\xi(T) \nearrow$ as T ↘
$\xi(T) \to \infty$ as $T = 0$.

The rigorous proof gives an idea of what is this length scale:
point to set correlations → $\xi_{(PTS)}$

between a point and whole set of points in the surrounding.

↳ for observable Θ: $\langle \Theta(\underline{r})\, f(\{\Theta(B)\}) \rangle_{\underline{\text{connected}}}$

in the bulk liquid

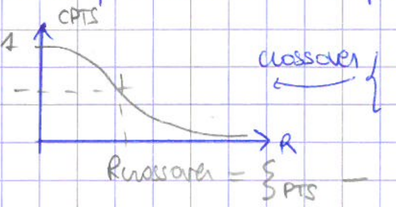
neighboring sub-system

7/7

take a spin-system with equilibrium configuration $\mathcal{C}_{eq} = \{\sigma_i\}$

↳ let's freeze the system in $\mathcal{C}_{eq}$ outside the subsystem B of size R
equilibrate ~~out~~ side ↳ configurations $\mathcal{C}' = \{\sigma_i'\} \rightarrow \langle \sigma_i' \rangle_B$

↳ similarity at i between original $\mathcal{C}_{eq}$ and all new sampled. $\langle \sigma_i \overbrace{\langle \sigma_i' \rangle_B}^{= f(\sigma_B)} \rangle_{eq} = \text{CPTS}$



crossover ← $\begin{cases} 0 \text{ if } R \rightarrow +\infty \\ 1 \text{ if } R \rightarrow 0 \end{cases}$

Super-Arrhenius, activated dynamics: $\tau(T) \sim \tau_0 \, e^{c\,\xi(T)^{\psi}/T}$

↳ let's call Tonset the point where the super arrhenius starts

$$\log\left[\frac{\tau(T_g)}{\tau(T_{onset})}\right] \sim 14-15 \rightarrow c\left[\frac{\xi(T_g)^{\psi}}{T_g} - \frac{\xi(T)^{\psi}}{T_{onset}}\right] \sim 34$$

$$\frac{T_{onset}}{T_g} \sim 1{,}5 \,, \quad c\,\frac{\xi(T_{onset})^{\psi}}{T_{onset}} \sim 2-3 \longrightarrow \left[\frac{\xi(T_g)}{\xi(T_{onset})}\right]^{\psi} \sim 8-12$$

↳ d = 3, assuming $\psi = 3$ (in the rigorous bound) $\frac{\xi_g}{\xi_{onset}} \sim 2 - 2{,}3$

$\psi = 2$ $\sim 2.8 - 3.5$

$\psi = 3/2$ $\sim 4 - 5.2$

CONCLUSION: THEORETICAL APPROACHES TO THE GLASS TRANSITION

1/ Great diversity of approaches actually exist:

Us	vs	OTHER VIEWS.
collective behavior	vs	local behavior
phase transitions criticality	vs	mecanism (singled out relaxat mecanism)
thermodynamic/ static	vs	purely dynamical

strength of landscape picture + rarefaction of available states
→ one can formulate the mean-field theory of the glass transition
↳ exact for hard sphere fluid in $d \rightarrow \infty$ _
↳ universality of the landscape _

→ from which one can compute a lot of thing: _ relation between glass-jamming.

yet in real 3-d world → fluctuations!

two strategies: { × MF + include fluctuations ↳ nucleation/instantons, ↳ RG } very hard
"Theory of simple glasses" F. Zamponi - HDR _
× guess important fluctuations in 3d.