WHAT IS A GLASS?

System formed in a disordered system.
This lecture will be restricted to structural glasses (formed by liquids).
E.g.: polymers, colloidal suspensions
High vs. small elastic conductivities.
Glasses are solid - don't flow
- resist to small shear.

Amorphous - homogeneous material (optical properties, windows)
Thermally quenched transitions, entropy, subcooled liquid.

Class formation = cooling a liquid.

But crystal formation can be by-passed (1st order transition) if cooling is done a smart way.

Instead we form a supercooled liquid (meltable).

The equilibrium metastable phase has a free energy higher than that of the crystal. Nevertheless, it is said to be at equilibrium because there is no experimental measurement that would allow us to say that it is not.

The system forgets the initial preparation:
- Properties independent of preparation
- Time translational invariance

\[ \langle A(t) \rangle = \langle A \rangle \]
\[ \langle A(t_1)A(t_2) \rangle = \langle A_0 \rangle A(t_1-t_2) \]

Fluctuation-dissipation relations

\[ \chi (t; t') = \frac{\langle A(t_1)A(t_2) \rangle}{T} \]

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

\[ \langle A(t) \rangle \text{ evolving very slowly with time} \]
\[ \langle A(t)A(t) \rangle \text{ does depend on age } t \text{ and } t-t' = At \text{ (nonspecific)} \]

At the glass transition, it is actually an observed "transition" corresponding to a Kauzmann crossover. So that it depends on the scale at which you look or the relaxation time of your system - no discontinuity.
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.

**Diversity of questions about glasses:**
- Nature and properties of the glass phase, glass temperature anomalies, aging behavior, non-linear rheology, plasticity.
- Relation between glass and jamming (jamming = zero temp, out of equilibrium, infinite pressure).
  - Lead spheres still have injection, jammed, dominated by Hooke's law.
  - Glass transition.
- How to avoid crystallization? Metallic glasses would need $10^6$ K/s speed of cooling, which is huge!
- Properties of the "glass transition" from the supercooled liquid.

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

**II.** Dramatic slow down of relaxation when $T < T_g$ in the supercooled liquid.

**Arhenius plot:**

where $\tau$ characterizes the time for the system to relax to equilibrium states:

$$\tau = \frac{A}{k_B T}$$

Super-Arrhenius behavior must arise from collective behavior.

- Interactions between organic molecules are more weak vdW → so build.
- This impregnative Arhenius activation energy everybody must be computing!

**Rh.: Sio2 has very weak super-Arrhenius behavior** (strong glass former)

**Angell classification (1984):**

- Organic molecules
  - Strong glass former (1)
  - Fragile (strong glass former)
How can we describe in formula the rise of the relaxation time?

\[ k_0 = \frac{A}{e^{E/T}} \]

Arrhenius: \( T \rightarrow e^{-E/T} \)

\[ E = \text{apparent activation (free) energy} \]

Super-Arrhenius: \( T \rightarrow e^{-E(t)/T} \) with \( E(t) \) increasing as \( T \) decreases.

Percus-Aizawa formula were introduced:

- Vogel-Fulcher-Tamman: \( T \rightarrow \frac{C}{e^{B/T}} \) diverges at \( T_0 \) that has \( T \rightarrow T_0 < T_g \).

- Bässler: \( T \rightarrow e^{-C/T} \) diverges only at \( T = 0 \).

- Haug et al (2010 iib) \( T \rightarrow e^{-C_1/T} \)

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

Another observation here:

The viscosity slow down = relaxation slow down, although a prior two different properties.

Relation between elasticity/viscosity and micro elasticity theory by Maxwell.

The short time looks like a solid (elastic) \( t \ll t_{\text{relax}} \)

(at long time looks like a liquid (viscous) \( t \gg t_{\text{relax}} \)

High frequency

Viscoelasticity shear modulus

\( \eta = G \ll T_{\text{relax}} \)

viscosity

\( \eta \) decreases 2-5 times when \( T \).

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

\[ \Phi(t) = \langle (A(0) - A)(A(t) - A(t)) \rangle \]

\[ e^{-\frac{t}{\beta}} \quad \text{skeletal exp.} \]

\( 0.01 < \beta < 1 \)

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 time, particles "marginal"-bouncing (pictorial new)
- at large time, will escape to equilibrium.

Note coupling theory.

About the static observables this line: There is very little changes in the observed data

- structure measured by \( S(q) = \langle S_q \cdot S_q \rangle \) where \( S_q = \text{density fluctuation at coordinate } q. \)

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= S2 almost identical, S2 few % change from Tm to Tg.
The only significant relaxation is for the entropy (of RA supercooled)

\[ \Delta S = S_{\text{liquid}} - S_{\text{solid}} = \Delta S \]

\[ T_1 \quad T_2 \quad T_3 \quad T_4 \quad T_5 \]

\[ \Delta S_{\text{melt}} \]

Kauzmann 1948

Extrapolation: Imagine cooling the liquid infinitely slowly. Imagine a state for which the entropy of the solid = entropy liquid \( \rightarrow \) entropy crisis

\[ \Delta S = 0 \text{ at } T = T_\text{cr} \]

Comment: The mean-field description of the REH on the p-spin is a matter of connection as they are descriptions idealized of low-temperature regimes.

**THE SLOWING DOWN OR RELAXATION: WHAT IS UNIQUE ABOUT THEglas TRANSITION?**

- **Non collective/non cooperative** \( \rightarrow \) Arrhenius law

  \[ \Delta S = \text{energy barrier} \quad \Delta S \gg T \]

  \[ T \sim T_\text{cr} \quad \Delta S / T \quad \text{nothing collective about forming the barrier, it is always exponentially unchanged by state} \]

- **Collective** \( \rightarrow \) critical slowing down (conventional, e.g., Curie Weiss para \( \rightarrow \) ferro)

  For temperatures just above \( T_\text{cr} \): \[ T \gg T_\text{cr} \]

  \[ \tau \sim \tau_0 \quad \tau \approx \tau_0 \tau_0 \quad z = \text{dynamic exponent} \quad = c(t) \]

  So that here the slowing down is in a peculiar and not exponential!

  So nothing comparable in simple model to supercooled liquid(s).

- **Activated dynamic scaling** \( \tau \sim e^{-\frac{\Psi}{T}} \) with \( \frac{\Psi}{T} \sim 1/1-T_\text{cr} \)

The models with quenched disorder: REHM, random elastic manifold, (P. Le Doussal)

Critical point controlled by a zero-temperature fixed point (0D)
(ii) Finite range, finite system: $\Phi(x)$ allowed to be inhomogeneous

- Classical theory of nucleation
- Field theory (instanton) \to I. Lang (68)

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

- Free energy change: $\Delta F(R) = -\Phi^2 R^3 + 6 R^{3/2}$

- As soon as $R > R_c$, system will prefer to turn to $S$.
- Consequentially, the time of relaxation for nucleation $T \sim e^{-\Delta F(R_c) / kT}$.

- At melting $R \to 0$, so $\Delta F = 0$ and the relaxation is infinite.

Cristallization

$T_c$ << Times of Typical

At cooling faster than this can avoid crystallization.

$\phi$ Theory: nucleation calculation: localized/inhomogeneous solution of effective Hamiltonian

$H_n$ Theory: $V(\phi) = \frac{1}{2} \phi^2 + \frac{3}{4} \phi^4$

$S(\phi) = \int \frac{1}{2} (\partial_x \phi(x))^2 + V(\phi(x))$

Consider the case:

\[ \phi \to \phi_0 \quad \text{for} \quad \Delta F \sim \Theta_{1-1} \]

Slightly more complicated:

$V(\phi) = \frac{3}{2} \phi^4 - \frac{3}{4} \phi^3 + \frac{3}{4} \phi^2$

$\phi_{ns} \to \phi_0$
IV. COLLECTIVE BEHAVIOR IN GLASS FORMATION: CHARACTERISTIC LENGTH SCALE

IV.1 Spatially heterogeneous character of the dynamics

\[ D \sim \frac{1}{n} \]  
decoupling between translational diffusion and viscosity \[ \sim \tau_c \]

fast and slow regions in the system
characteristic rates of these regions depend on the temperature

Can we be more quantitative about that?

Define \( f_{ij}(t'; t+t) = \text{Re} \left\{ e^{i(t' - t)/\tau_c} \langle \xi_i(t') \xi_j(t) \rangle \right\} \)  

measure of the displacement

\( \text{mobility field} \) \[ f_{ij}(t, t+t) = \frac{1}{\rho} \sum_{i=1}^{N} \frac{f_{ij}(t', t+t)}{s_i(t - t', t')} \]

\( \text{average dynamics} \) \[ \phi(t) = \frac{1}{\sqrt{N}} \int d^3r \langle f_{ij}(r, t, t+t) \rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \langle f_{ij}(t', t+t) \rangle \]

\[ = \langle f_{ij}(t, t) \rangle \] self-averaging

\[ \Rightarrow \text{fluctuations in dynamics} \] \[ \vec{f} \cdot \langle \vec{f} \rangle = 0 \]

\( 4p \) th correlation function

\[ \chi_4(t, t) = \rho \left( \frac{1}{\sqrt{N}} \sum_{i=1}^{N} \langle s_i(t', t) \rangle \right) \]

\( \text{dynamical} \) correlation length \( \xi_d(t) \)

\[ \Rightarrow \text{correlation length} \] \[ \xi_d(t) \]

\[ \text{small and large time} \rightarrow \text{homogeneous} \]

\[ \tau_c \rightarrow t \]

experimental estimates: \( \tau_c \sim 5-10 \) molecules

\[ \text{If there is a relevant static correlation} \] \[ \sim \]

\[ 2^S \]  
\[ \text{independent sub-systems} \rightarrow \Gamma_{\text{relax}} \sim \Gamma_{\text{relax (sub-system)}} \]

\[ \text{which implies} \] \[ \Gamma_{\text{relax}} \sim \Gamma_{\text{relax (sub-system)}} \]

\[ \text{in the case of activated dynamics, what is the biggest possible barrier in a finite size system? (worst-case scenario)} \]

\[ \rightarrow \Delta E \sim \xi_d^2 \]

\[ \text{rigorously} \] \[ \text{Guillermo Andra 2006} \]

\[ \text{The rigorous proof gives an idea of what is this length scale:} \]

\[ \text{point to set correlations} \rightarrow \xi_d^2 (\text{pts}) \]

\[ \text{between a point and whole set of points in the surrounding} \]

\[ \text{for observable} \] \[ \langle \xi(\mathbf{x}) \rangle \]

\[ \text{in the bath liquid} \]
take a spin system with equilibrium configuration \( \langle 6, 3 \rangle \).

Let's freeze the system in Eq. outside the subsystem B of size \( A \) and equilibrate each side to configuration \( \langle 6, 3 \rangle \). 

Similarly, if \( \beta \) between original Eq. and all new examples \( \langle 6, 3 \rangle \) are CPMS.

Super-Arrhenius, activated dynamics: \( T \) vs. \( T_{\text{cr}} \),

We call \( T_{\text{cr}} \) the point where the super-arrhenius starts.

\[
C \left( \frac{\varepsilon(T_g)}{T_g} \right)^n \sim 14 - 15 \rightarrow c \left[ \frac{\varepsilon(T_g)}{T_g} \right]^n \sim 34
\]

\[
\frac{T_{\text{cr}}}{T_g} \sim 2.5, \quad c \left[ \frac{\varepsilon(T_g)}{T_g} \right]^n \sim 2 - 3 \rightarrow \left[ \frac{\varepsilon(T_g)}{T_g} \right]^n \sim 8 - 12
\]

So \( n = 3 \), assuming \( \varepsilon = 3 \) (in the rigorous bound).

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**Conclusion: Theoretical Approaches to the Glass Transition**

vs. vs. Other Views

1/ Great diversity of approaches actually exist:
- Collective behavior vs. local behavior
- Phase transitions vs. mechanism
- Criticality vs. mechanism
- Thermodynamic vs. purely static/dynamical

Strength of landscape picture + large fraction of available states

- One can formulate the mean-field theory of the glass transition
- From each spin to spin fluid in \( d = \infty \)
- Universality of the landscape

Yet in real 3d world \( \rightarrow \) fluctuations?

Two strategies:

1. RIF + include fluctuations \( \sim \) RG
   - Theory of simple glasses, from point HDR
   - Very important fluctuations in 3d.