Lectures on "glass transition"
Summer School on Statistical physics
September 2023

First lecture

• who am I?
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Homepage / Scholar
PhD ~ 20 years ago

→ Statistical mechanics
nonequilibrium and disordered systems

- many models
- soft matter
- active / bio matter
- amorphous solids

→ Physics of glass transition has impacts on all those topics.

Fundamental: it's a difficult problem in Stat mech with series of progress since at least 1960's [60 years]

Applications
* new theoretical ideas diffuse to many areas → { soft matter, active systems }

* Even for simple molecular glasses new technological progress are being made which require input of fundamental physicists [Ligo, Smartphones]

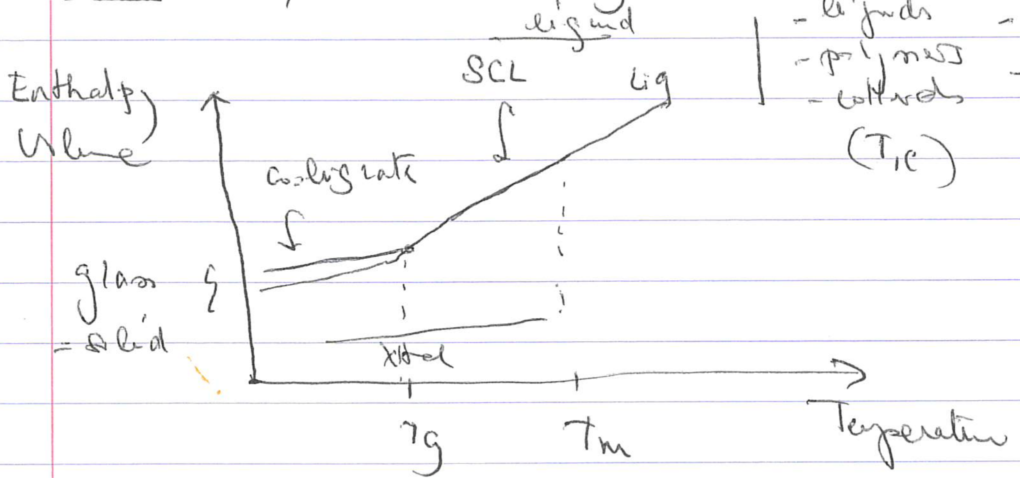
Global outline of 5 lectures

1) Basics of glass transition
2) Mean field theory [1990 - 2020]
3) Lattice models : new physics
4) Atomistic models : tests in finite d.
5) Nonequilibrium glass physics | Active, UG, Rheology, Jamming

I) Basics of glass transition physics

a) What is the pb? why is it interesting? A fluid to solid transition

| - liquids - polymers - colloids (T, c) | - animals - cells |



SCL : looks equilibrated (even if unstable wrt xtal)

- $C_{AB}(t,t') = \langle A(t) B(t') \rangle = C_{AB}(t-t')$

- $R_{AB}(t,t') = \frac{\delta \langle A(t) \rangle}{\delta h_B(t')} = R_{AB}(t-t') = -\frac{1}{T} \frac{\partial C_{AB}(t-t')}{\partial t'}$

Glass: not equilibrated — Corr (t,t') explicitly
- FDT not obeyed
- depends on history

Many questions can be asked:
- xtal
- stat + dynamics, thermodynamics
- nature of phase change, description, universality
- Glass state: aging, transport in amorphous solids? (xtal in textbooks)

→ many of them are still research questions today

b) Structure of liquids and glasses

positions $\{\vec{r}_i;\ i=1,\dots N\}$

density $\rho(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i)$

$\rho_0 = \langle \rho(\vec{r}) \rangle = \frac{1}{V}\int d\vec{r}\, \rho(\vec{r}) = \frac{N}{V}$ average number density

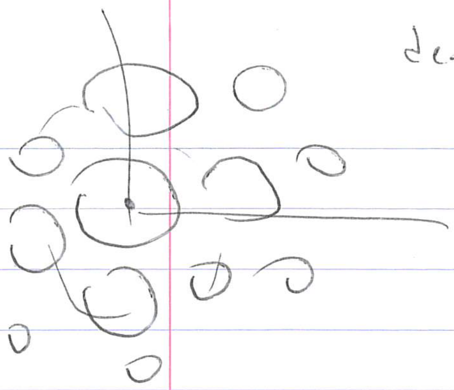
fluctuations $\delta\rho(\vec{r}) = \rho(\vec{r}) - \rho_0$

$G(\vec{r},\vec{r}') = \langle \delta\rho(\vec{r})\, \delta\rho(\vec{r}') \rangle$

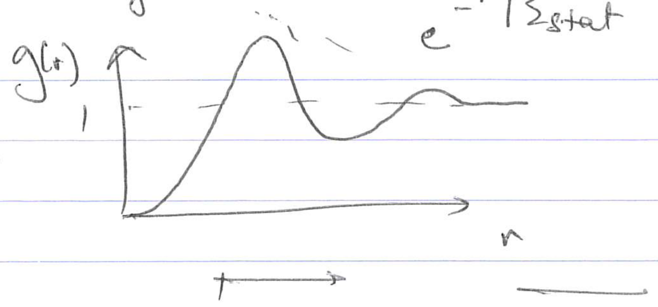
$= \rho_0 \delta(\vec{r}-\vec{r}') + \rho_0^2 g(\vec{r},\vec{r}') - \rho_0^2$ spatial homogeneity ↓

$\rho_0^2 g(\vec{r},\vec{r}') = \langle \sum_{i\neq j} \delta(\vec{r}-\vec{r}_i)\, \delta(\vec{r}'-\vec{r}_j) \rangle = \rho_0^2 g(\vec{r}-\vec{r}')$

pair correlation function: $\rho_0 g(\vec{r}) =$ density at $\vec{r}$ given one particle at $\vec{r}=\vec{0}$



dense liquids



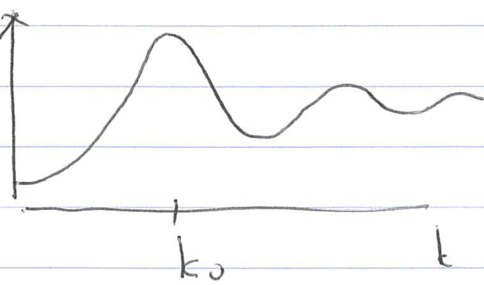
$\xi_{stat} \sim (1-2)\sigma$ weakly T dependent

Fourier domain $\delta\rho(\vec{r}) \to \delta\rho(\vec{k}) = \sum_{i=1}^{N} e^{i\vec{k}\cdot\vec{r}_i}$

$$S(k) = \frac{1}{N}\langle \delta\rho(\vec{k})\,\delta\rho(-\vec{k})\rangle$$ (scattering experiments)

$$= \frac{1}{N}\Big\langle \sum_{ij} e^{i\vec{k}\cdot[\vec{r}_i - \vec{r}_j]}\Big\rangle$$

$$S(\vec{k}) = 1 + \rho_0 \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\,[g(\vec{r}) - 1]$$



$$S(k\to 0) = 1 + \rho_0 \int d\vec{r}\,[g(\vec{r}) - 1]$$

$$= \rho_0 k_B T\, \chi_T$$

Isothermal compressibility

Critical fluids

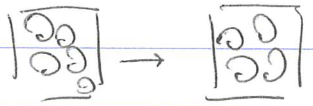
$\xi \to \infty$

$\chi_T \to \infty$

"opalescence"

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big|_T$$

- liquids & glass have random disordered structure with no long-range order in ⟨δρ δρ⟩ –
- mysticism: glass is a solid! xtal → periodicity –



c) Dynamics

t dependent → motion, transport

- $F(\vec{q},t) = \frac{1}{N} \langle \delta\rho(\vec{k},t)\, \delta\rho(-\vec{k},0) \rangle$

$$= \frac{1}{N} \left\langle \sum_{ij} e^{i\vec{k}\cdot[\vec{r}_i(t) - \vec{r}_j(0)]} \right\rangle$$

intermediate scattering function (exp) ISF

- Self part

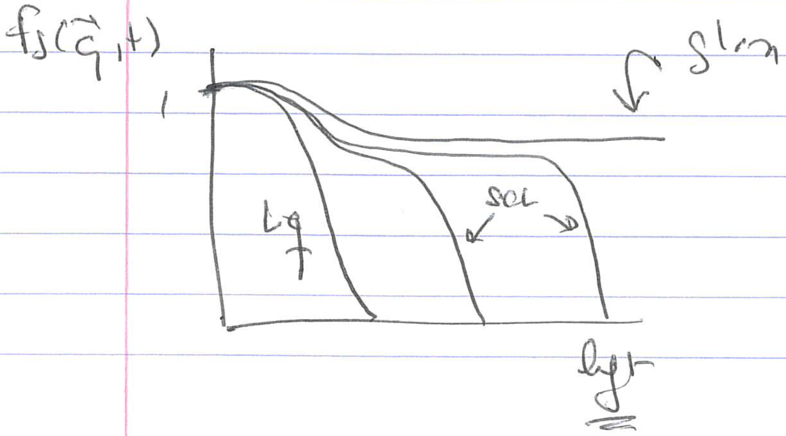
$$F_s(\vec{q},t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{i\vec{k}\cdot[\vec{r}_i(t) - \vec{r}_i(0)]} \right\rangle$$

self ISF ↑ single particle motion.

- k→0 related to

$$\Delta^2(t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} [\vec{r}_i(t) - \vec{r}_i(0)]^2 \right\rangle$$

mean-squared displacement (easy interpretation)

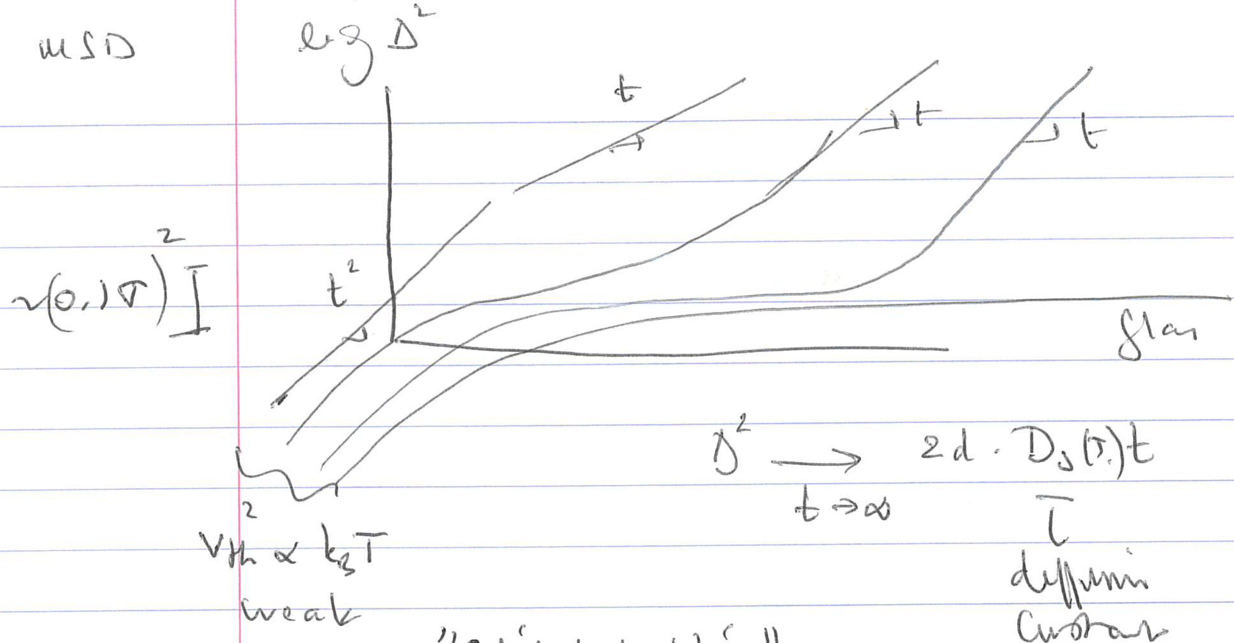


- 2-step decay (vib + leave)
- slow part

$$\propto \exp\left(-\left(\frac{t}{\tau_\alpha(T)}\right)^{\beta(T)}\right)$$

stretched "distrib"

MSD

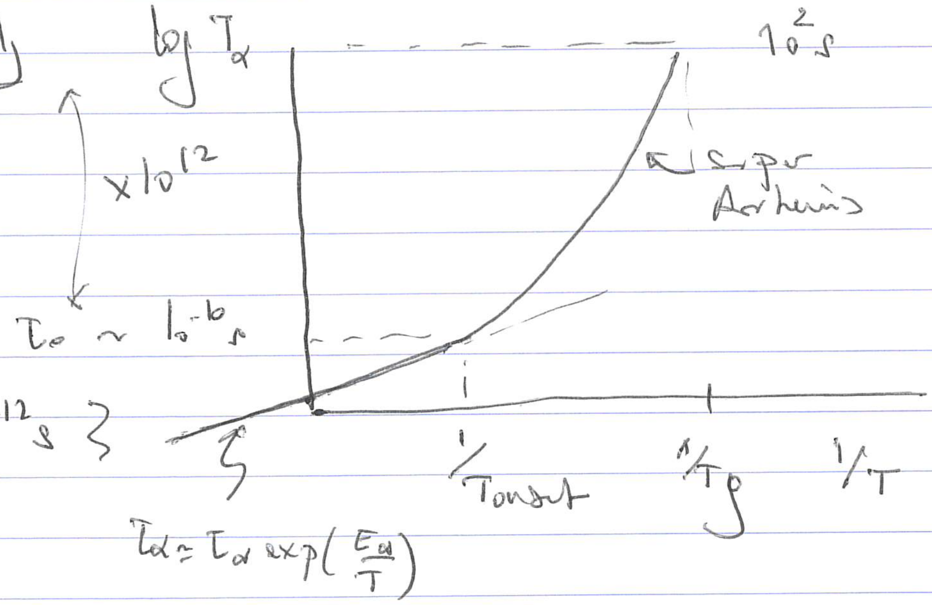


$\Delta^2 \xrightarrow[t\to\infty]{} 2d \cdot D_s(T) t$ — D_s: diffusion constant (strong fn T)

"Solid at short time"

Both $\tau_\alpha(T)$ and $D_s(T)$ change rapidly with T
→ dynamics slow at particle level

Typically for molecular liquids



NB colloidal glasses (cells, bacteria)

$\tau_{mic} \sim 1$ ms
GT ~ 10^2 s } ×10⁵

7 orders of magnitude difference!

Super Arrhenius $\rightarrow \tau_\alpha \sim \tau_0 \exp\left(\frac{\Delta(T)}{T}\right)$

| with $\Delta(T) \nearrow$ when $T \downarrow$

Hint of collective physics!

Functional forms for $\Delta(T)$ not known!

$\Delta(T) = \frac{1}{T - T_0}$ Vogel Fulcher Tammann

$\Delta(T) = \frac{1}{T^2}$ Bässler

$\Delta =$ const

"strong glasses" SiO_2

Many others from expt

overall variation of Δ in factor of 3-4 max

but then goes into $\exp\left(\frac{\Delta}{T}\right)$ → explodes.

We will never know!

× Not easy to predict $\Delta(T)$

- Arrhenius → wrong
- Critical phenomena → wrong $\tau = |T - T_c|^{-z\nu}$
- Disordered critical point $\xi(T)$

  $\rightarrow \tau \propto \exp\left(\xi^\psi / T\right)$ ✓
- Nucleation near 1st order transition

  $\tau \sim \exp\left(\frac{\Delta F^*}{T}\right)$ ✓

× "Decoupling" diffusion $\partial_t \rho = D \nabla \rho \rightarrow \rho(k,t) = \rho(k,0) e^{-Dk^2 t}$

$$\tau(k) = \frac{1}{Dk^2}$$

$\left[\tau \sim \frac{1}{D}\right.$ with $\frac{1}{k^2}$ dependence$\left.\right]$ ~~not valid in SCL~~

<u>In fluids</u> | $\tau \sim \eta \sim \frac{1}{D}$ Stokes Einstein

$D = \frac{k_B T}{6\pi\sigma\eta}$

<u>In SCL</u> $\underline{\tau \sim \eta} \neq \frac{1}{D}$ Stokes Einstein not obeyed

Stronger T-dependence than $1/D$

d) <u>Thermodynamics = Configurational Entropy</u>

"excess" or "configurational" Entropy i.e. remove momenta to focus on positions only

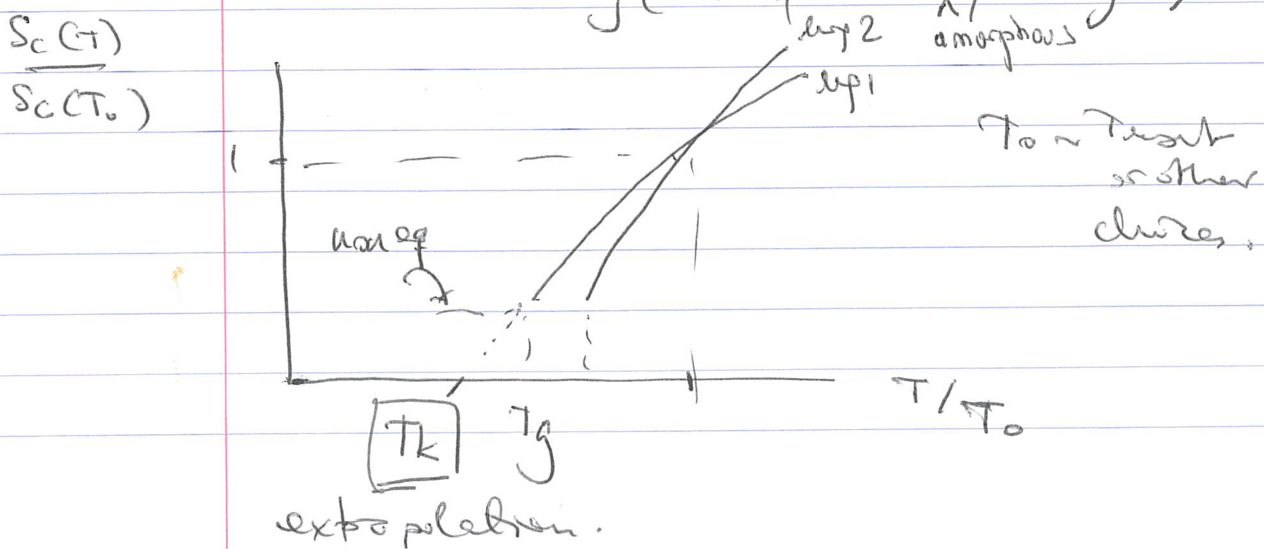
$S_c = \underline{S_{liquid}} - S_{xtal}$

↳ exp. $S(T) = S_{ref} + \int_{T_{ref}}^{T} dT' \frac{C_p(T')}{T'}$

calorimetry along rev. paths.

<u>Idea</u> | $S_{liq} \sim \log(\#\text{config})$
| $S_{xtal} \sim \log(\#\text{config with unique structure})$

$S_c \sim \log(\#\text{ of distinct packings})$ (amorphous)



Kauzmann (1948) notes that $S_c(T \to T_K) = 0$?!?

No amorphous states available $\Rightarrow$ glass state

→ possible underlying liq → glass phase transition kinetically avoided at T_g

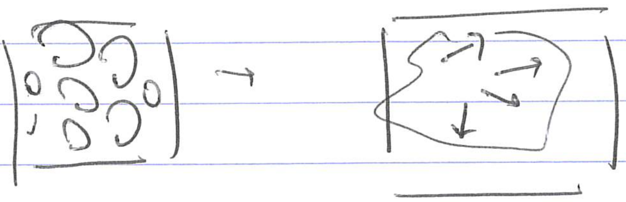
→ physics driven by rarefaction of available amorphous states rather than specific "structure" of states

→ 70 years later: exactly realized in MF theory of glass (lecture 2)

c) Dynamic Heterogeneity

Statics boring; dynamics is not!

$t = 0 \longrightarrow t \sim \tau_\alpha \quad (|\Delta \vec{r}_i| \sim \sigma)$



spatially correlated particle motion!

$$f_i(t) = e^{i\vec{q}\cdot[\Delta\vec{r}_i(t)]}$$

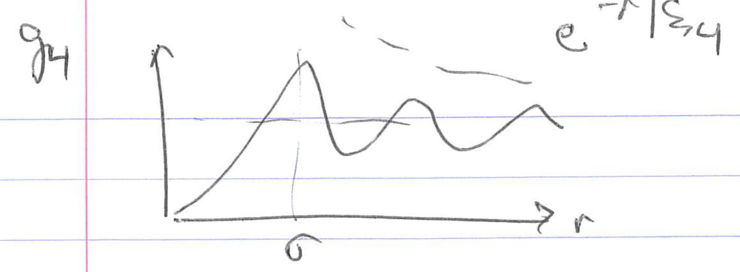
$$\langle f_i \rangle = F_S(q,t)$$

$\delta f_i(t) = f_i(t) - \langle f_i \rangle$ fluct. around average

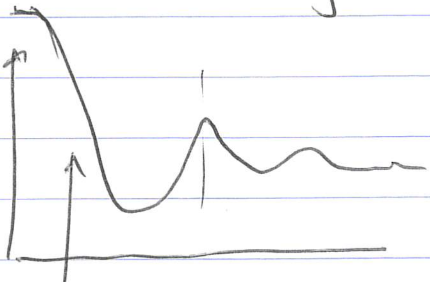
↓

$$g_4(r,t) = \frac{1}{N}\sum_{ij} \delta f_i(t)\, \delta f_j(t)\, \delta\left(\vec{r} - |\vec{r}_i(0) - \vec{r}_j(0)|\right)$$

are fluc of i and j correlated



$$S_4(k,t) = \frac{1}{N}\sum_{ij} \delta f_i(t)\,\delta f_j(t)\, e^{i k\cdot[\vec{r}_i(0)-\vec{r}_j(0)]}$$



growing peak $\quad S_4(k,t) \simeq \frac{S_4(0,t)}{1+(k\xi)^2}$

$$S_4(k\to 0,t) = \frac{1}{N}\left\langle\left(\frac{1}{N}\sum_i \delta f_i\right)^2\right\rangle$$

$$= \chi_4(t) \simeq \xi_4^d$$

↑ diverging susceptibility

<u>χ_4, g_4, S_4 well studied → $\xi_4(T)$ ↑ when T ↘</u>

<u>A lot of work (1990 – 2010)</u> measurements in molecules near T_g are still missing today.

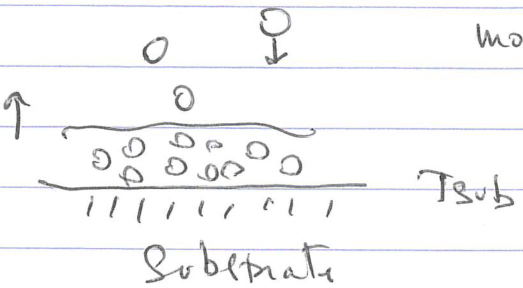
f) <u>Ultrastable glasses</u>

<u>Q</u> How to equilibrate glasses below T_g?

(1) Wait very long times → eg amber glass $\tau_{prep} \simeq 10^6$ years

(2) Be clever!

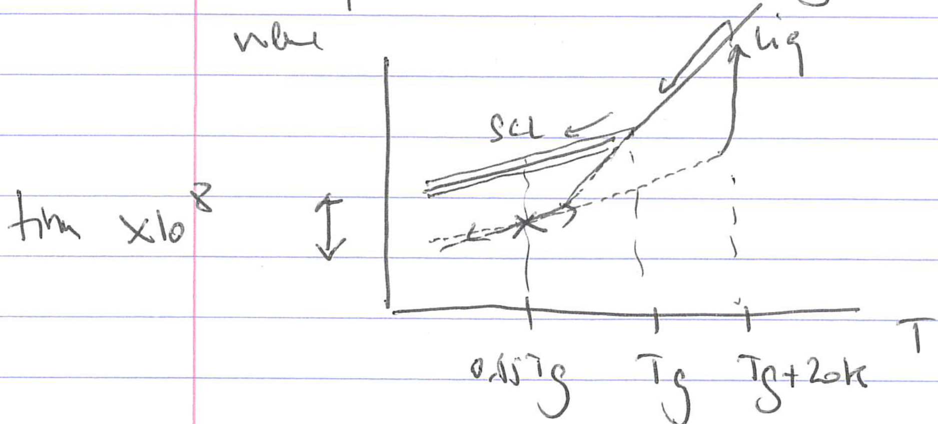
Protocol: physical vapor deposition



molecules arrive "one by one"
ie very slowly

Two control parameters = $\begin{cases} T_{sub} \\ \gamma_{dep} = \frac{dh}{dt} \sim nm/s \end{cases}$

2007 Ediger finds that (slow γ_{dep} + $T_{sub} \sim 0.85\,T_g$)
produces "ultrastable glasses"



glass remain "stable" in liq phase

Since 2007: many systems, applications, etc.

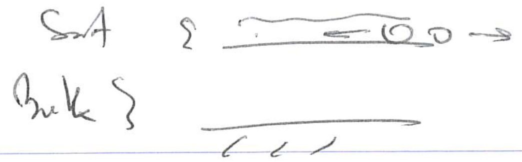
As if system is cooled 10^8 times slower!

↳ Very old glasses in 1 afternoon

Q What is the miracle?

Bulk: cooling rate $\frac{dT}{dt}$ competes with $\tau_\alpha^{\text{Bulk}}$

ie: $x^{\text{Bulk}} = \frac{dT}{dt} \times \frac{\tau_\alpha}{T}$ $\ll 1$ eq ; $\gg 1$ glass



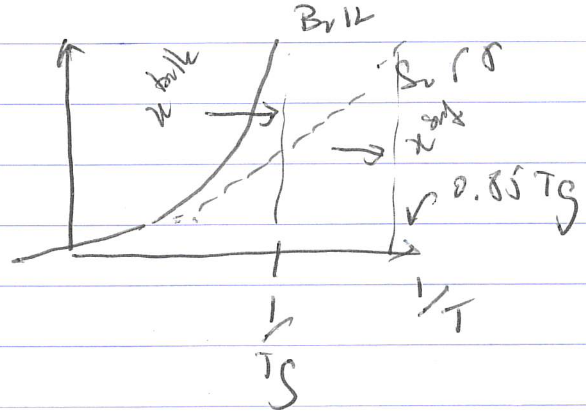
For the Surface:

$$x^{surface} = \gamma_{dep} \times \frac{\tau_\alpha^{surf}}{\sigma}$$

$\ll 1$ eq

$\gg 1$ glass

key finding $\tau_\alpha^{surf} \ll \tau_\alpha^{Bulk}$



Surface freezes below Tg and helps maintain eq at T<Tg

Rem: Novel technological applications are being developed → pharmaceuticals

→ smartphone displays

→ LIGO / quantum computing