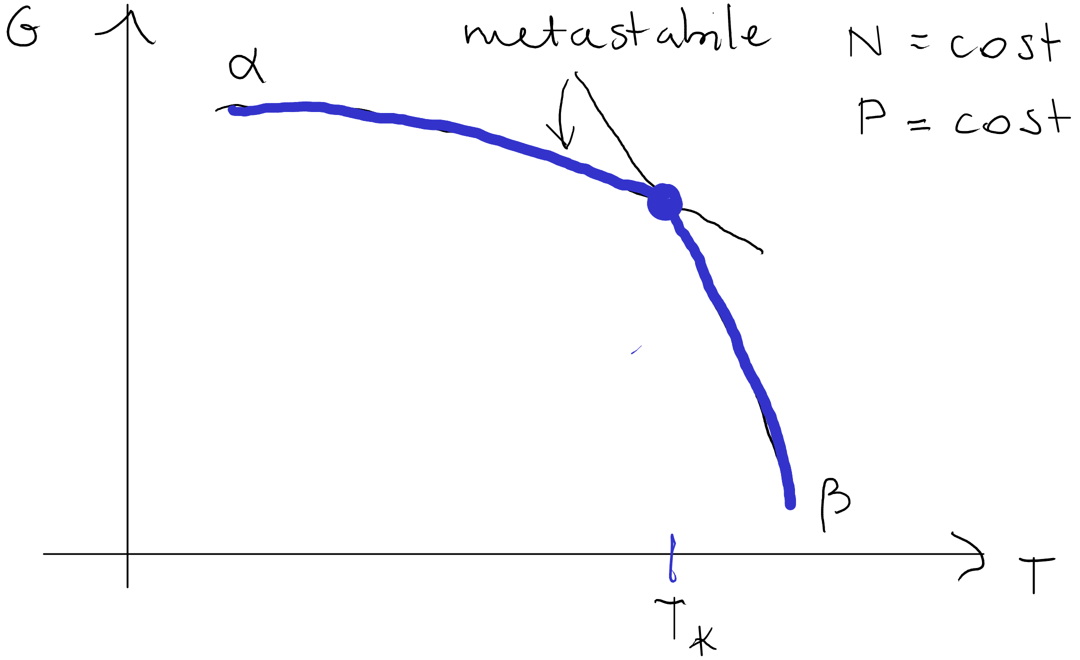
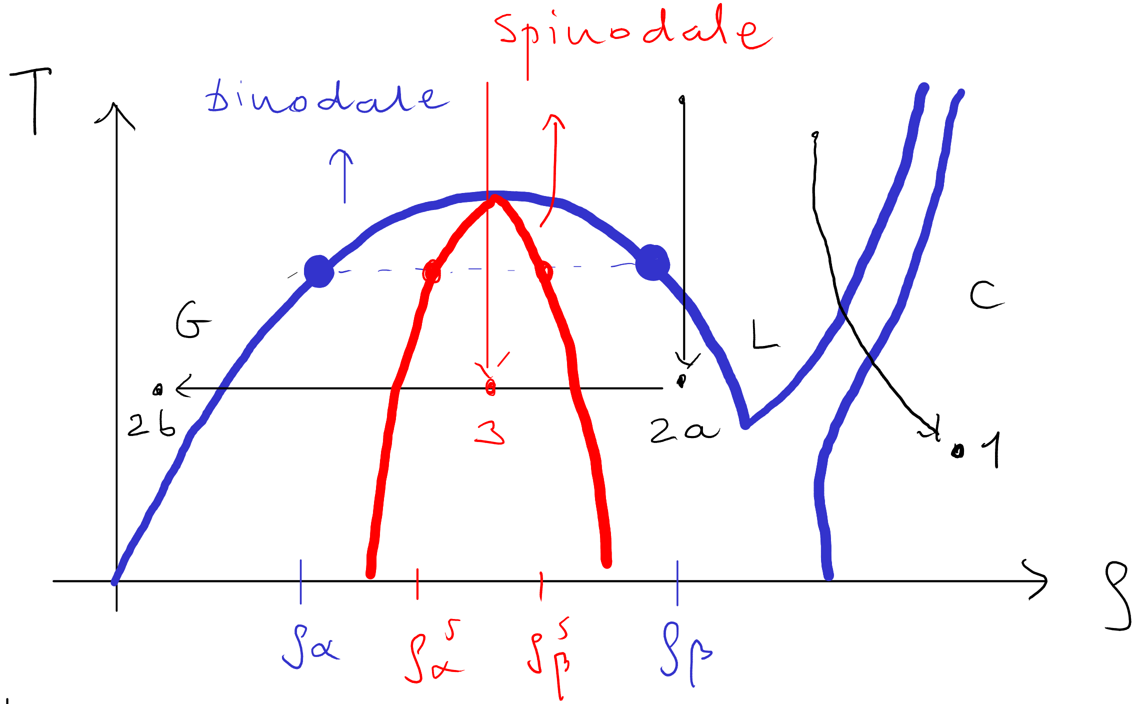
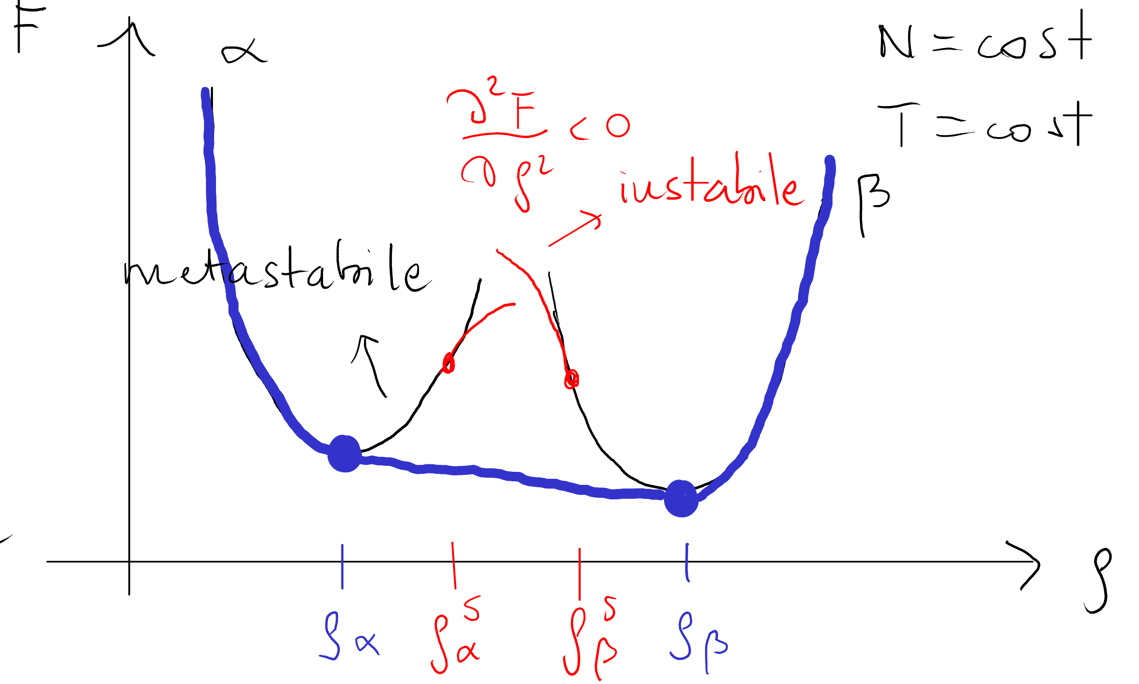
FLUIDI METASTABILI E INSTABILI





1. metastabile rispetto al cristallo
2a. —//— a liquido + gas } ①
2b. —//— al gas
3. instabile a liquido + gas ②

① nucleazione + crescita ② decomposizione spinodale



1) Nucleazione

Teoria fenomenologica: teoria classica della nucleazione (CNT)

α: metastabile, β: stabile

tensione di superficie

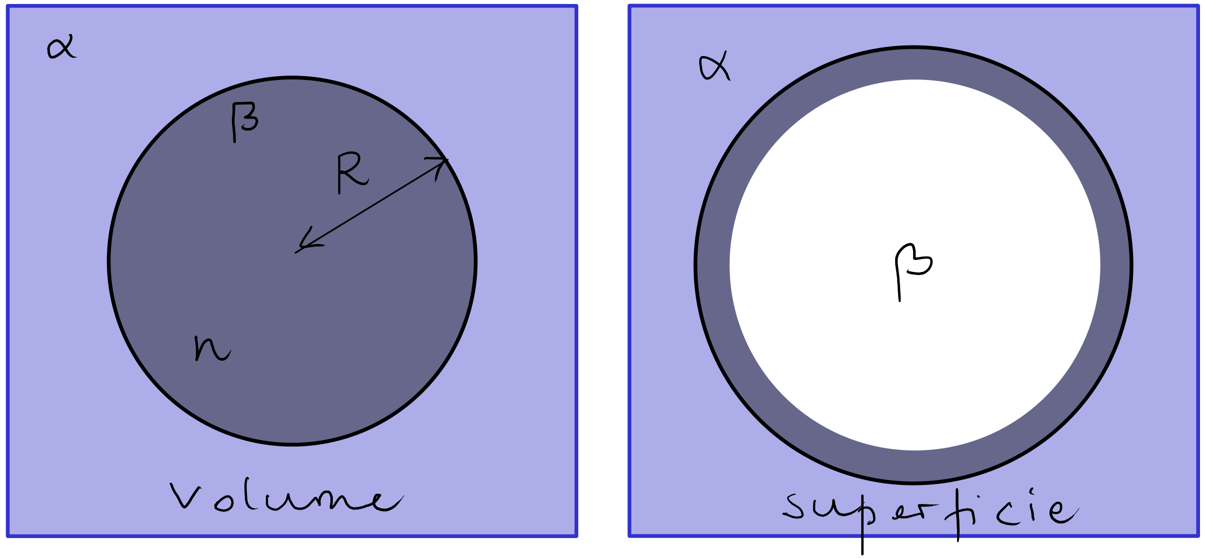
$$\Delta G(R) = \underset{\sim\sim}{\frac{4}{3}\pi R^3}\,\Delta g_v + 4\pi R^2 \gamma$$

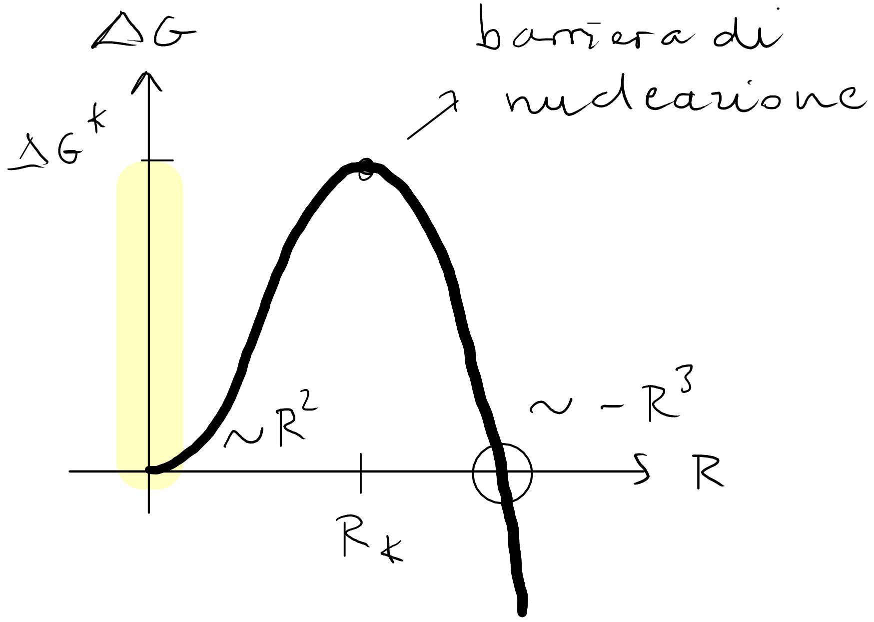
$$\Delta G = n(\overbrace{g_\beta - g_\alpha}^{\Delta g})$$

$$= V_\beta g_\beta^v - V_\alpha g_\alpha^v$$

$$= V_\beta \left(g_\beta^v - \frac{V_\alpha}{V_\beta} g_\alpha^v \right)$$

$$= \underset{\sim}{V_\beta} \underbrace{\left(g_\beta^v - \frac{\rho_\beta}{\rho_\alpha} g_\alpha^v \right)}_{\Delta g_v}$$





$$\frac{d\Delta G}{dR} = \cancel{4\pi} R^{\cancel{2}} \Delta g_v + \overset{2}{\cancel{8}}\cancel{\pi}\cancel{R}\gamma = 0 \Rightarrow R_* = -\frac{2\gamma}{\Delta g_v}$$

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

Cinetica della nucleazione

- ΔG paesaggio di energia
- sistema → grado di libertà effettivo $R \rightarrow n$ variabile continua
- moto browniano senza inerzia in campo esterno

Eq. Smoluchowski $p(x,t) \rightarrow p(n,t)$; $U \rightarrow \Delta G$ $\quad D = \frac{k_B T}{\xi}$ $\quad D = D(n)$

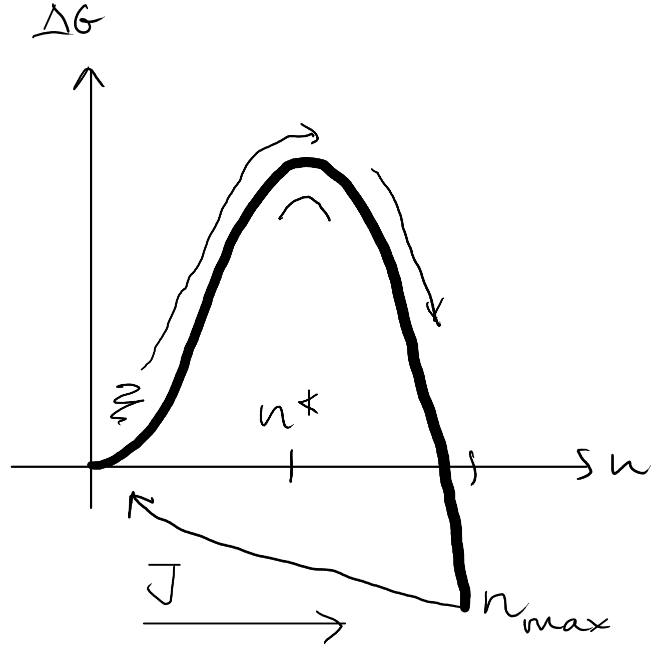
$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial n}\left[D \frac{\partial p}{\partial n} + \frac{1}{\xi}\frac{d\Delta G}{dn} p \right] = \frac{\partial}{\partial n}\left[D \left(\frac{\partial p}{\partial n} + \frac{1}{k_B T}\frac{d\Delta G}{dn} p \right)\right]$$

$\Delta G \gg k_B T$ problema di Kramers

BH 10.6 → dinamica attivata

Tempo di nucleazione : tempo di uscita dalla buca

$$\underset{\substack{\uparrow \\ 1\ \text{nucleo}}}{\tau_X} = \underbrace{\frac{1}{D(n^*)}}_{\substack{\text{prefattore}\\ \text{cinetico}}} \underbrace{\frac{1}{\left(-\frac{1}{2\pi k_B T} \left.\frac{d^2 \Delta G}{dn^2}\right|_{n^*} \right)^{1/2}}}_{\substack{\text{prefattore}\\ \text{termodinamico}\\ \text{fattore di Zeldovich}}} \underbrace{\exp\left(\frac{\Delta G^*}{k_B T}\right)}_{\text{fattore di Arrhenius}}$$



Tasso di nucleazione : $I = \frac{N}{\tau_x}\frac{1}{V} = \rho\,\frac{1}{\tau_x}$ numero di nuclei critici per unità di tempo e di volume

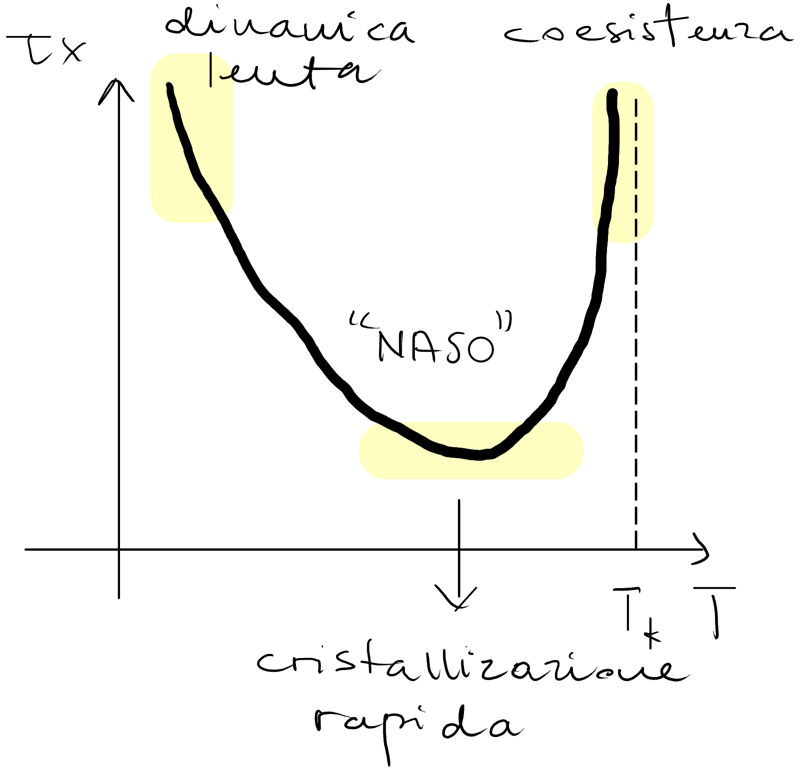
Dipendenza da T di τ_x :

- $D(n^*) \sim D \sim \exp\left(-\frac{\Delta E_d}{K_B T}\right)$
- $T \simeq T_*$: $\Delta g(T) \sim (T - T_*)$

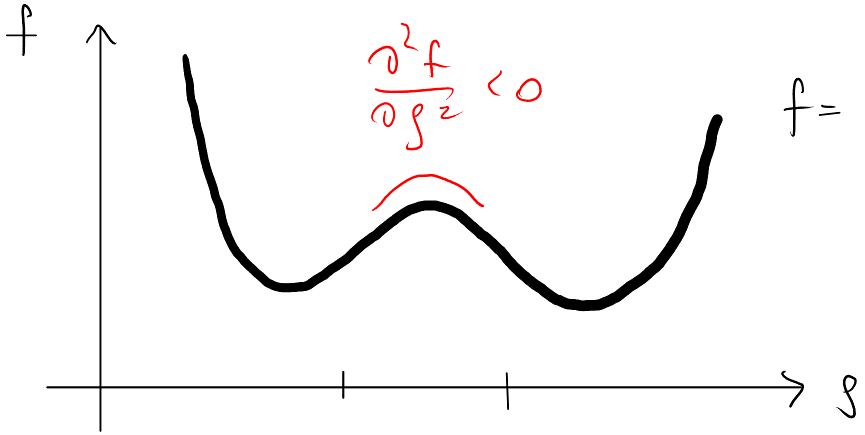
$$\Delta G^* \sim \frac{1}{(\Delta g^v)^2} \sim \frac{1}{\Delta g^2} \sim \frac{1}{(T-T_*)^2}$$

$$\exp\left(\frac{\Delta G^k}{K_B T}\right) \sim \exp\left(\frac{B}{T(T-T_*)^2}\right)$$

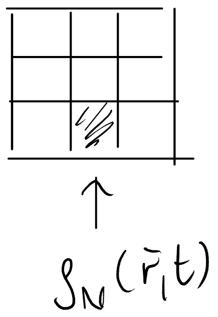
$$\tau_x \sim \exp\left(+\frac{A}{T}\right)\exp\left(+\frac{B}{T(T-T_*)^2}\right)$$



2) Decomposizione spinodale



$f = \frac{F}{V}$



T = cost

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

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

LDA : $\mu[\rho_N(\vec{r},t)]$

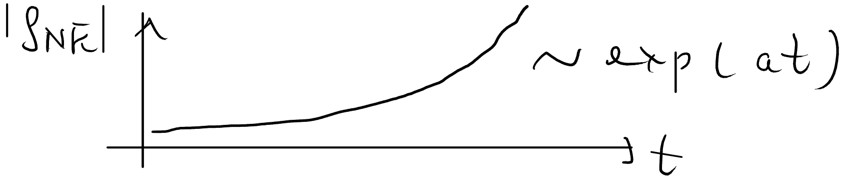
$$= \vec{\nabla}\cdot\left(\underbrace{\frac{L_{NN}}{T}\frac{\partial \mu}{\partial \rho_N}}_{D_c}\vec{\nabla}\rho_N\right)$$

coeff. diff. collettivo

$$\frac{\partial \rho_N}{\partial t} = D_c \nabla^2 \rho_N$$ (eq. diffusione) regime lineare

$$\mu = \left.\frac{\partial F}{\partial N}\right|_T = \left.\frac{\partial f}{\partial \rho_N}\right|_V \Rightarrow \left.\frac{\partial \mu}{\partial \rho_N}\right|_T = \left.\frac{\partial^2 f}{\partial \rho_N^2}\right|_T \Rightarrow D_c < 0\ !$$ instabilità

$$\rho_{N,\vec{k}}(t) = \rho_{N,\vec{k}}(0)\exp\left(+|D_c|\,|\vec{k}|^2 t\right)$$



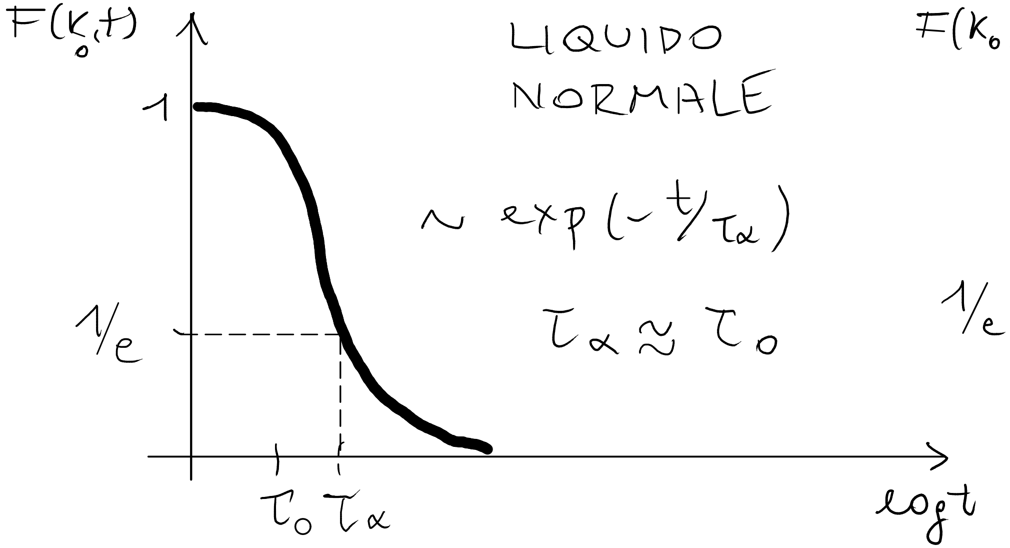
Eq. Cahn-Hilliard : $$\frac{\partial \rho_N}{\partial t} = \frac{L_{NN}}{T}\nabla^2\left[\frac{\partial^2 f}{\partial \rho_N^2}\rho_N - \frac{k_B T\,\xi_0^2}{\rho_N}\nabla^2\rho_N\right]$$ regime non lineare

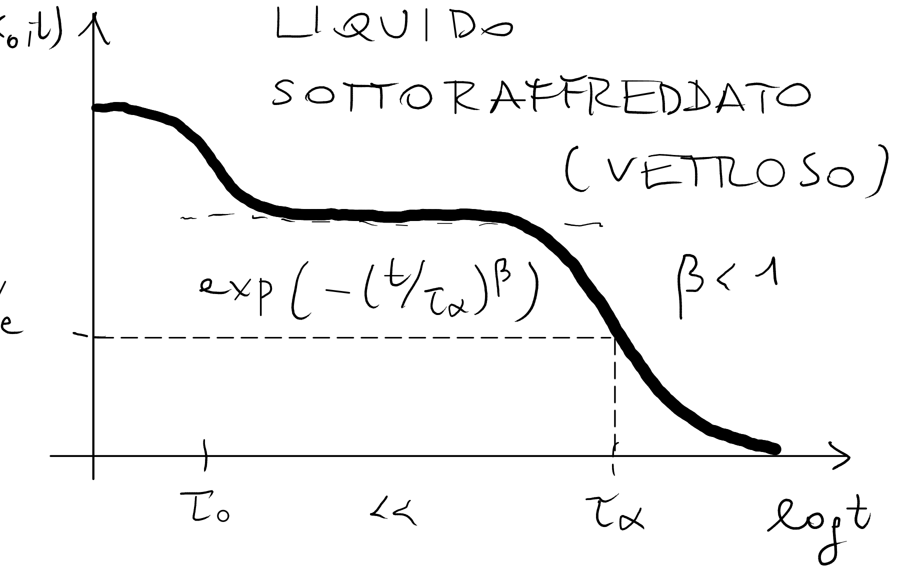
FENOMENOLOGIA DELLA TRANSIZIONE LIQUIDO - VETRO

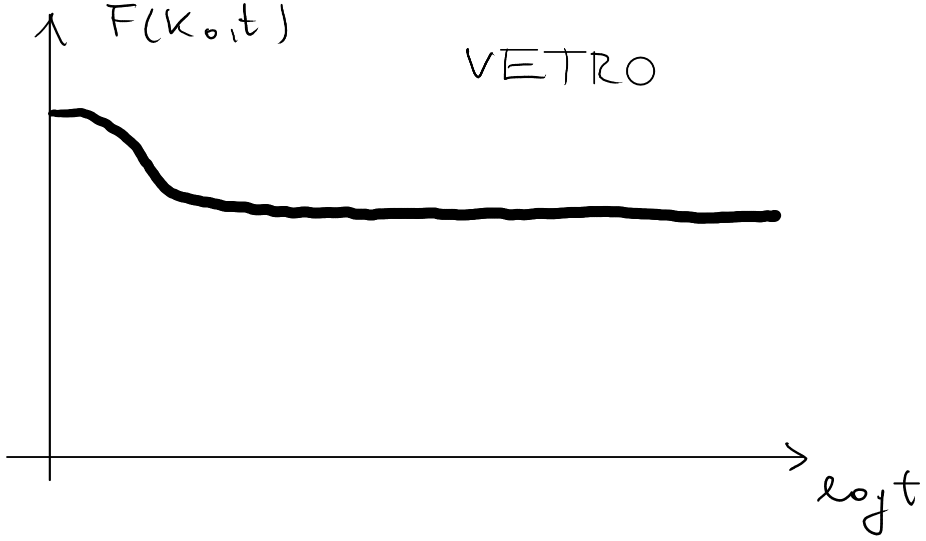
Liquido sottoraffreddato : $T<T_m$ Vetro : → dinamica → scale di tempo

1) Tempo di rilassamento strutturale : τ_α $F(k_0,t) = \frac{1}{N} \langle \rho_{\bar{k}_0}(t) \cdot \rho_{-\bar{k}_0}(0) \rangle$

$k_0 \to$ picco di $S(k)$ $k_0 \approx \frac{2\pi}{\xi_0}$







$$\frac{F(k_0,\tau_\alpha)}{F(k_0,0)} = \frac{1}{e}$$

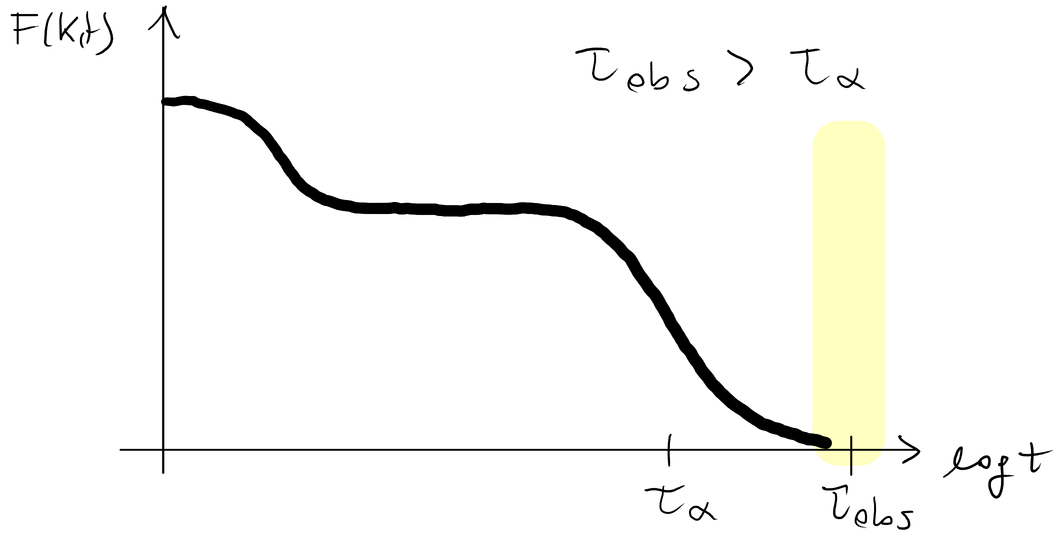
$T \lesssim T_{onset}$

Modello di Maxwell

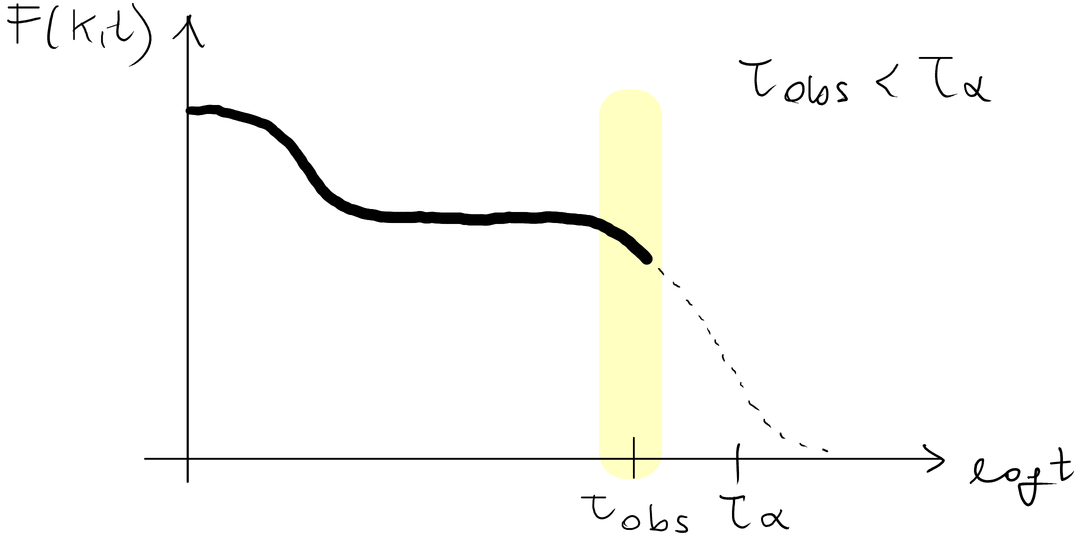
$$\eta = G_\infty \tau_\alpha$$

$$\xrightarrow{\hspace{6cm}} 1/T$$

2) Tempo di osservazione: τ_{obs}



equilibrio metastabile



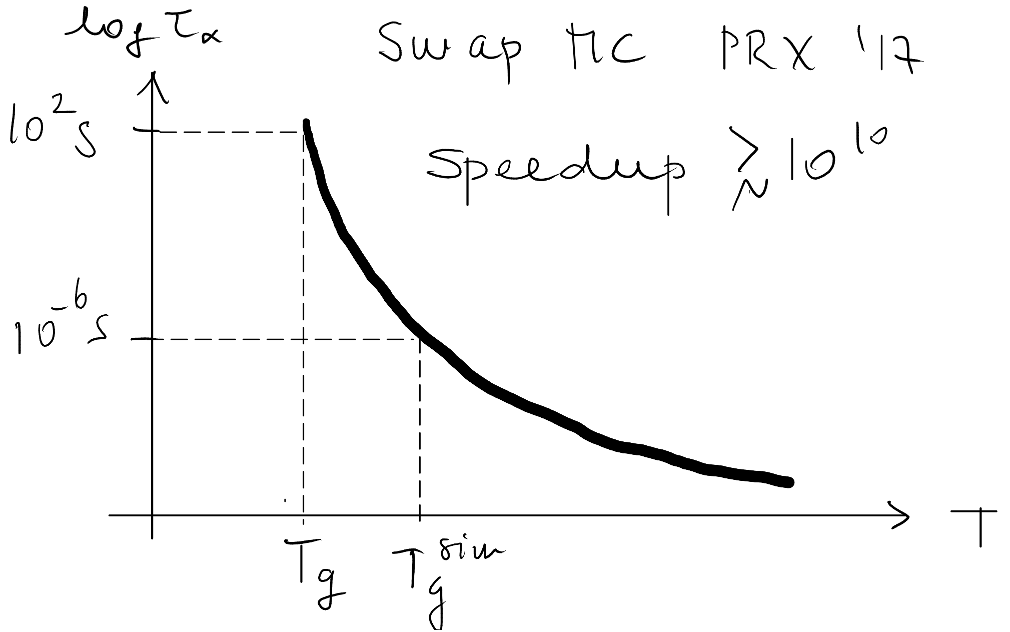
fuori equilibrio

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

Def. operativa della transizione liquido vetro:

$$\eta(T_g) \cong 10^{12}\ \text{Pa}\cdot\text{s} \Rightarrow \tau_\alpha(T_g) \approx 10^{2}\ \text{s}$$

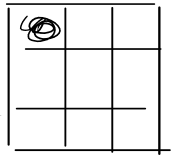
$$\frac{10^{-7}\ \text{s}}{\text{step} \times \text{particella}} : \quad \underset{\text{PBC}}{N=10^{3}} \to \frac{10^{-4}\ \text{s}}{\text{step}} = \frac{10^{-4}\ \text{s}}{10^{-14}\ \text{s}} \sim 10^{10}$$



Swap MC PRX '17

Speedup $\gtrsim 10^{10}$

3) Tempo di nucleazione : τ_x (cf. CNT)



$$\tau_x(N) \sim \frac{1}{N} \exp\left(\frac{\Delta G^*}{k_B T}\right) \frac{1}{D(n^*)}$$

⚠

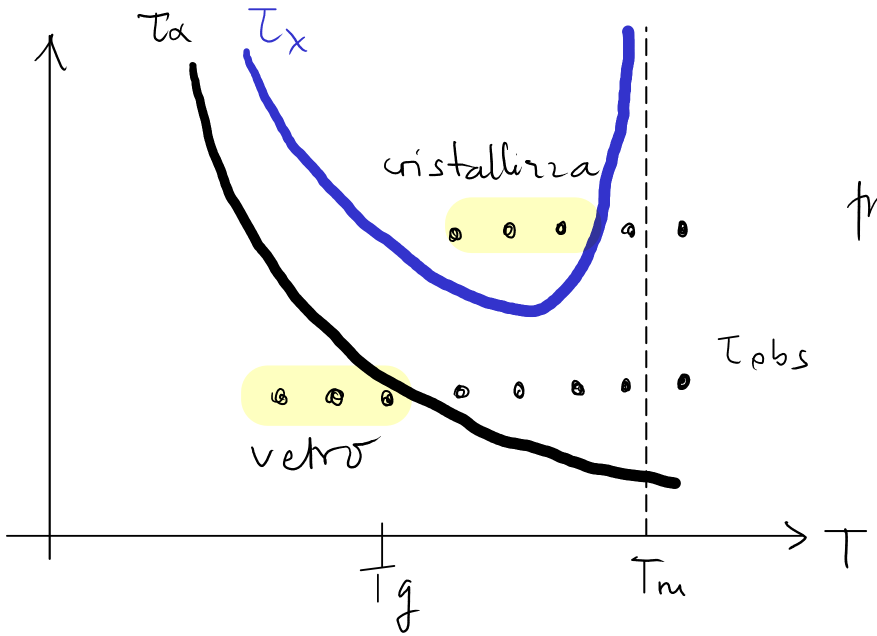
$\exists\, N_0 : \tau_x(N_0) \approx \tau_x$ (dimensioni minime affinché si osservi un solo nucleo cristallino nel sistema)

Diagramma tempo – temperatura – trasformazione (TTT)

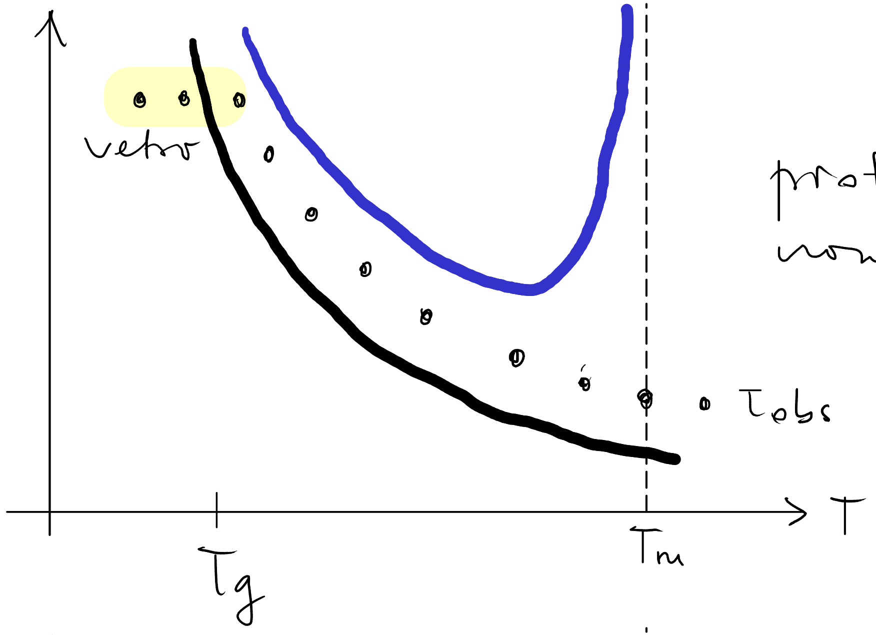
1. rilassare fluttuazioni di densità 2. evitare cristallizzazione $\tau_\alpha \ll \tau_{obs} \ll \tau_x$

buon formatore di vetro

$\tau_x > \tau_\alpha$



protocollo lineare

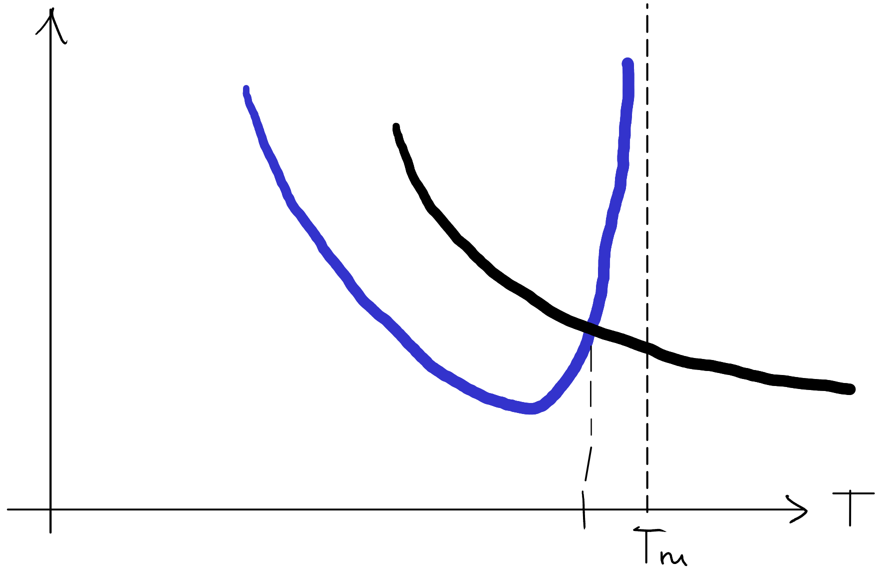


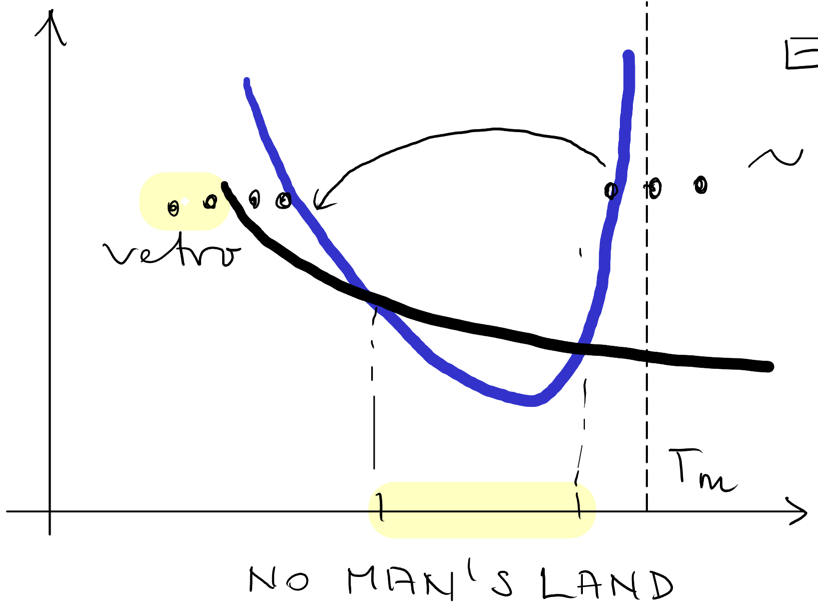
protocollo non-lineare

$\frac{\tau_{obs}}{\tau_\alpha} \simeq cost$

cattivo formatore di vetro

$\tau_x < \tau_\alpha$





Es. H_2O,

~ 160K – 230K

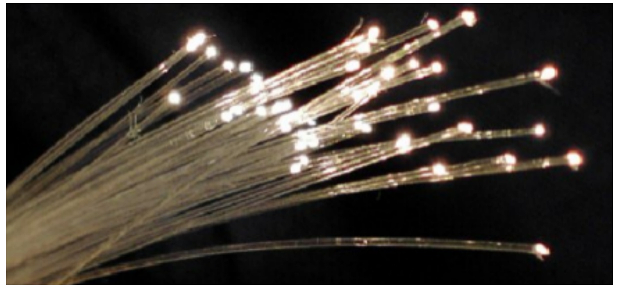
($P = P_{atm}$)

vetri metallici

Formatori di vetro

Ossidi

Silicati : SiO_2 (silice)



B_2O_3

gorilla glass©

Vetro da finestra

SiO_2 : 70%

NaO_2 : 20%

CaO : 10%

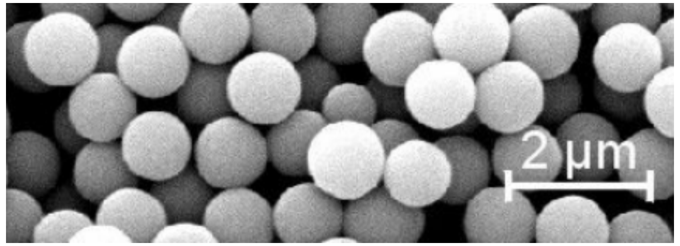
Polimeri

polistirene

PMMA

Metalli

Colloidi

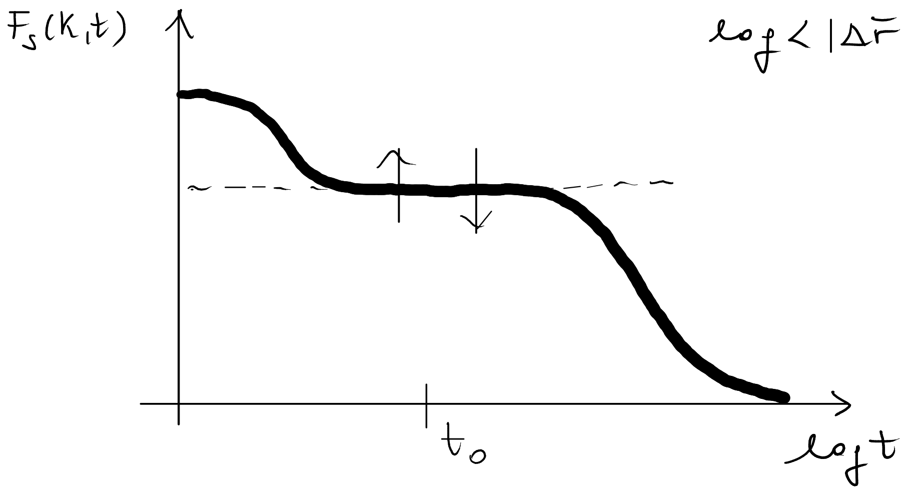


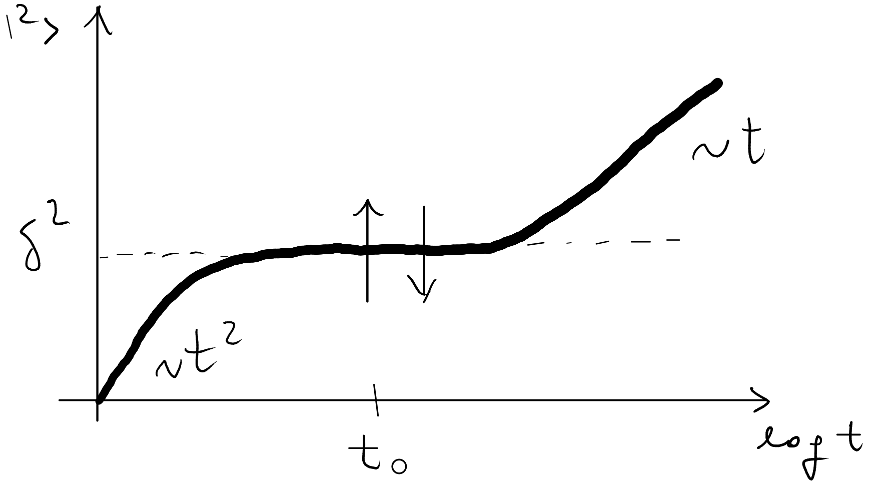
Vetri organici

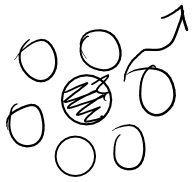
Substance	T_g
SiO_2	1473[g]
B_2O_3	532[m]
nPOH	97[h]
PropGlyc	167[d]
3-MePent	77[f]
3-Br-P	108[a]
glycerol	190[d]
BMPC	243[h]
salol	220[a]
MTHF	91[a]
OTP	246[h]
PropCarb	158[i]
triPhenPhos	203[k]
CKN	333[g]

Richert & Angell JCP 1998

Dinamica







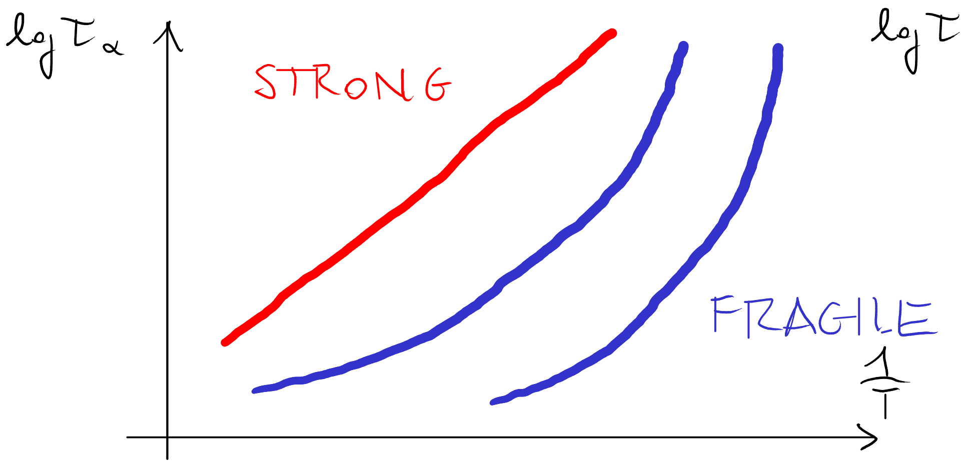
$t < t_0$

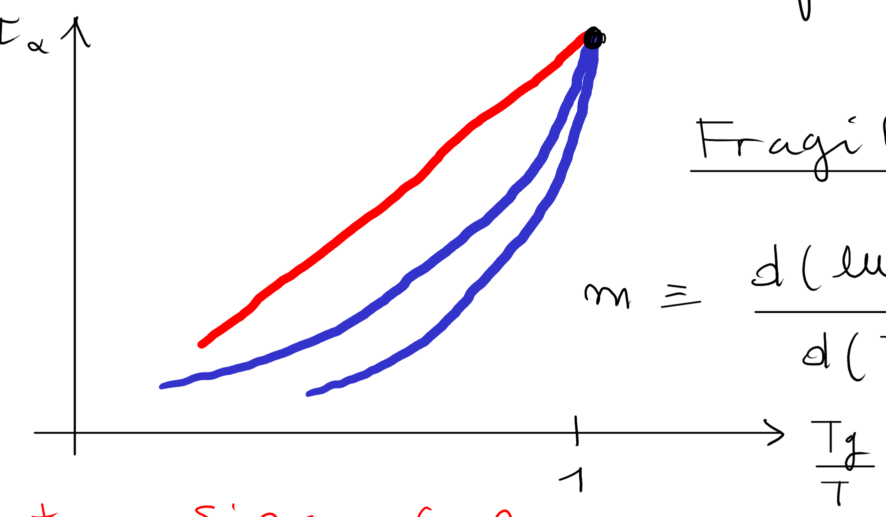
cage effect

es. $\delta^2 \leftrightarrow T$?

es. $F(k,t_0) \leftrightarrow \delta^2$

Classificazione di Angell

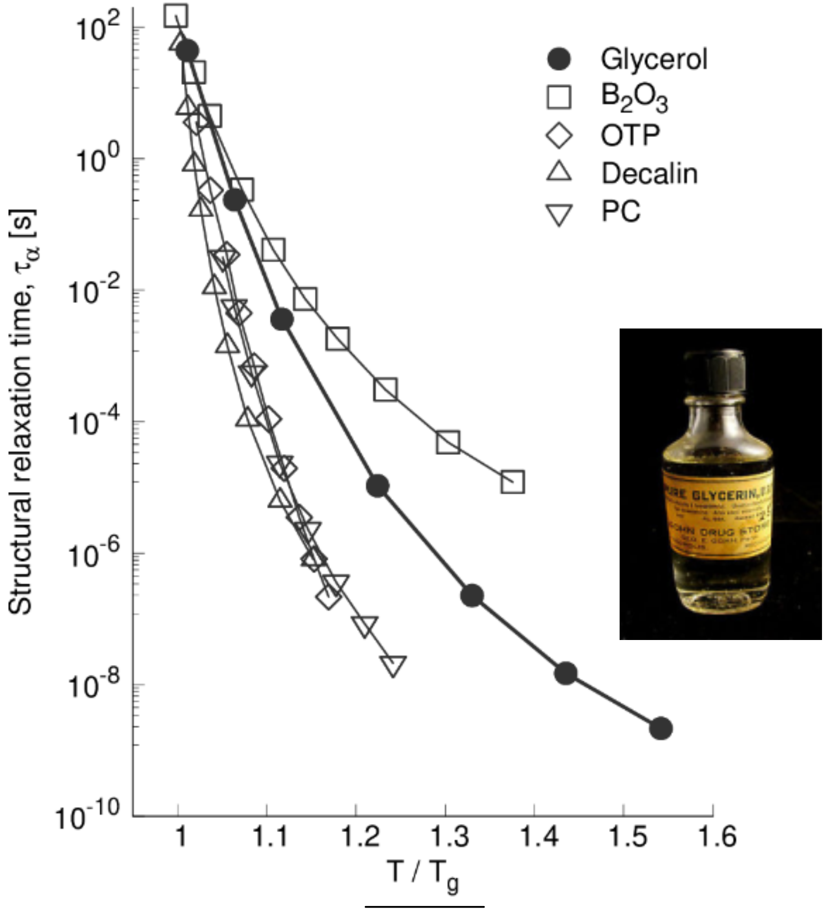




Angell plot

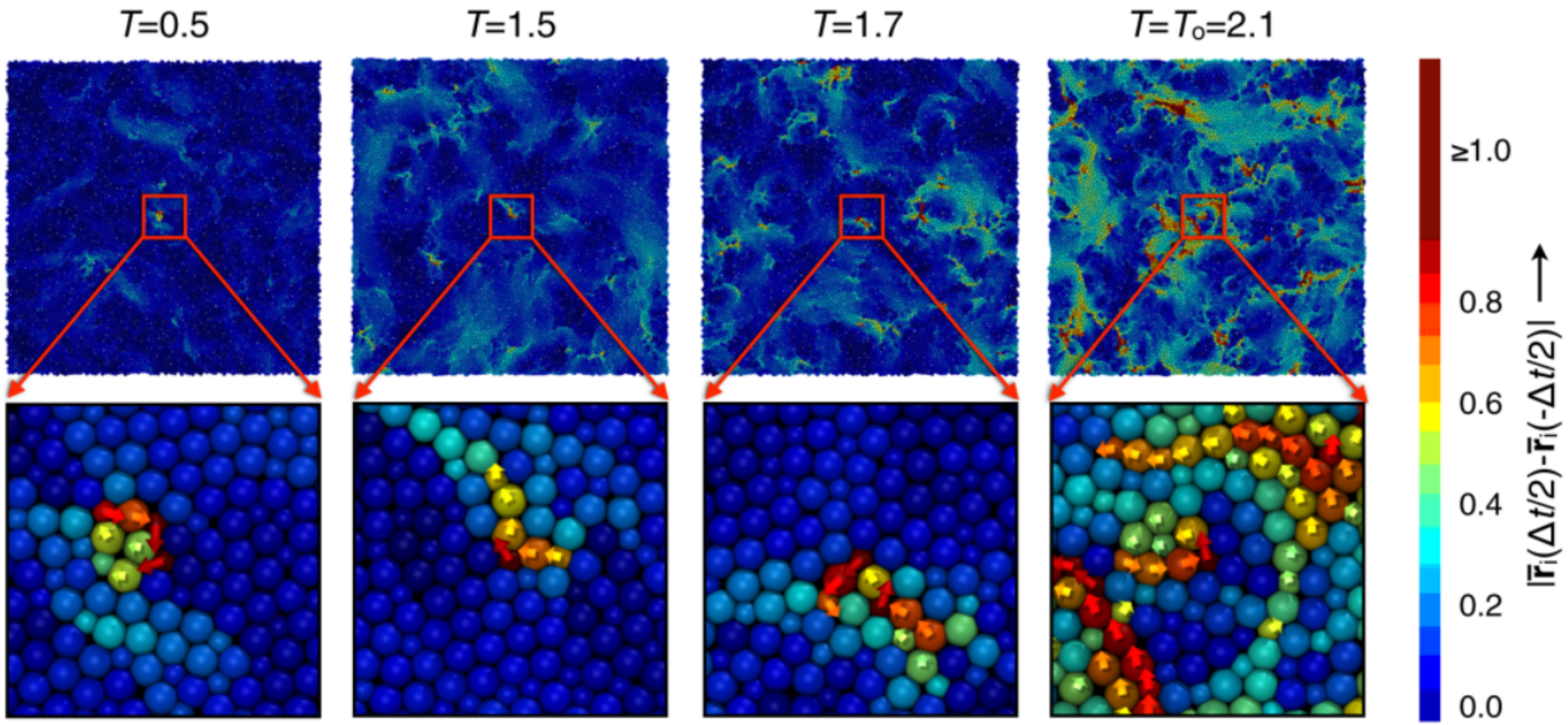
Fragilità :

$$m = \left.\frac{d\left(\ln \tau_\alpha/\tau_0\right)}{d\left(T_g/T\right)}\right|_{T_g}$$



$\tau_\alpha \sim \exp\left(\frac{\Delta E}{k_B T}\right)$ $\Delta E = \text{cost}$ SiO_2, GeO_2

$\tau_\alpha \sim \exp\left(\frac{\Delta E(T)}{k_B T}\right)$ $\Delta E(T) \uparrow$ $T \downarrow$ super-Arrhenius



Keys et al. PRX 2011

Termodinamica

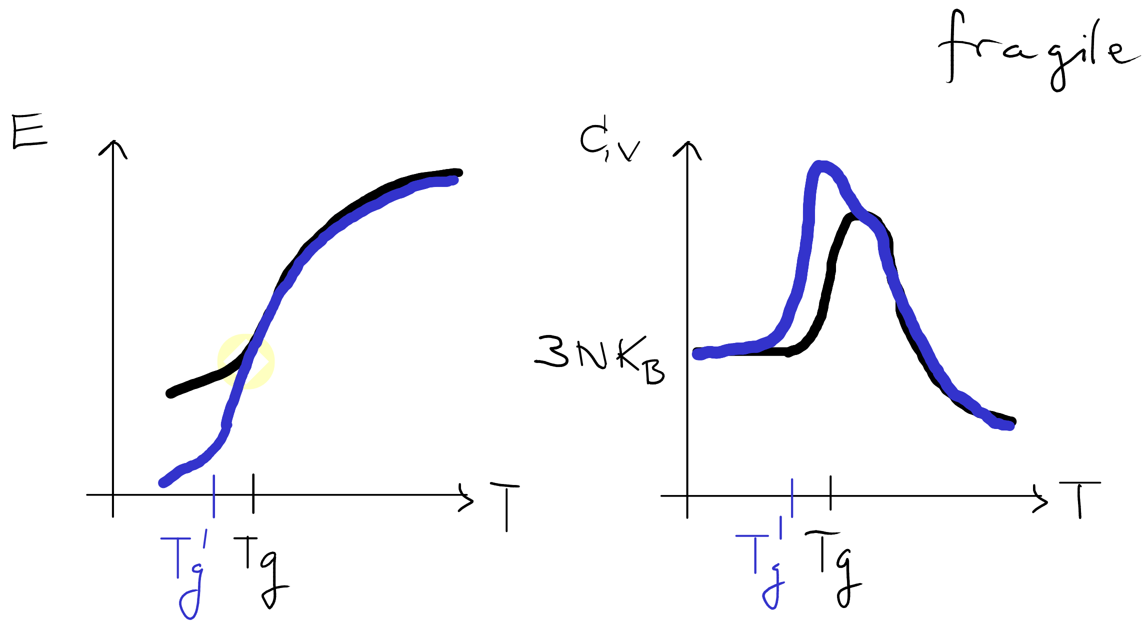
Energia interna E

Capacità termica $C_V = \left.\frac{\partial E}{\partial T}\right|_V$ (V = cost)

Entropia : $dS = \frac{1}{T} dE + \cancel{\frac{P}{T} dV}$

$$S = S(T_0) + \int_{T_0}^{T} \frac{C_V}{T}\, dT \quad \left\langle \begin{array}{l} \text{g.p.} \\ \text{solido armonico} \end{array} \right.$$

↑ V = cost



congelamento dei dof "configurazionali"

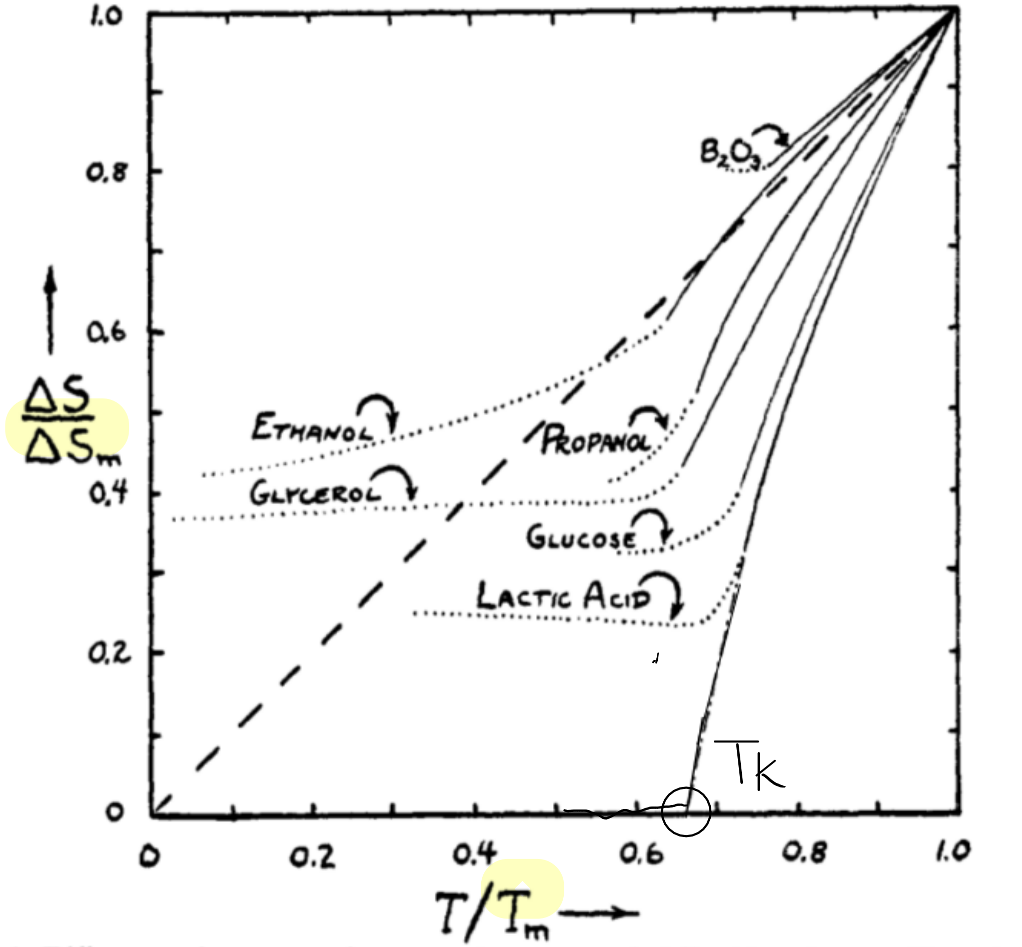
Entropia configurazionale

difetti

- cristallo perfetto : $S = \underbrace{S_{vib}} \;(+ S_c)$
- liquido : $S = ?$
- liquido sottoraffreddato : $S \approx S_c + \underbrace{S_{vib}}$

1948 Kauzmann $\Delta S = S_{liq} - S_{crist} \approx S_c + \underbrace{S_{vib} - S_{crist}}_{\approx 0} \approx S_c$

Paradosso di Kauzmann

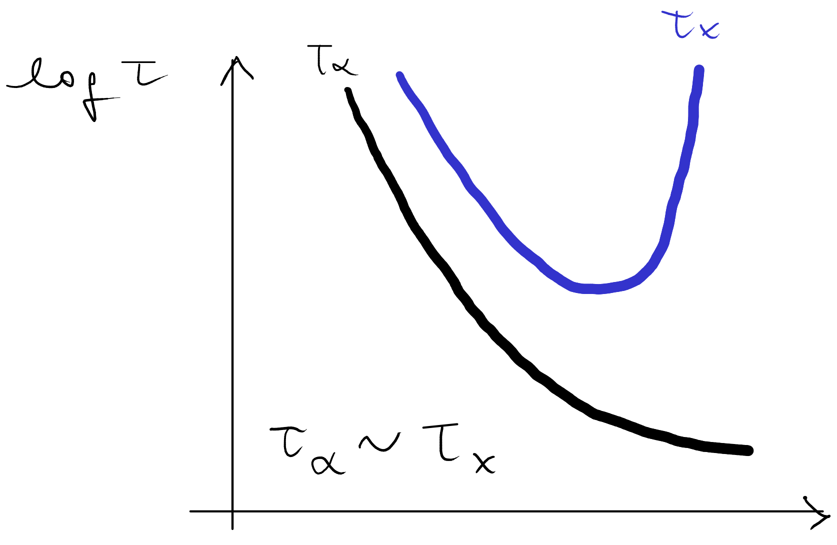


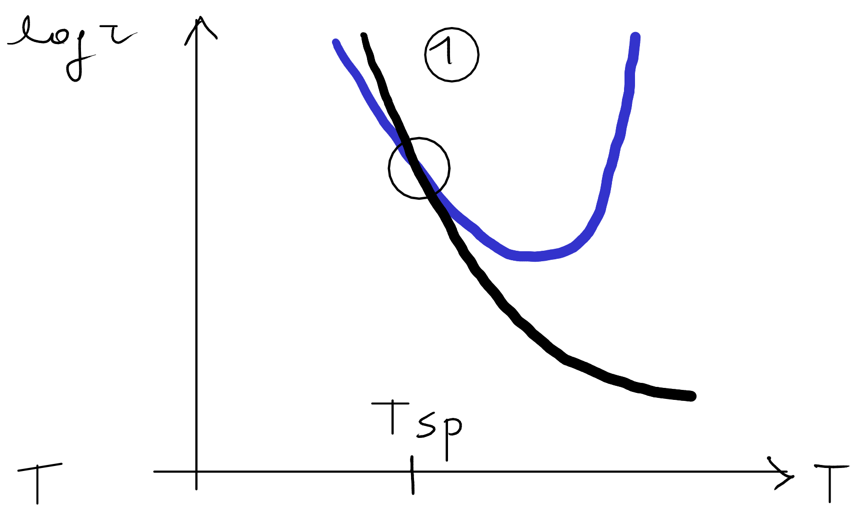
4. Differences in entropy between the supercooled liquid and crystalline ph

Kauzmann Chemical Reviews 1948

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.



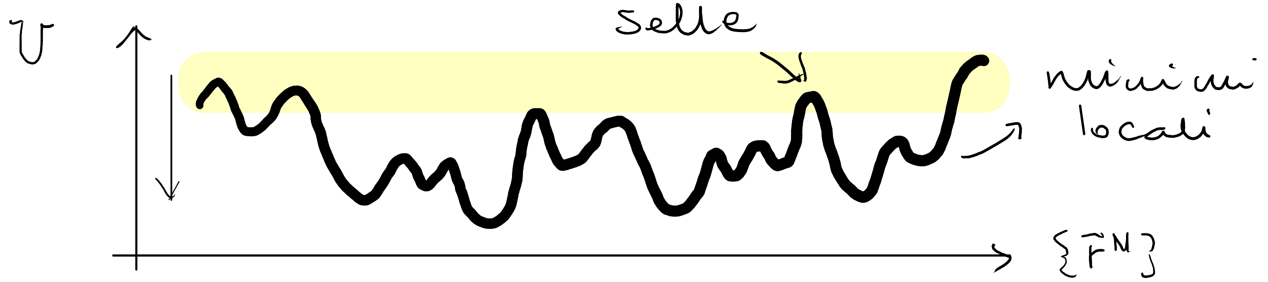


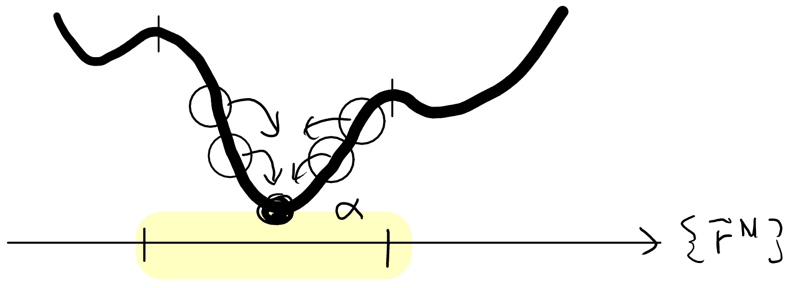
① spinodale cinetica: $T < T_{sp}$ $T_K < T_{sp}$

② Transizione di fase a vetro ideale

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape (PEL)





R_α
bacino di attrazione

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

'80 Stillinger Weber

"struttura inerente"

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

$$\mathcal{H} = \left(\frac{\partial^2 U}{\partial r_{i\alpha}\,\partial r_{j\beta}}\right)_{i,j,\alpha,\beta}$$

Funzione di partizione N,V,T fissati

$$Z(T) = \mathrm{Tr}\left[\exp(-\beta H(\{\vec r^N,\vec p^N\}))\right] \qquad U = U_{m\alpha} + (U - U_{m\alpha})$$

$$= \sum_\alpha \exp(-\beta U_m)\,\frac{1}{\Lambda^{3N}} \int_{R_\alpha} d\vec r^N \exp(-\beta(U - U_m))$$

$u_m = \frac{U_m}{N}$ → densità di stati : $\Omega(u_m) = \sum_\alpha \delta(u_{m\alpha} - u_m)$

$\Omega(u_m)\, du_m$ n. minimi con energia tra u_m e $u_m + du_m$

$$Z(T) \simeq \int du_m\, \Omega(u_m) \exp(-\beta N u_m)\, Z(u_m, T)$$

- $F_{basin}(u_m, T) = -K_B T \ln Z(u_m, T) \quad \rightarrow \quad f_{basin} = \frac{F_{basin}}{N}$

$$\Omega(u_m)\, du_m = \exp(N s_c)\, du_m$$

- $S_c(u_m) = K_B \ln(\Omega(u_m)) \quad \rightarrow \quad s_c = \frac{S_c}{N}$

$$Z(T) = \int du_m \exp\left[-\beta N (u_m + f_{basin} - T s_c)\right]$$

1) Approssimazione armonica

$$f_{basin}(u_m, T) \approx f_{vib}(u_m, T) \qquad \frac{\partial f_{vib}}{\partial u_m} \approx 0$$

2) Approssimazione di punto sella

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

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

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

$$Z(T) \overset{\overset{1)}{\downarrow}}{\approx} \int du_m \exp\left[-\beta N\left(u_m + f_{vib} - Ts_c\right)\right]$$

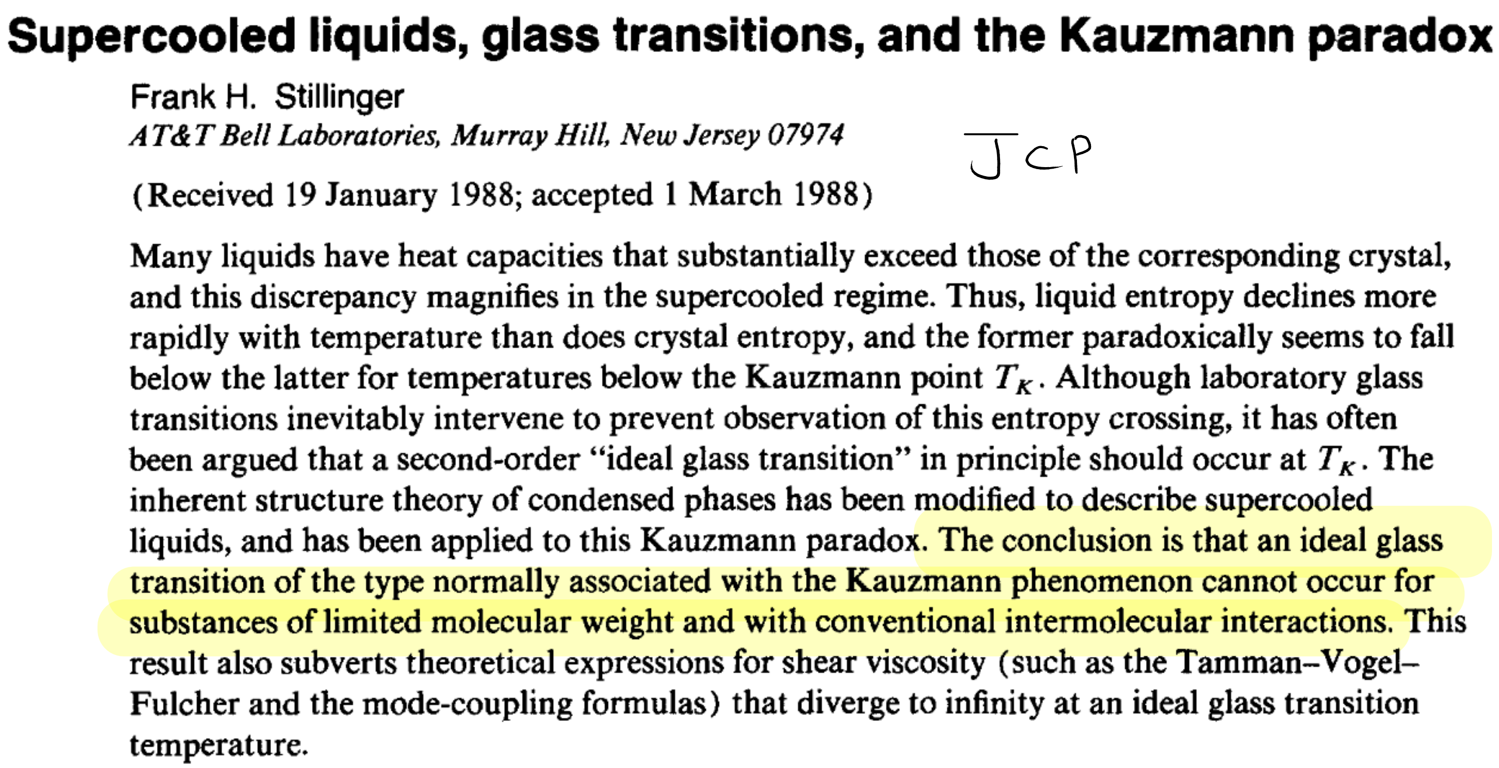
Scelgo u_m tale che $-\beta\,(u_m + f_{vib} - T s_c)$ sia massimo !

$$\left\{ \begin{aligned} & Z(T) \overset{2)}{\underset{\downarrow}{\approx}} A(N)\,\exp\left[-\beta N\,(u_m + f_{vib} - T s_c)\right] \\ & -1 - \underset{\approx 0}{\frac{\partial f_{vib}}{\partial u_m}} + T\,\frac{\partial s_c}{\partial u_m} = 0 \quad \Rightarrow \quad \frac{\partial s_c}{\partial u_m} = \frac{1}{T} \end{aligned} \right.$$

Paradosso di Kauzmann :

① $S_c = 0$ se $u_m \le u_K$

② $\dfrac{\partial S_c}{\partial u_m} = \dfrac{1}{T_K}$ es. Landscape gaussiano



Supercooled liquids, glass transitions, and the Kauzmann paradox

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

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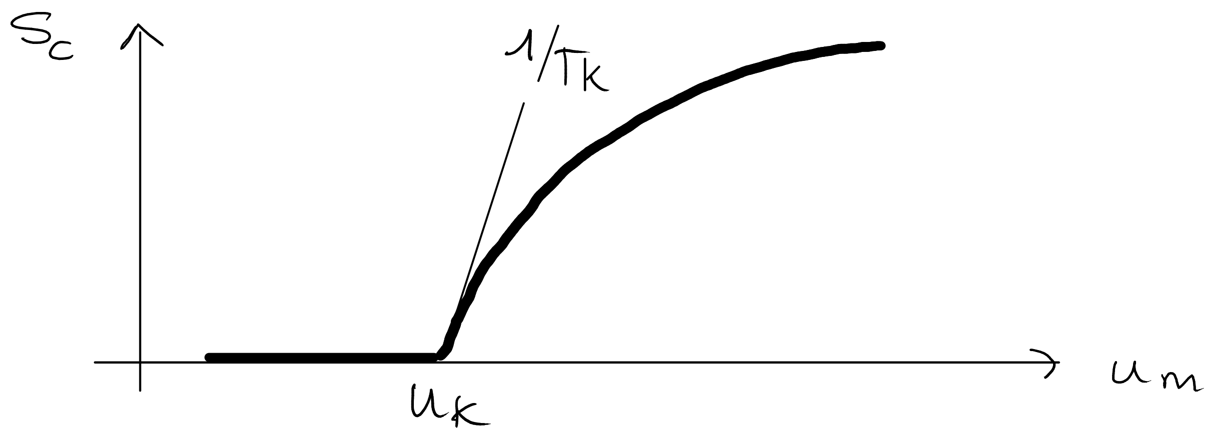
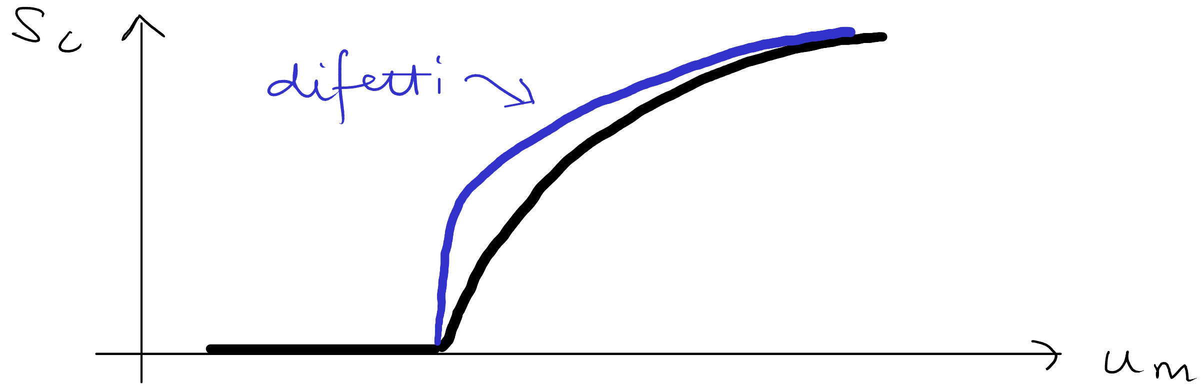
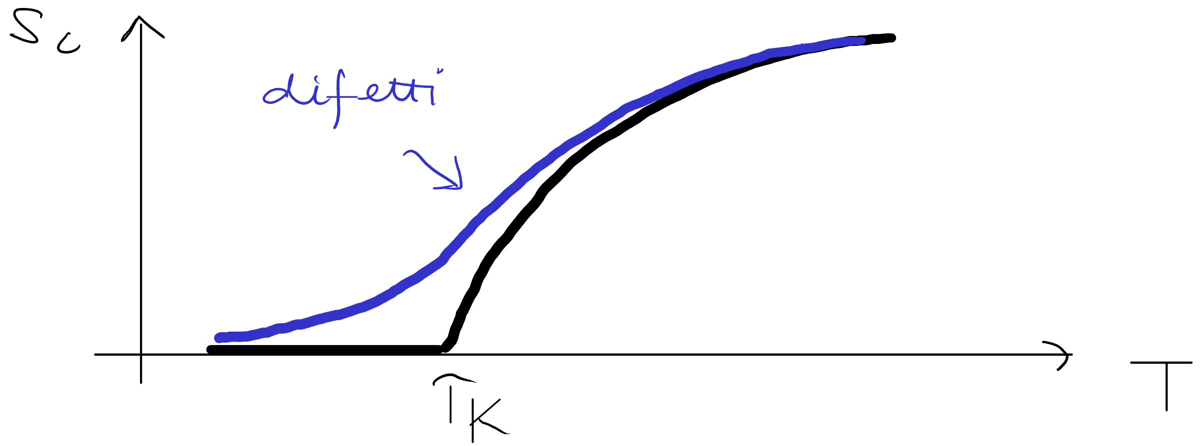
Many liquids have heat capacities that substantially exceed those of the corresponding crystal, and this discrepancy magnifies in the supercooled regime. Thus, liquid entropy declines more rapidly with temperature than does crystal entropy, and the former paradoxically seems to fall below the latter 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.

JCP

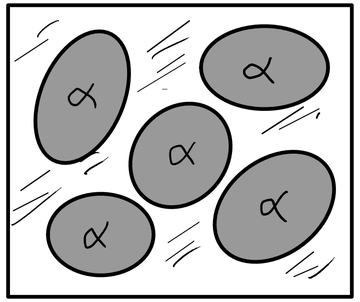






Modello di Adam e Gibbs 1965

CRR ≡ cooperatively rearranging regions



N : n. particelle

n : n. particelle in CRR

α : n. stati per CRR

N. di stati accessibili

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

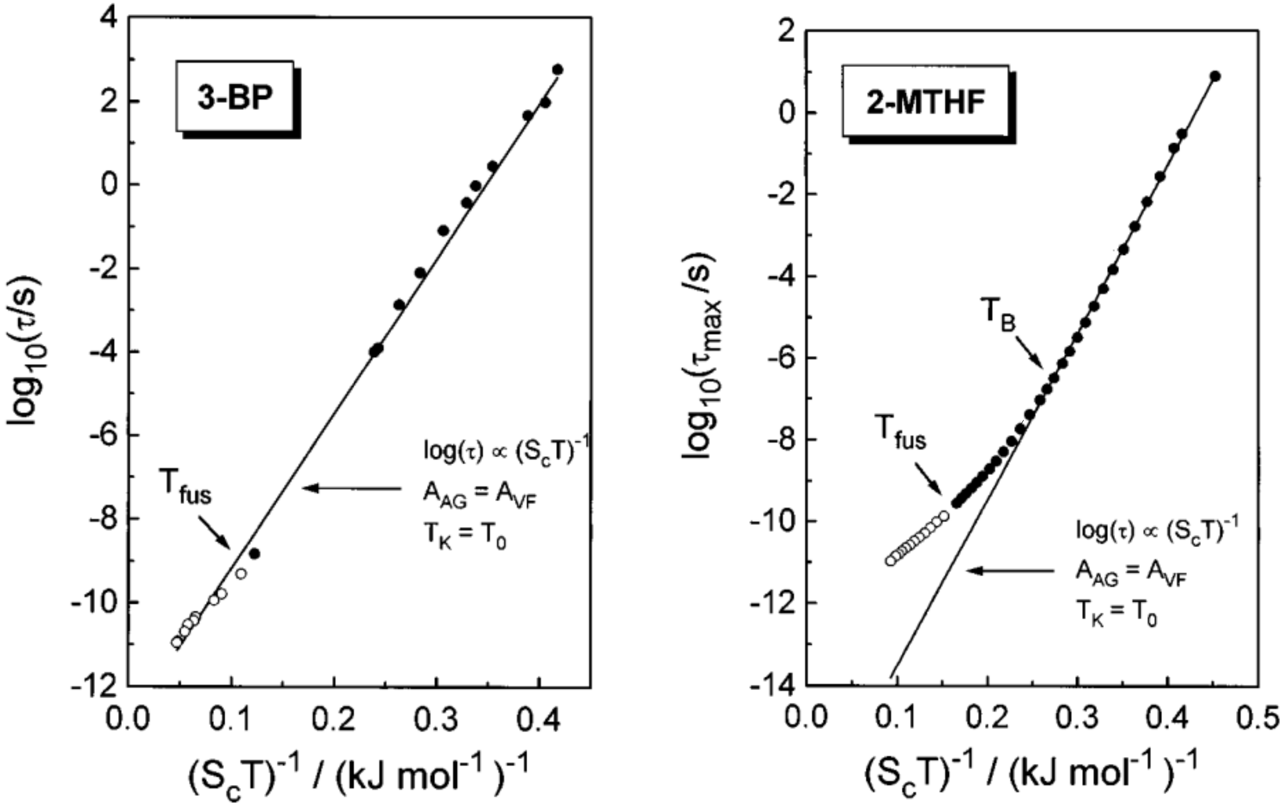
Entropia configurazionale

$$S_c = \frac{1}{N} K_B \ln \Omega = \frac{K_B}{n} \ln \alpha \sim \frac{1}{n}$$

Dinamica attivata relazione Adam-Gibbs

$$\tau_\alpha = \tau_0 \exp\left(\frac{\Delta E}{K_B T}\right) \underset{\uparrow}{=} \tau_0 \exp\left(\frac{A}{T S_c}\right) \swarrow$$

$$\Delta E \sim n \sim \frac{1}{S_c}$$



Richert & Angell JCP 1998

Per $T \approx T_K$ transizione ideale

$$S_c \approx \frac{1}{T_K}(T - T_K)$$

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

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

Teoria mode-coupling

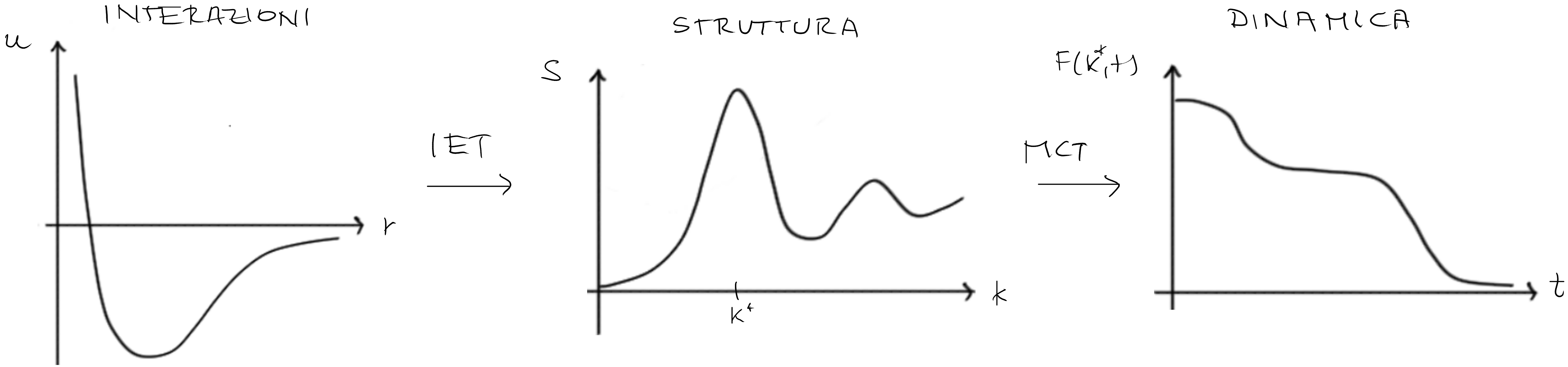
Formalismo dell' operatore di proiezione (Mori e Zwanzig '60)

'80 Götze + collaboratori

Goals:

1) 2-step relaxation + stretched exponential

2) $\tau_\alpha(T)$: $\exists$ transizione vetrosa ideale?



Eq. del moto esatta per $A(t)$

- osservabili lente : $\rho_{\vec{k}}(t)$, $\vec{J}_{\vec{k}}(t)$
- osservabili veloci

Prodotto scalare : $(A|B) \equiv \langle A B^* \rangle$ $\quad (\sigma \langle \delta A \, \delta B^* \rangle)$

Eq. Langevin generalizzata per A

$$\frac{dA}{dt} = \underset{\substack{\uparrow \\ i\Omega = \frac{\left(\frac{dA}{dt}, A\right)}{(A,A)}}}{i\Omega A(t)} - \int_0^t ds \, \underset{\substack{\uparrow \\ \text{funzione di memoria}}}{M(t-s)} A(s) + \Theta(t) \leftarrow \text{forza stocastica} \quad \underset{=0}{(\Theta(t)|A)}$$

funzione di memoria : $M \sim (\Theta(t)|\Theta)$

$$\frac{dC}{dt} = i\Omega C(t) - \int_0^t ds \, M(t-s) \, C(s) \leftarrow \text{esatta} \qquad C(t) = (A(t)|A)$$

Funzione intermedia di scattering : $F(k,t) = \frac{1}{N} \langle \rho_{\bar{k}}(t) \, \rho_{-\bar{k}}(0) \rangle$

$$\frac{d^2F}{dt^2} + \frac{k_B T k^2}{m S(k)} F(k,t) + \int_0^t ds \, M(k,t-s) \frac{dF}{ds}(k,s) = 0$$

$$M(k,t) = \frac{\rho\, k_B T}{16\,\pi^3 m}\int d\bar{k}'\,\left|V_{\bar{k},\bar{k}-\bar{k}'}\right|^2 F(k,t)\,F(|\bar{k}-\bar{k}'|,t) \qquad M \sim \rho_{\bar{k}_1}(t)\,\rho_{\bar{k}_2}(t)$$

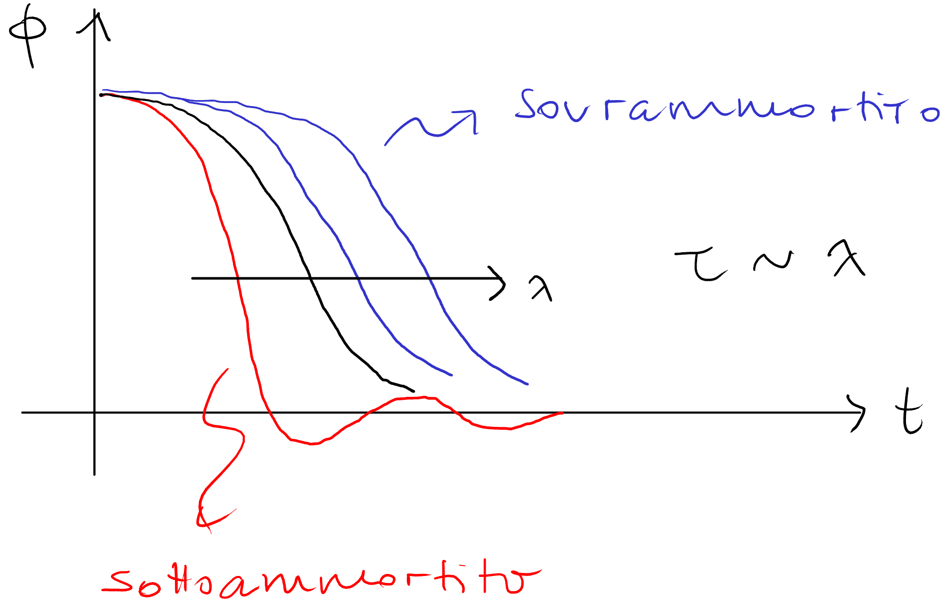
$\uparrow$

vertice $\to S(k)$

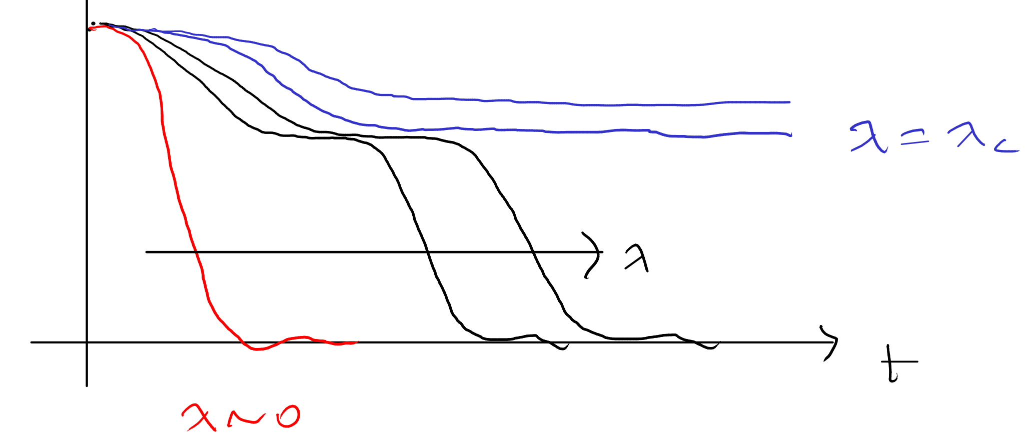
Versione schematica : $\phi(t) = F(k_*,t)$

$$\ddot{\phi} + \Omega^2\phi + \lambda\dot{\phi} = 0 \qquad\qquad \ddot{\phi} + \Omega^2\phi + \lambda\int_0^t ds\,\phi^2(t-s)\,\dot{\phi}(s) = 0$$

$\circlearrowleft$ feedback (es.)



$\tau \sim \lambda$



$f > 0$ se $\lambda \geq \lambda_c$

$f = 0$ se $\lambda < \lambda_c$

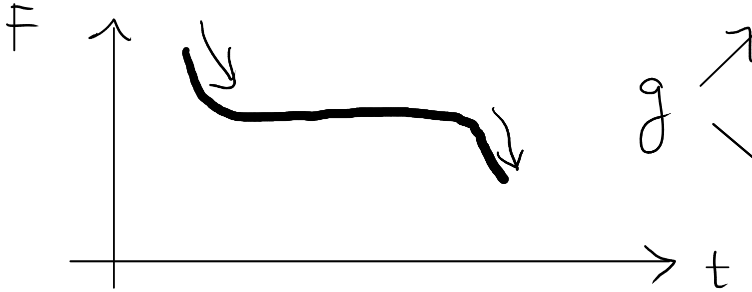
$f = \phi(t \to \infty)$ fattore di non ergodicità

Predizioni generali della MCT

1) **2-step relaxation** $f(k) > 0$ se $T < T_c$

- β - relaxation

$$F(k,t) \approx f(k) + \sqrt{|T-T_c|}\, h(k)\, g(t/\tau_\beta)$$



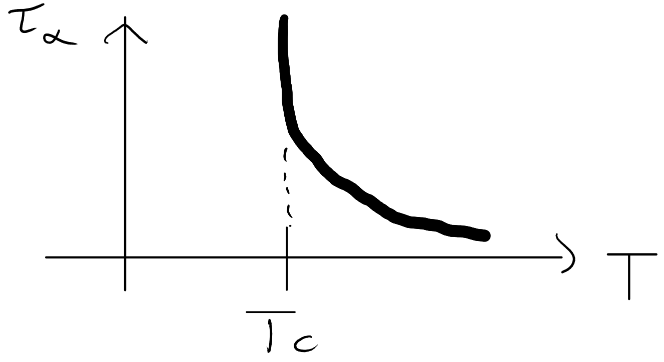
$$g \begin{cases} \nearrow (t/\tau_\beta)^{-a} \\ \searrow (t/\tau_\beta)^{b} \end{cases}$$

- α - relaxation

$$F(k,t) \approx \exp\left[-(t/\tau_\alpha)^\beta\right] \qquad \beta \sim 0.6-0.7 \qquad k \to \infty \text{ esatta}$$

2) **$\tau_\alpha(T)$** legge di potenza

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



3) $D, \eta, \dots$

Verifica predizioni della MCT

miscela binaria
Kob-Andersen

$T_{onset} \sim 0.8-1.0$

$T_c^{(pp)} = 0.92$

$T_g^{(sim)} = 0.4$

1) Da "principi primi" $(S(K) \to F(K,t))$

T_c è troppa alta (il sistema è ancora liquido)

2) Fit : T_c, γ, a, b parametri liberi

$T_c^{(fit)} \approx 0.43$ per miscela Kob-Andersen

funziona abbastanza bene

$$T_{onset} > T_c > T_g > T_K$$

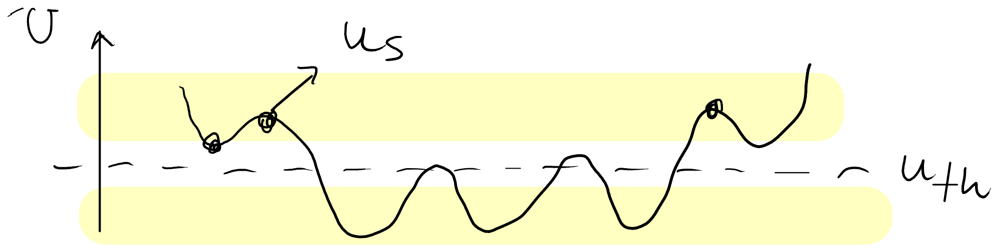
T_{onset} ↑ crossover

T_c ↑ evitata ↓ processi attivati

T_g ↑ convenzionale

T_K ↖ evitata ↓ difetti

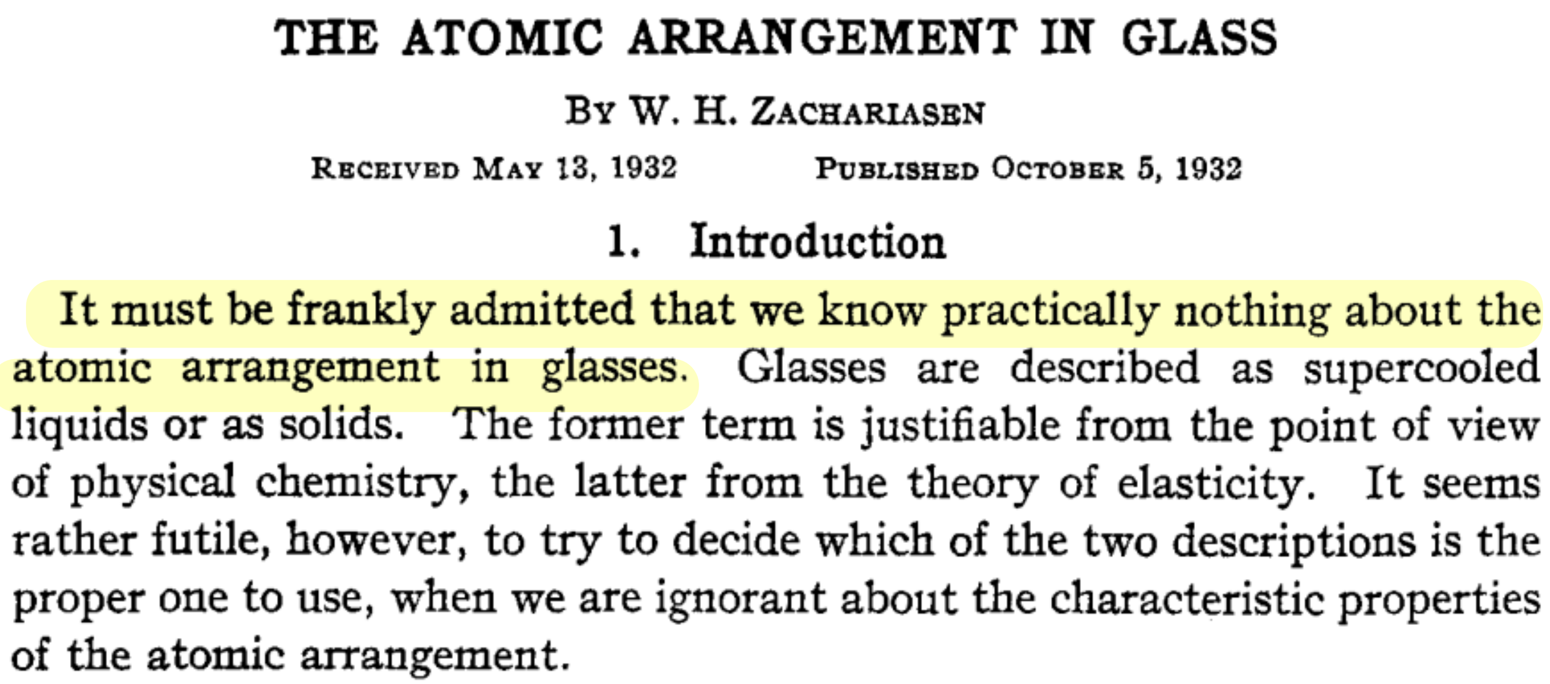
cf. review di Cavagna



$u_s > u_{th} \Rightarrow$ MCT

$u_s < u_{th} \Rightarrow$ dinamica attivata

STRUTTURA DEI VETRI



THE ATOMIC ARRANGEMENT IN GLASS

BY W. H. ZACHARIASEN

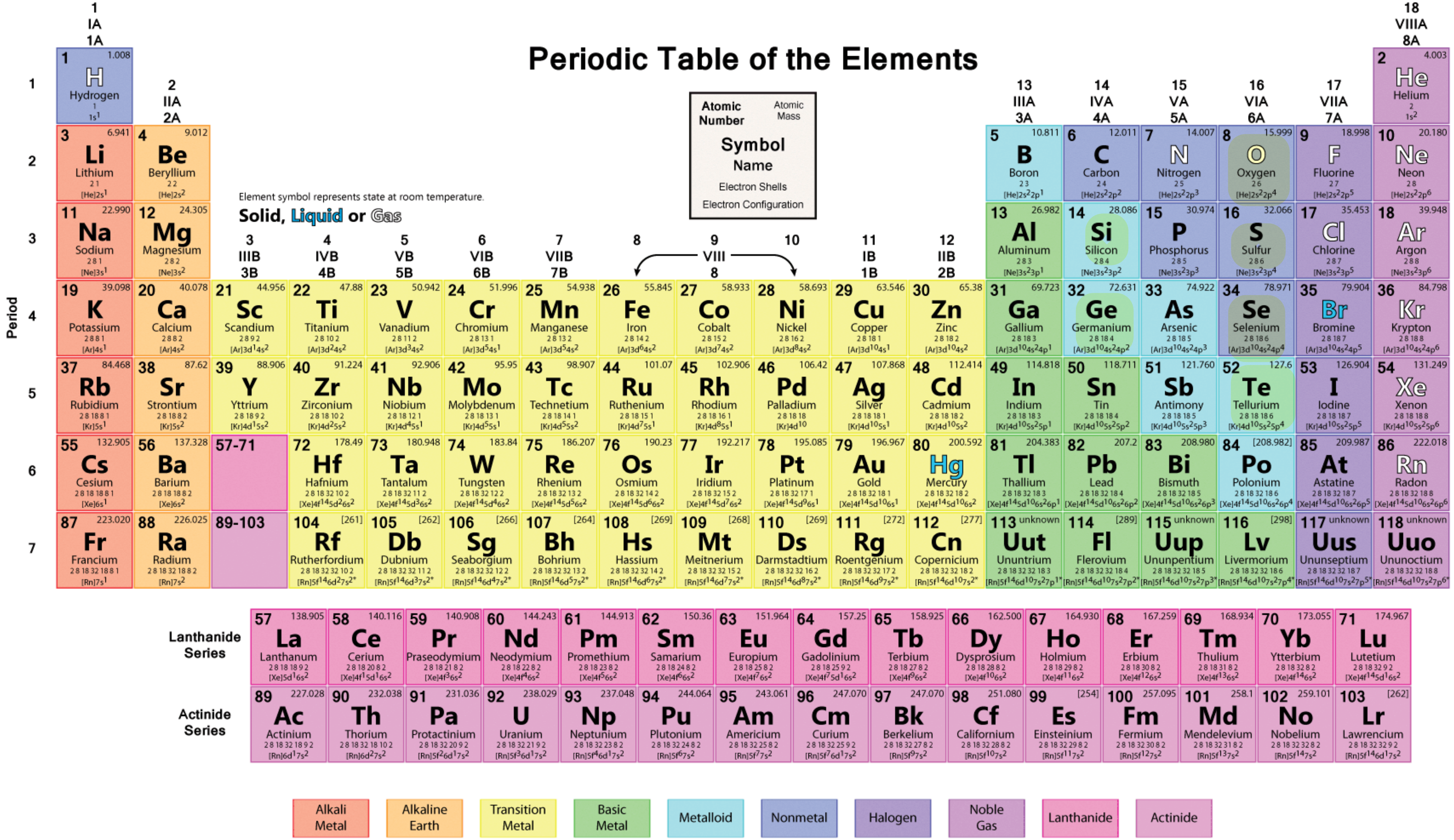
RECEIVED MAY 13, 1932 PUBLISHED OCTOBER 5, 1932

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.

- network-forming glasses → SiO_2, GeO_2, ...
- close-packed glasses → metalli, colloidi, 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	9 VIII 8	10	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 $[Rn]5f^{14} 6d^{10} 7s^2 7p^{6*}$

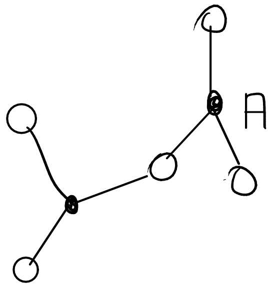
Lanthanide Series	57 138.905 La Lanthanum 2 8 18 18 9 2 $[Xe]5d^1 6s^2$	58 140.116 Ce Cerium 2 8 18 20 8 2 $[Xe]4f^1 5d^1 6s^2$	59 140.908 Pr Praseodymium 2 8 18 21 8 2 $[Xe]4f^3 6s^2$	60 144.243 Nd Neodymium 2 8 18 22 8 2 $[Xe]4f^4 6s^2$	61 144.913 Pm Promethium 2 8 18 23 8 2 $[Xe]4f^5 6s^2$	62 150.36 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 → $A_m O_n$ → Zachariasen

calcogenuri → S, Se, Te + Ge, As

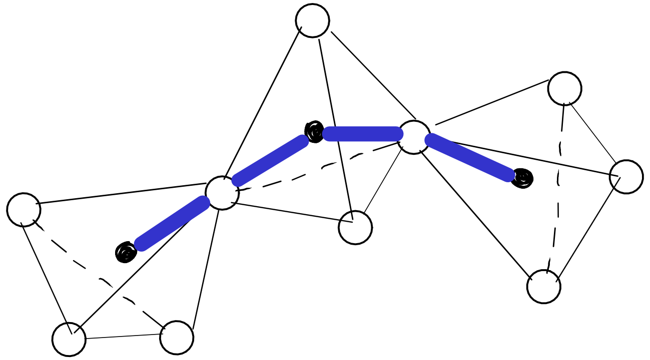


z_A } numero di

z_O } coordinazione

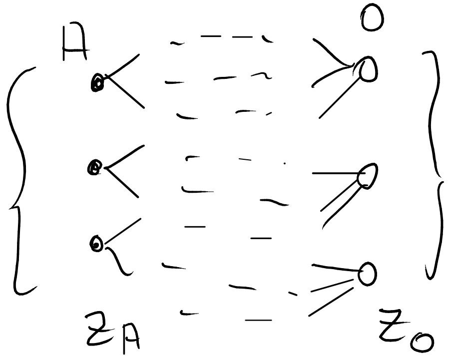
x_A } concentrazioni

x_O } chimiche



Es. Dati z_A, z_O cerco x_A, x_O tali che tutti i legami sono saturati.

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



SiO_2 : $z_{Si} = 4$, $z_O = 2$

$$\overset{2}{\cancel{4}} x_{Si} = (1 - x_{Si}) \cancel{2} \qquad 3 x_{Si} = 1$$

$x_{Si} = 1/3$ $x_O = 2/3$

es. : Ge+O, B+O, Ge+Se, As+Se

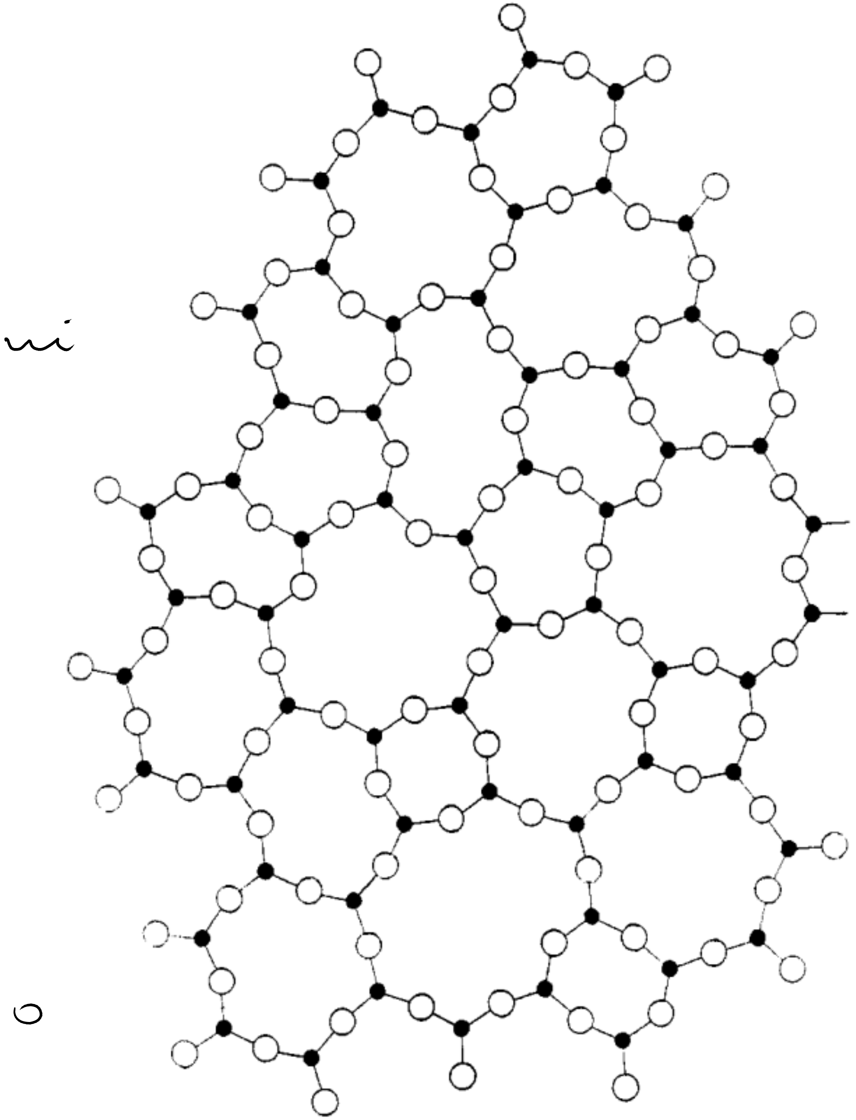
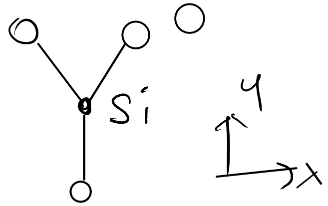
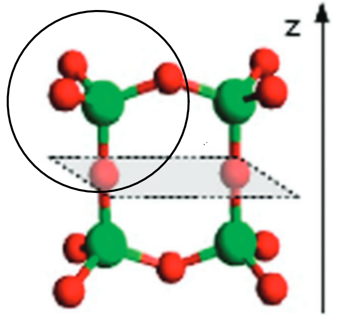


Fig. 1b.

Zachariasen 1932

Silice 2d   es. x_{Si} , x_O ?





Teoria della rigidità

1) Gupta – Cooper (1978 – 1990)
2) Phillips – Thorpe (1979 – 1985)
   → estensioni a T finita

marginal rigidity / isostaticità

criterio di Maxwell (1864)

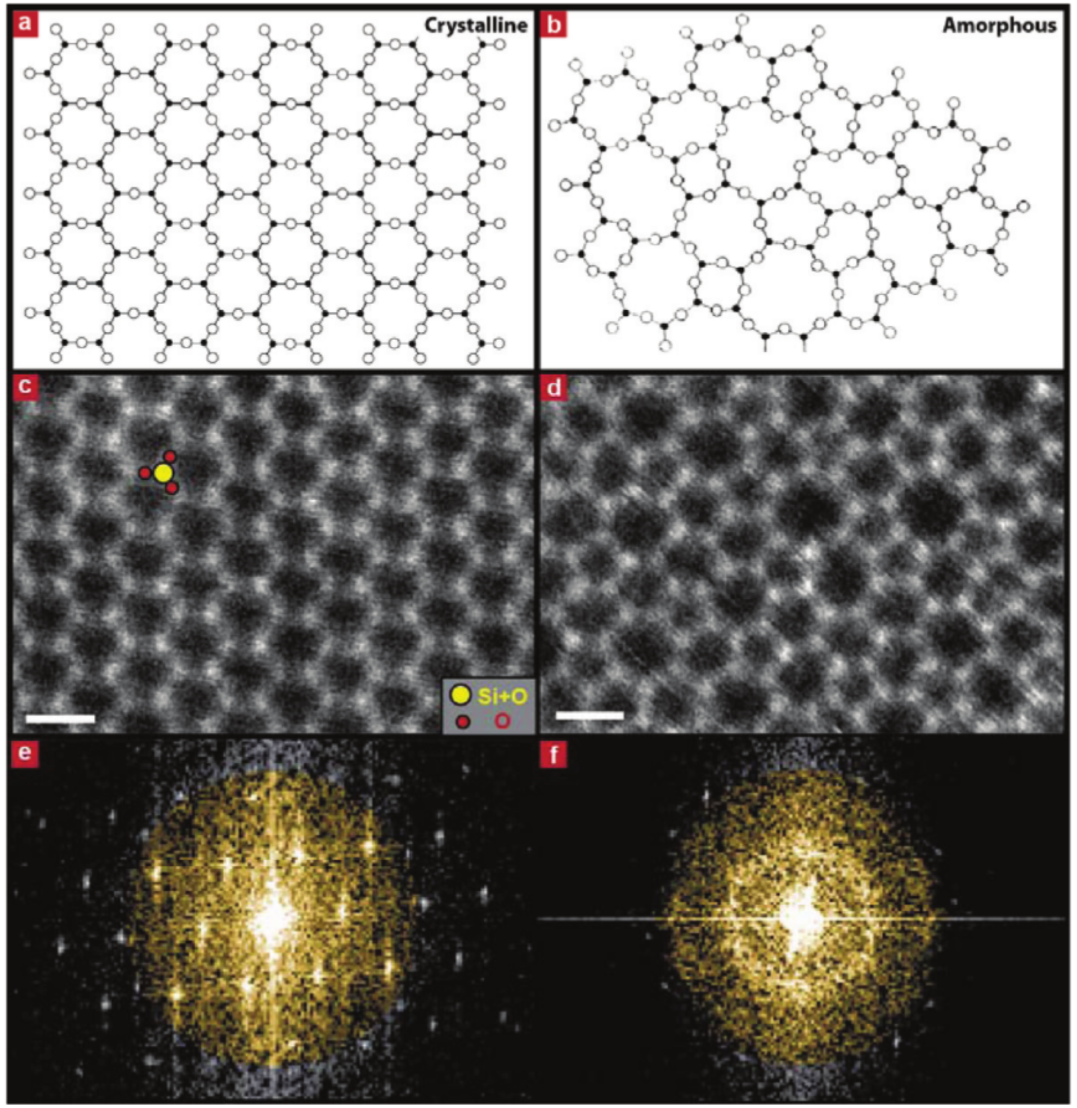
$$\text{n. vincoli} = \text{n. dof}$$

$$N_v = N_{dof}$$

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



$T = 0$ fissiamo legami e angoli , specie $\alpha \rightarrow z_\alpha , x_\alpha$

$$\begin{cases} N_{dof} = 3N \\ N_v = \sum_\alpha \Big\{ \underset{\substack{\uparrow \\ \text{legami}}}{N_\alpha \frac{z_\alpha}{2}} + \underset{\substack{\uparrow \\ \text{angoli}}}{N_\alpha (2 z_\alpha - 3)} \Big\} \end{cases} \qquad \langle z \rangle = \sum_\alpha x_\alpha z_\alpha$$

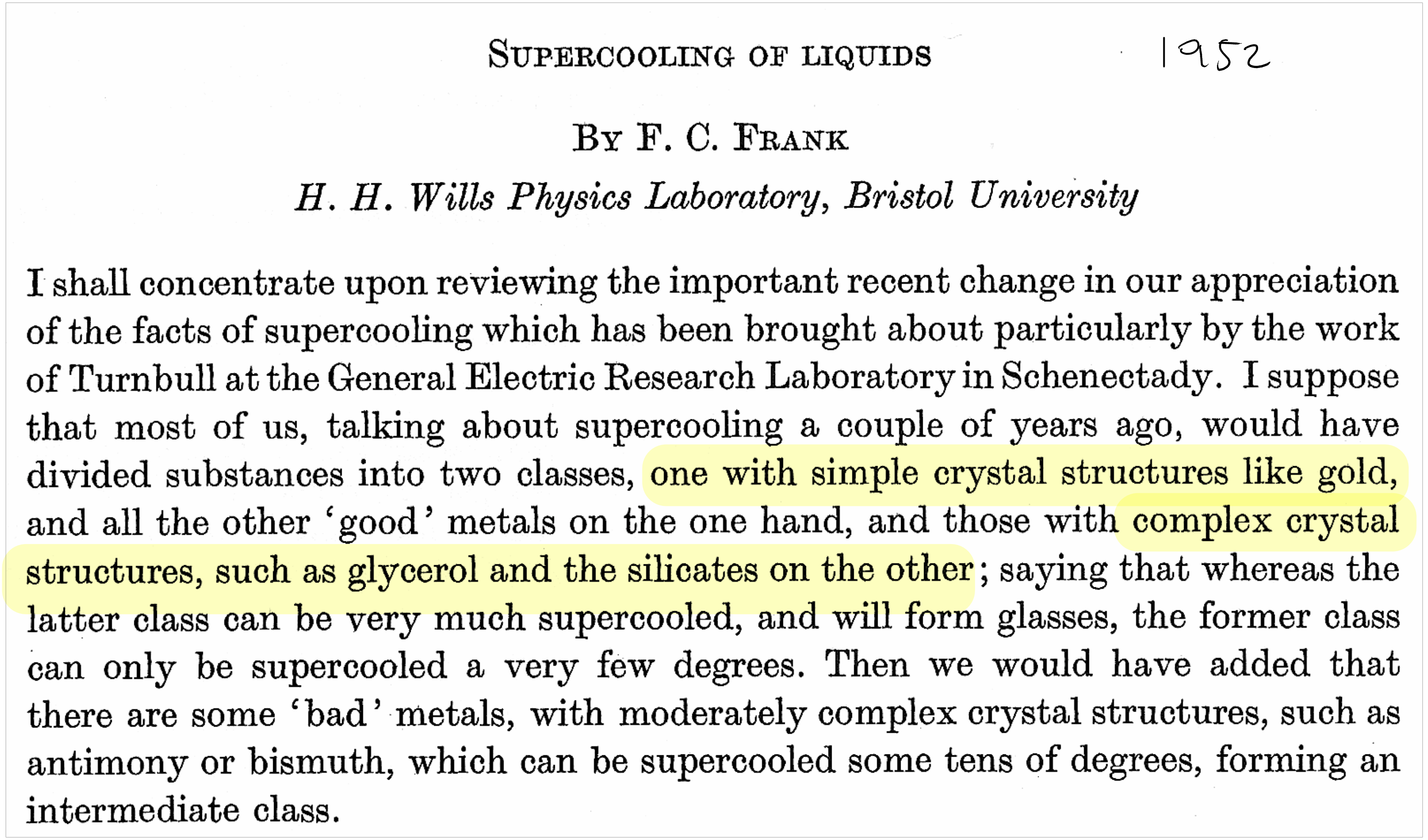
$$\frac{N_v}{N} = \sum_\alpha x_\alpha \left(\frac{z_\alpha}{2} + 2 z_\alpha \right) - 3 \sum_\alpha x_\alpha = \frac{5}{2} \langle z \rangle - 3$$

Criterio Maxwell : $3N = N_v \rightarrow 3 = \frac{5}{2} \langle z \rangle - 3 \rightarrow \frac{5}{2} \langle z \rangle = 6$

$$\Rightarrow \underline{\langle z \rangle = 2.4}$$

SiO_2 : $\langle z \rangle = \frac{1}{3} 4 + \frac{2}{3} 2 = \frac{8}{3} = 2.\overline{6} \gtrsim 2.4$

Close-packed glasses

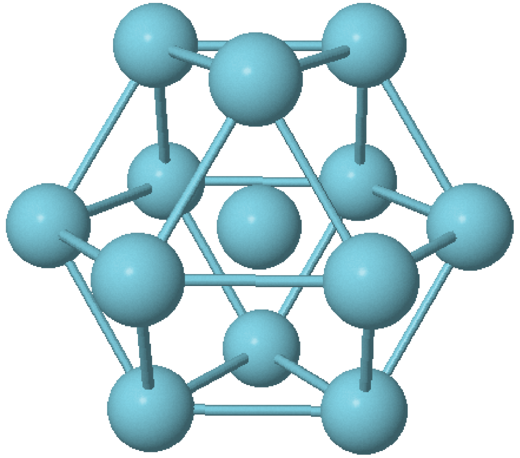


SUPERCOOLING OF LIQUIDS 1952

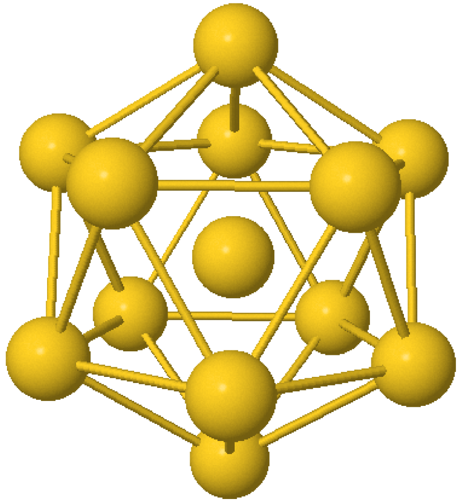
BY F. C. FRANK

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.



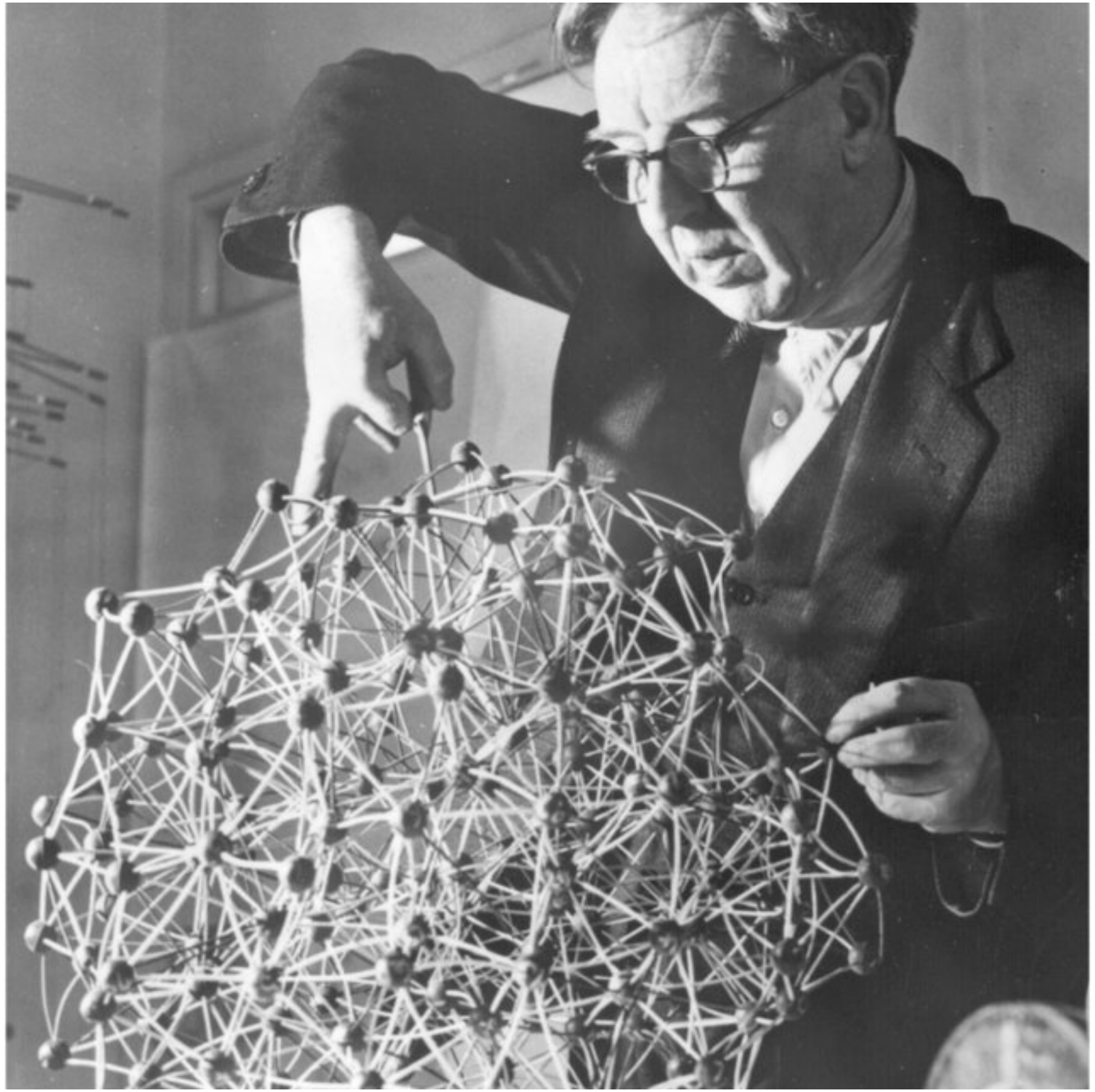
FCC



ICOSAEDRO

$U_{ICO} < U_{FCC}$ 8%

frustrazione geometrica



Bernal 1964

Tassellazione di Voronoi

→ Wigner-Seitz

cella → poliedro

$$\left.\begin{array}{l} f = \text{n. facce} \\ p = \text{n. vertici} \end{array}\right\} \quad \bar{f} = \frac{12}{6-\bar{p}}$$

Segnature:

$(f_3, f_4, f_5, \dots)$

icosaedro $(0, 0, 12)$

Congettura Eulero: $\phi_{FCC} = 0.74$

Random close packing: $\phi_{RCP} \sim 0.68$

Isostaticità: $dN = N\frac{z}{2} \Rightarrow z = 2d$

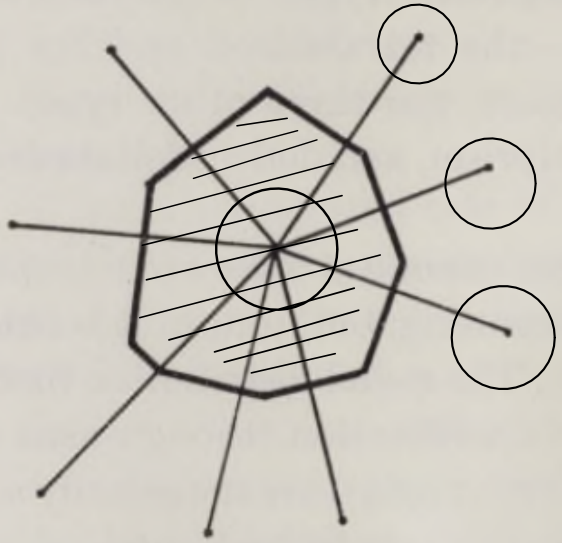


FIGURE 1

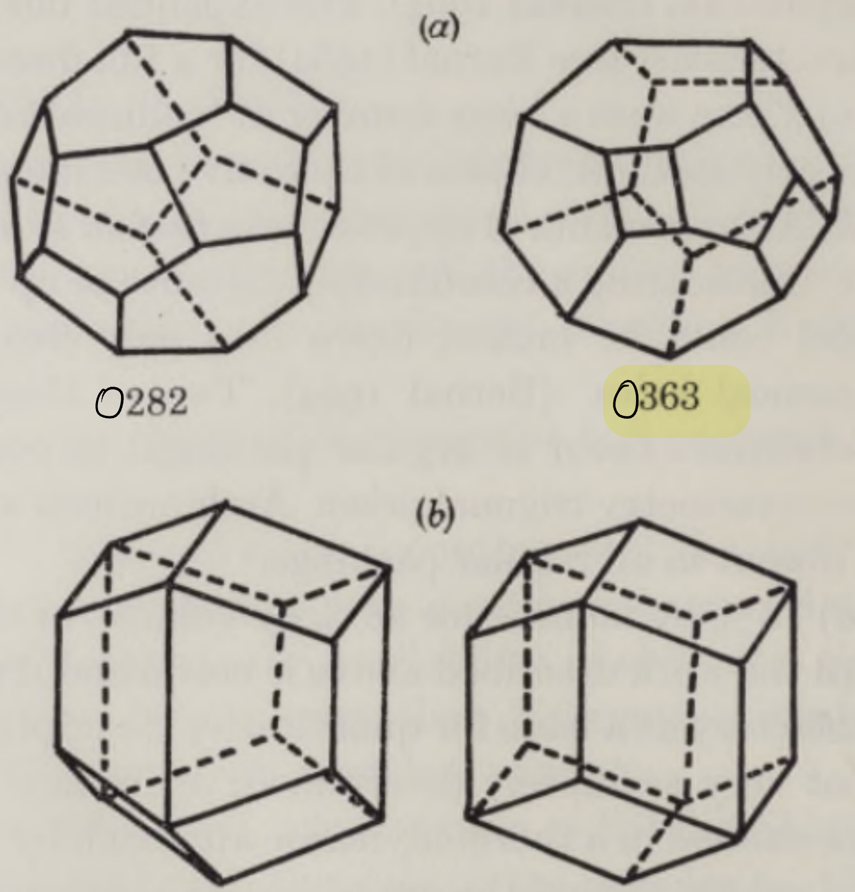


FIGURE 2

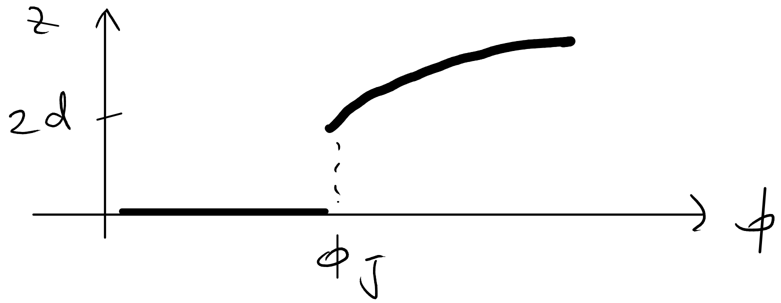
FIGURE 1. Construction of a two-dimensional Voronoi polygon.

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

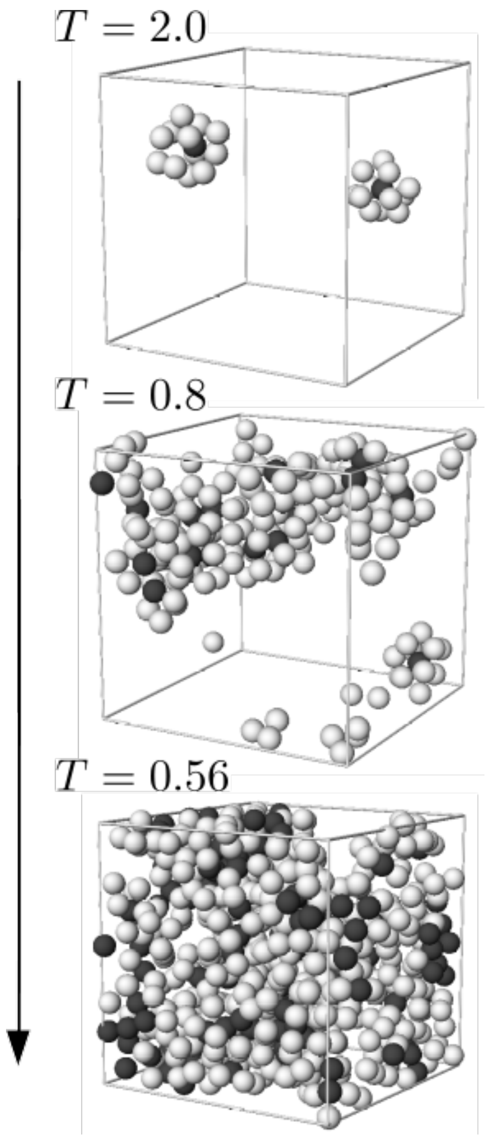
Finney & Bernal 1972

Jamming !

$$\begin{cases} z = 0 & \phi < \phi_J \\ z = 2d + A(\phi - \phi_J)^{1/2} & \phi \geq \phi_J \end{cases}$$



Strutture localmente favorite (LFS)

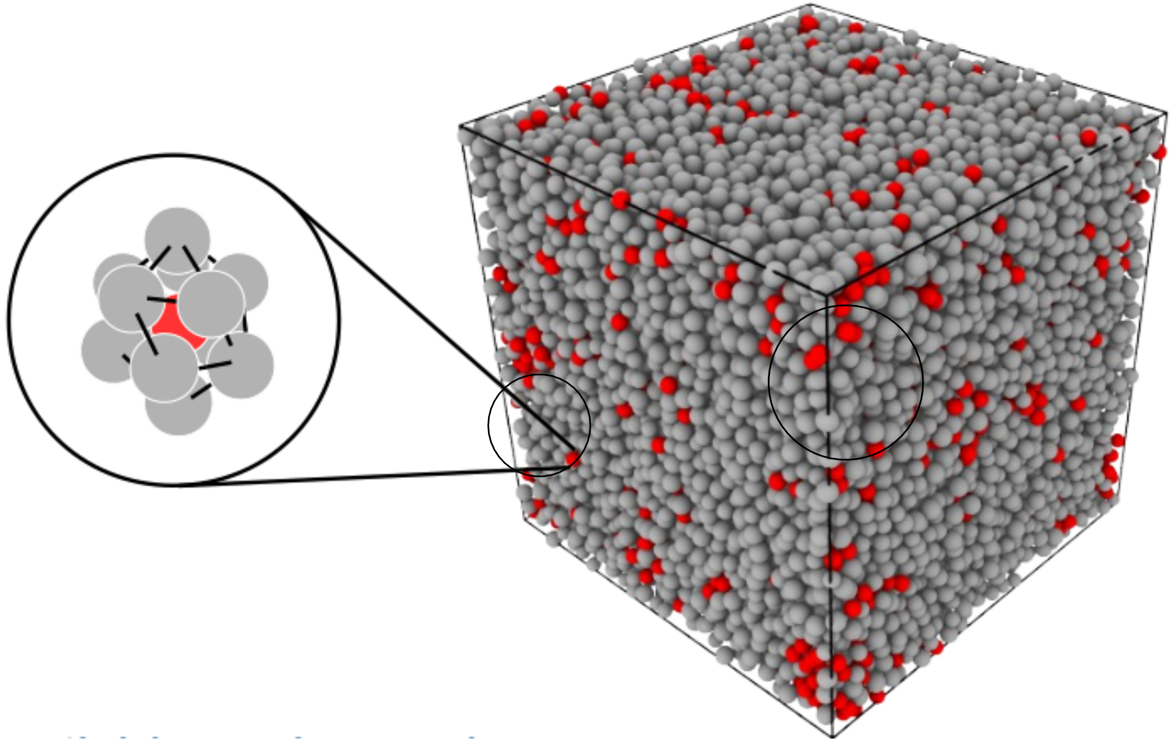


Coslovich Pastore JCP 2007

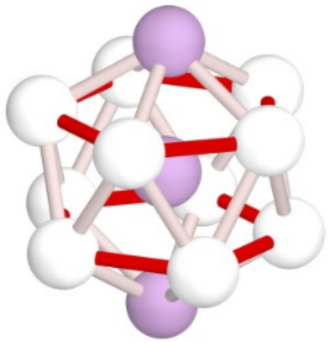
Miscela binaria di
WAHNSTRÖM

$T_{onset} \approx 1.0$

$T_c \approx 0.55$

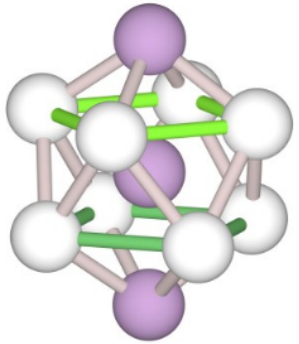


(0,0,12)

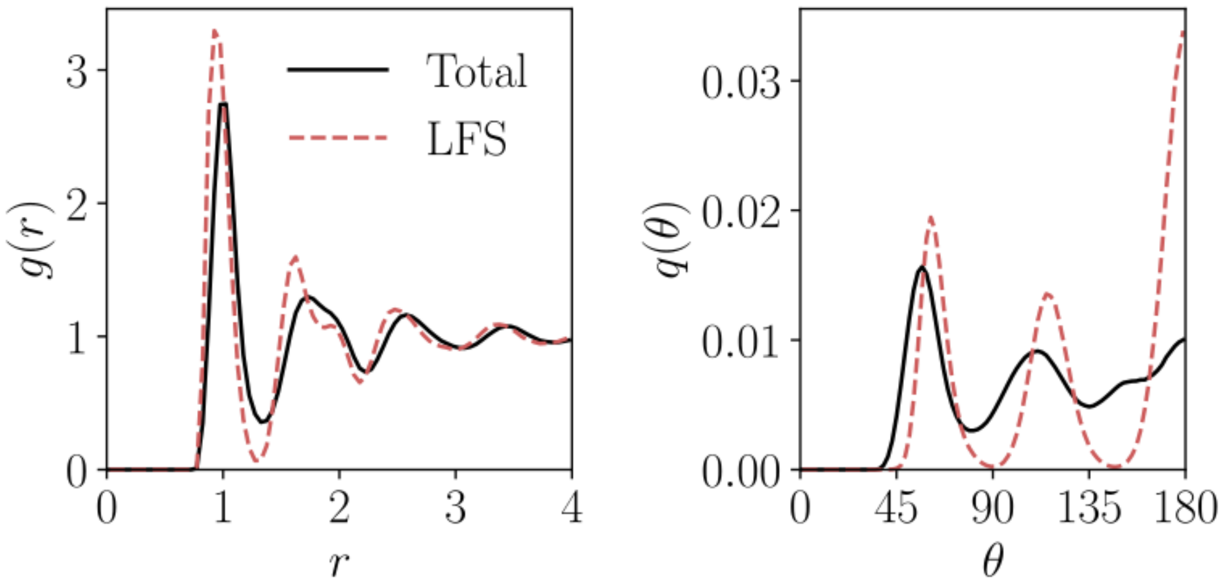


Wahnström
mixture

(0,2,8)

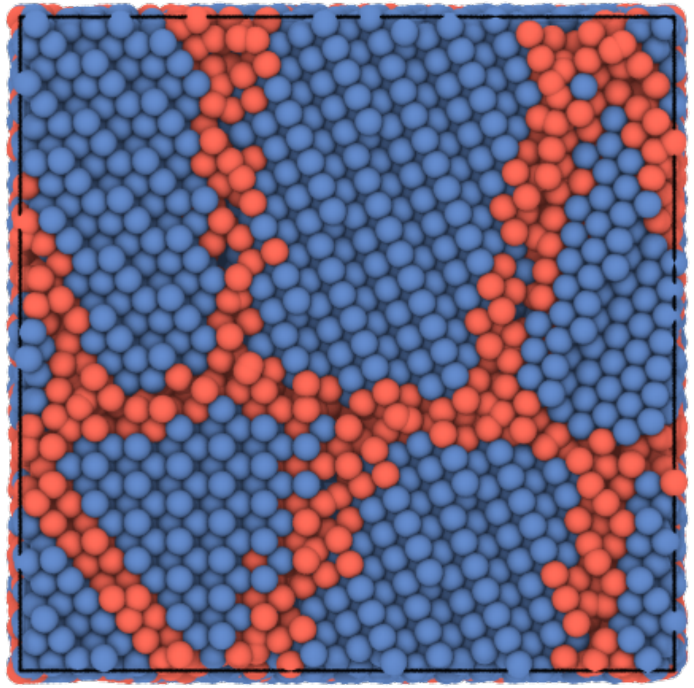


Kob - Andersen
mixture



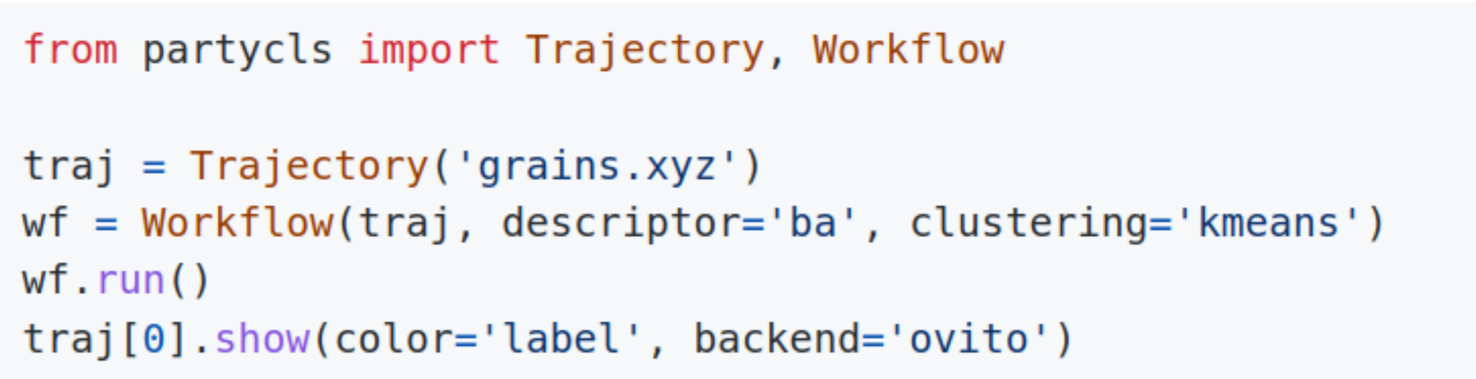
Paret, Jack, Coslovich JCP 2019

UNSUPERVISED LEARNING



partycls

https://github.com/jorisparet/partycls



```python
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