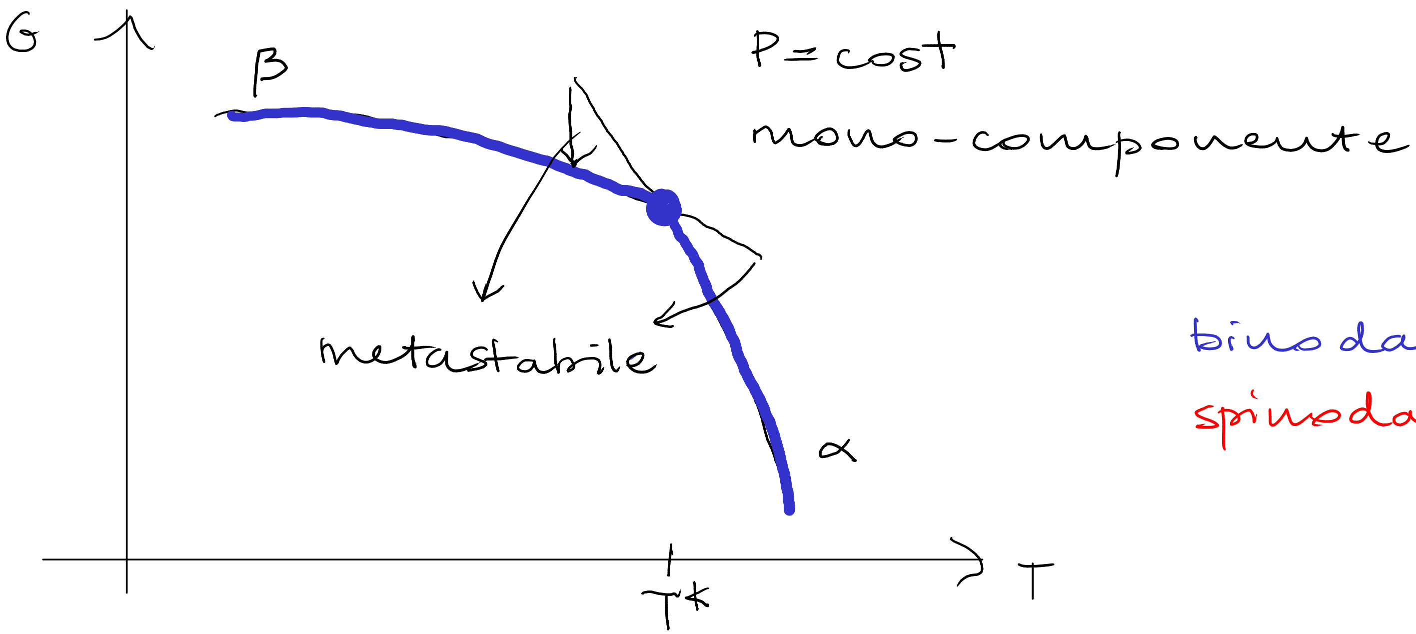
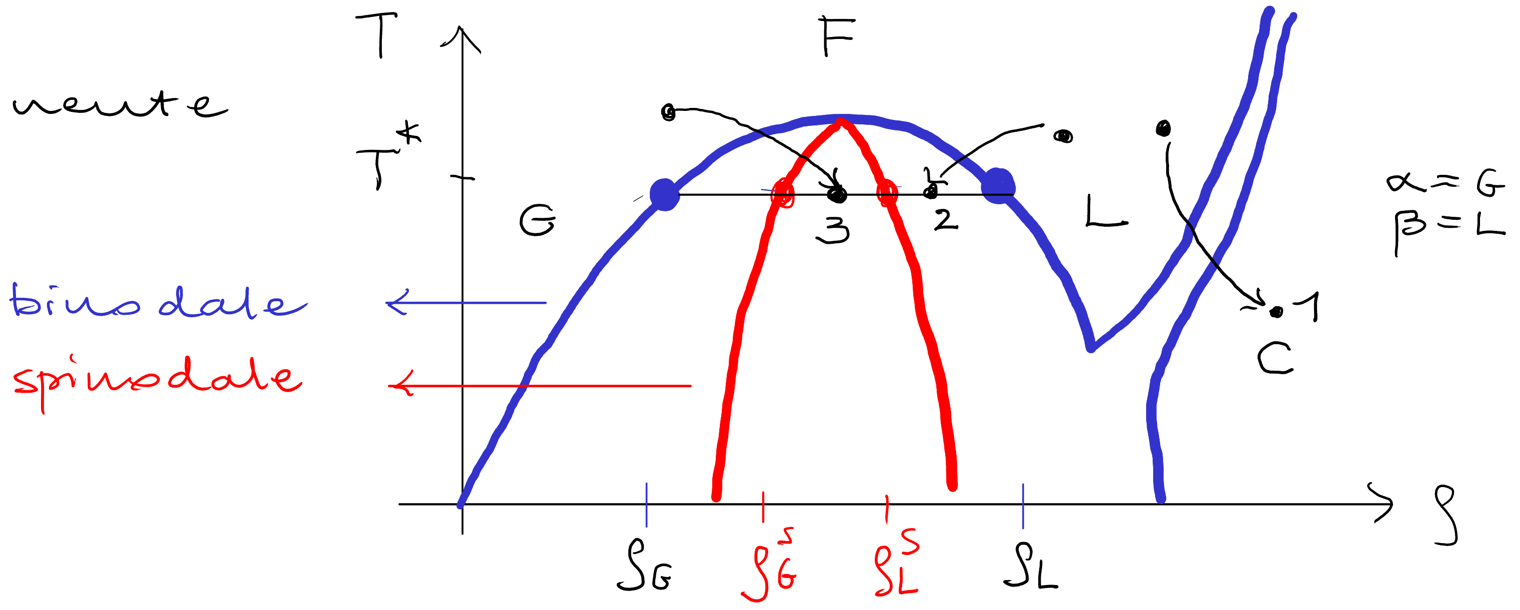
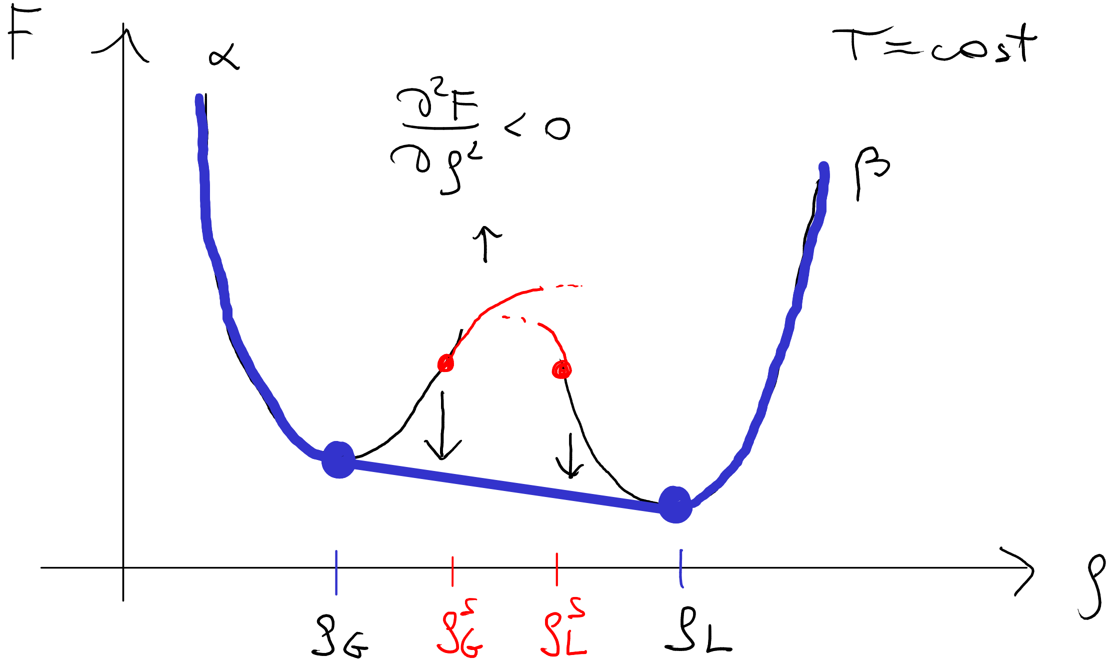
FLUIDI METASTABILI E INSTABILI





1. metastabile rispetto a cristallo } ①
2. metastabile rispetto a liquido + gas } ①
3. instabile rispetto a liquido + gas ②



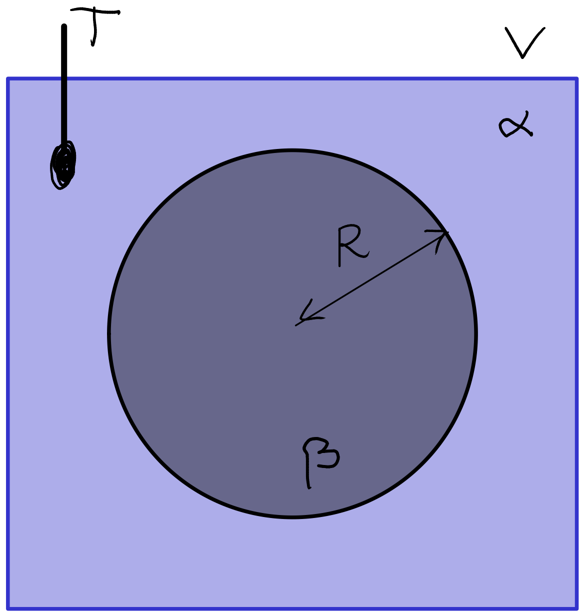
① nucleazione + crescita

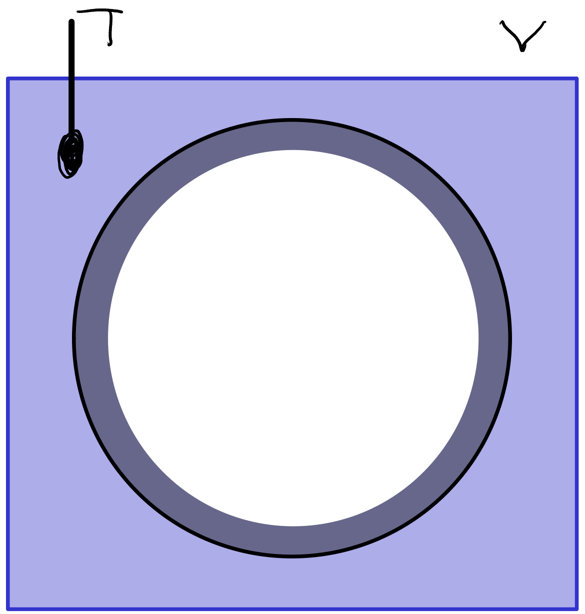
② decomposizione spinodale

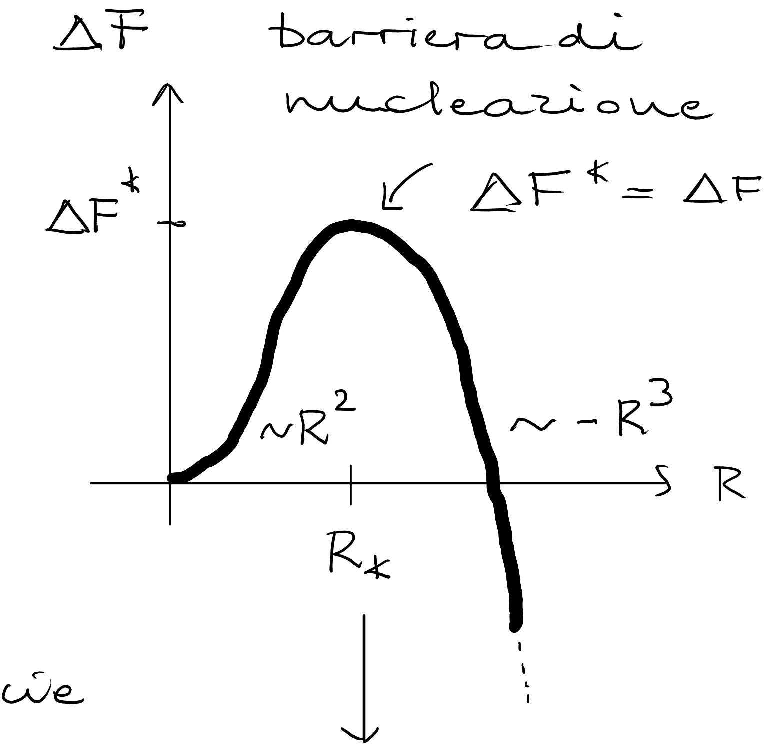
1) Nucleazione

CNT : fenomenologica α = metastabile β = stabile $f = \frac{F}{V}$ $f_\beta < f_\alpha$

$\Delta f = f_\beta - f_\alpha$







barriera di nucleazione

$\Delta F^* = \Delta F(R_*)$

nucleo critico

$$\Delta F = \frac{4}{3}\pi R^3 \Delta f + 4\pi R^2 \cdot \gamma \rightarrow \text{tensione di superficie}$$

$$\left.\frac{d\Delta F}{dR}\right|_{R^*} = 0 \; : \; \cancel{4\pi} R_*^{\cancel{2}} \Delta f + {}^{2}\cancel{8}\cancel{\pi}\cancel{R}_* \gamma = 0 \Rightarrow R_* = -\frac{2\gamma}{\Delta f}$$

$$\Delta F^* = \frac{4}{3}\pi\left(-\frac{8\gamma^3}{\Delta f^3}\right)\Delta f + 4\pi \frac{4\gamma^2}{\Delta f^2}\gamma = \frac{4\pi}{3}\frac{12-8}{\Delta f^2}\gamma^3 = \frac{16\pi}{3}\frac{\gamma^3}{\Delta f^2} \sim \frac{1}{\Delta f^2}$$

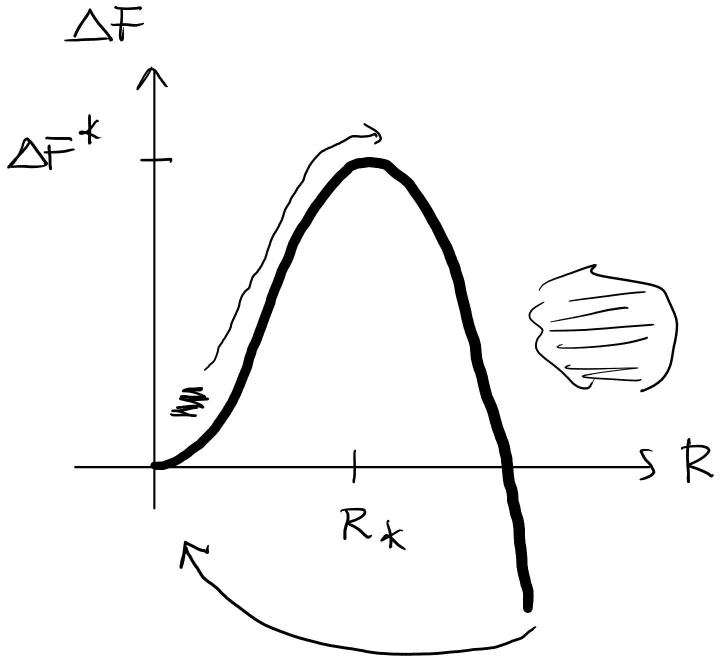
Cinetica della nucleazione

- $\Delta F(R)$ paesaggio di energia
- 1 dof : R del nucleo
- particella browniana senza inerzia in campo esterno

Eq. Smoluchowski : $\Delta U \to \Delta F$, $x \to R$, $D = \frac{k_B T}{\xi} = D(R)$

BH 10.6 $\Rightarrow p(R,t)$

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial R}\left[D(R)\frac{\partial p}{\partial R} + \frac{1}{\xi}\frac{d\Delta F}{dR}\, p \right] \qquad \Delta F^* \gg k_B T$$



problema di kramers

$\Delta U \gg k_B T$

Tempo di nucleazione τ_x (1 nucleo critico)

= tempo di uscita

$$\tau_x = \frac{1}{D(R_*)} \cdot \frac{1}{\left(-\frac{1}{2\pi k_B T} \left.\frac{d^2 \Delta F}{dR^2}\right|_{R_*} \right)^{1/2}} \cdot \exp\left(\frac{\Delta F^*}{k_B T} \right) \leftarrow \text{fattore di Arrhenius}$$

↑ fattore cinetico ↑ fattore termodinamico (Zeldovich)

Tasso di nucleazione : nuclei / tempo / volume

$$I = \frac{N}{\tau_x} \cdot \frac{1}{V} = \frac{S}{\tau_x}$$

Dipendenza di τ_x dalla temperatura

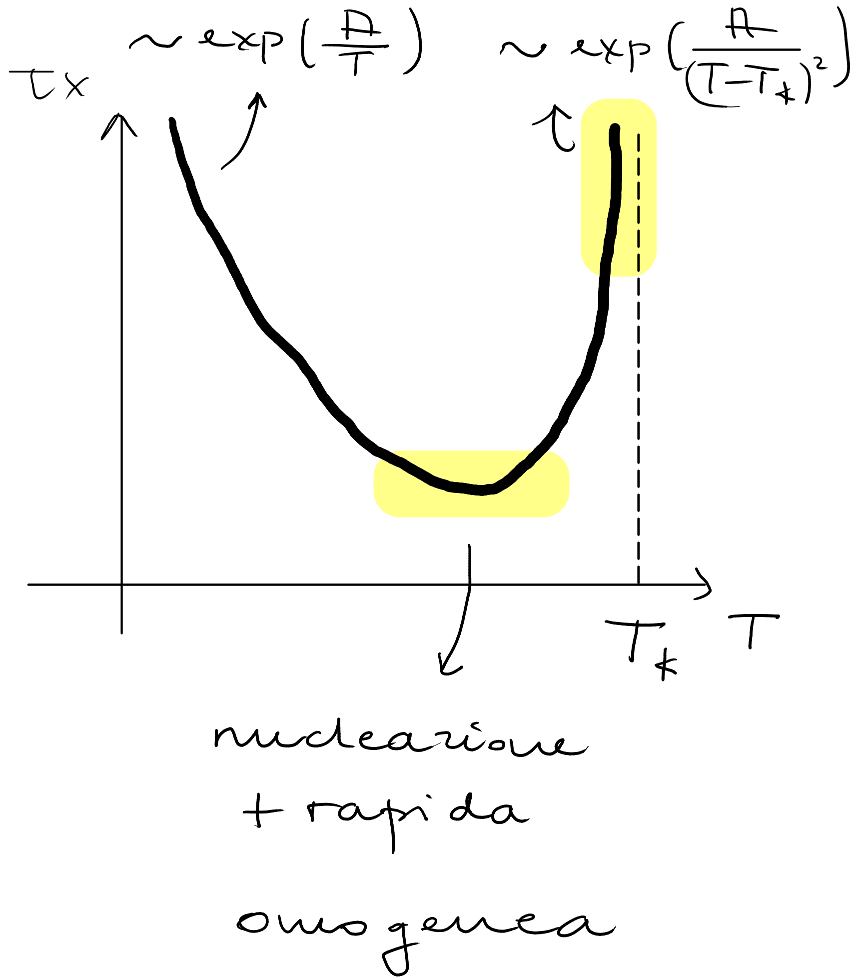
$T \ll T_*$: $D(R^*) \sim \exp\left(-\frac{\Delta E_d}{k_B T}\right)$

$$\tau_x \sim \exp\left(\frac{\Delta E_d}{k_B T}\right) \cdot \exp\left(\frac{\Delta F^*}{k_B T}\right)$$

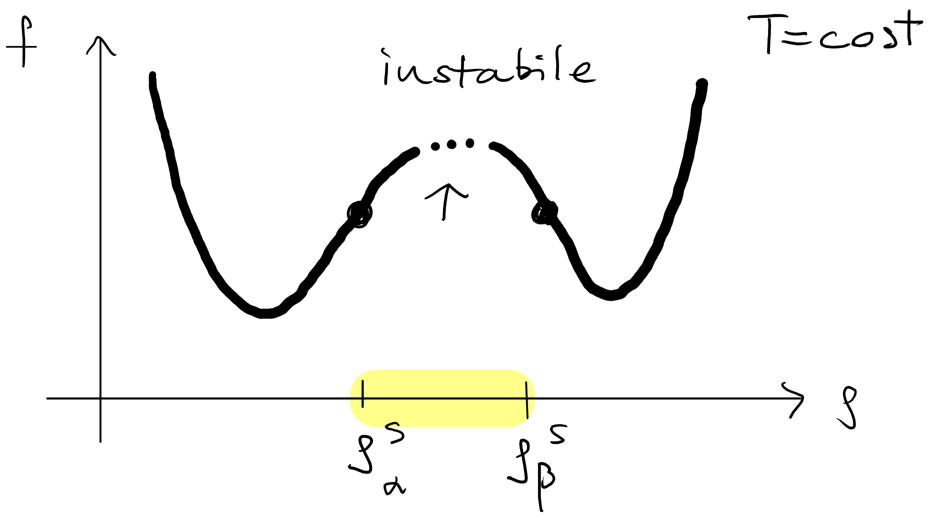
$T \approx T_*$: $\Delta f \sim (T - T_*)$

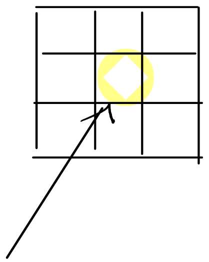
$$\Delta F^* \sim \frac{1}{\Delta f^2} \sim \frac{1}{(T-T_*)^2}$$

$$\tau_x \sim \exp\left(\frac{A}{T(T-T_*)^2}\right)$$



2) Decomposizione spinodale





$$\rho_N(\vec r,t) = \rho(\vec r,t)$$

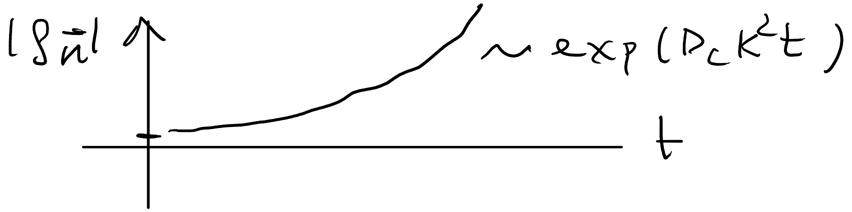
$$\frac{\partial\rho}{\partial t} = -\vec\nabla\cdot\left(L_{NN}\vec\nabla\left(-\frac{\mu}{T}\right)\right)$$

$$= \vec\nabla\cdot\left(\frac{L_{NN}}{T}\vec\nabla\mu\right)$$

$$\mu = \mu[\rho(\vec r,t)] \nearrow \quad = \vec\nabla\cdot\left(\underbrace{\frac{L_{NN}}{T}\frac{\partial\mu}{\partial\rho}}_{D_c}\vec\nabla\rho\right)$$

$$\frac{\partial F}{\partial N}\Big|_T = \mu = \frac{\partial f}{\partial\rho}\Big|_T$$

$$\frac{\partial^2 f}{\partial\rho^2}\Big|_T = \frac{\partial\mu}{\partial\rho}\Big|_T < 0 \quad\Rightarrow\quad D_c < 0 \quad !!$$



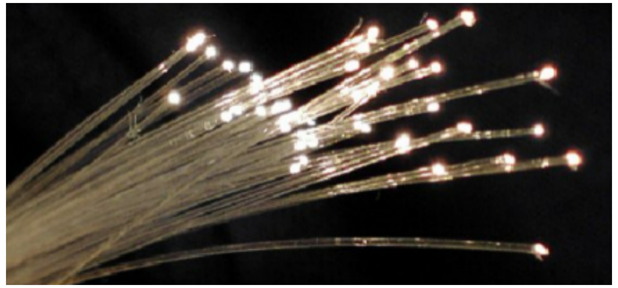
$$\frac{\partial\rho}{\partial t} = D_c\vec\nabla^2\rho \quad\Rightarrow\quad \rho_{\vec k}(t) = \rho_{\vec k}(0)\exp\left(-D_c k^2 t\right) \simeq \rho_{\vec k}(0)\exp\left(+|D_c|k^2 t\right)$$

Cahn-Hilliard : $$\frac{\partial\rho}{\partial t} = \frac{L_{NN}}{T}\nabla^2\left[\frac{\partial^2 f}{\partial\rho^2}\rho_N - \frac{k_B T\xi_0^2}{\rho}\nabla^2\rho\right]$$

Formatori di vetro

Ossidi

Silicati : SiO_2 (silice)



B_2O_3

gorilla glass©

vetro da finestre

SiO_2 : 70%
NaO_2 : 20%
CaO : 10%

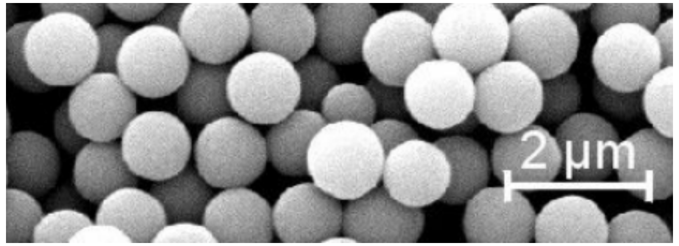
Polimeri

polistirene

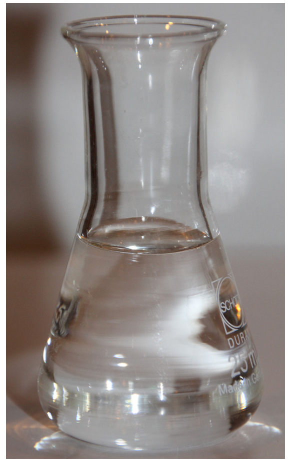
PMMA

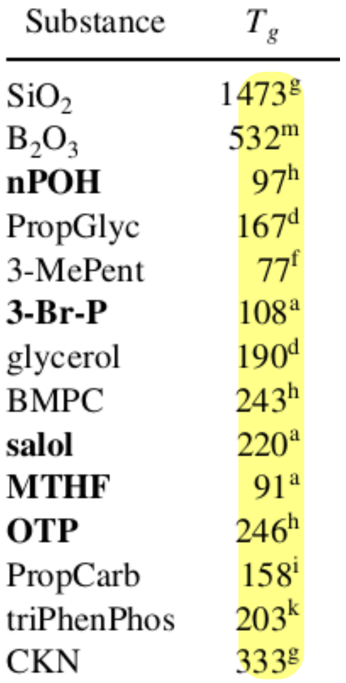
Metallici

Colloidi



Organici





Substance	T_g
SiO_2	1473[g]
B_2O_3	532[m]
nPOH	97[h]
PropGlyc	167[d]
3-MePent	77[f]
3-Br-P	108[a]
glycerol	190[d]
BMPC	243[h]
salol	220[a]
MTHF	91[a]
OTP	246[h]
PropCarb	158[i]
triPhenPhos	203[k]
CKN	333[g]

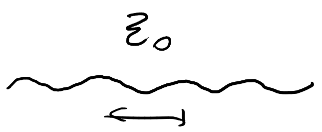
Richert & Angell JCP 1998

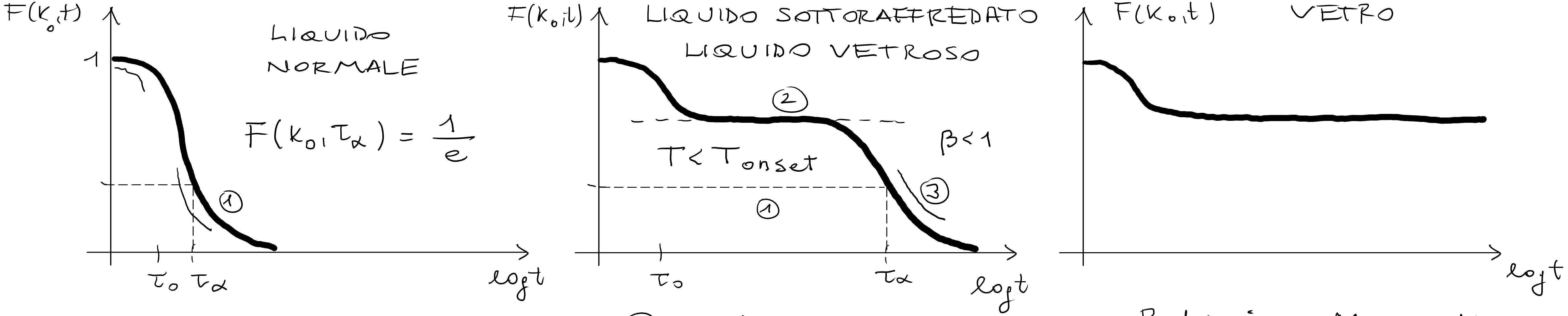
FENOMENOLOGIA DELLA TRANSIZIONE LIQUIDO - VETRO

Liquido sottoraffreddato : $T < T_m$ Vetro : $T < T_g$

1) Tempo di rilassamento strutturale

$$F(k,t) = \frac{\langle \hat{\rho}_{\bar{k}}(t)\, \hat{\rho}_{-\bar{k}}(0) \rangle}{\langle \hat{\rho}_{\bar{k}}(0)\, \hat{\rho}_{-\bar{k}}(0) \rangle} \qquad k_0 \approx \frac{2\pi}{\xi_0}$$





$$F(k_0, \tau_\alpha) = \frac{1}{e}$$

① $F(k_0,t) \sim \exp(-t/\tau_\alpha)$

① $\tau_\alpha \gg \tau_0$

② two-step

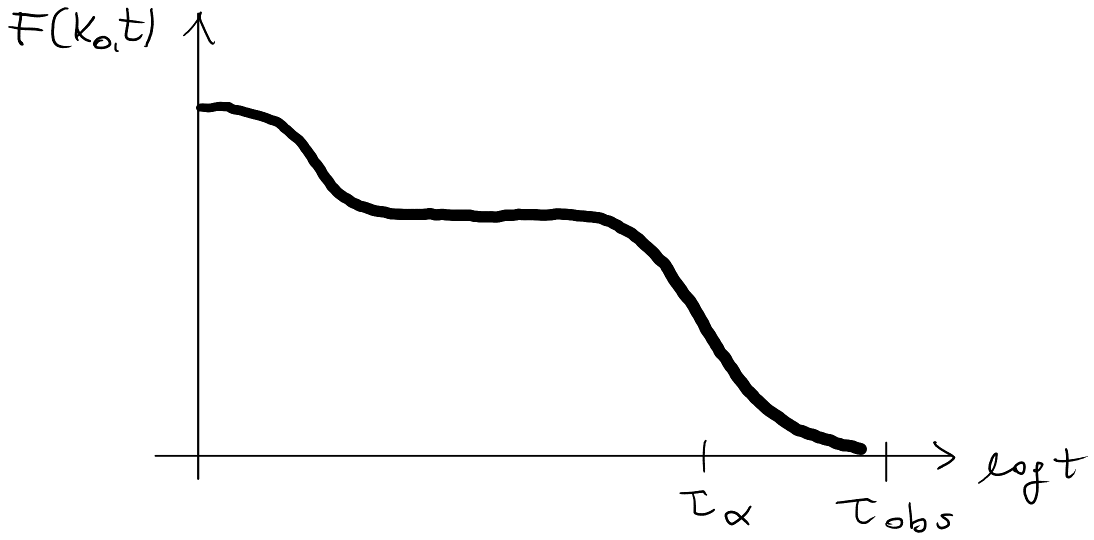
③ $F(k_0,t) \sim \exp\left(-(t/\tau_\alpha)^\beta\right)$

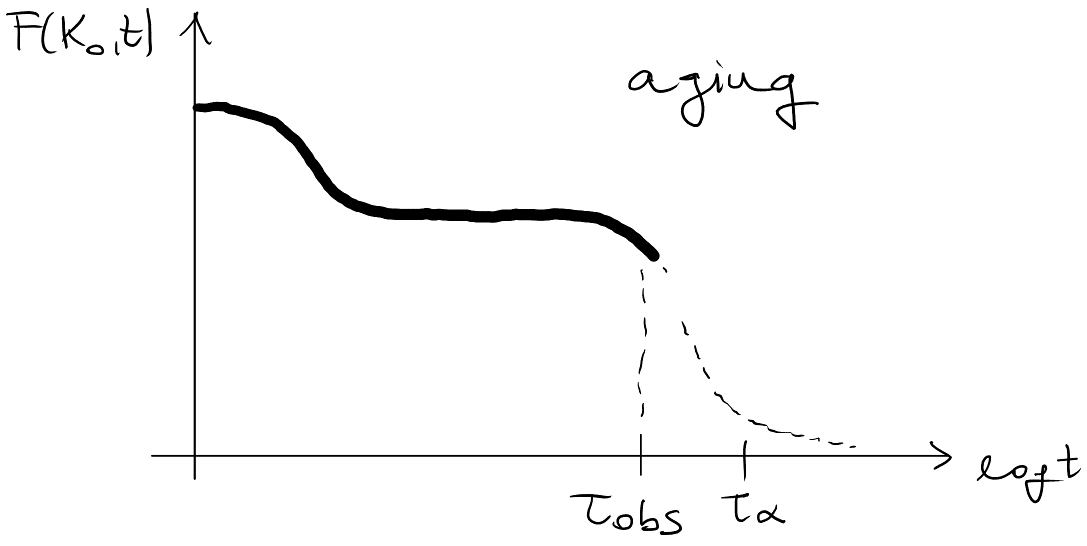
Relazione Maxwell

$$\eta = G_0 \tau_\alpha$$

$\xrightarrow{\qquad\qquad} 1/T$

2) Tempo di osservazione: τ_{obs}



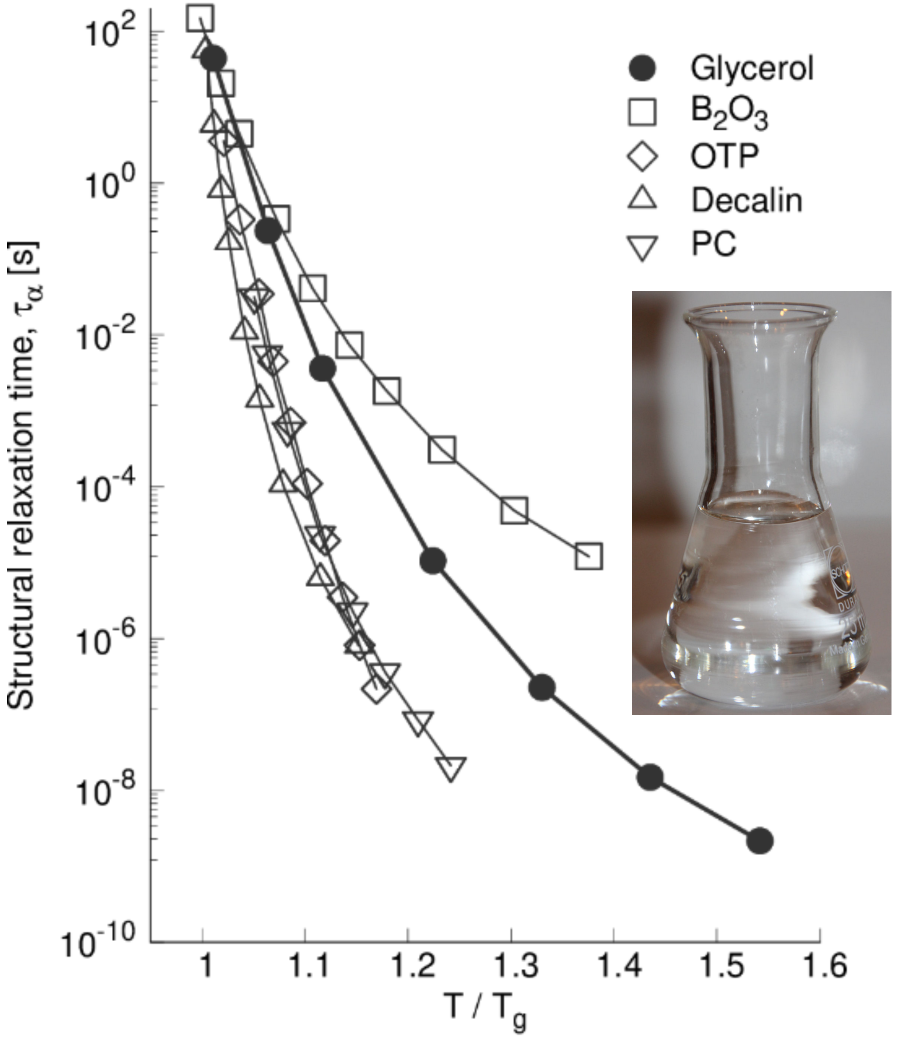


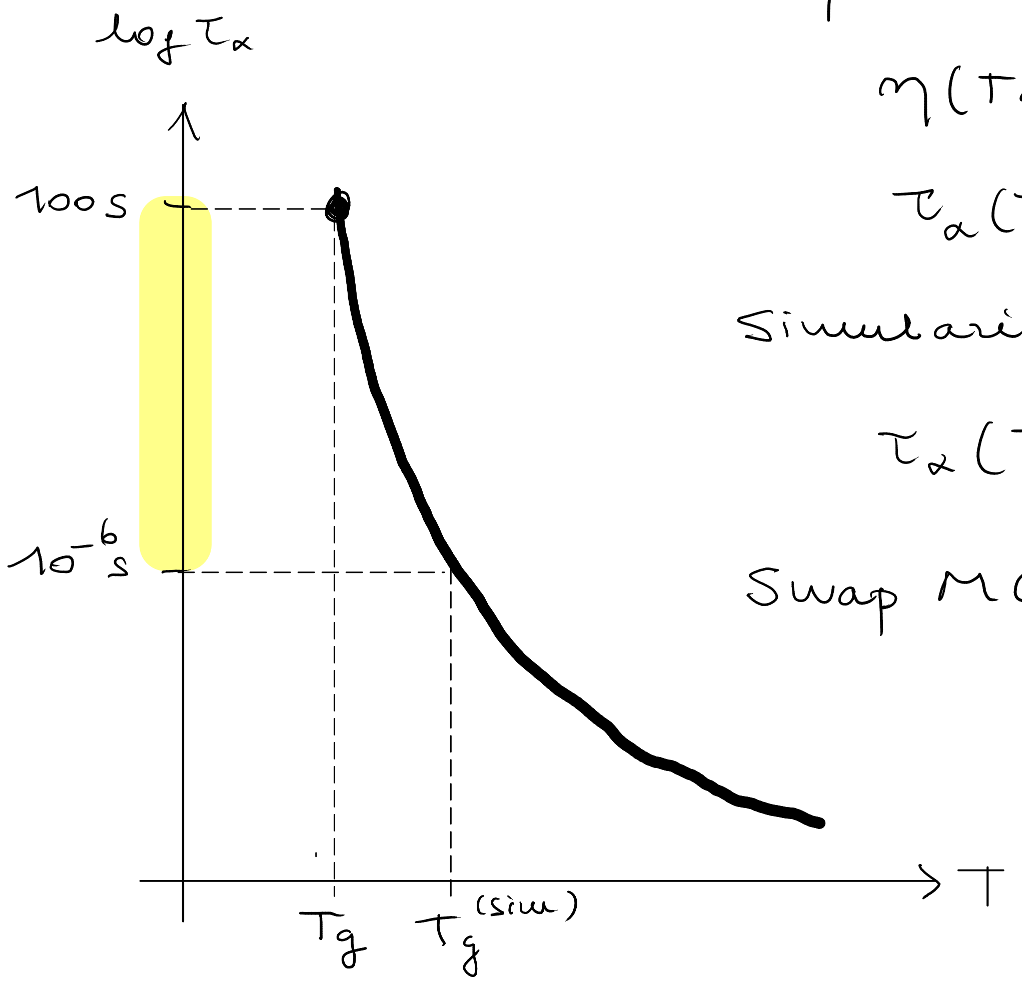
non-ergodico
fuori-equilibrio

Def. di equilibrio di Feynman: "when all the fast things have happened and all the slow ones not"

Def. operativa della transizione vetrosa:

$$\boxed{\tau_\alpha(T_g) = \tau_{obs}} \qquad \tau_\alpha = \tau_\alpha(T)$$





Esperimenti :

$$\eta(T_g) = 10^{12} \text{ Pa}\cdot\text{s}$$

$$\tau_\alpha(T_g) \approx 10^{2} \text{ s}$$

Simulazioni :

$$\tau_\alpha(T_g^{(sim)}) \approx 10^{-6} \text{ s}$$

Swap MC PRX 2017

$\text{timestep} = \frac{\tau_0}{100}$ $\quad 10^{-6} \frac{\text{s}}{\text{step}\cdot\text{part}}$ $\quad N = 10^{3}$ $\quad t_1 = 10^{-3}\text{ s}$ $\quad \frac{t_1^{reale}}{\text{timestep}} \approx 10^{-3} \times 10^{14}$

$\tau_0 \sim 10^{-12}\text{ s}$ $\quad \underline{= 10^{9}}$

3) Tempo di cristallizzazione : τ_x

$$\tau_x \sim \frac{1}{D(R_*)} \exp\left(\frac{\Delta F^*}{K_B T}\right)$$

$$\tau_{x,N} \sim \frac{1}{N}$$

$$\exists\, N_0 : \tau_{x,N_0} = \tau_x$$

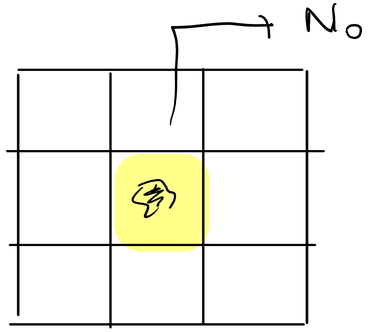
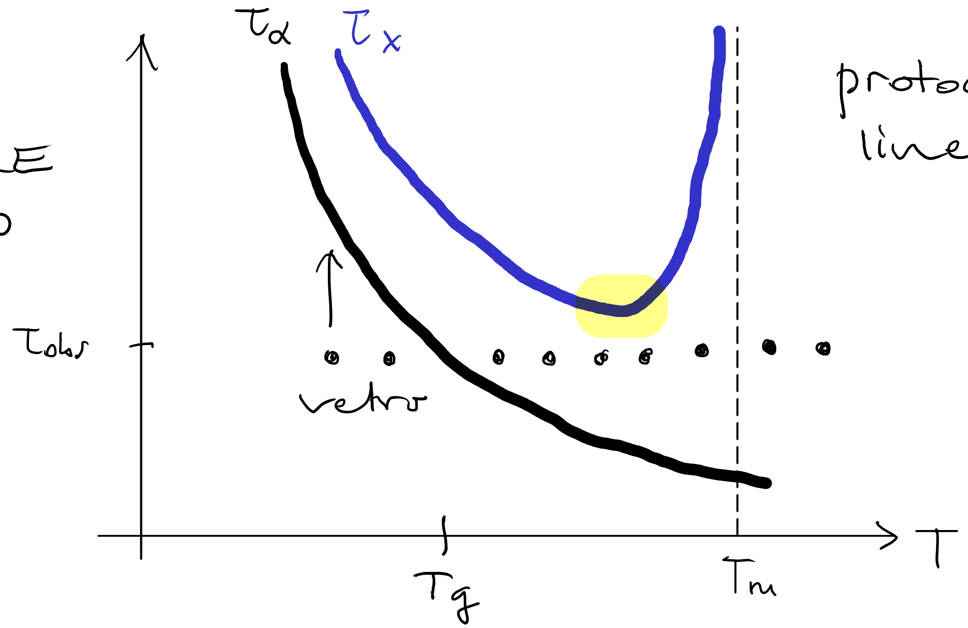


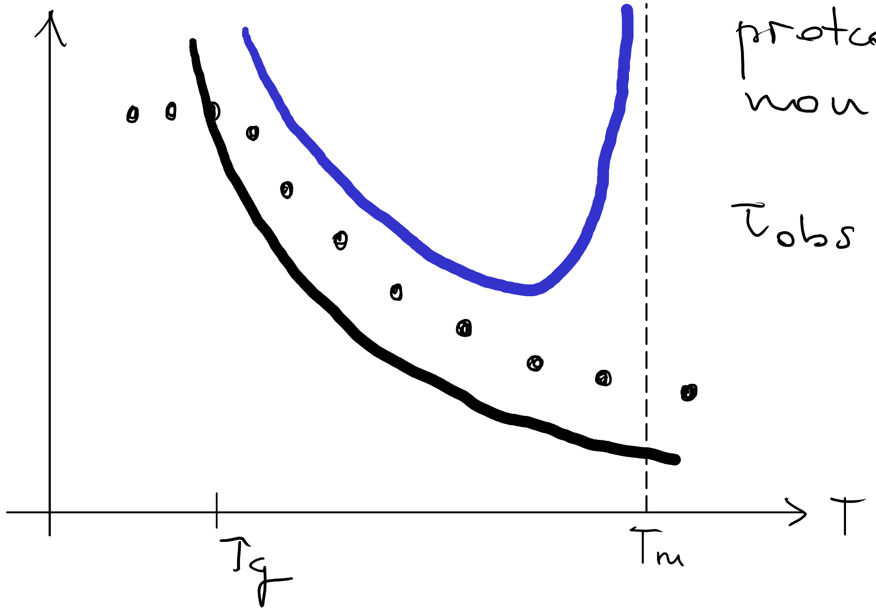
Diagramma tempo – temperatura – trasformazione (TTT)

① rilassare dofs lenti ($\hat{\rho}_{\bar{\pi}_0}$) ② evitare cristallo $\tau_\alpha < \tau_{obs} < \tau_x$

BUON FORMATORE DI VETRO



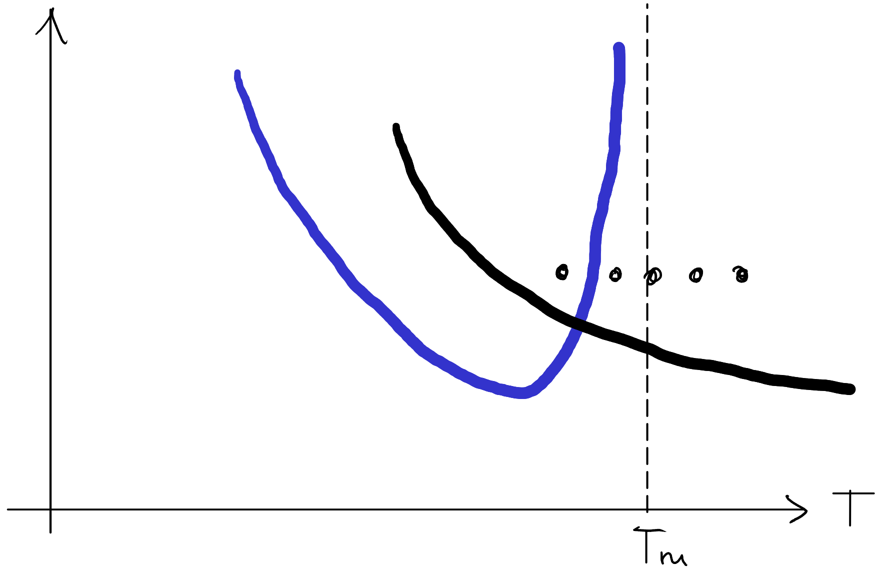
protocollo lineare

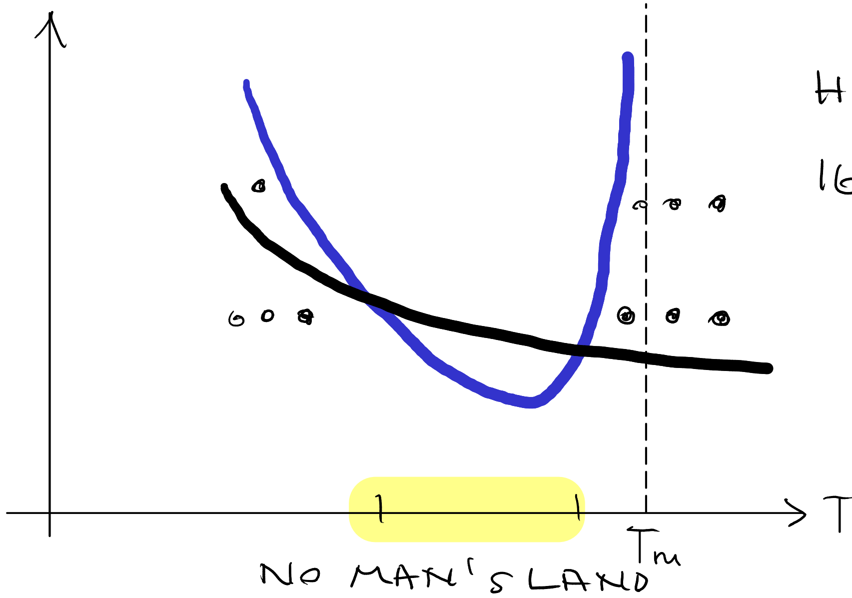


protocollo non-lineare

$\tau_{obs} \sim \tau_\alpha$

CATTIVO FORMATORE DI VETRO

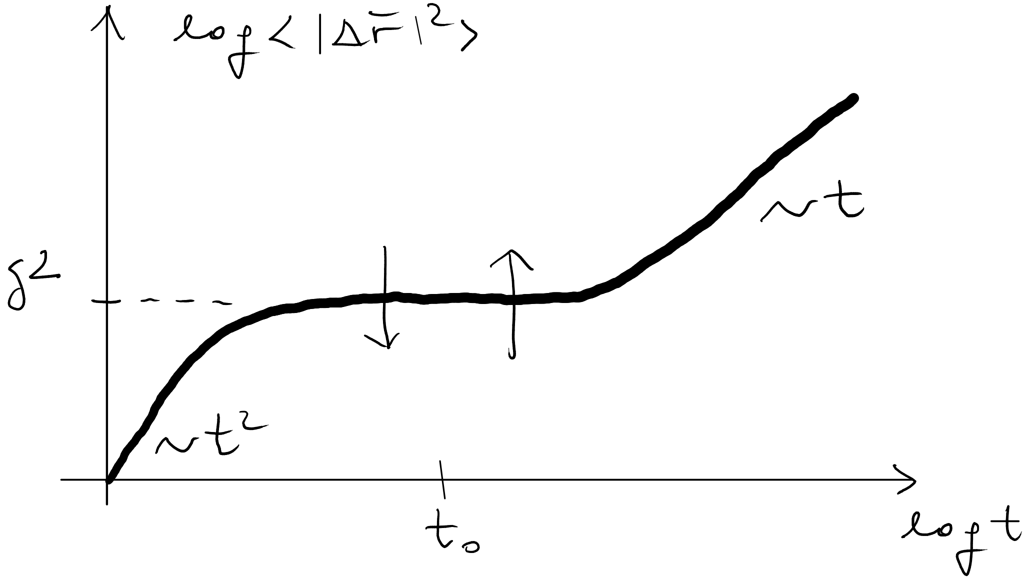




H_2O P_{atm}

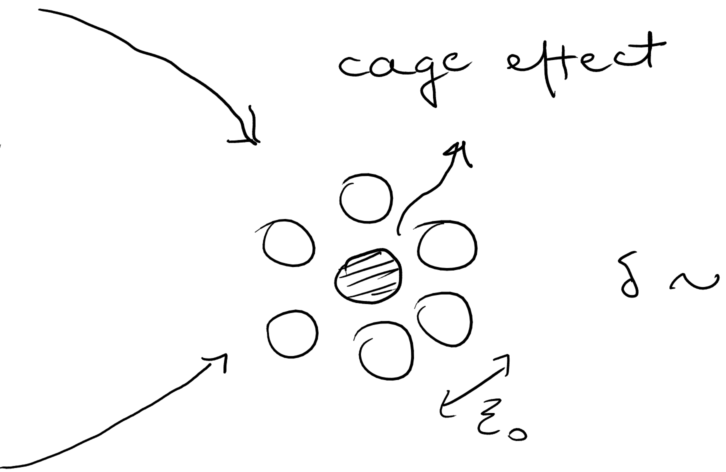
160 K – 230 K

Dinamica

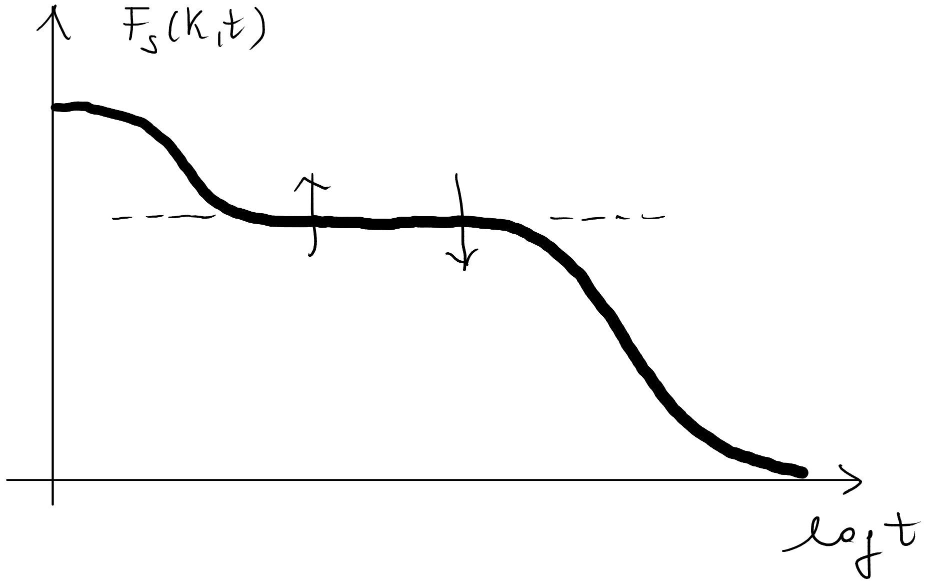


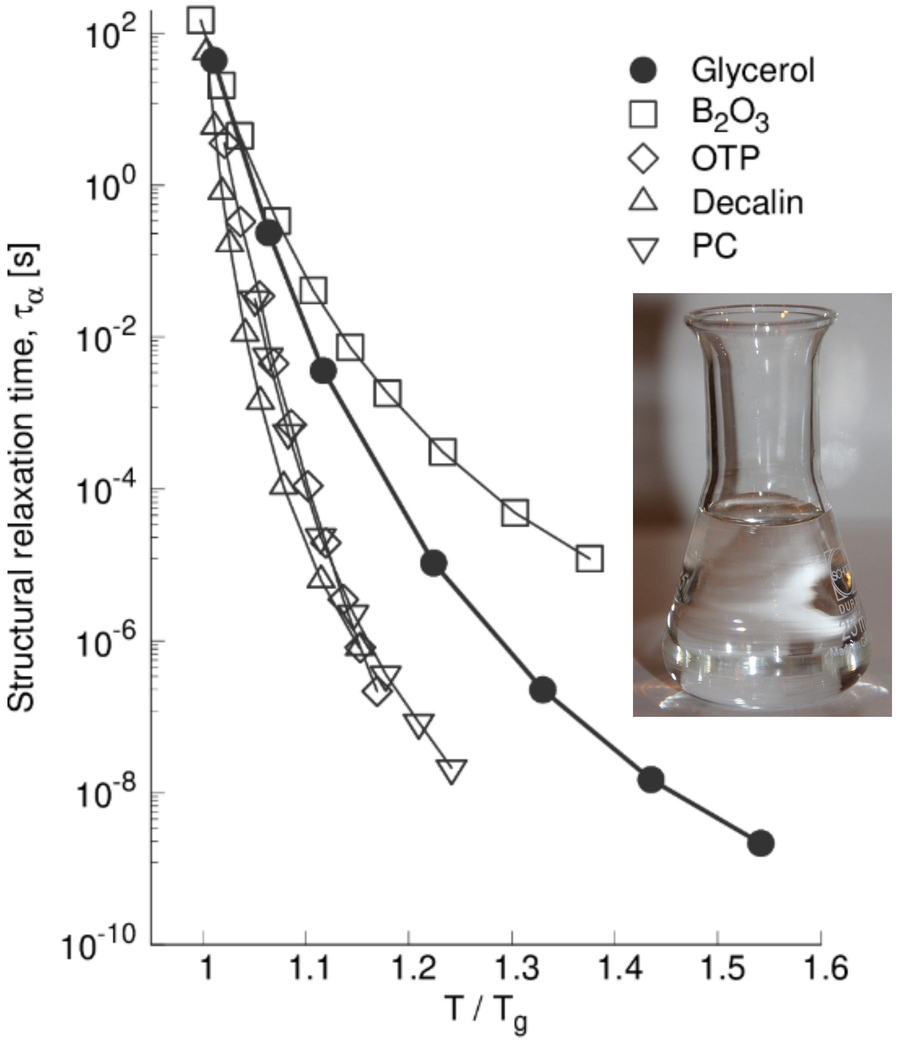
$$\delta^2 = \langle|\Delta\bar{r}(t_0)|^2\rangle$$

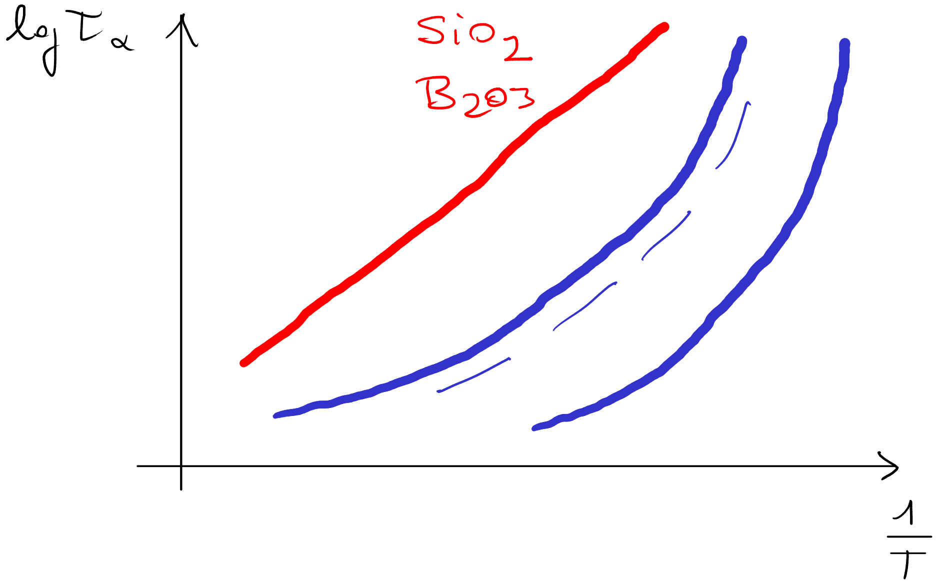
$\delta^2 \leftrightarrow T$ es.

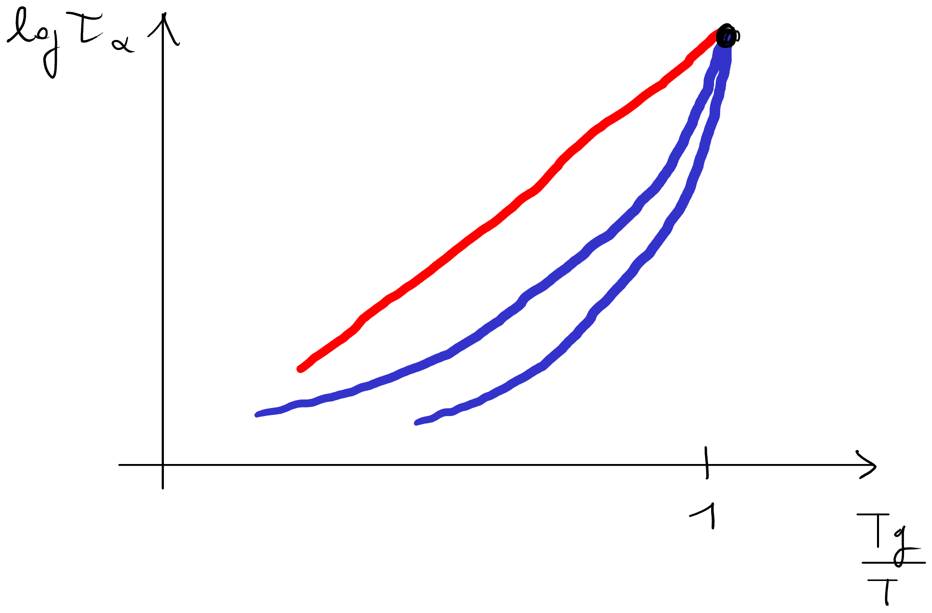


$\delta \sim 0.2\,\xi_0$









Arrhenius

$$\tau_\alpha \sim \exp\left(\frac{\Delta E}{k_B T}\right)$$

STRONG

Super-Arrhenius

$$\tau_\alpha \sim \exp\left(\frac{\Delta E(T)}{k_B T}\right)$$

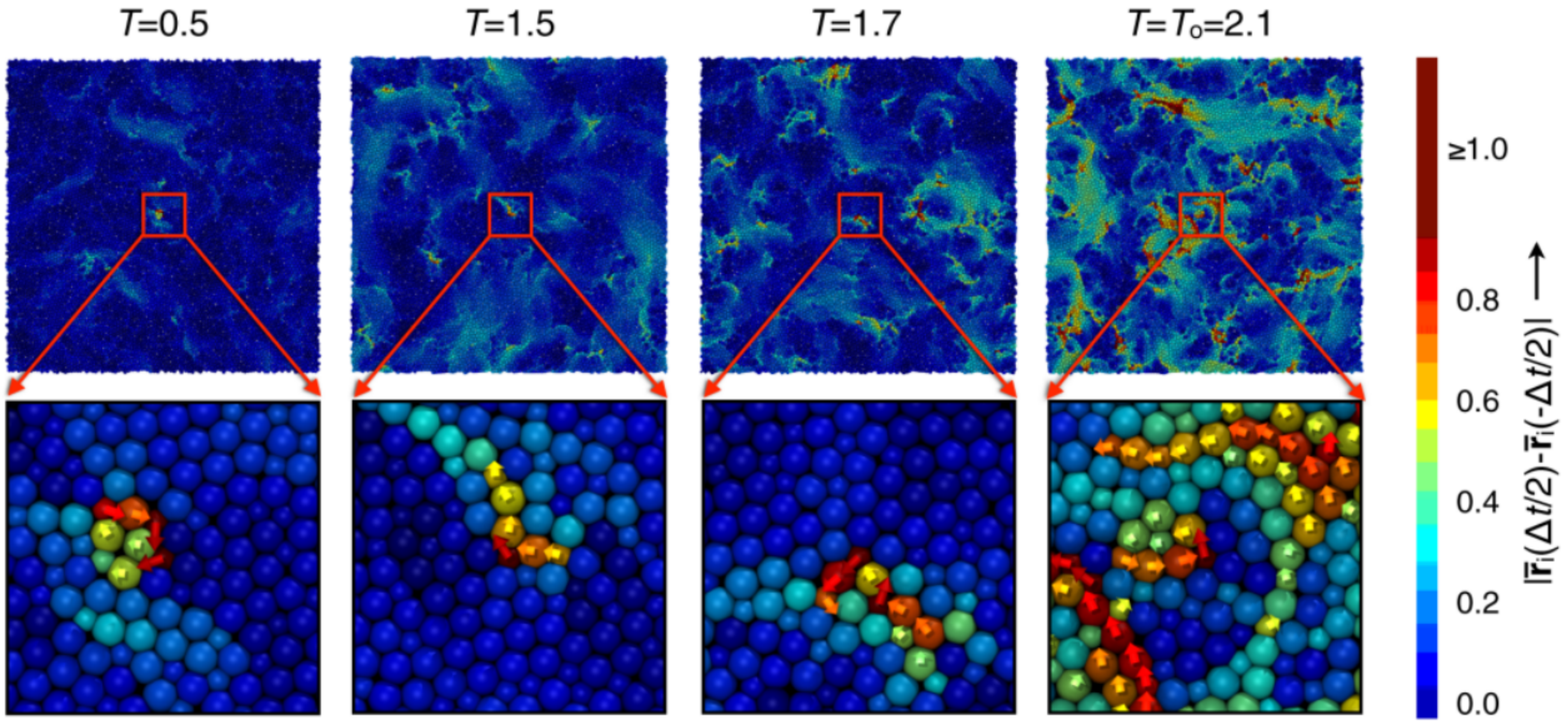
$\Delta E \nearrow \quad T \searrow$

FRAGILE

Classificazione di Angell: fragilità

$$m = \left.\frac{d \log \tau_\alpha}{d(T/T_g)}\right|_{T=T_g}$$

Eterogeneità dinamiche



Keys et al. PRX 2011

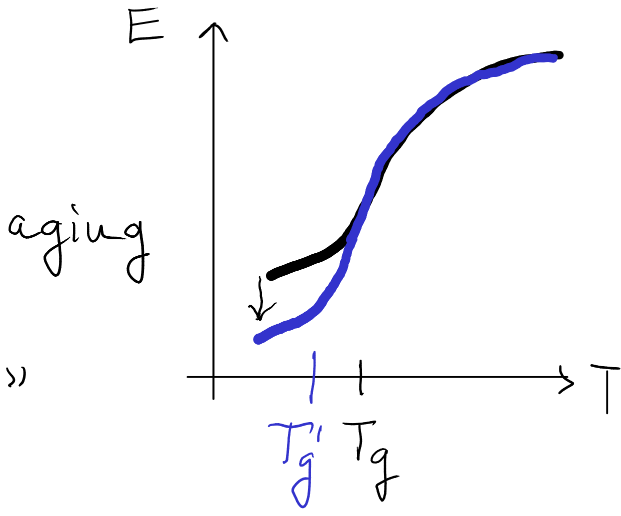
Termodinamica

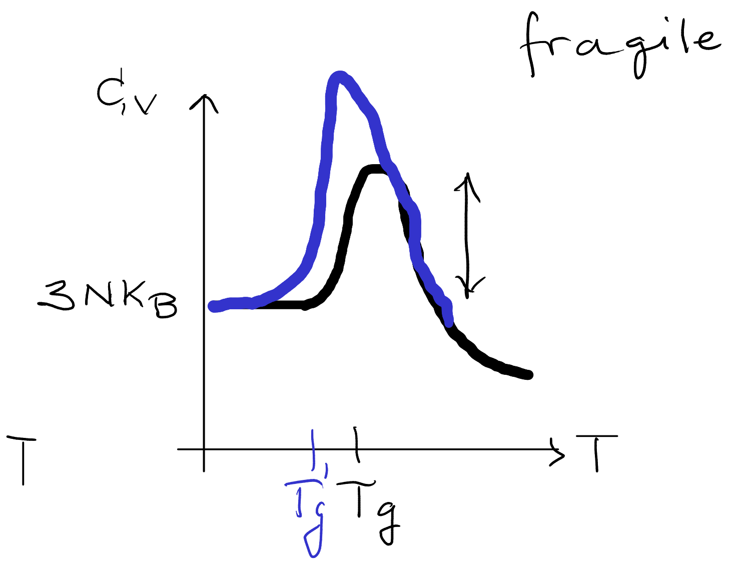
Energia interna : E

Capacità termica : $C_V = \frac{\partial E}{\partial T}\Big|_V$

Approx armonica : $E \approx 3 N k_B T$

Congelamento di defs "configurazionali"





N = cost   V = cost

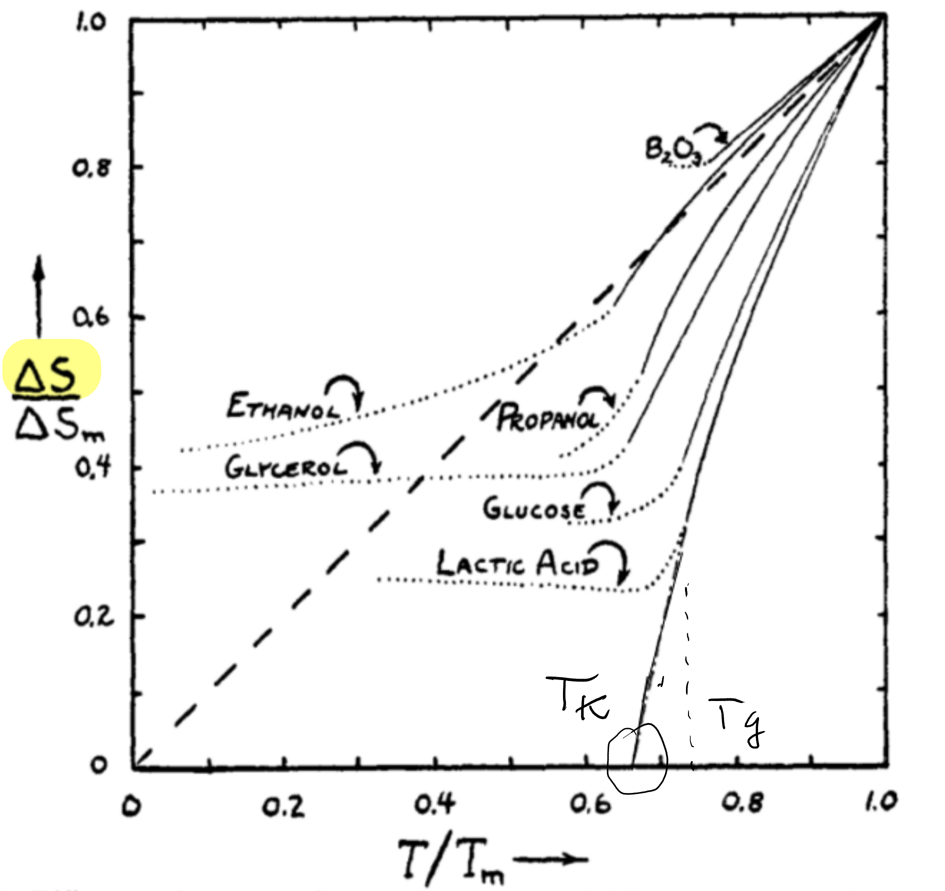
Entropia : $dS = \frac{1}{T} dE - \underbrace{\frac{P}{T} dV}_{\approx 0} + \underbrace{\frac{\mu}{T} dN}_{\approx 0}$

$$S(T) = S(T_0) + \int_{T_0}^{T} \frac{1}{T} dE = S(T_0) + \int_{T_0}^{T} \frac{C_V}{T} dT$$

< gas perfetto / solido armonico   integrazione termodinamica

- ☐ cristallo perfetto : $S = S_{vib}$
- ☐ cristallo + difetti : $S = S_{vib} + S_c$
- ☐ liquido : S
- ☐ liquido sottoraffredato : $S \approx S_{vib} + S_c$

$$\Delta S = S_{liq} - S_{crist} \approx (\underset{\sim\sim}{S_{vib}} + S_c) - (\underset{\sim\sim}{S_{vib}}) \approx S_c$$

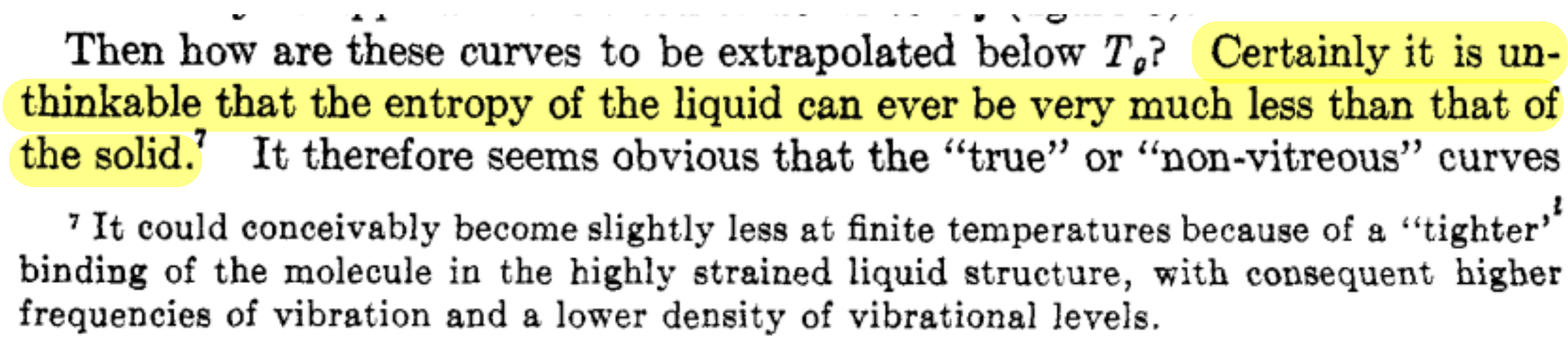


4. Differences in entropy between the supercooled liquid and crystalline ph

Kauzmann Chemical Reviews 1948

Paradosso di Kauzmann

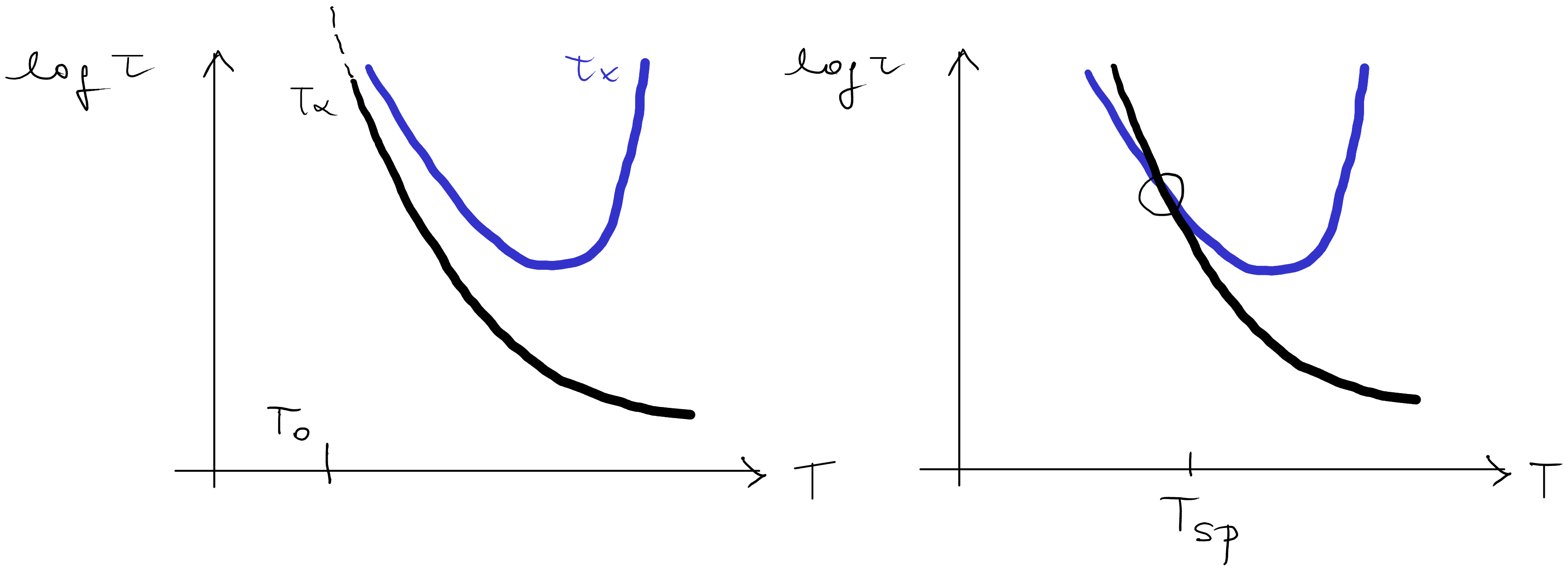
“Entropy crisis”



Then how are these curves to be extrapolated below T_g? Certainly it is unthinkable that the entropy of the liquid can ever be very much less than that of the solid.[7] It therefore seems obvious that the “true” or “non-vitreous” curves

---

[7] It could conceivably become slightly less at finite temperatures because of a “tighter” binding of the molecule in the highly strained liquid structure, with consequent higher frequencies of vibration and a lower density of vibrational levels.



$$\tau_\alpha \sim \exp\left(\frac{A}{T-T_0}\right)$$

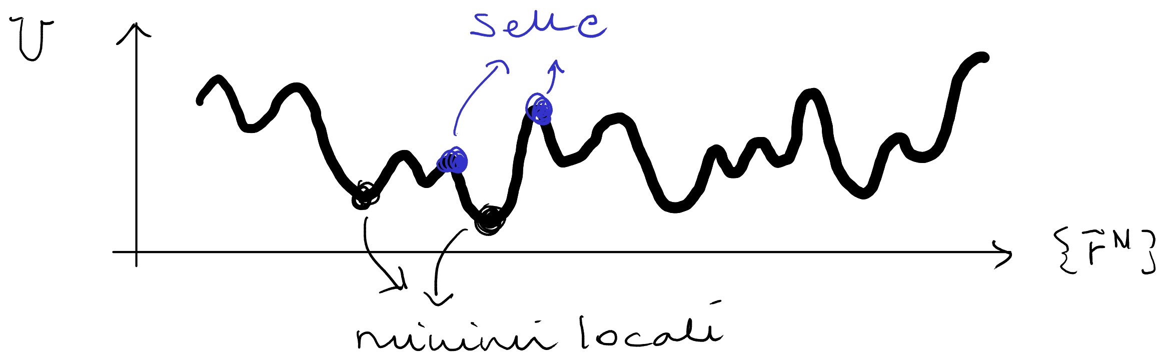
Vogel-Fulcher

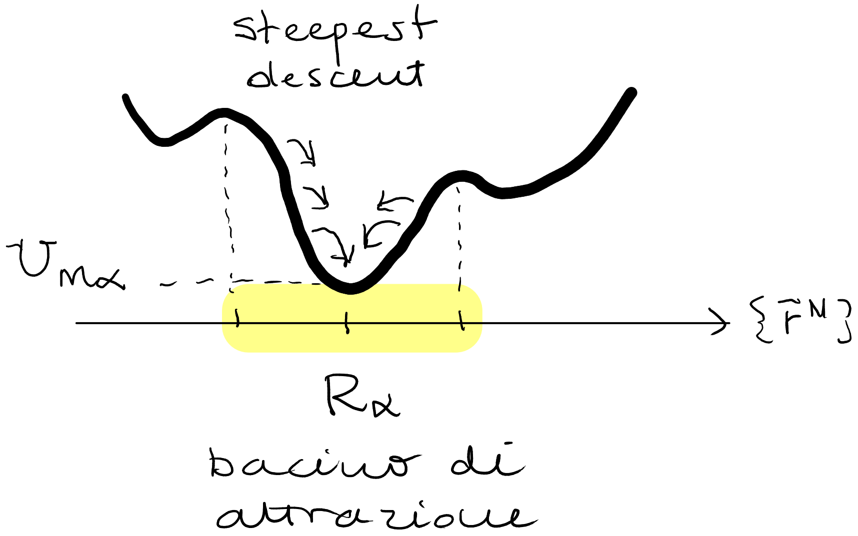
① vetro ideale

① cristalizzazione

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape (PEL)





$U = U(\{\vec r^N\})$

Stillinger Weber '80

"struttura inerente"

punti stazionari : $\vec\nabla U = \vec 0$

Hessiana : $\mathcal{H} = \left(\dfrac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} \right)$ $\quad i,j = 1,\dots,N$ $\quad \alpha,\beta = x,y,z$

$N = \text{cost} \qquad V = \text{cost} \qquad \Lambda = \dfrac{h}{\sqrt{2\pi m k_B T}}$

$$Z(T) = \mathrm{Tr}\left[\exp\left(-\beta H(\{\vec r^N, \vec p^N\})\right)\right] = \sum_\alpha \frac{1}{\Lambda^{3N}} e^{-\beta U_{m\alpha}} \int_{R_\alpha} d\vec r^N \, e^{-\beta[U(\{\vec r^N\}) - U_{m\alpha}]}$$

$$u_{m\alpha} = \frac{U_{m\alpha}}{N} \qquad U(\{\vec r^N\}) = \left(U(\{\vec r^N\}) - U_{m\alpha}\right) + U_{m\alpha}$$

$$Z(T) = \sum_\alpha e^{-\beta U_{m\alpha}} \frac{1}{\Lambda^{3N}} \int_{R_\alpha} d\vec r^N \, e^{-\beta[U(\{\vec r^N\}) - U_{m\alpha}]}$$

Densità di stati : $\Omega(u_m)$ $\quad$ $\Omega(u_m)\,du_m$: n. minimi con energia tra u_m e $u_m + du_m$

$$Z(T) = \int du_m\, \Omega(u_m)\, e^{-\beta N u_m}\, Z(u_m, T)$$

↳ funzione di partizione vincolata

$$F_{basin}(u_m, T) = -k_B T \ln\left[Z(u_m, T) \right] \qquad f_{basin} = \frac{F_{basin}}{N}$$

$$= \int du_m\, \Omega(u_m)\, e^{-\beta N (u_m + f_{basin})}$$

Entropia configurazionale :

$$S_c = k_B \ln \Omega(u_m) \qquad s_c = \frac{S_c}{N}$$ ⚠

$$Z(T) = \int du_m\, e^{-\beta N (u_m + f_{basin} - T s_c)}$$

1) Approx armonica:

$$f_{basin} \approx f_{vib} \qquad \frac{\partial f_{vib}}{\partial u_m} \approx 0$$

2) $N \to \infty$ Approx di punto sella (metodo di Laplace)

$\int_a^b e^{Nf(x)}\,dx$ f ha un massimo in x_0 per $N \to \infty$

$$\approx \int_a^b e^{N\left[f(x_0) - \frac{1}{2}|f''(x_0)|(x-x_0)^2\right]}dx = e^{Nf(x_0)} \int_{-\infty}^{\infty} e^{-\frac{1}{2}N|f''(x_0)|(x-x_0)^2}dx$$

$$\approx \sqrt{\frac{2\pi}{N|f''(x_0)|}}\, e^{Nf(x_0)}$$

$$Z(T) \approx \int du_m\, e^{-\beta N\left(u_m + \overset{\swarrow ①}{f_{vib}} - T s_c\right)} \qquad N \to \infty$$

$$\begin{cases} Z(T) \approx A(N)\, e^{-\beta N (u_m + f_{vib} - T s_c)} & \leftarrow \textcircled{2} \\ 1 + \underset{\uparrow\ \textcircled{1} \approx 0}{\dfrac{\partial f_{vib}}{\partial u_m}} - T \dfrac{\partial s_c}{\partial u_m} = 0 \end{cases}$$

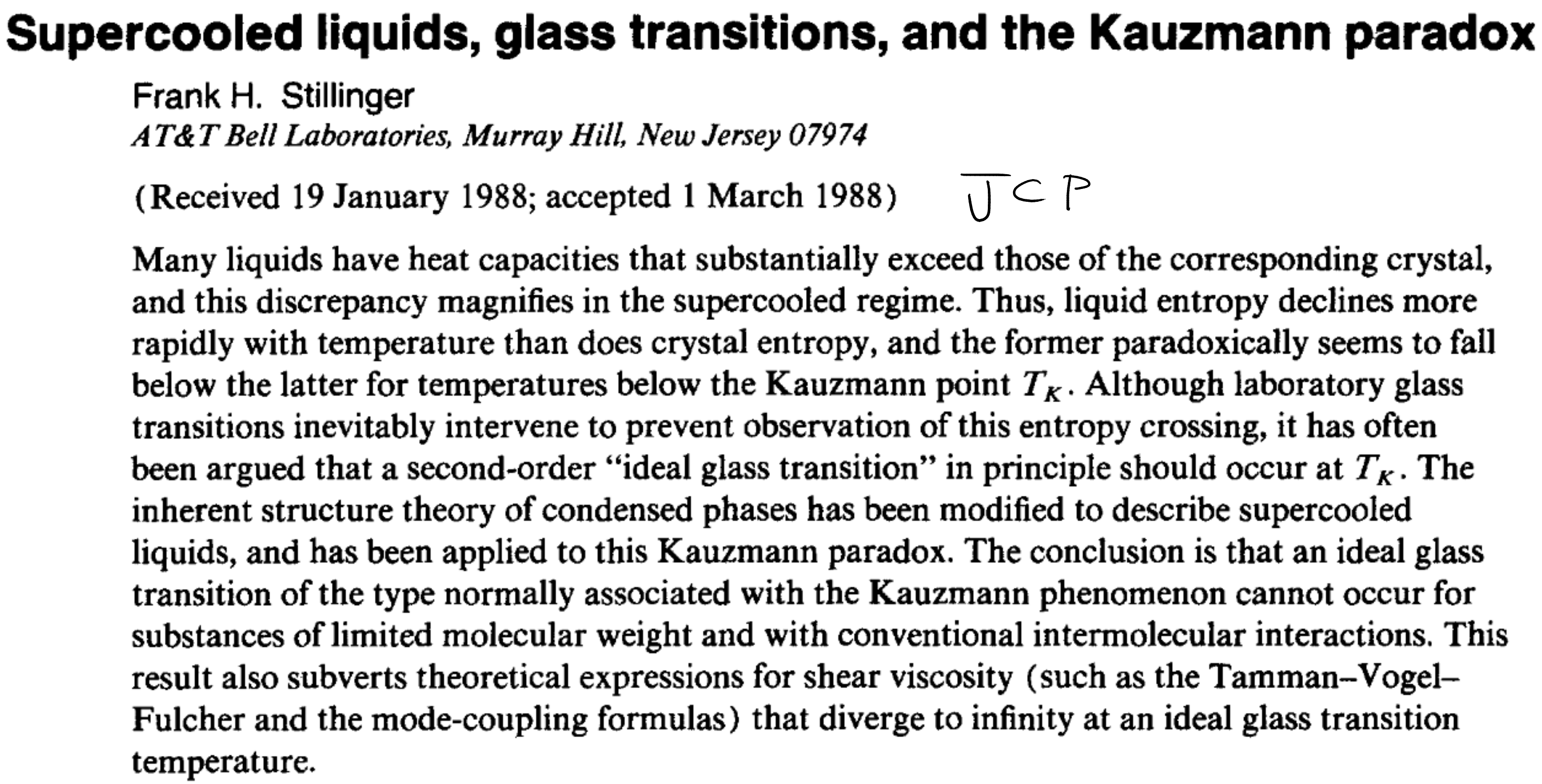
$$\begin{cases} Z(T) \approx e^{-\beta N (u_m + f_{vib} - T s_c)} \quad \Longrightarrow \quad \text{termodinamica} \\ \dfrac{\partial s_c}{\partial u_m} = \dfrac{1}{T} \end{cases}$$

$$s_c = s_c(u_m)$$

Paradosso Kauzmann :

1) $S_c = 0 \qquad u_m \lesssim u_K$

2) $\left.\dfrac{\partial S_c}{\partial u_m}\right|_{u_K} = \dfrac{1}{T_K}$

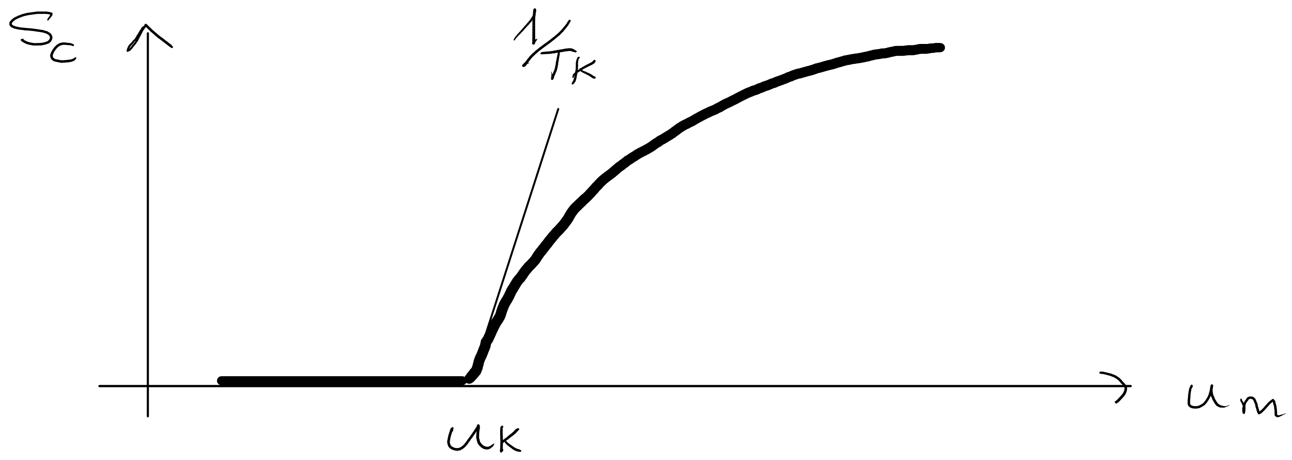


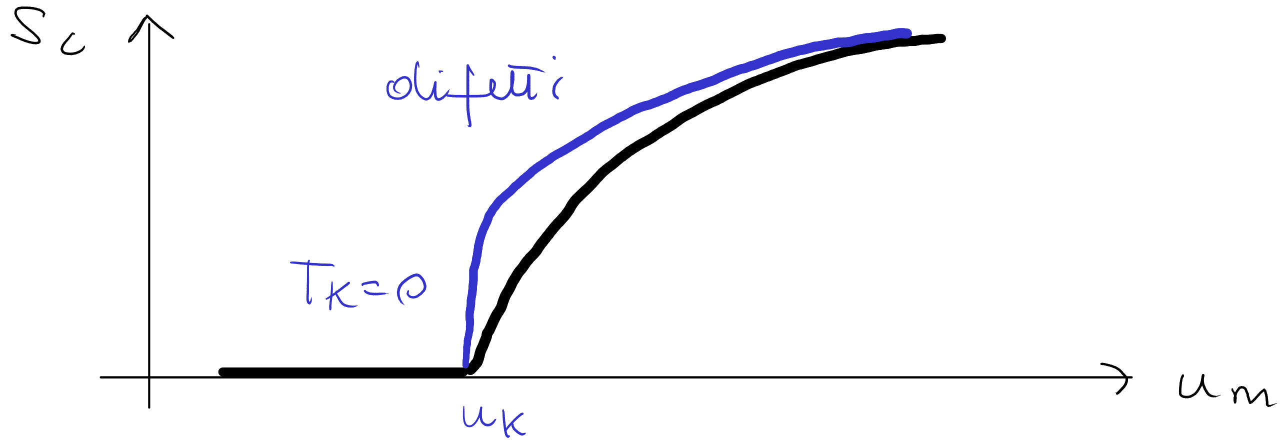
Supercooled liquids, glass transitions, and the Kauzmann paradox

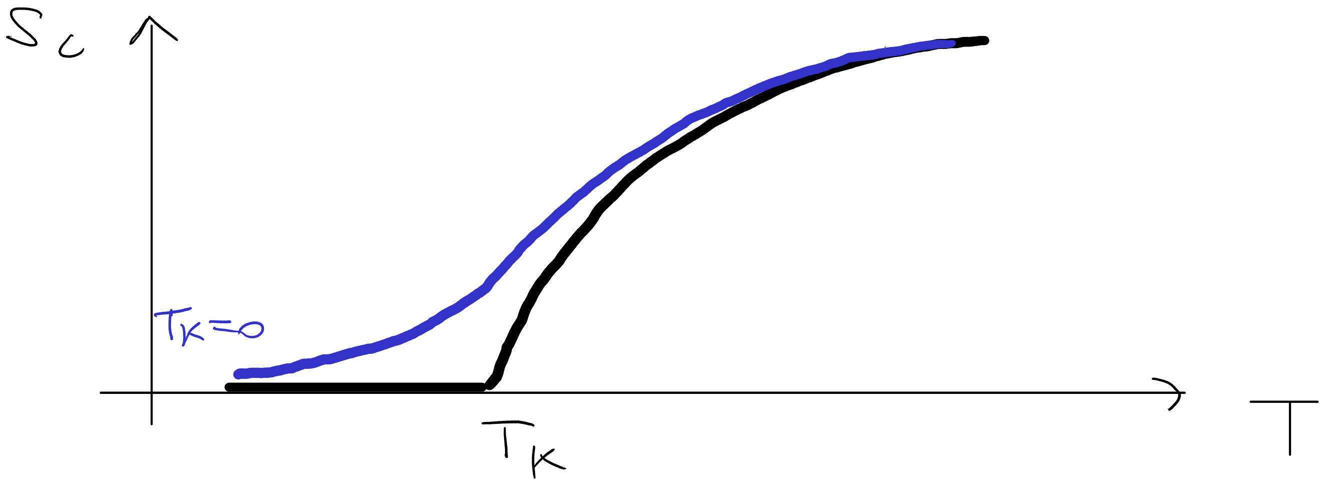
Frank H. Stillinger
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 19 January 1988; accepted 1 March 1988) JCP

Many liquids have heat capacities that substantially exceed those of the corresponding crystal, and this discrepancy magnifies in the supercooled regime. Thus, liquid entropy declines more rapidly with temperature than does crystal entropy, and the former paradoxically seems to fall below the latter for temperatures below the Kauzmann point T_K. Although laboratory glass transitions inevitably intervene to prevent observation of this entropy crossing, it has often been argued that a second-order "ideal glass transition" in principle should occur at T_K. The inherent structure theory of condensed phases has been modified to describe supercooled liquids, and has been applied to this Kauzmann paradox. The conclusion is that an ideal glass transition of the type normally associated with the Kauzmann phenomenon cannot occur for substances of limited molecular weight and with conventional intermolecular interactions. This result also subverts theoretical expressions for shear viscosity (such as the Tamman–Vogel–Fulcher and the mode-coupling formulas) that diverge to infinity at an ideal glass transition temperature.

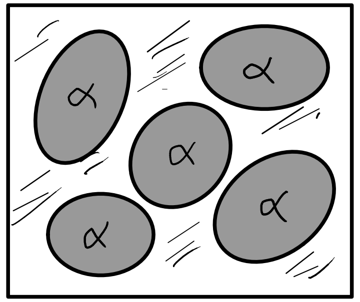






Modello di Adam e Gibbs (1965)

CRR = regioni che rilassano in modo cooperativo



N particelle

n particelle / CRR

α n. stati / CRR

N. stati accessibili

$$\Omega = \alpha^{N/n}$$

Entropia configurazionale per particella

$$s_c = \frac{1}{N} k_B \ln \Omega = \frac{K_B}{n} \ln \alpha \sim \frac{1}{n} \qquad n \sim \frac{1}{s_c}$$

Rilassamento termicamente attivato $\Delta E \sim n \sim \frac{1}{s_c}$

$$\tau_\alpha = \tau_0 \exp\left(\frac{\Delta E}{K_B T}\right) = \tau_0 \exp\left(\frac{A}{T s_c}\right)$$

relazione di Adam & Gibbs

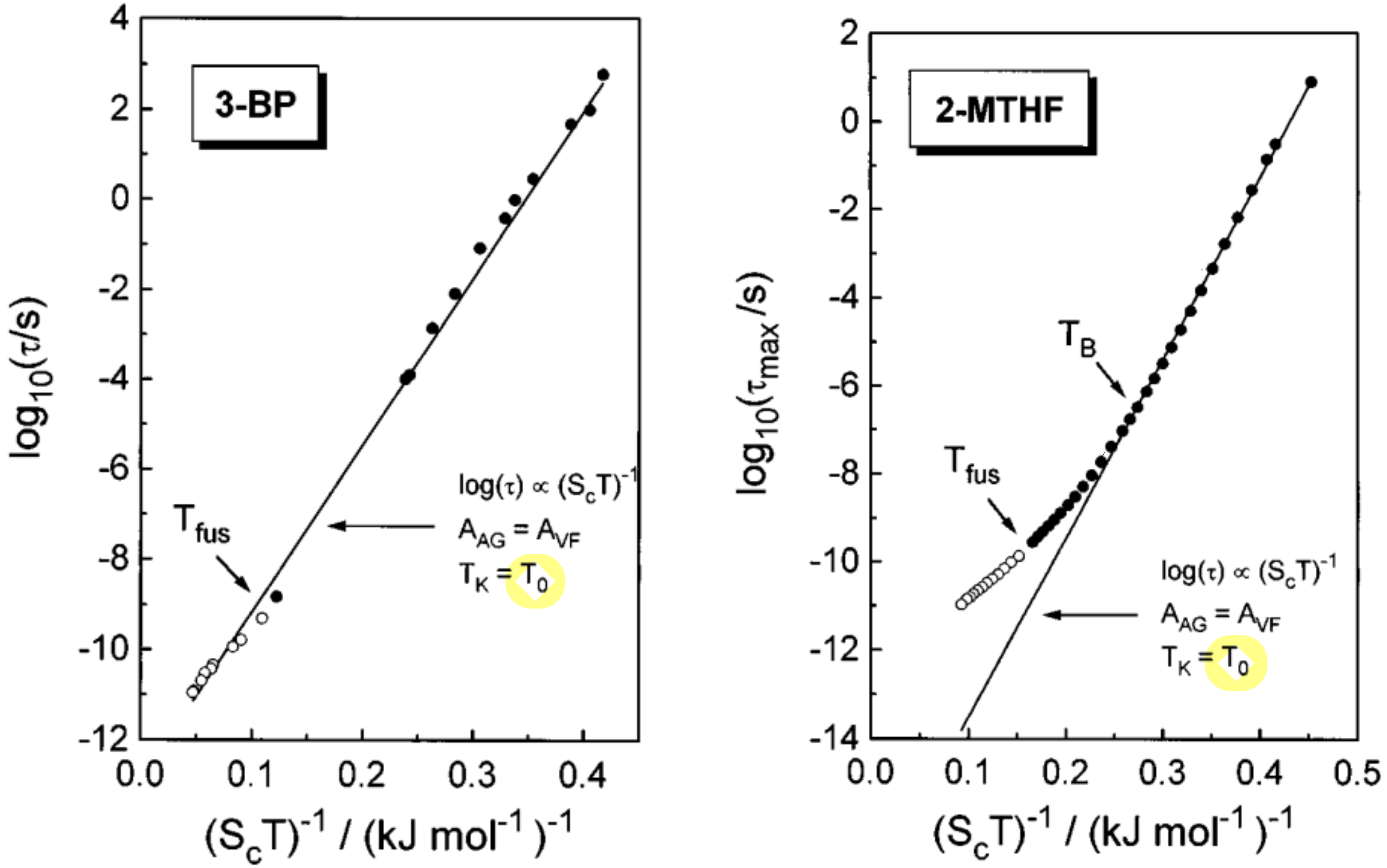
Transizione ideale T_K : $T \simeq T_K >> 0$

$$S_c \sim \frac{1}{T_K}\left(T - T_K\right)$$

$$\tau_\alpha \approx \tau_0 \exp\left(\frac{T_K B}{T(T-T_K)}\right)$$

$$\left\{ \begin{array}{l} \tau_\alpha \approx \tau_0 \exp\left(\dfrac{C}{T - T_K}\right) \\ \text{Vogel-Fulcher} \end{array} \right.$$

$\nwarrow T_0$



Richert & Angell JCP 1998

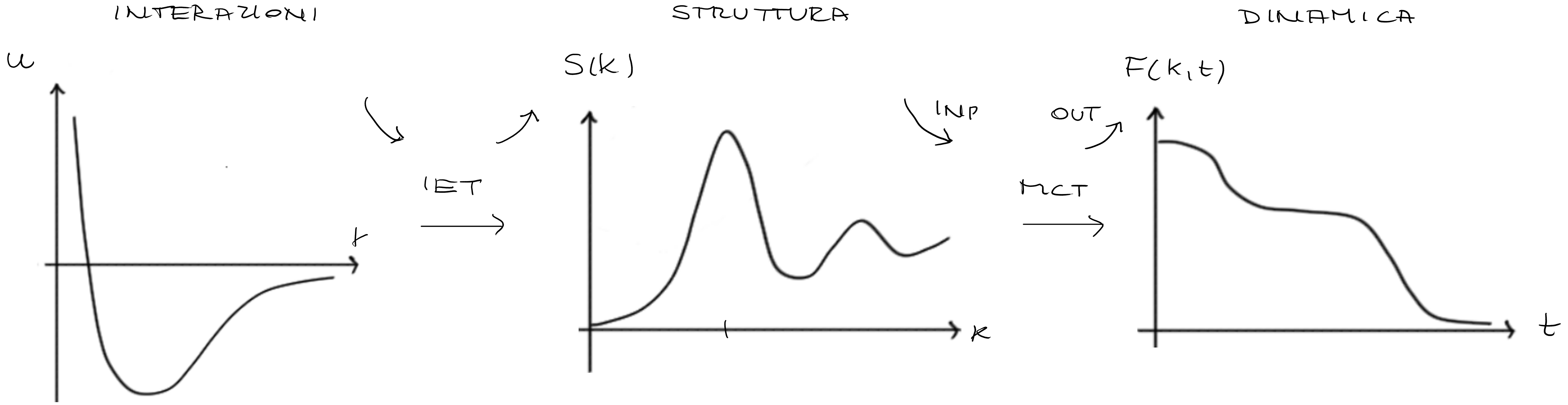
Teoria mode-coupling

Operatore di proiezione → Mori e Zwanzig '1960

1984 Götze → transizione vetrosa

① 2-step relaxation + stretched exponential

② $\tau_\alpha(T)$ → vetro ideale



Variabile rilevante $A(t)$ $\{A_1, \dots, A_M\}$

lente $\hat{\rho}_{\vec{k}}(t)$, $\hat{\vec{J}}_{\vec{k}}(t)$ $\hat{J}(\vec{r},t) = \sum_{i=1}^{N} \vec{v}_i\, \delta(\vec{r}-\vec{r}_i(t))$

resto

Prodotto Scalare

$$(B|A) = \langle A B^* \rangle \qquad (\langle \delta A\, \delta B^* \rangle)$$

Eq. moto per A formalmente esatta : eq. Langevin generalizzata

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t ds\, M(t-s)\, A(s)\, ds + \theta(t) \leftarrow$$

forza stocastica

$\downarrow$

$$\langle \theta(t) A^* \rangle = 0$$

$$(A|\theta(t)) = 0$$

$\uparrow$ matrice delle frequenze $\sim \dfrac{(A|\dot{A})}{(A|A)}$

$\uparrow$ funzione di memoria $\sim \dfrac{(\theta|\theta(t))}{(A|A)}$

Funzione di correlazione : $C(t) = \dfrac{\langle A(t) A^*(0) \rangle}{\langle A(0) A^*(0) \rangle}$

$$\frac{dc}{dt} = i\Omega\, c(t) - \int_0^t ds\, M(t-s)\, C(s)\, ds \qquad C(0) \to C(t)$$

Approssimazione mode-coupling : $M \sim \hat{\rho}_{\bar{k}_1}(t)\, \hat{\rho}_{\bar{k}_2}(t) \Rightarrow F(k,t)$

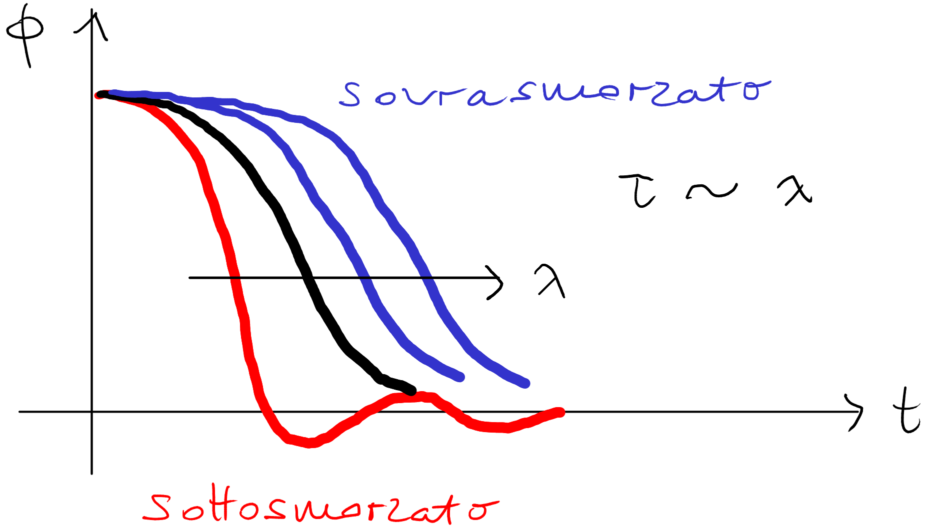
$$\begin{cases} \dfrac{d^2F}{dt^2} + \dfrac{k_BT\, k^2}{m\, S(k)} F(k,t) + \displaystyle\int_0^t ds\, M(k,t-s)\, \frac{dF}{ds}(k,s) = 0 \\[2ex] M(k,t) = \dfrac{\rho\, k_BT}{16\pi^3 m} \displaystyle\int d\bar{k}'\, \underset{\substack{\uparrow \\ \text{vertici} \to S(k)}}{\left|V_{\bar{k},\bar{k}-\bar{k}'}\right|^2} F(k,t)\, F(|\bar{k}-\bar{k}'|,t) \end{cases}$$

Modello schematico : $S(k) = \delta(k-k_0)$ $\qquad \phi(t) = F(k_0,t)$

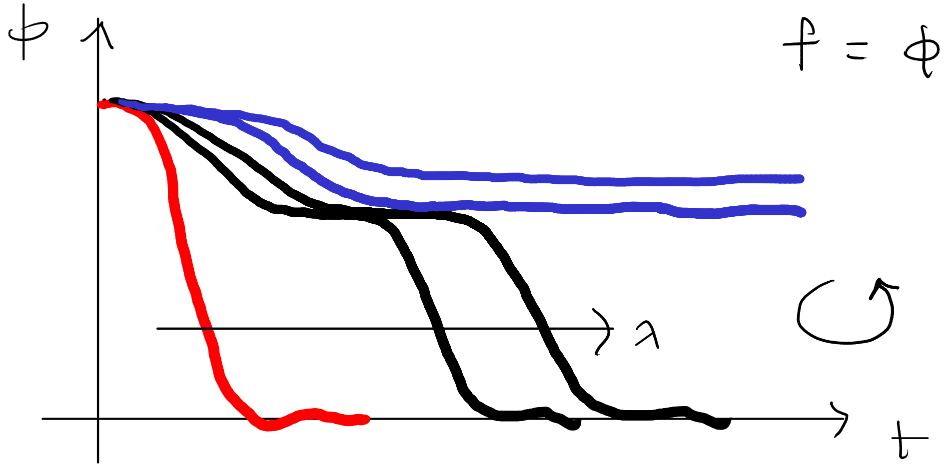
① $\dfrac{d^2\phi}{dt^2} + \Omega^2\phi + \lambda\displaystyle\int_0^t ds\, \phi^2(t-s)\, \frac{d\phi}{ds} = 0$ → memoria

② $\dfrac{d^2\phi}{dt^2} + \Omega^2\phi + \lambda\, \dfrac{d\phi}{dt} = 0$ oscillatore armonico smorzato

②



①



$f = \phi(\infty)$

$x < x_c$: $f = 0$

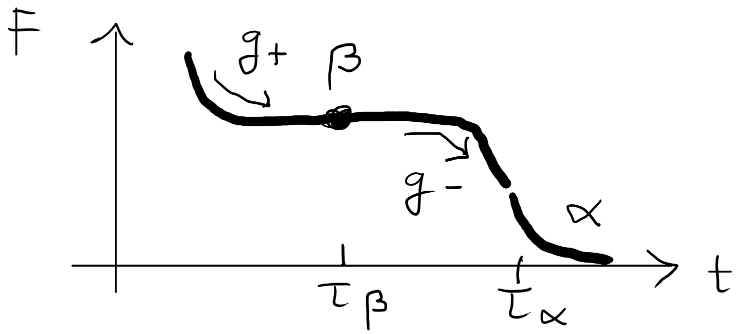
$x \geq x_c$: $f > 0$

Predizioni generali della MCT

↗ principi primi : $S(k) \rightarrow F(k,t)$ → numeriche

↘ sviluppi asintotici in prossimità di T_c → analitiche

1) Two step relaxation + stretched



- β relaxation

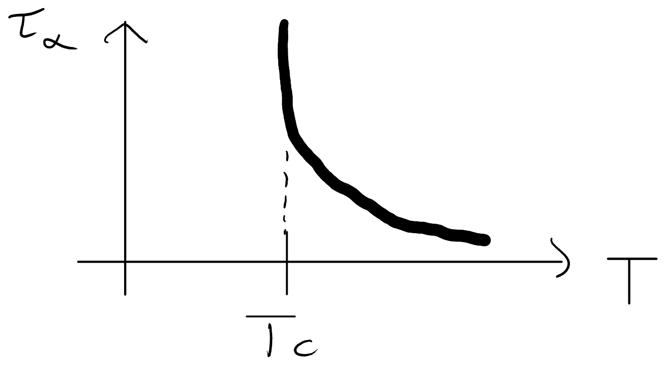
$$F(k,t) \approx f(k) + |T-T_c|\, h(k)\, g_\pm(t/\tau_\beta)$$

$$g_+ = (t/\tau_\beta)^{-a} \qquad g_- \sim (t/\tau_\beta)^{b}$$

- α relaxation

$$F(k,t) \approx \exp(-(t/\tau_\alpha)^\beta) \qquad \beta \sim 0.6-0.7$$

2) $\tau_\alpha(T)$



$$\tau_\alpha \sim \frac{1}{|T-T_c|^\gamma} \qquad \gamma \sim 2 \qquad a, b, \gamma$$

3) η, D, ...

Verifica predizioni della MCT

1) Principi primi : $S(k) \rightarrow F(k,t)$

2) Fit

miscela binaria
Kob-Andersen

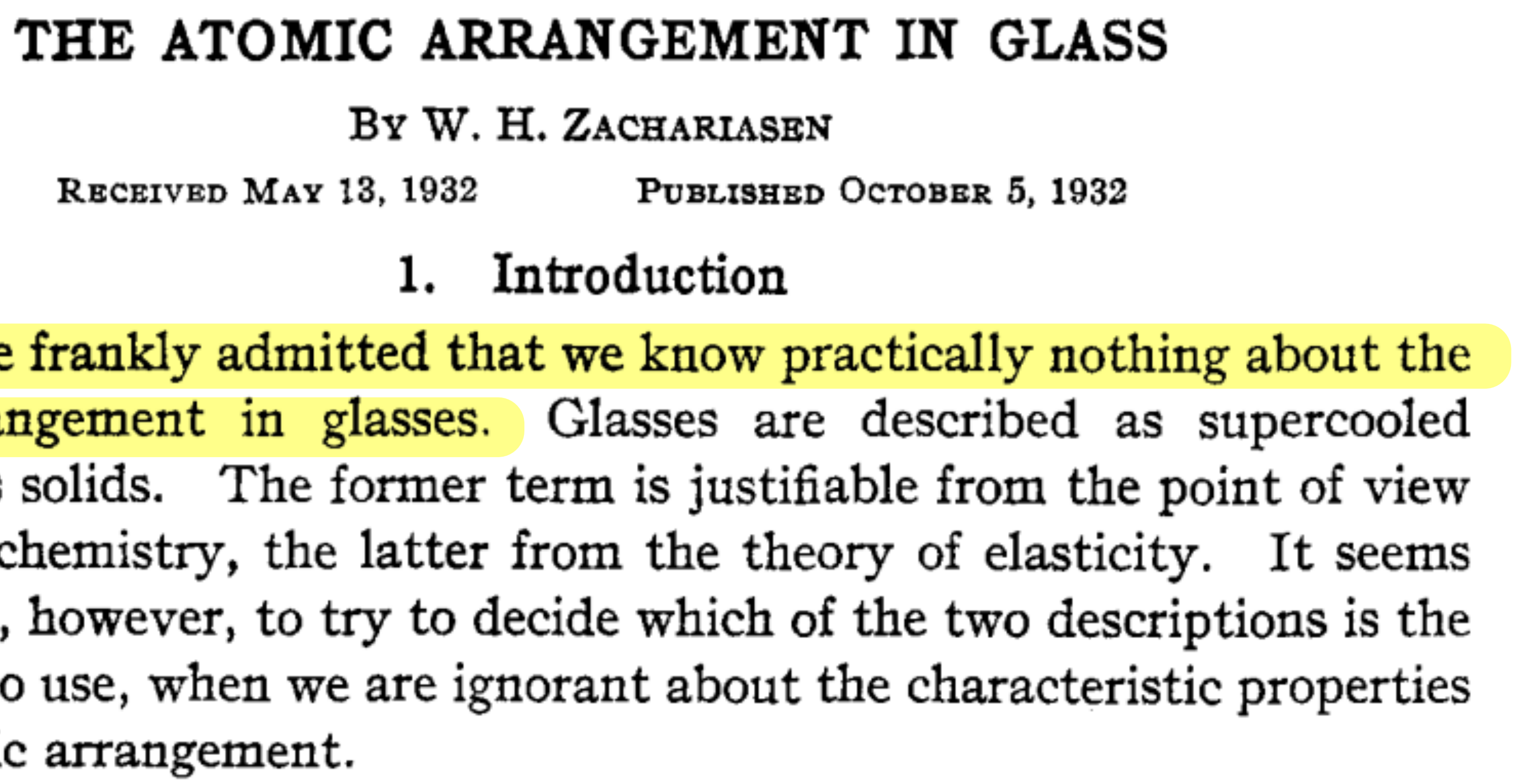
$T_{onset} \sim 0.9 - 1.0$

$T_c^{(pp)} = 0.92$

$T_c^{(fit)} = 0.435$

$T_g^{(sim)} = 0.4$

STRUTTURA DEI VETRI



THE ATOMIC ARRANGEMENT IN GLASS

By W. H. Zachariasen

Received May 13, 1932 Published October 5, 1932

1. Introduction

It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses. Glasses are described as supercooled liquids or as solids. The former term is justifiable from the point of view of physical chemistry, the latter from the theory of elasticity. It seems rather futile, however, to try to decide which of the two descriptions is the proper one to use, when we are ignorant about the characteristic properties of the atomic arrangement.

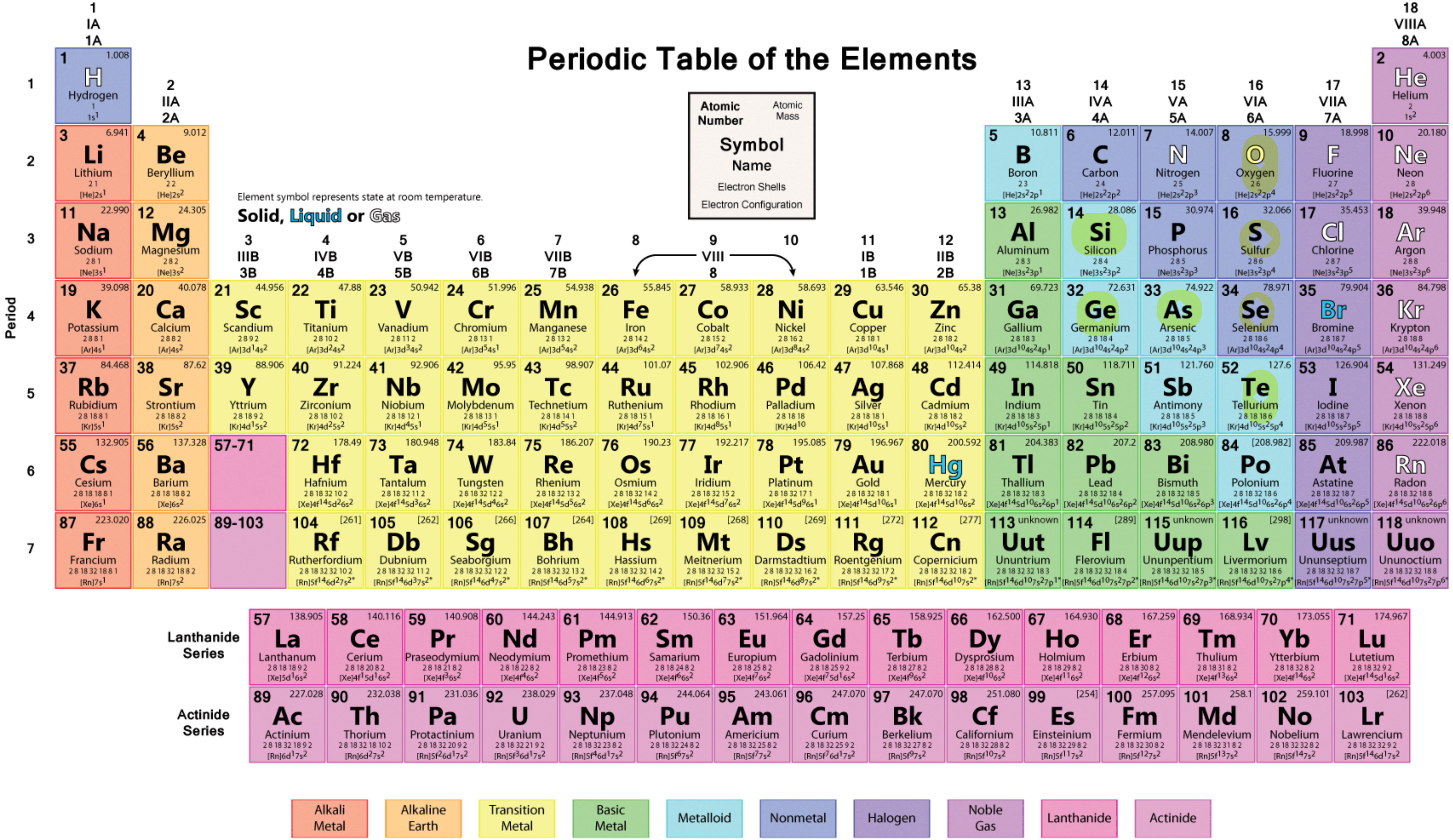
- continuous random network
- crystallites theory

- random close packing
- frustrazione geometrica

→ network-forming ① ← ossidi, silicati, calcogenidi

→ close-packed ② ← colloidi, vetri metallici, polimeri

Periodic Table of the Elements



Atomic Number — Atomic Mass
Symbol
Name
Electron Shells
Electron Configuration

Element symbol represents state at room temperature.
Solid, Liquid or Gas

Period	1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1	1 1.008 **H** Hydrogen 1 $1s^{1}$																	2 4.003 **He** Helium 2 $1s^{2}$
2	3 6.941 **Li** Lithium 2 1 $[He]2s^{1}$	4 9.012 **Be** Beryllium 2 2 $[He]2s^{2}$											5 10.811 **B** Boron 2 3 $[He]2s^{2}2p^{1}$	6 12.011 **C** Carbon 2 4 $[He]2s^{2}2p^{2}$	7 14.007 **N** Nitrogen 2 5 $[He]2s^{2}2p^{3}$	8 15.999 **O** Oxygen 2 6 $[He]2s^{2}2p^{4}$	9 18.998 **F** Fluorine 2 7 $[He]2s^{2}2p^{5}$	10 20.180 **Ne** Neon 2 8 $[He]2s^{2}2p^{6}$
3	11 22.990 **Na** Sodium 2 8 1 $[Ne]3s^{1}$	12 24.305 **Mg** Magnesium 2 8 2 $[Ne]3s^{2}$											13 26.982 **Al** Aluminum 2 8 3 $[Ne]3s^{2}3p^{1}$	14 28.086 **Si** Silicon 2 8 4 $[Ne]3s^{2}3p^{2}$	15 30.974 **P** Phosphorus 2 8 5 $[Ne]3s^{2}3p^{3}$	16 32.066 **S** Sulfur 2 8 6 $[Ne]3s^{2}3p^{4}$	17 35.453 **Cl** Chlorine 2 8 7 $[Ne]3s^{2}3p^{5}$	18 39.948 **Ar** Argon 2 8 8 $[Ne]3s^{2}3p^{6}$
4	19 39.098 **K** Potassium 2 8 8 1 $[Ar]4s^{1}$	20 40.078 **Ca** Calcium 2 8 8 2 $[Ar]4s^{2}$	21 44.956 **Sc** Scandium 2 8 9 2 $[Ar]3d^{1}4s^{2}$	22 47.88 **Ti** Titanium 2 8 10 2 $[Ar]3d^{2}4s^{2}$	23 50.942 **V** Vanadium 2 8 11 2 $[Ar]3d^{3}4s^{2}$	24 51.996 **Cr** Chromium 2 8 13 1 $[Ar]3d^{5}4s^{1}$	25 54.938 **Mn** Manganese 2 8 13 2 $[Ar]3d^{5}4s^{2}$	26 55.845 **Fe** Iron 2 8 14 2 $[Ar]3d^{6}4s^{2}$	27 58.933 **Co** Cobalt 2 8 15 2 $[Ar]3d^{7}4s^{2}$	28 58.693 **Ni** Nickel 2 8 16 2 $[Ar]3d^{8}4s^{2}$	29 63.546 **Cu** Copper 2 8 18 1 $[Ar]3d^{10}4s^{1}$	30 65.38 **Zn** Zinc 2 8 18 2 $[Ar]3d^{10}4s^{2}$	31 69.723 **Ga** Gallium 2 8 18 3 $[Ar]3d^{10}4s^{2}4p^{1}$	32 72.631 **Ge** Germanium 2 8 18 4 $[Ar]3d^{10}4s^{2}4p^{2}$	33 74.922 **As** Arsenic 2 8 18 5 $[Ar]3d^{10}4s^{2}4p^{3}$	34 78.971 **Se** Selenium 2 8 18 6 $[Ar]3d^{10}4s^{2}4p^{4}$	35 79.904 **Br** Bromine 2 8 18 7 $[Ar]3d^{10}4s^{2}4p^{5}$	36 84.798 **Kr** Krypton 2 8 18 8 $[Ar]3d^{10}4s^{2}4p^{6}$
5	37 84.468 **Rb** Rubidium 2 8 18 8 1 $[Kr]5s^{1}$	38 87.62 **Sr** Strontium 2 8 18 8 2 $[Kr]5s^{2}$	39 88.906 **Y** Yttrium 2 8 18 9 2 $[Kr]4d^{1}5s^{2}$	40 91.224 **Zr** Zirconium 2 8 18 10 2 $[Kr]4d^{2}5s^{2}$	41 92.906 **Nb** Niobium 2 8 18 12 1 $[Kr]4d^{4}5s^{1}$	42 95.95 **Mo** Molybdenum 2 8 18 13 1 $[Kr]4d^{5}5s^{1}$	43 98.907 **Tc** Technetium 2 8 18 14 1 $[Kr]4d^{5}5s^{2}$	44 101.07 **Ru** Ruthenium 2 8 18 15 1 $[Kr]4d^{7}5s^{1}$	45 102.906 **Rh** Rhodium 2 8 18 16 1 $[Kr]4d^{8}5s^{1}$	46 106.42 **Pd** Palladium 2 8 18 18 $[Kr]4d^{10}$	47 107.868 **Ag** Silver 2 8 18 18 1 $[Kr]4d^{10}5s^{1}$	48 112.414 **Cd** Cadmium 2 8 18 18 2 $[Kr]4d^{10}5s^{2}$	49 114.818 **In** Indium 2 8 18 18 3 $[Kr]4d^{10}5s^{2}5p^{1}$	50 118.711 **Sn** Tin 2 8 18 18 4 $[Kr]4d^{10}5s^{2}5p^{2}$	51 121.760 **Sb** Antimony 2 8 18 18 5 $[Kr]4d^{10}5s^{2}5p^{3}$	52 127.6 **Te** Tellurium 2 8 18 18 6 $[Kr]4d^{10}5s^{2}5p^{4}$	53 126.904 **I** Iodine 2 8 18 18 7 $[Kr]4d^{10}5s^{2}5p^{5}$	54 131.249 **Xe** Xenon 2 8 18 18 8 $[Kr]4d^{10}5s^{2}5p^{6}$
6	55 132.905 **Cs** Cesium 2 8 18 18 8 1 $[Xe]6s^{1}$	56 137.328 **Ba** Barium 2 8 18 18 8 2 $[Xe]6s^{2}$	57-71	72 178.49 **Hf** Hafnium 2 8 18 32 10 2 $[Xe]4f^{14}5d^{2}6s^{2}$	73 180.948 **Ta** Tantalum 2 8 18 32 11 2 $[Xe]4f^{14}5d^{3}6s^{2}$	74 183.84 **W** Tungsten 2 8 18 32 12 2 $[Xe]4f^{14}5d^{4}6s^{2}$	75 186.207 **Re** Rhenium 2 8 18 32 13 2 $[Xe]4f^{14}5d^{5}6s^{2}$	76 190.23 **Os** Osmium 2 8 18 32 14 2 $[Xe]4f^{14}5d^{6}6s^{2}$	77 192.217 **Ir** Iridium 2 8 18 32 15 2 $[Xe]4f^{14}5d^{7}6s^{2}$	78 195.085 **Pt** Platinum 2 8 18 32 17 1 $[Xe]4f^{14}5d^{9}6s^{1}$	79 196.967 **Au** Gold 2 8 18 32 18 1 $[Xe]4f^{14}5d^{10}6s^{1}$	80 200.592 **Hg** Mercury 2 8 18 32 18 2 $[Xe]4f^{14}5d^{10}6s^{2}$	81 204.383 **Tl** Thallium 2 8 18 32 18 3 $[Xe]4f^{14}5d^{10}6s^{2}6p^{1}$	82 207.2 **Pb** Lead 2 8 18 32 18 4 $[Xe]4f^{14}5d^{10}6s^{2}6p^{2}$	83 208.980 **Bi** Bismuth 2 8 18 32 18 5 $[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$	84 [208.982] **Po** Polonium 2 8 18 32 18 6 $[Xe]4f^{14}5d^{10}6s^{2}6p^{4}$	85 209.987 **At** Astatine 2 8 18 32 18 7 $[Xe]4f^{14}5d^{10}6s^{2}6p^{5}$	86 222.018 **Rn** Radon 2 8 18 32 18 8 $[Xe]4f^{14}5d^{10}6s^{2}6p^{6}$
7	87 223.020 **Fr** Francium 2 8 18 32 18 8 1 $[Rn]7s^{1}$	88 226.025 **Ra** Radium 2 8 18 32 18 8 2 $[Rn]7s^{2}$	89-103	104 [261] **Rf** Rutherfordium 2 8 18 32 32 10 2 $[Rn]5f^{14}6d^{2}7s^{2*}$	105 [262] **Db** Dubnium 2 8 18 32 32 11 2 $[Rn]5f^{14}6d^{3}7s^{2*}$	106 [266] **Sg** Seaborgium 2 8 18 32 32 12 2 $[Rn]5f^{14}6d^{4}7s^{2*}$	107 [264] **Bh** Bohrium 2 8 18 32 32 13 2 $[Rn]5f^{14}6d^{5}7s^{2*}$	108 [269] **Hs** Hassium 2 8 18 32 32 14 2 $[Rn]5f^{14}6d^{6}7s^{2*}$	109 [268] **Mt** Meitnerium 2 8 18 32 32 15 2 $[Rn]5f^{14}6d^{7}7s^{2*}$	110 [269] **Ds** Darmstadtium 2 8 18 32 32 16 2 $[Rn]5f^{14}6d^{8}7s^{2*}$	111 [272] **Rg** Roentgenium 2 8 18 32 32 17 2 $[Rn]5f^{14}6d^{9}7s^{2*}$	112 [277] **Cn** Copernicium 2 8 18 32 32 18 2 $[Rn]5f^{14}6d^{10}7s^{2*}$	113 unknown **Uut** Ununtrium 2 8 18 32 32 18 3 $[Rn]5f^{14}6d^{10}7s^{2}7p^{1*}$	114 [289] **Fl** Flerovium 2 8 18 32 32 18 4 $[Rn]5f^{14}6d^{10}7s^{2}7p^{2*}$	115 unknown **Uup** Ununpentium 2 8 18 32 32 18 5 $[Rn]5f^{14}6d^{10}7s^{2}7p^{3*}$	116 [298] **Lv** Livermorium 2 8 18 32 32 18 6 $[Rn]5f^{14}6d^{10}7s^{2}7p^{4*}$	117 unknown **Uus** Ununseptium 2 8 18 32 32 18 7 $[Rn]5f^{14}6d^{10}7s^{2}7p^{5*}$	118 unknown **Uuo** Ununoctium 2 8 18 32 32 18 8 $[Rn]5f^{14}6d^{10}7s^{2}7p^{6*}$

Lanthanide Series	57 138.905 **La** Lanthanum 2 8 18 18 9 2 $[Xe]5d^{1}6s^{2}$	58 140.116 **Ce** Cerium 2 8 18 20 8 2 $[Xe]4f^{1}5d^{1}6s^{2}$	59 140.908 **Pr** Praseodymium 2 8 18 21 8 2 $[Xe]4f^{3}6s^{2}$	60 144.243 **Nd** Neodymium 2 8 18 22 8 2 $[Xe]4f^{4}6s^{2}$	61 144.913 **Pm** Promethium 2 8 18 23 8 2 $[Xe]4f^{5}6s^{2}$	62 150.36 **Sm** Samarium 2 8 18 24 8 2 $[Xe]4f^{6}6s^{2}$	63 151.964 **Eu** Europium 2 8 18 25 8 2 $[Xe]4f^{7}6s^{2}$	64 157.25 **Gd** Gadolinium 2 8 18 25 9 2 $[Xe]4f^{7}5d^{1}6s^{2}$	65 158.925 **Tb** Terbium 2 8 18 27 8 2 $[Xe]4f^{9}6s^{2}$	66 162.500 **Dy** Dysprosium 2 8 18 28 8 2 $[Xe]4f^{10}6s^{2}$	67 164.930 **Ho** Holmium 2 8 18 29 8 2 $[Xe]4f^{11}6s^{2}$	68 167.259 **Er** Erbium 2 8 18 30 8 2 $[Xe]4f^{12}6s^{2}$	69 168.934 **Tm** Thulium 2 8 18 31 8 2 $[Xe]4f^{13}6s^{2}$	70 173.055 **Yb** Ytterbium 2 8 18 32 8 2 $[Xe]4f^{14}6s^{2}$	71 174.967 **Lu** Lutetium 2 8 18 32 9 2 $[Xe]4f^{14}5d^{1}6s^{2}$
Actinide Series	89 227.028 **Ac** Actinium 2 8 18 32 18 9 2 $[Rn]6d^{1}7s^{2}$	90 232.038 **Th** Thorium 2 8 18 32 18 10 2 $[Rn]6d^{2}7s^{2}$	91 231.036 **Pa** Protactinium 2 8 18 32 20 9 2 $[Rn]5f^{2}6d^{1}7s^{2}$	92 238.029 **U** Uranium 2 8 18 32 21 9 2 $[Rn]5f^{3}6d^{1}7s^{2}$	93 237.048 **Np** Neptunium 2 8 18 32 23 8 2 $[Rn]5f^{4}6d^{1}7s^{2}$	94 244.064 **Pu** Plutonium 2 8 18 32 24 8 2 $[Rn]5f^{6}7s^{2}$	95 243.061 **Am** Americium 2 8 18 32 25 8 2 $[Rn]5f^{7}7s^{2}$	96 247.070 **Cm** Curium 2 8 18 32 25 9 2 $[Rn]5f^{7}6d^{1}7s^{2}$	97 247.070 **Bk** Berkelium 2 8 18 32 27 8 2 $[Rn]5f^{9}7s^{2}$	98 251.080 **Cf** Californium 2 8 18 32 28 8 2 $[Rn]5f^{10}7s^{2}$	99 [254] **Es** Einsteinium 2 8 18 32 29 8 2 $[Rn]5f^{11}7s^{2}$	100 257.095 **Fm** Fermium 2 8 18 32 30 8 2 $[Rn]5f^{12}7s^{2}$	101 258.1 **Md** Mendelevium 2 8 18 32 31 8 2 $[Rn]5f^{13}7s^{2}$	102 259.101 **No** Nobelium 2 8 18 32 32 8 2 $[Rn]5f^{14}7s^{2}$	103 [262] **Lr** Lawrencium 2 8 18 32 32 9 2 $[Rn]5f^{14}6d^{1}7s^{2}$

Alkali Metal
Alkaline Earth
Transition Metal
Basic Metal
Metalloid
Nonmetal
Halogen
Noble Gas
Lanthanide
Actinide

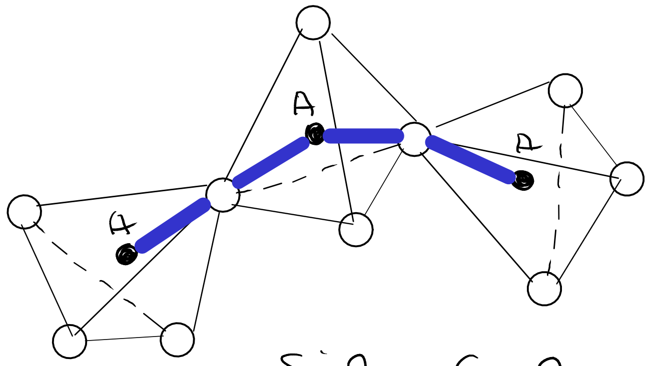
Network-forming glasses

ossidi : A + O

calcogenidi : As, Ge + S, Se, Te

$x_A = \frac{N_A}{N}$, $x_O = \frac{N_O}{N}$ concentrazioni chimiche

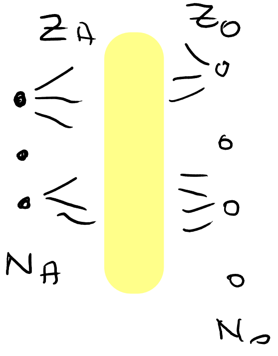
$z_A, z_O = 2$ valenza → numeri di coordinazione



SiO_2, GeO_2

Es.: $z_A, z_O \to x_A, x_O = ?$

$$\begin{cases} x_A + x_O = 1 \\ N_A z_A = N_O z_O \end{cases}$$



$$\begin{cases} x_A + x_O = 1 \\ x_A z_A = x_O z_O \end{cases}$$

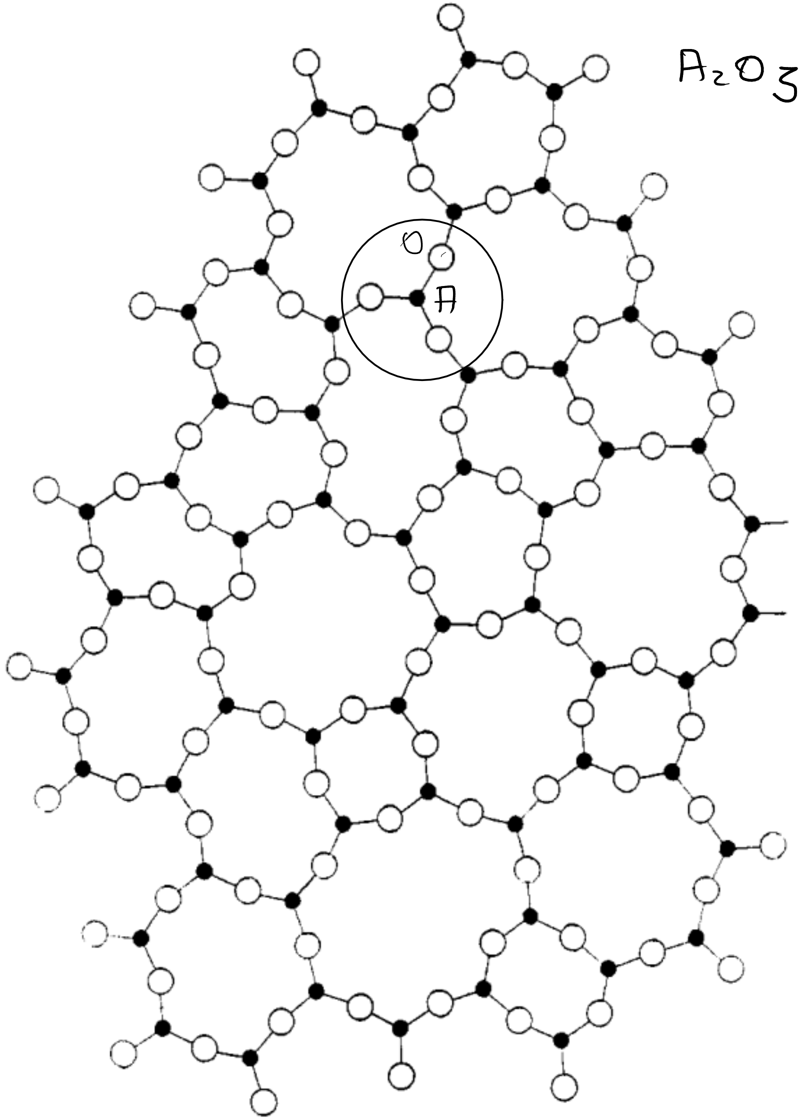


Fig. 1b.

Zachariasen 1932

$$x_A z_A = (1 - x_A) z_O$$

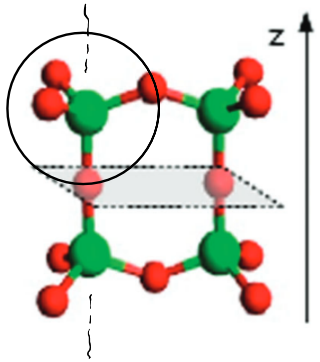
$$x_A = \frac{z_O}{z_O + z_A}$$

$z_{Si} = 4$ $z_O = 2$ $x_{Si} = \frac{2}{6} = \frac{1}{3}$ $x_O = \frac{2}{3}$ SiO_2 → As, Se Ge, Se → ?

bilayer SiO_2

$z_{Si} = 3$ $z_O = 2$

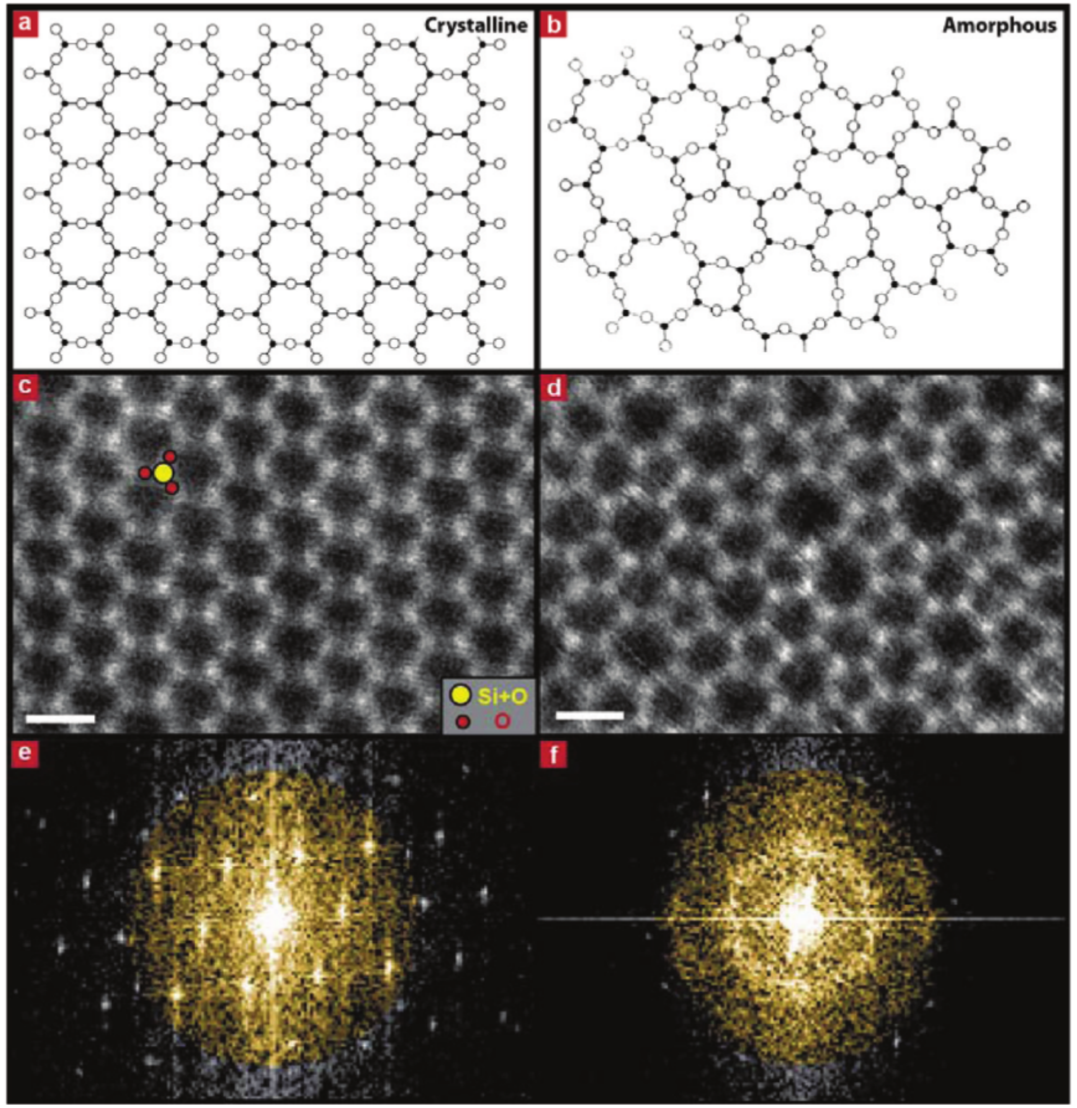
in 2d : Si_2O_3 (A_2O_3)

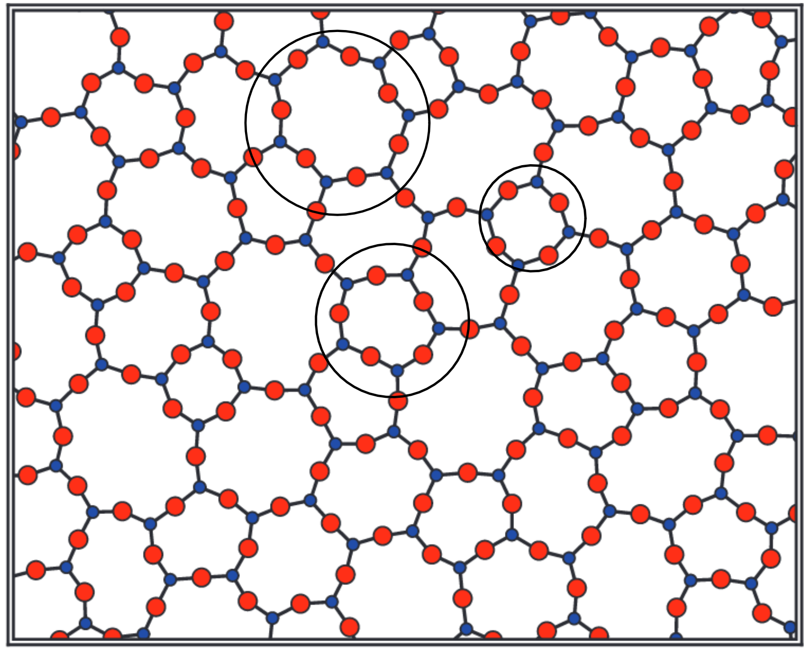


Direct Imaging of a Two-Dimensional Silica Glass on Graphene

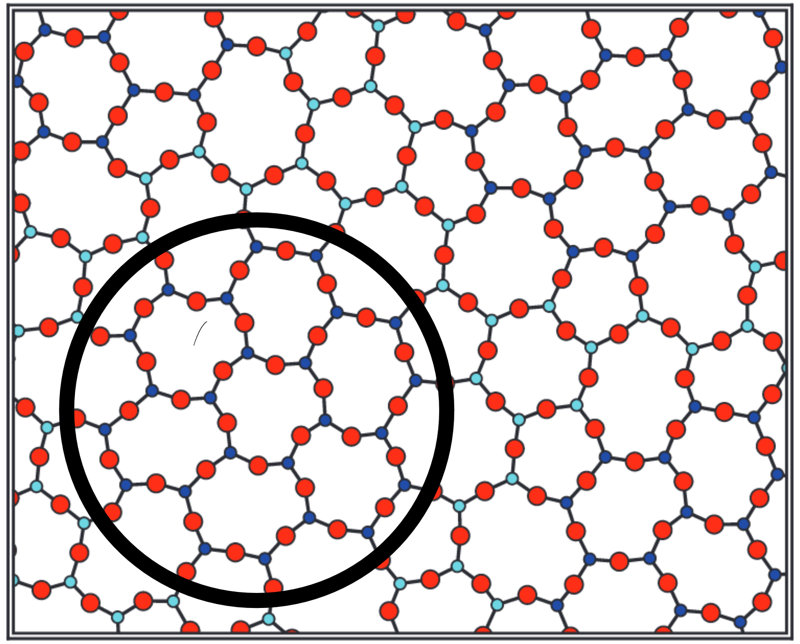
Pinshane Y. Huang,[†,■] Simon Kurasch,[‡,■] Anchal Srivastava,[§,○] Viera Skakalova,[§,∥] Jani Kotakoski,[∥,⊥] Arkady V. Krasheninnikov,[⊥,¶] Robert Hovden,[†] Qingyun Mao,[†] Jannik C. Meyer,[‡,∥] Jurgen Smet,[§] David A. Muller,[*,†,□] and Ute Kaiser[*,‡]

Nano Lett. 2012, 12, 1081–1086



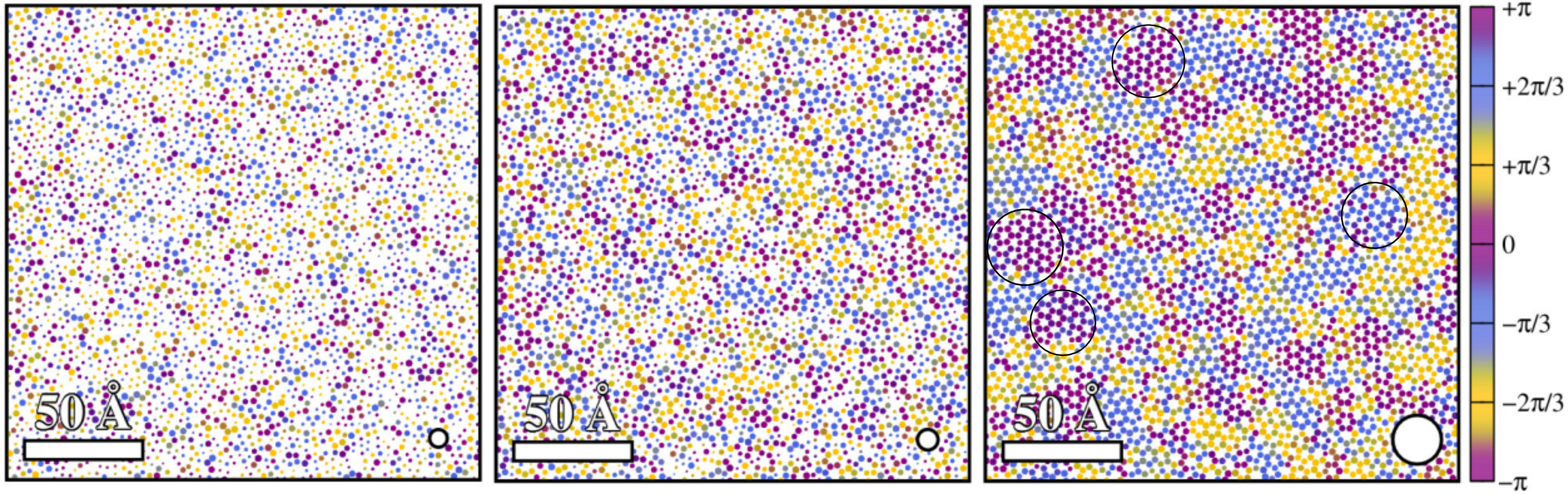


CRN



Wright

$\longrightarrow$ $1/T$



$$\psi_{nj} = \frac{1}{n} \sum_{l=1}^{n} e^{in\theta_{jl}}$$

$n = 3$

Dirindin
Coslovich 2024

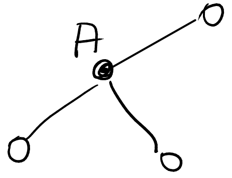
Teoria della rigidità

- Gupta – Cooper ~ Zachariasen '78 – '80 campo medio
- Phillips – Thorpe '79 – '85 $T = 0$

Isostaticità : Maxwell (1864) stabilità meccanica

n. vincoli = n. dofs

Es.: d dimensioni, N particelle $dN = zN \Rightarrow z = d$



$z_\alpha, x_\alpha \qquad \alpha = A, O \qquad d = 3$

$$3N = \sum_\alpha \Big(\underset{\overset{\uparrow}{\text{legami}}}{\frac{1}{2} N_\alpha z_\alpha} + \underset{\overset{\uparrow}{\text{angoli}}}{N_\alpha (2 z_\alpha - 3)} \Big) \qquad \sum_\alpha x_\alpha z_\alpha = \langle z \rangle$$

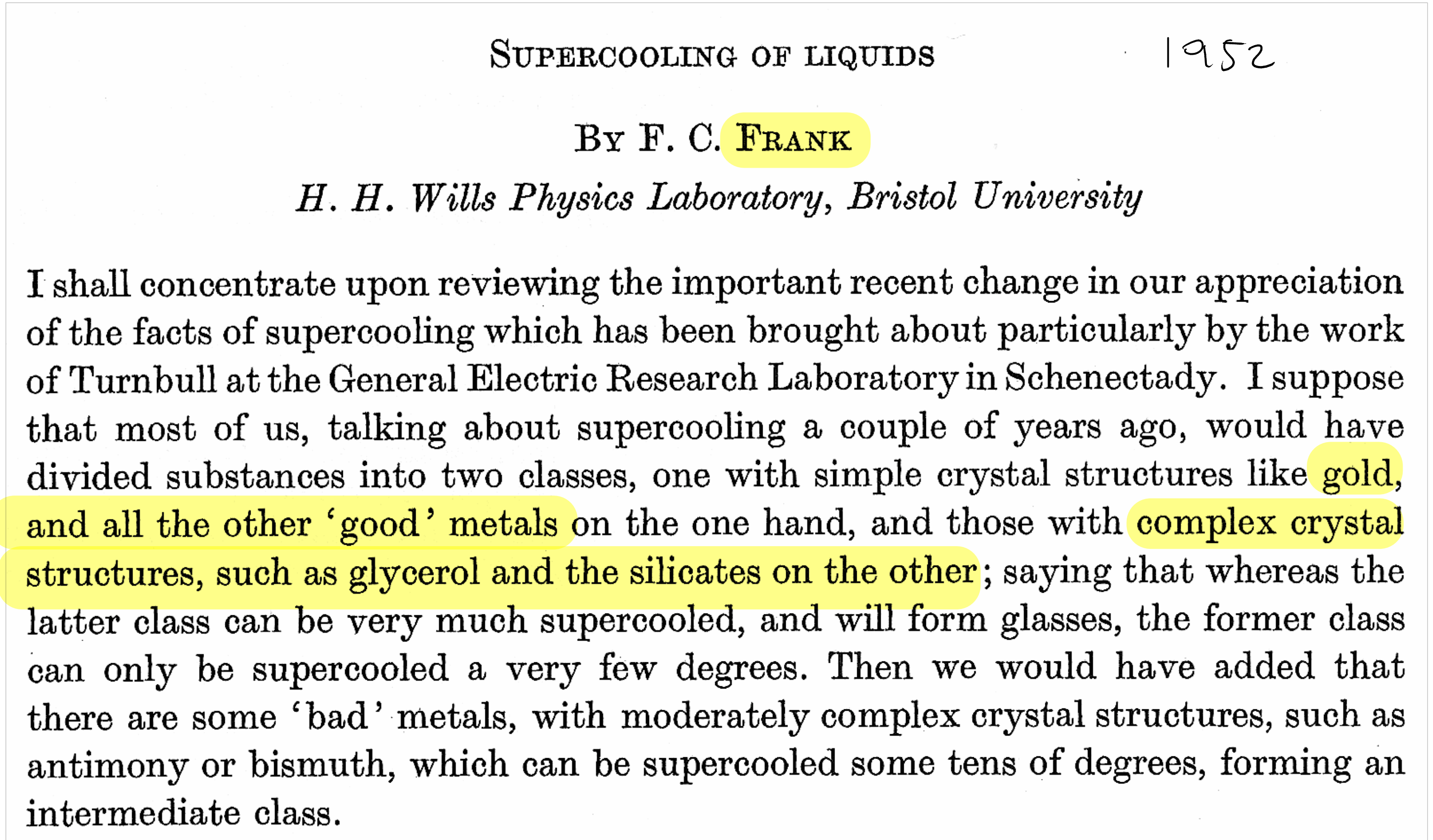
$$3 = \sum_\alpha \Big(\frac{1}{2} x_\alpha z_\alpha + x_\alpha (2 z_\alpha - 3) \Big) = \frac{5}{2} \langle z \rangle - 3$$

$$\langle z \rangle = \frac{12}{5} = 2{,}4$$

Es.: SiO_2 $\langle z \rangle = z_{Si} x_{Si} + z_O x_O = 4 \cdot \frac{1}{3} + 2 \cdot \frac{2}{3} = \frac{8}{3}$

$= 2.\bar{6} \gtrsim 2.4$

Close-packed glasses



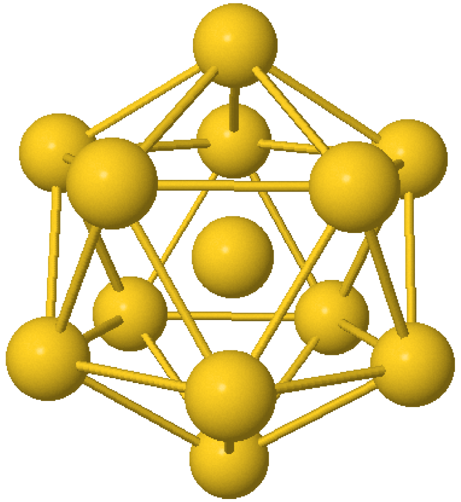
SUPERCOOLING OF LIQUIDS 1952

BY F. C. FRANK

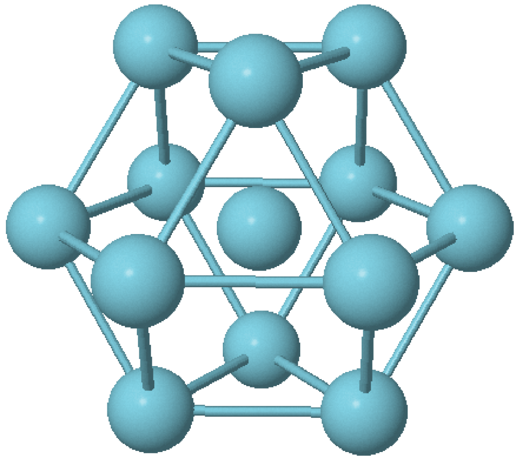
H. H. Wills Physics Laboratory, Bristol University

I shall concentrate upon reviewing the important recent change in our appreciation of the facts of supercooling which has been brought about particularly by the work of Turnbull at the General Electric Research Laboratory in Schenectady. I suppose that most of us, talking about supercooling a couple of years ago, would have divided substances into two classes, one with simple crystal structures like gold, and all the other 'good' metals on the one hand, and those with complex crystal structures, such as glycerol and the silicates on the other; saying that whereas the latter class can be very much supercooled, and will form glasses, the former class can only be supercooled a very few degrees. Then we would have added that there are some 'bad' metals, with moderately complex crystal structures, such as antimony or bismuth, which can be supercooled some tens of degrees, forming an intermediate class.

LJ



ICOSAEDRO

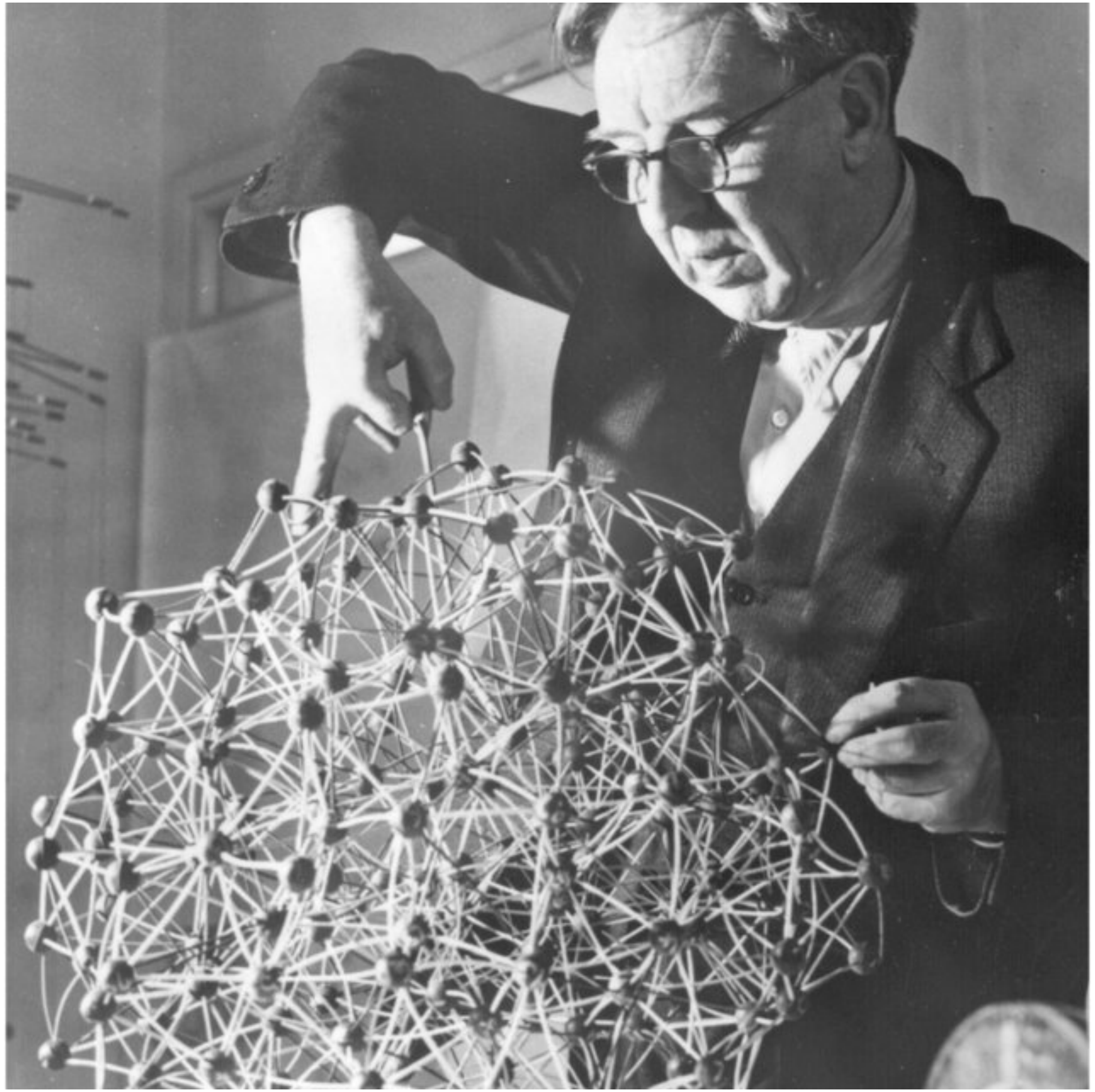


FCC

ΔU : -8%

↓

frustrazione geometrica



Bernal 1964

Tassellazione di Voronoi

→ Wigner - Seitz

poliedri di Voronoi

n = n. facce

p = n. vertici faccia

$$\bar{f} = \frac{12}{6 - \bar{p}}$$

Segnatura

$$(n_3, n_4, n_5, \dots) \qquad (n_p)_p$$

icosaedri : $(0, 0, 12)$

Close packing : 74% (FCC)

Random close packing : 64% - 68%

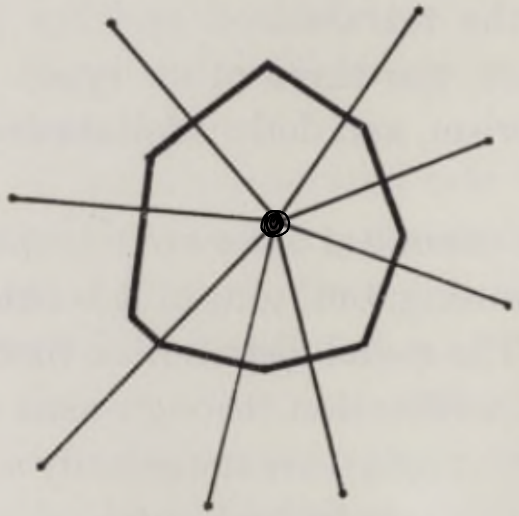


FIGURE 1

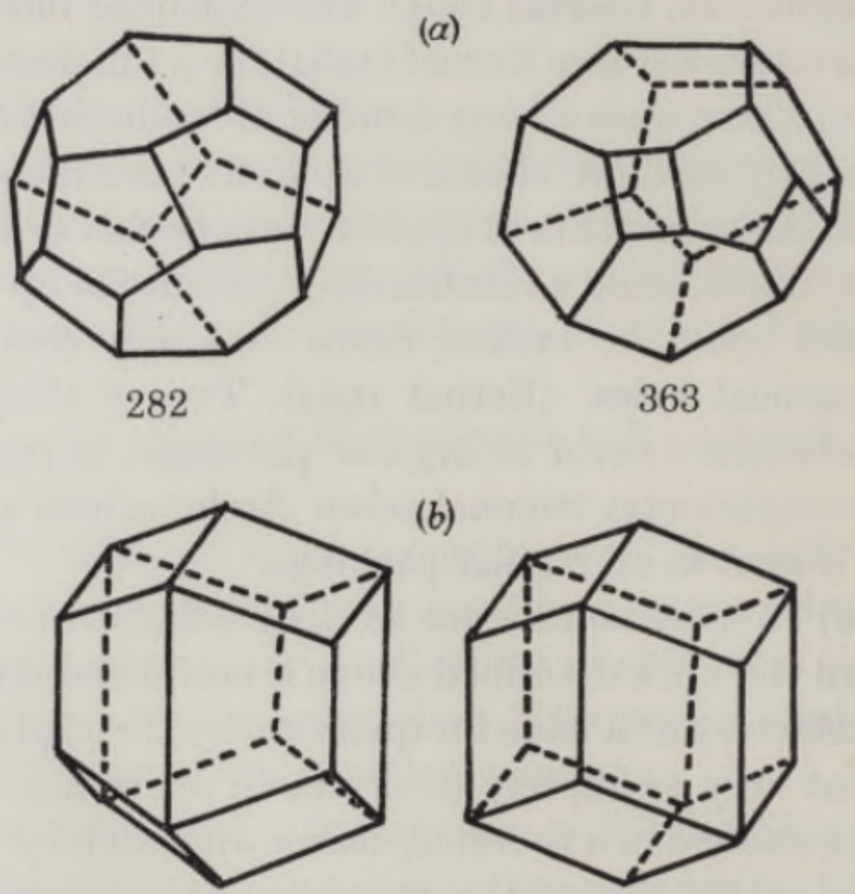


FIGURE 2

FIGURE 1. Construction of a two-dimensional Voronoi polygon.

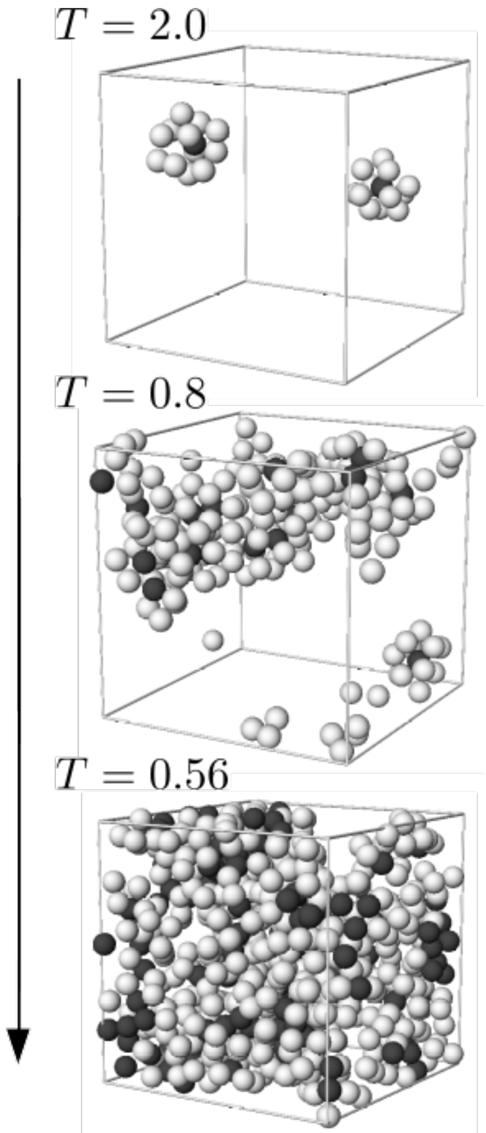
FIGURE 2. (*a*) Two typical irregular Voronoi polyhedra. (*b*) Two regular Voronoi polyhedra, derived from hexagonal and cubic close-packing respectively.

Finney & Bernal 1972

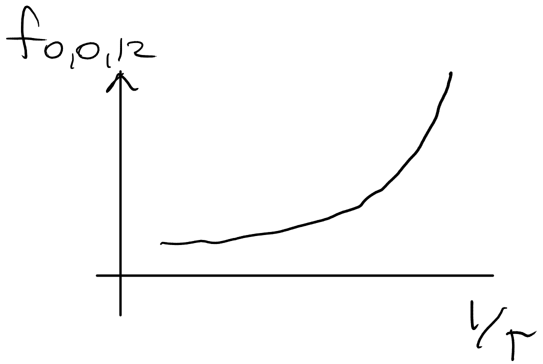
Wahnström
Lennard-Jones
mixture

$T_{onset} \approx 1.0$

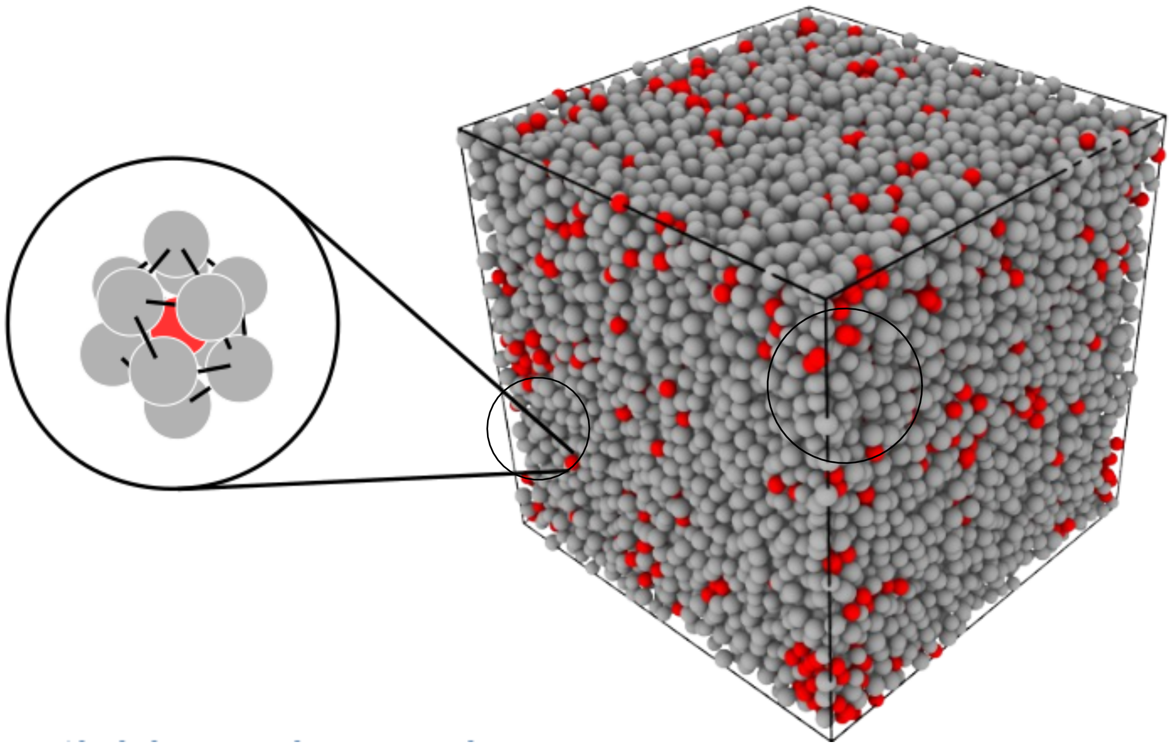
$T_c \approx 0.55$



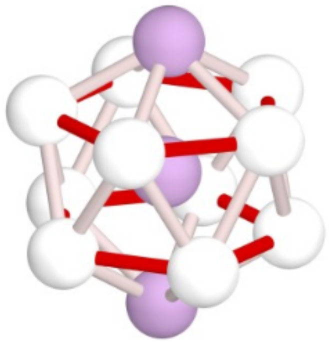
Coslovich Pastore JCP 2007



LFS

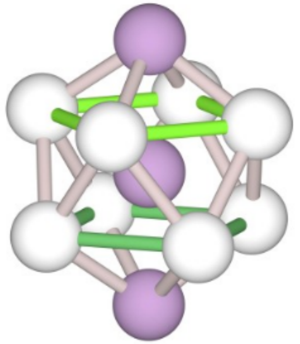


(0,0,12)

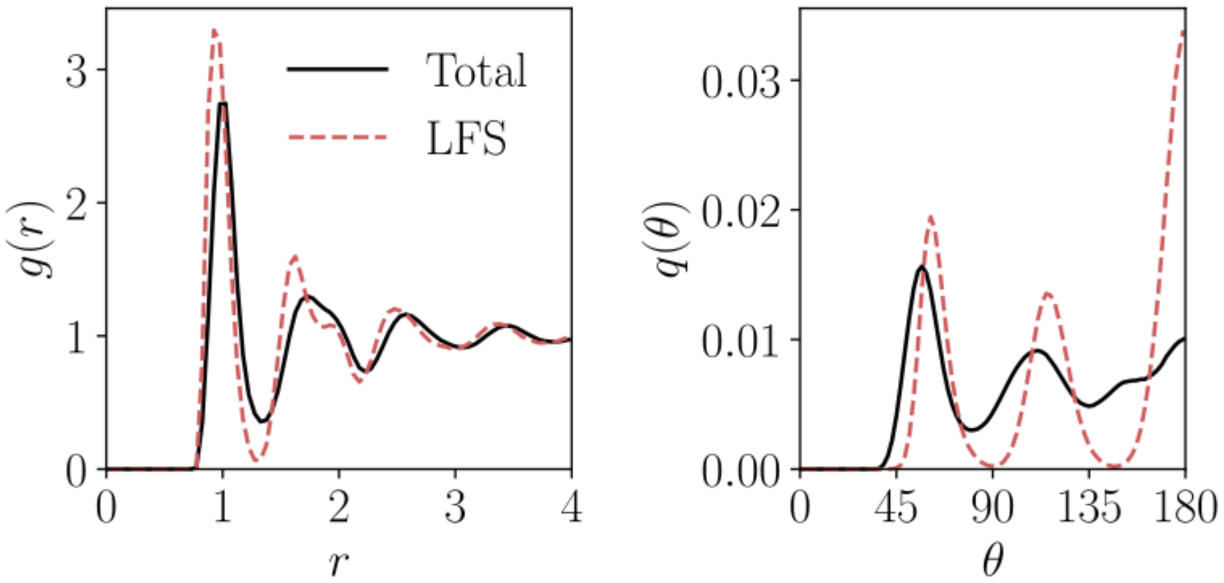


Wahnström
mixture

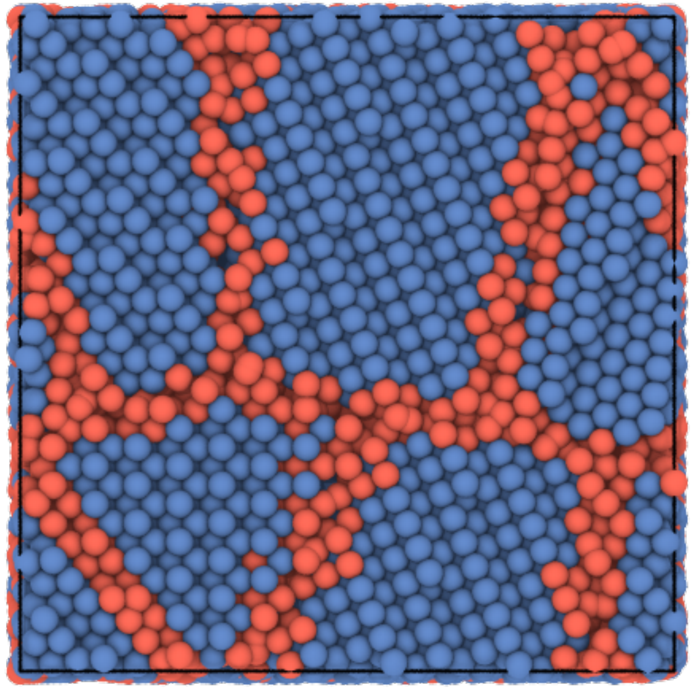
(0,2,8)



Kob - Andersen
mixture

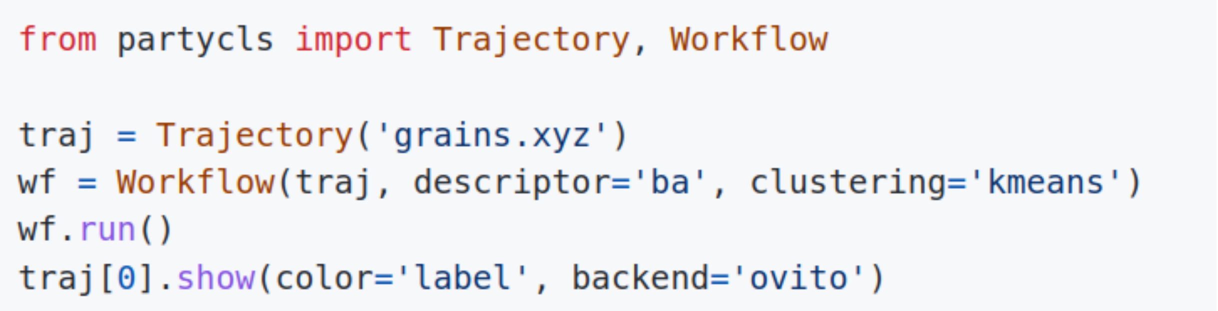


Paret, Jack, Coslovich JCP 2019



partycls

https://github.com/jorisparet/partycls



```
from partycls import Trajectory, Workflow

traj = Trajectory('grains.xyz')
wf = Workflow(traj, descriptor='ba', clustering='kmeans')
wf.run()
traj[0].show(color='label', backend='ovito')
```

Paret, Coslovich JOSS 2021