FLUIDI METASTABILI E INSTABILI

monocomponente

$N = cost$
$P = cost$

$dG = -SdT + VdP$
$= 0$

α
metastabile
β
T^*

binodale
spinodale
T^*
G
L
C
F
2
3
ρ_G ρ_G^s ρ_L^s ρ_L

α = L
ρ = G
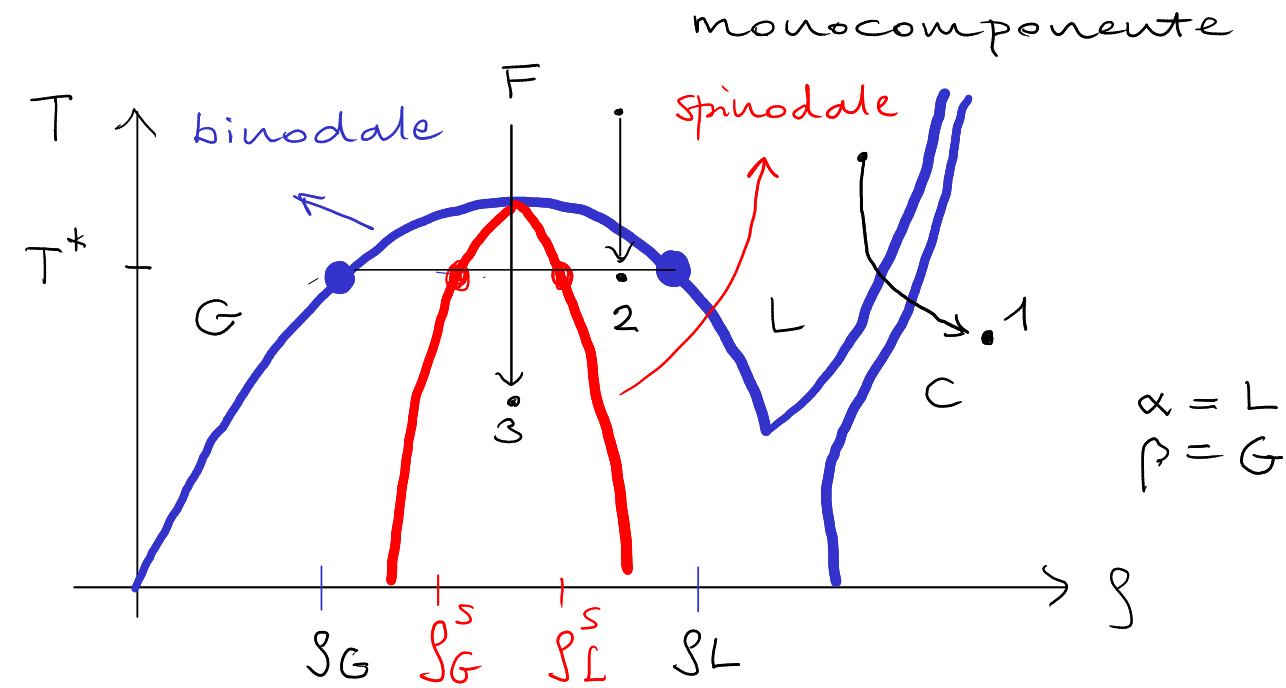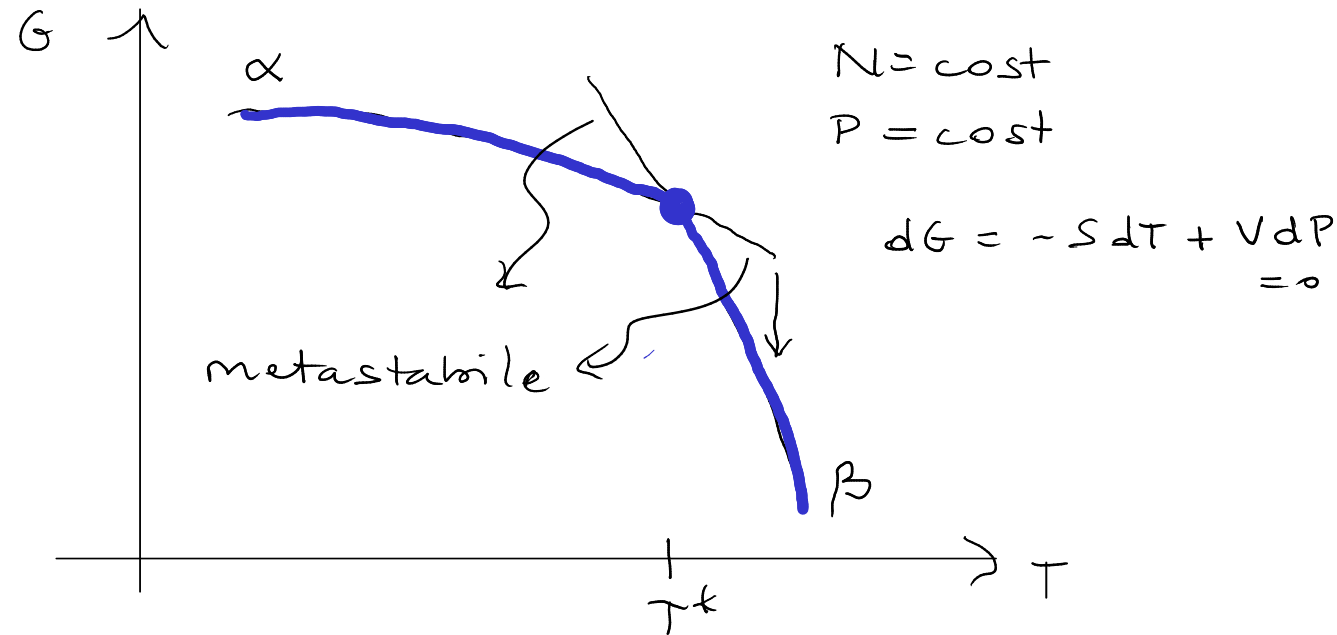
1. metastabile wrt cristallo   ⎱ ①
2. metastabile wrt liquido + gas ⎰
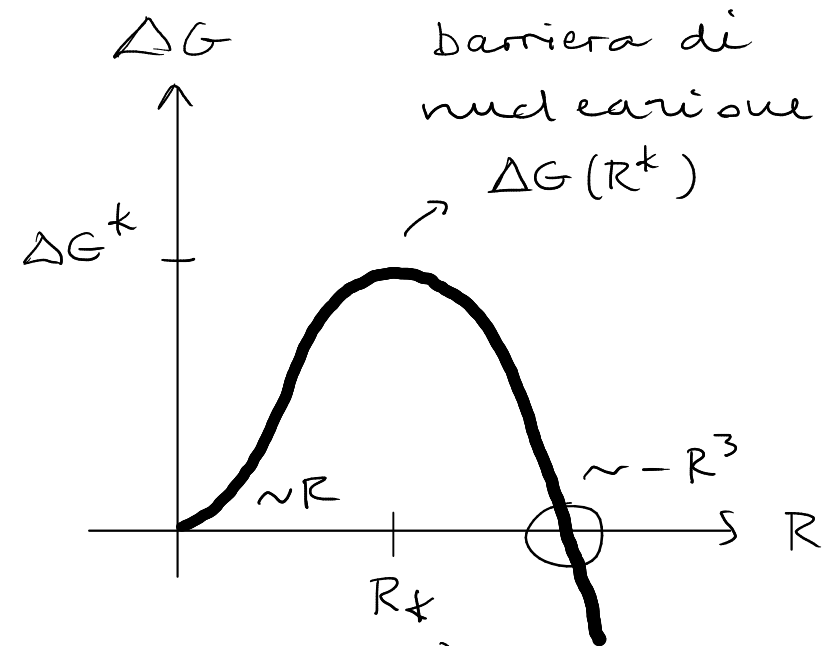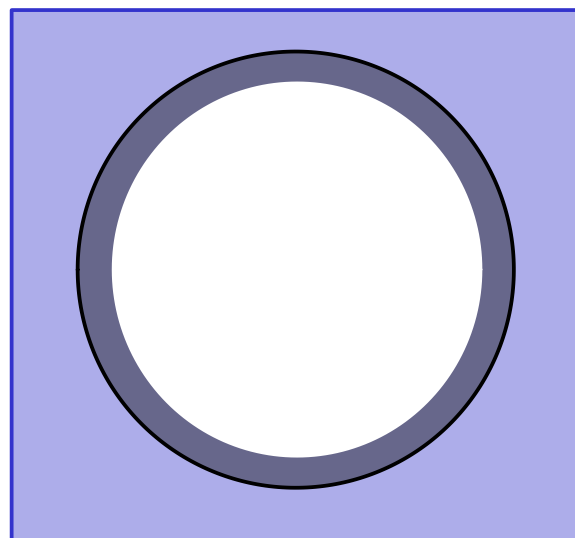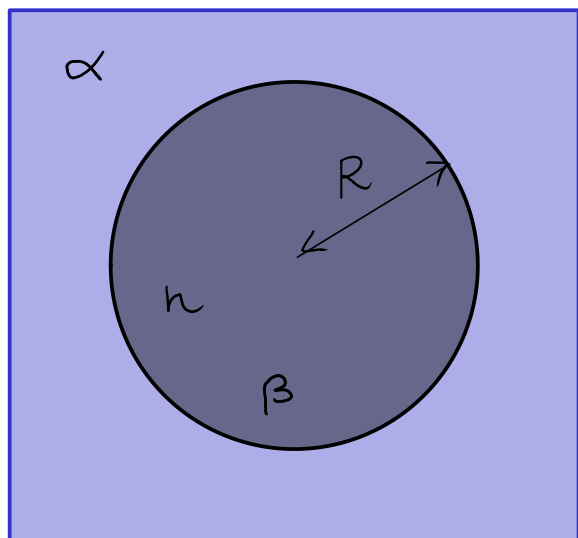3. instabile wrt liquido + gas   ②

① nucleazione e crescita   ② decomposizione spinodale

F
G
L
$N = cost$
$T = cost$

— metastabile
— instabile

ρ_G ρ_G^s ρ_L^s ρ_L
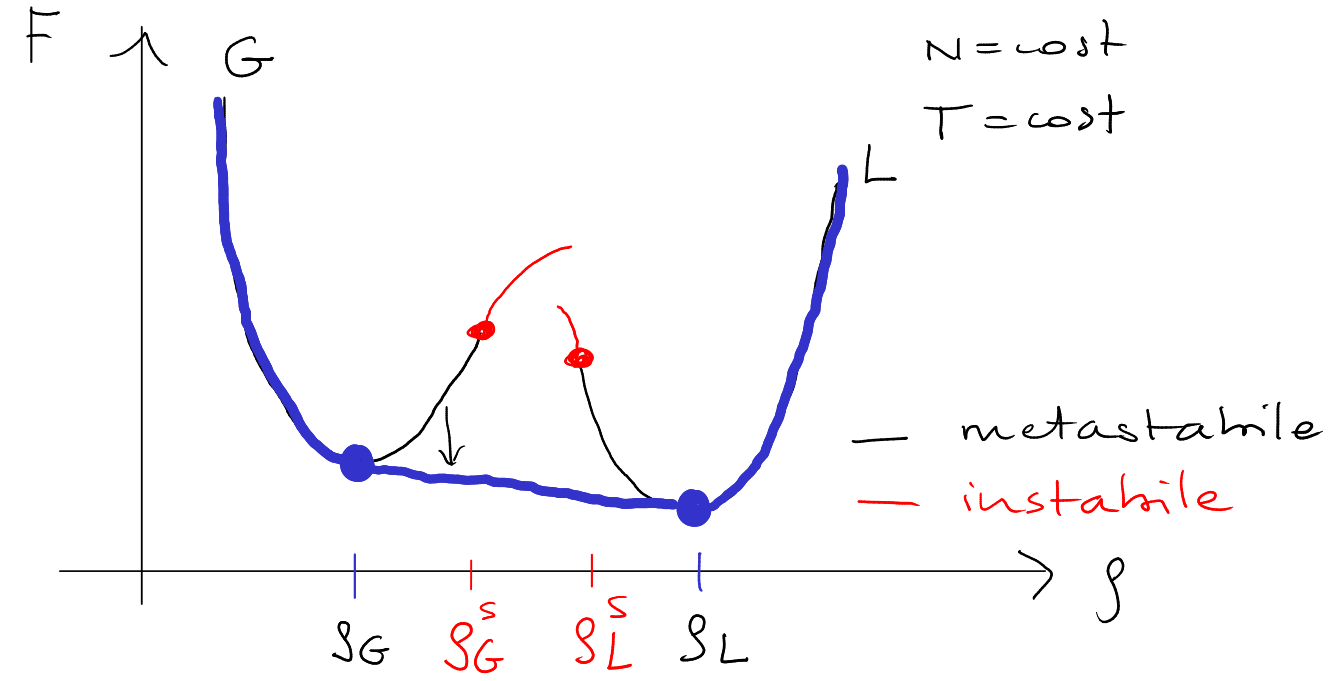
1) Nucleazione

Teoria classica della nucleazione (CNT) ← fenomenologica $\quad g = \frac{G}{V}$

$\alpha =$ metastabile $\quad \beta =$ stabile $\quad \Delta g = g_\beta - g_\alpha \leq 0$

$$\Delta G = \frac{4}{3}\pi R^3 \cdot \Delta g \quad + \quad 4\pi R^2 \cdot \gamma$$

volume $\qquad\qquad$ superficie $\qquad$ ⤴ tensione superficiale

$$\Delta G = V_\beta g_\beta + (V - V_\beta) g_\alpha \quad \to \quad V g_\alpha = V_\beta (g_\beta - g_\alpha) = V_\beta \Delta g \quad (= n \Delta g^{(n)})$$

$$\frac{d\Delta G}{dR} = 4\pi R^2 \Delta g + 8\pi R\gamma \qquad 4\pi R_k^2 \Delta g = -8\pi R_k \gamma \implies R_* = -\frac{2\gamma}{\Delta g}$$

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

Cinetica della nucleazione

- $\Delta G(R)$ paesaggio di energia
- dof: R raggio del nucleo (n particelle nel nucleo)
- particella browniana senza inerzia in campo esterno

Eq. Smoluchowski : $x \to R$, $U \to \Delta G$, $D = \frac{k_B T}{z} \implies p(R, t)$

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial R}\left[D(R)\frac{\partial p}{\partial R} + \frac{1}{z}\frac{d\Delta G}{dR}p\right] \qquad D = D(R) \qquad \underline{BH\ 10.6}$$

$\to$ problema di kramers $\quad \Delta G \gg k_B T$

Tempo di nucleazione : 1 nucleo

$$\tau_x = \frac{1}{D(R^{\ddagger})} \cdot \frac{1}{\left(-\frac{1}{2\pi k_B T}\frac{d^2\Delta G}{dR^2}\Big|_{R^\gamma}\right)^{1/2}} \cdot \exp\left(\frac{\Delta G^k}{k_B T}\right) \leftarrow \text{Arrhenius}$$
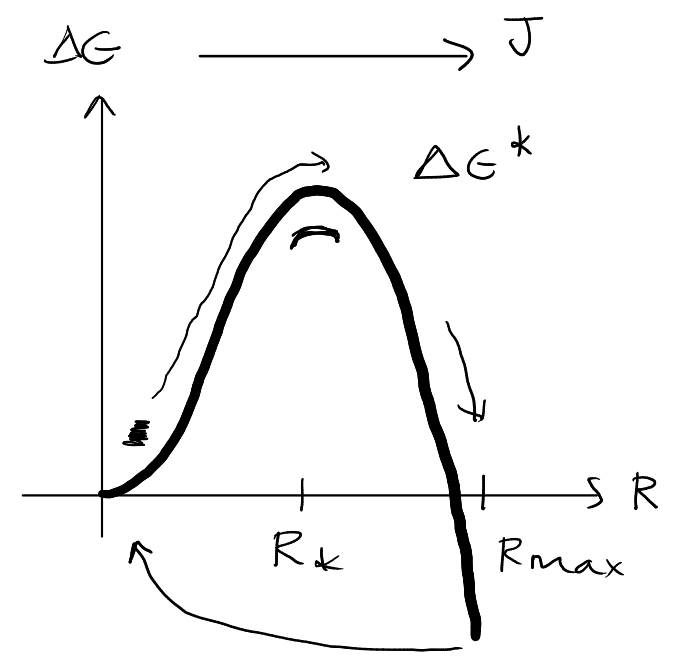
$$\underset{\text{cinetico}}{\uparrow} \qquad \underset{\text{termodinamico}}{\uparrow}$$

==Tasso di nucleazione== : n. nuclei per unità di tempo e di volume

$$I = \frac{N}{\tau_x} \frac{1}{V} = \frac{S}{\tau_x} \qquad \boxed{?}$$

Dipendenza da T

- $T \ll T_k$: $\quad D(R_k) \sim D \sim \exp\left(\frac{\Delta E_d}{K_B T} \right)$

- $T \approx T_k$: $\quad \Delta G^* \sim \frac{1}{\Delta g^2} \nearrow \sim \frac{1}{(T - T_k)^2}$

$$\Delta g \sim (T - T_k)$$

$$\tau_x \sim \exp\left(\frac{A}{K_B T} \right) \exp\left(\frac{B}{K_B T (T - T_k)^2} \right)$$

τ_x — $\sim$ Arrhenius $\quad \sim \exp\left(-\frac{1}{(T-T_k)^2} \right)$

"nose"

Coesistenza

$T_k \quad T$

cristallizzazione rapida !

2) **Decomposizione Spinodale**

$$\frac{\partial^2 f}{\partial \varphi^2} < 0$$

$T = cost$
$N = cost$

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

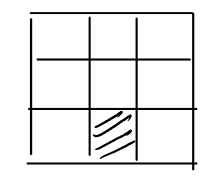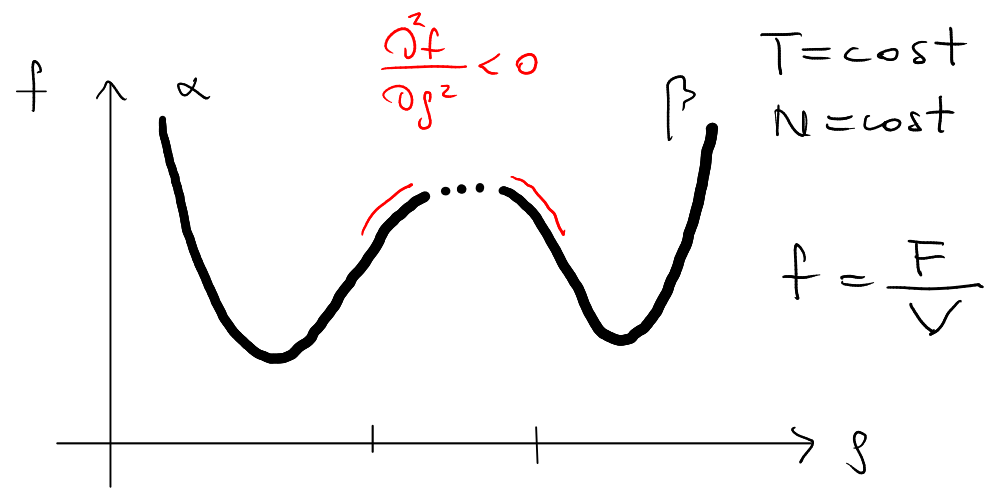$$\varphi_N(\bar{r}, t) = \varphi(\bar{r}, t)$$
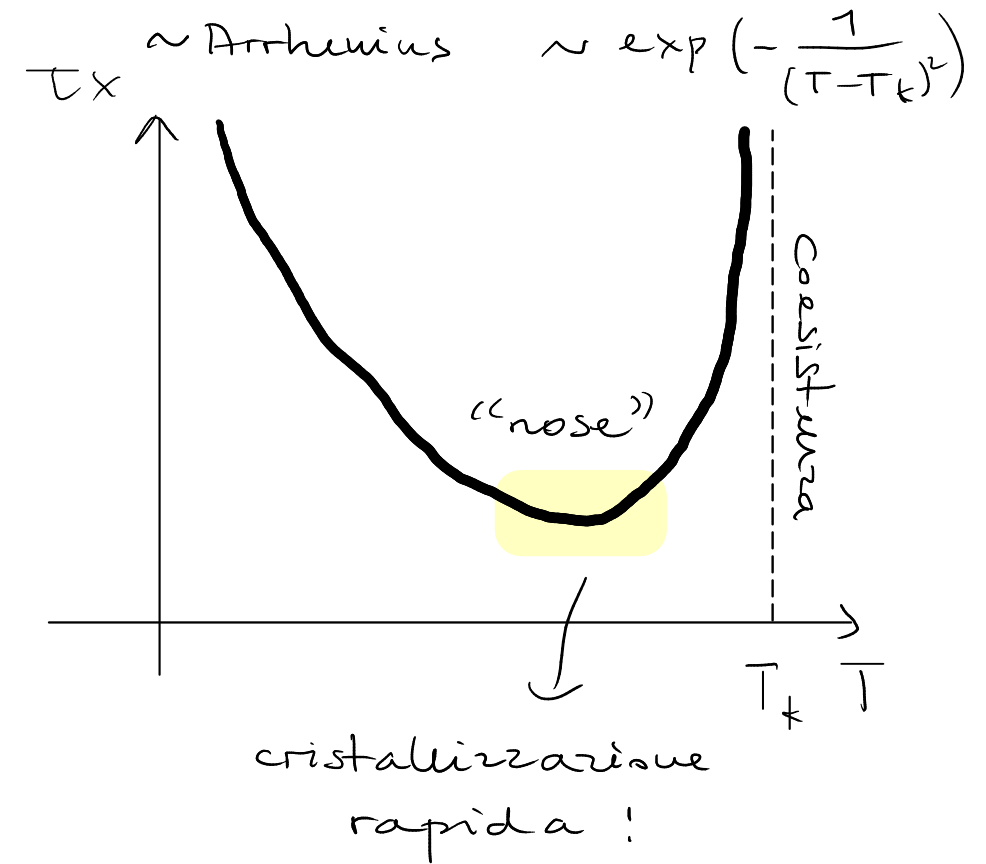
coeff. di diffusione collettivo

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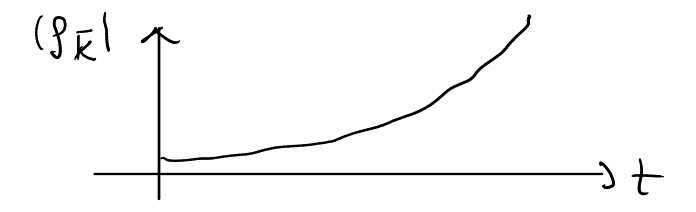
$$= \widehat{\nabla} \cdot \left(\frac{L_{NN}}{T} \frac{\partial \mu}{\partial \varphi} \vec{\nabla} \varphi \right) = \vec{\nabla} \cdot \left(D_c \vec{\nabla} \varphi \right)$$

LDA: $\mu = \mu [\varphi(\bar{r}, t)]$

$$\mu = \frac{\partial F}{\partial N} \Big|_T = \frac{\partial f}{\partial \varphi} \Big|_T \quad \rightarrow \quad \frac{\partial \mu}{\partial \varphi} = \frac{\partial^2 f}{\partial \varphi^2} < 0 \quad \Rightarrow \quad D_c < 0$$

$$\frac{\partial \varphi}{\partial t} = D_c \nabla^2 \varphi \quad \Rightarrow \quad \varphi_{\bar{k}}(t) = \varphi_{\bar{k}}(0) \; \exp\left(+ |D_c| \, k^2 \, t \right)$$

$\Rightarrow$ INSTABILITA'

Cahn - Hilliard

$$\frac{\partial \varphi}{\partial t} = \frac{L_{NM}}{T} \nabla^2 \left(\frac{\partial^2 f}{\partial \varphi^2} \varphi - \frac{k_B T \, z_o^2}{\varphi} \nabla^2 \varphi_N \right) \quad \rightarrow \quad \text{coarsening}$$

Formatori di vetro

Ossidi

Silicati : SiO_2 (Silice)
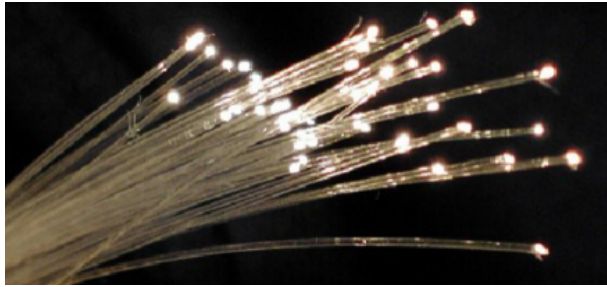
B_2O_3

gorilla glass©

Vetro da finestra

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

Polimeri
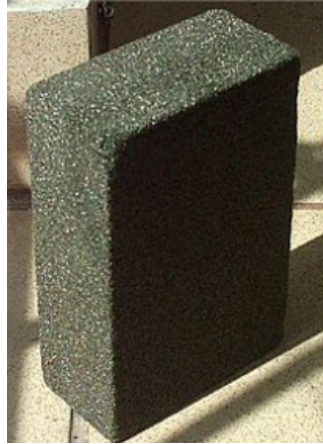
polistirene

PMMA

Metalli

Colloidi

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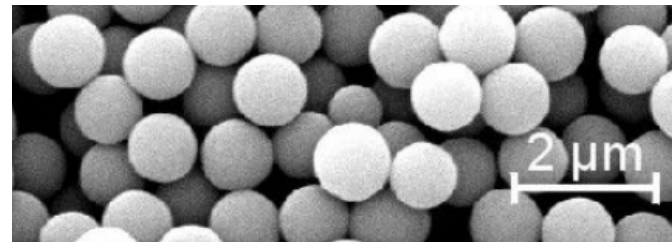
Vetri organici
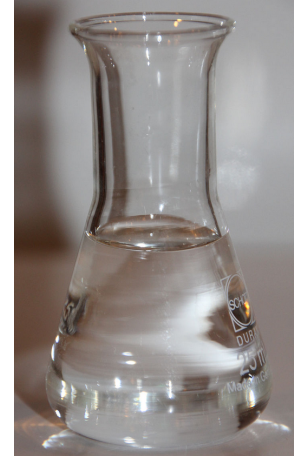
Substance	T_g
SiO_2	1473[g]
B_2O_3	532[m]
nPOH	97[h]
PropGlyc	167[d]
3-MePent	77[f]
3-Br-P	108[a]
glycerol	190[d]
BMPC	243[h]
salol	220[a]
MTHF	91[a]
OTP	246[h]
PropCarb	158[i]
triPhenPhos	203[k]
CKN	333[g]

Richert & Angell JCP 1998

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

1) Tempo di rilassamento strutturale : τ_α

$$F(\bar{K}, t) = \frac{\langle \hat{\rho}_{\bar{k}}(t) \, \hat{\rho}_{-\bar{k}}(0) \rangle}{\langle \hat{\rho}_{\bar{k}} \, \hat{\rho}_{-\bar{k}} \rangle} \qquad |\bar{k}_0| \approx \frac{2\pi}{\xi_0} \qquad |\bar{k}_0| \simeq \text{primo picco di } S(k)$$

ξ_0

$F(k_0, t)$ LIQUIDO NORMALE

1

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

$\frac{1}{e}$

$\tau_0 \quad \tau_\alpha \qquad \log t$

$\tau_\alpha \sim \tau_0$

$$F(k_0, t) \approx \exp\left(-\frac{t}{\tau_\alpha}\right)$$

$F(k_0, t)$ LIQUIDO SOTTORAFFREDATO

LIQUIDO VETROSO

$T < T_{onset}$

⚠️

$\frac{1}{e}$

$\tau_0 \qquad \qquad \tau_\alpha \quad \log t$
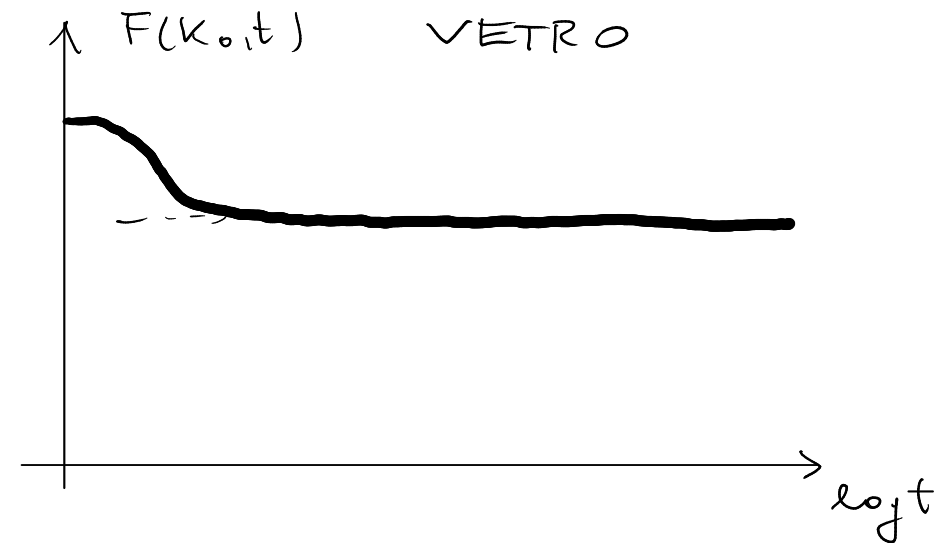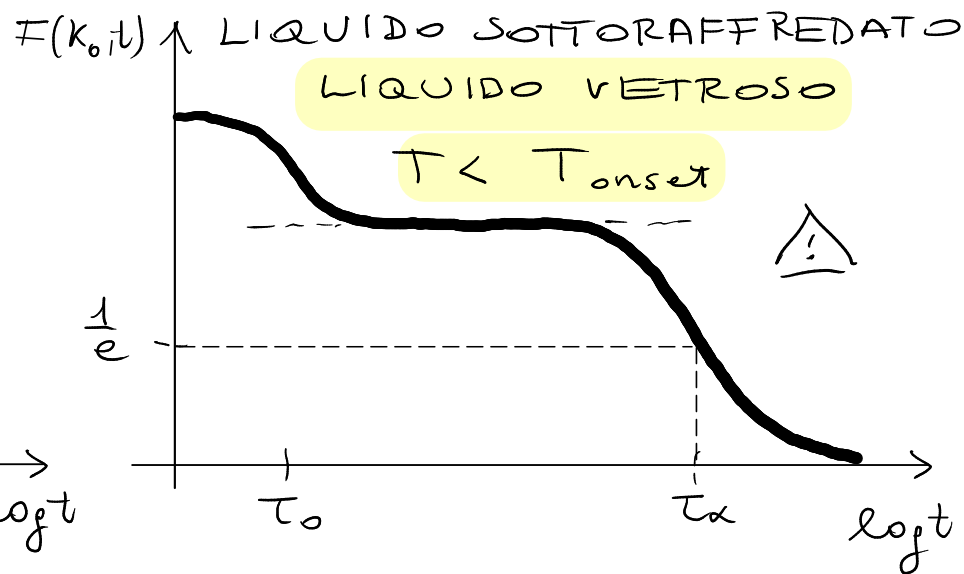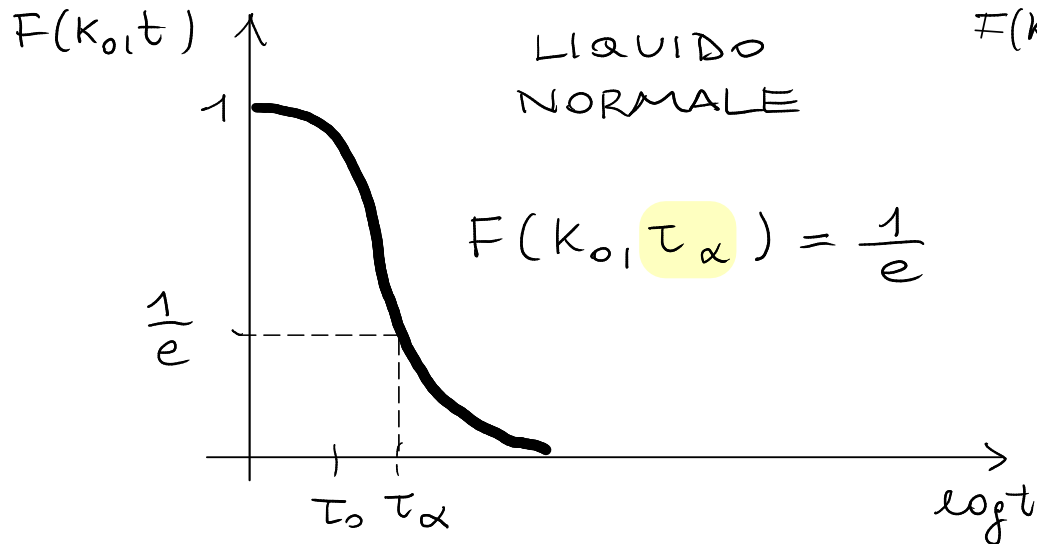
① $\tau_\alpha \gg \tau_0$

② two-step $\beta < 1$

③ $F(k_0, t) \approx \exp\left(-\left(\frac{t}{\tau_\alpha}\right)^\beta\right)$

$F(k_0, t)$ VETRO

$\log t$

Modello di Maxwell

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

$\longrightarrow \quad 1/T$

2) Tempo di osservazione : τ_{obs}
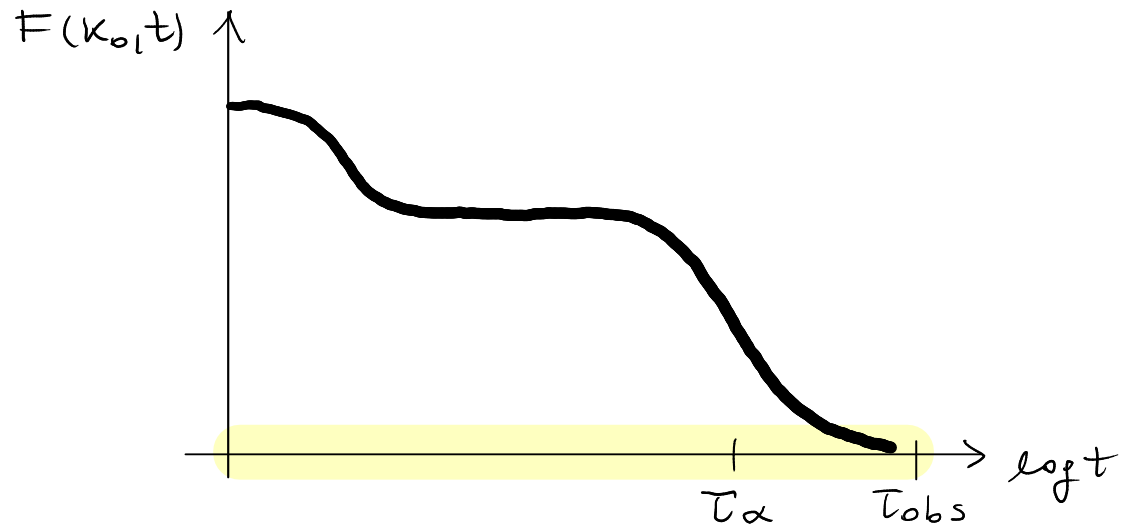
$\tau_{obs} \gg \tau_\alpha$

equilibrio metastabile
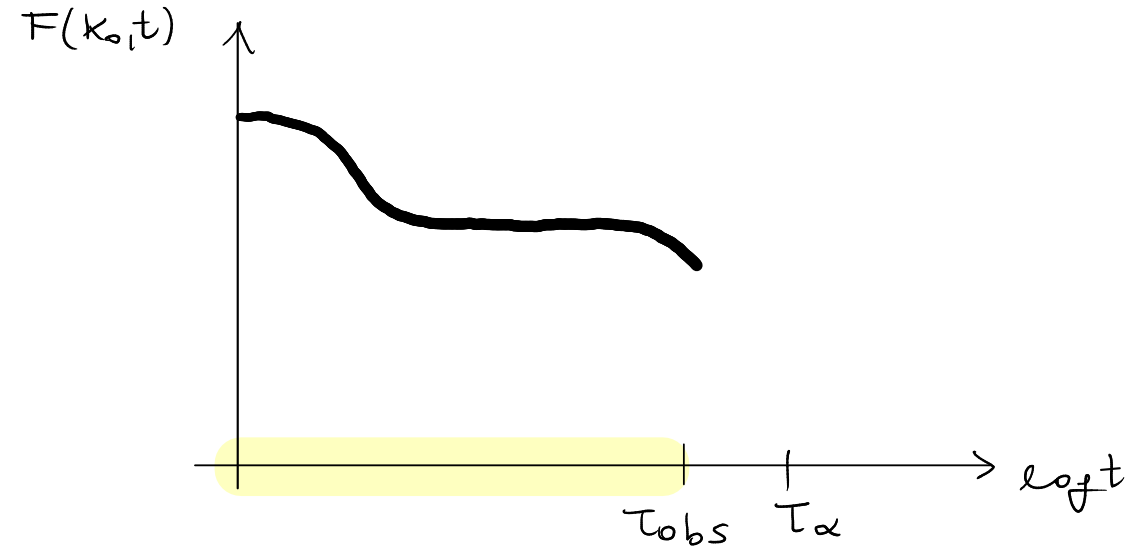
$\tau_{obs} < \tau_\alpha$

fuori equilibrio, non-ergodico

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

Def. operativa di temperatura di transizione vetrosa $\tau_\alpha = \tau_\alpha (T)$

$\tau_\alpha (T_g) = \tau_{obs}$ $T < T_g$ convenzionale

Structural relaxation time, τ_α [s] vs T/T_g

- Glycerol
- B_2O_3
- OTP
- Decalin
- PC

$\log \tau_\alpha$

$10^2 s$

$10^{-6} s$

T_g $T_g^{(sim)}$ T

- Esperimenti:

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

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

- Simulazioni:

$$\tau_\alpha(T_g^{(sim)}) \approx 10^{-6} \ s$$
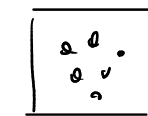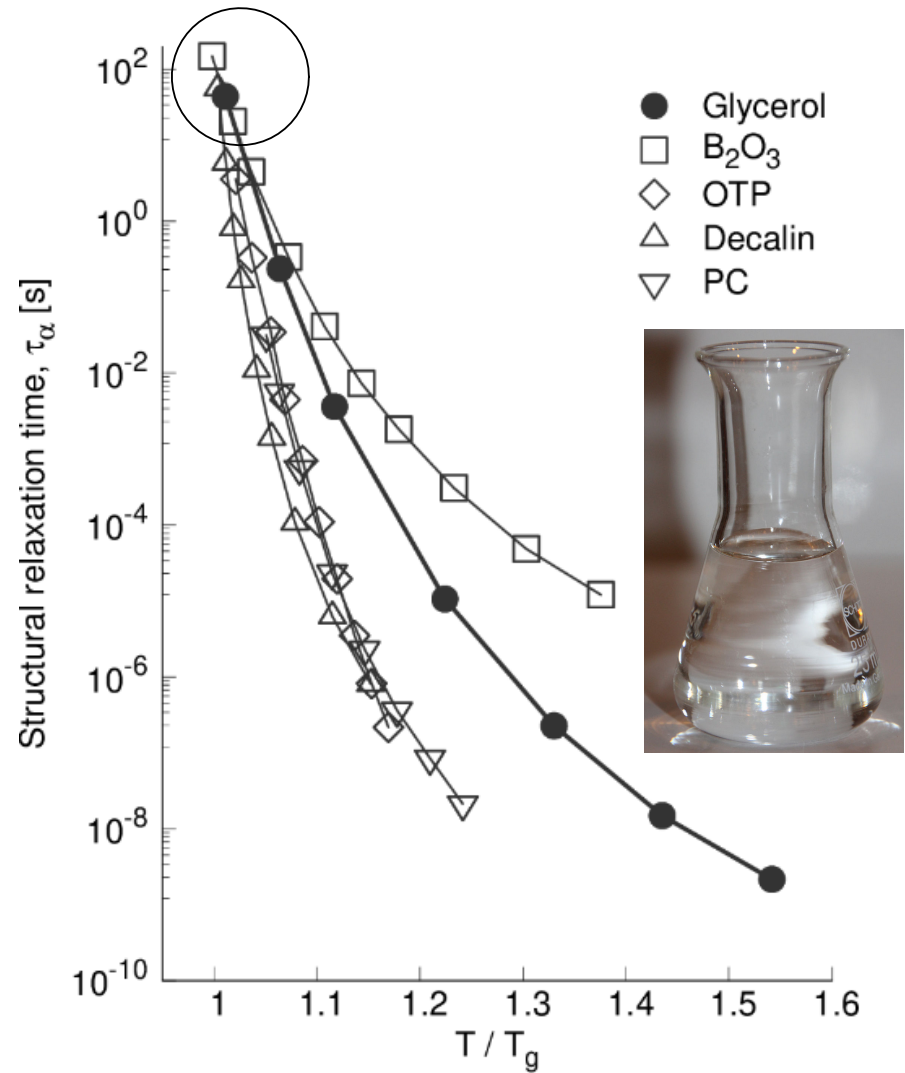
cf. swap MC [PRX 2017]

N
PBC

$$\frac{10^{-7} \ s}{step \times particella}$$

$$\frac{10^{-7} \ s}{step} \times 10^3 = \frac{10^{-4} \ s}{step} \approx \frac{10^{-4} \ s}{10^{-2} \times T_0} \approx 10^{10}$$

$\uparrow N$

$\uparrow 10^{-12} s$

3) <mark>Tempo di nucleazione</mark> : τ_x

$$\tau_x \sim \frac{1}{D(R_*)} \exp\left(\frac{\Delta G}{K_B T}\right) \qquad \Delta G = \Delta G(T)$$

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

$$\exists \; N_0 \; \text{t.c.} \quad \tau_{x,N_0} = \tau_x$$
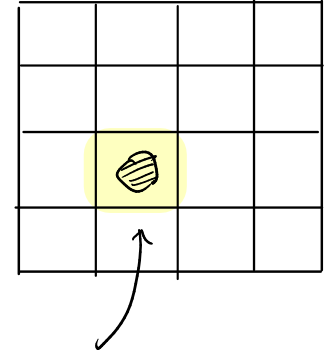
1 nucleo critico

Diagramma tempo − temperatura − trasformazione (TTT)

1) Equilibrare i dofs lenti ($\hat{S}_{K_0}(t)$) 2) Evitare XTAL $\Rightarrow$

$$\underset{1)}{\tau_\alpha} \ll \underset{2)}{\tau_{obs}} \ll \tau_x$$

"BUON" FORMATORE DI VETRO

τ_α τ_x

protocollo lineare

vetro ... τ_{obs}

T_g T_m → T
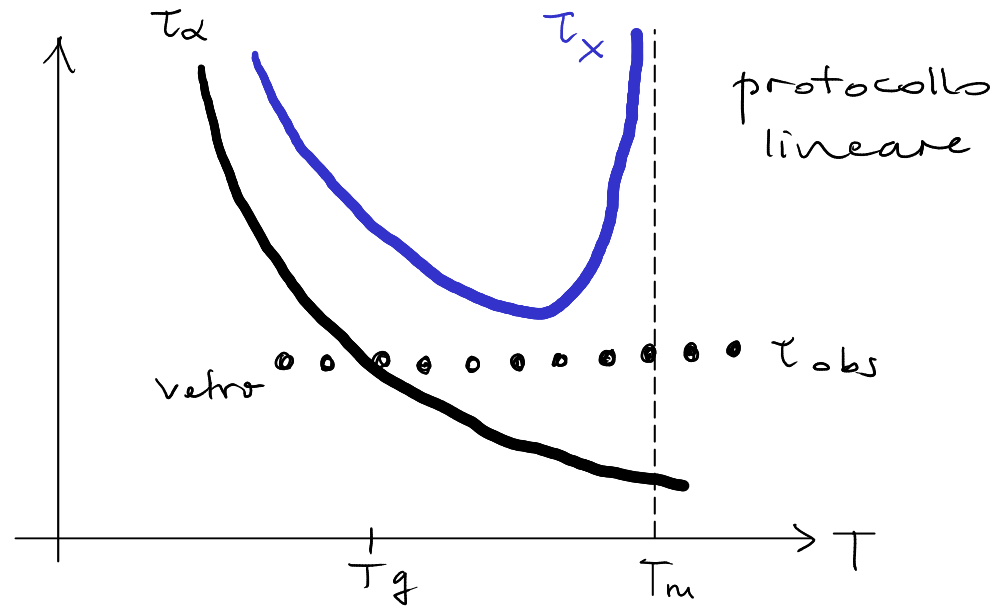
protocollo non-lineare

$\dfrac{\tau_{obs}}{\tau_\alpha} \approx cost$

T_g T_m → T

"CATTIVO" FORMATORE DI VETRO

T_m → T
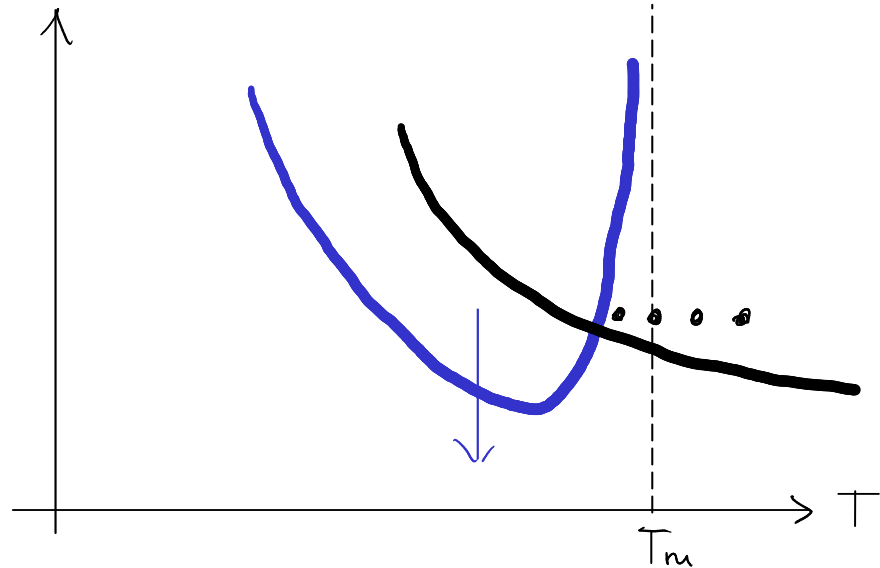
es. H_2O @ P_{amb} 160K − 230K

T_M → T

No MAN's LAND

$\log \langle |\Delta \bar{r}|^2 \rangle$

$\sim t$

δ^2

$\sim t^2$

t_o

$\log t$

$F_s(K, t)$

1

t_o

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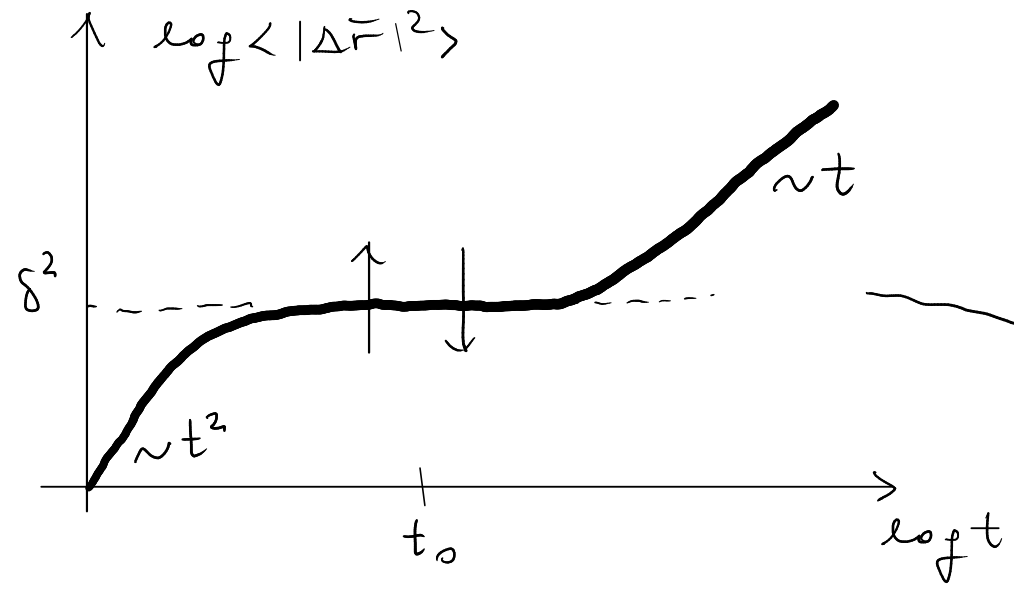
$$\langle |\Delta \bar{r}^2(t_o)|^2 \rangle = \delta^2$$

$$\delta^2 \leftrightarrow T \quad ?$$

(es.)

"cage effect"

$$\delta^2 \leftrightarrow F_s(K_o, t_o)$$
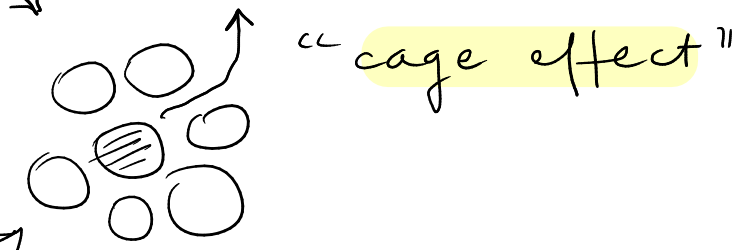
(es.)
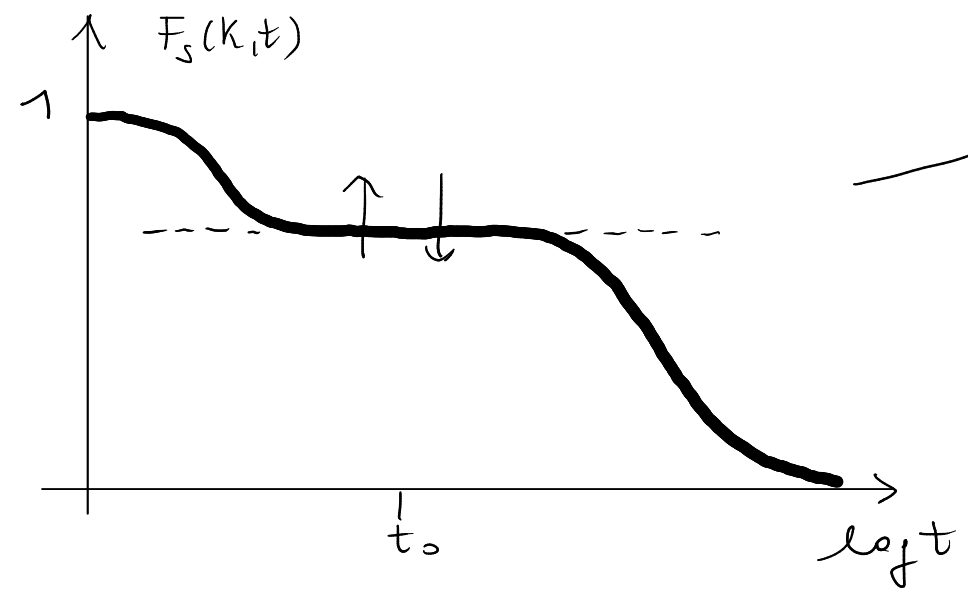
Classificazione di Angell
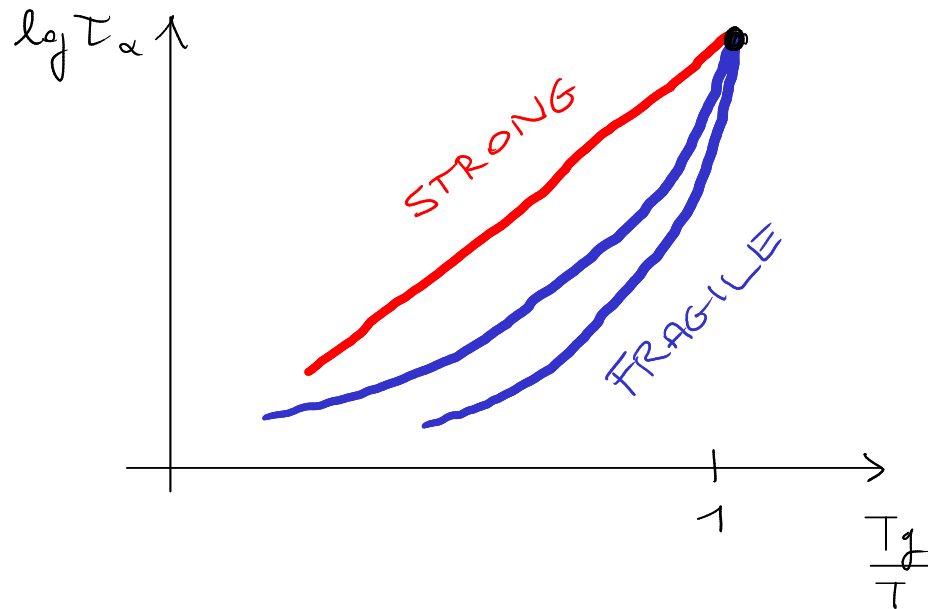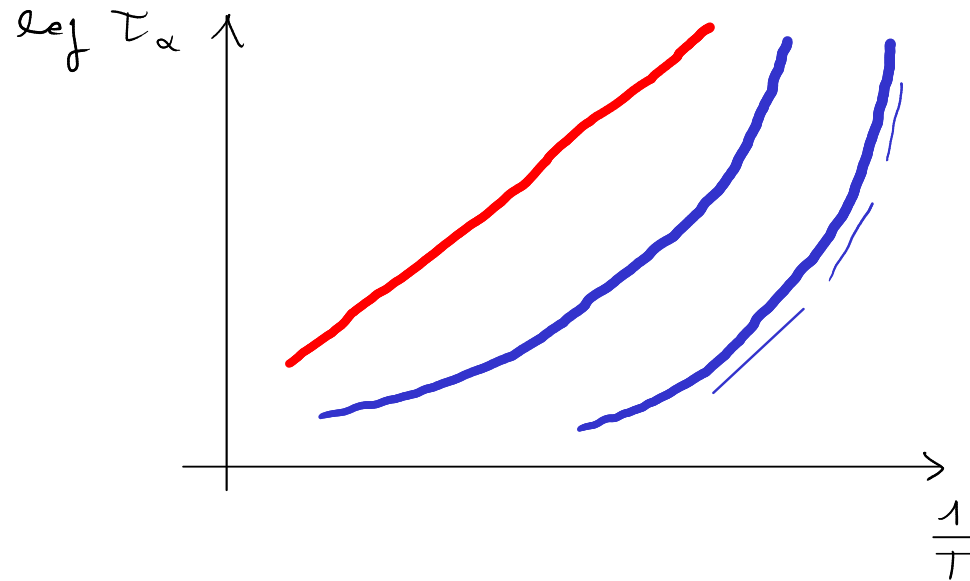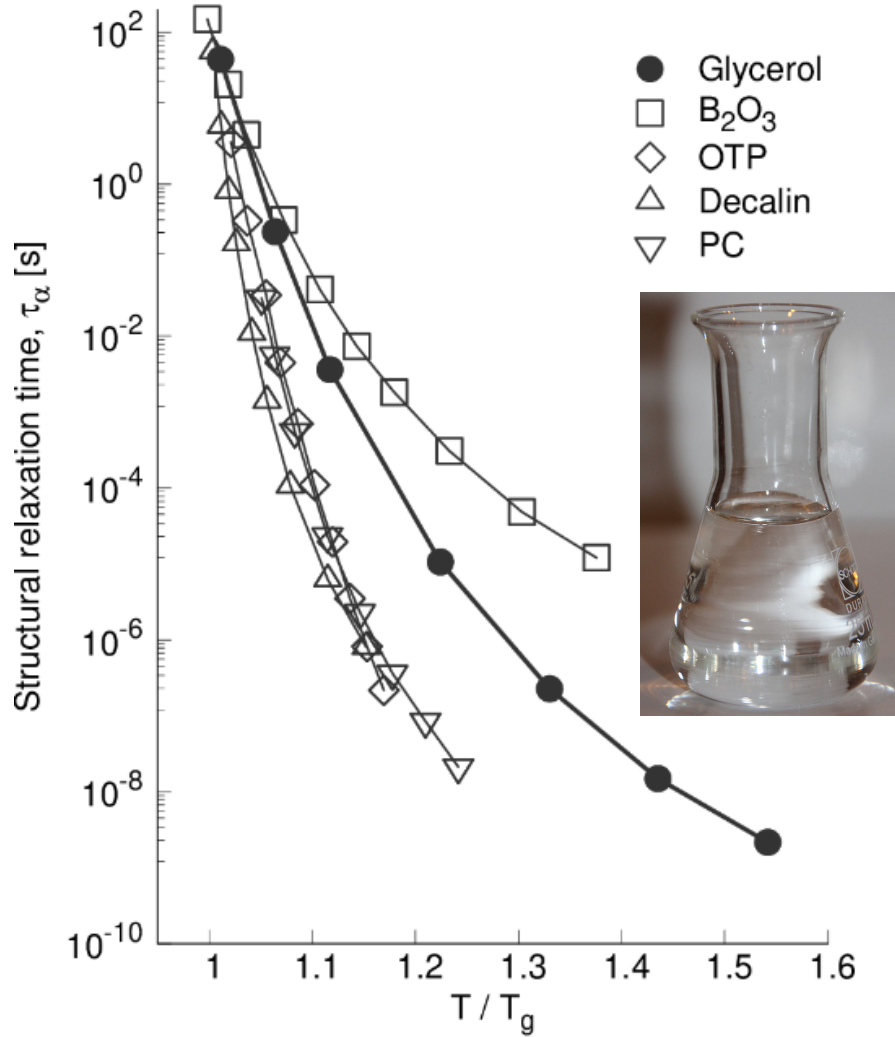
Arrhenius

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

$$\Delta E \approx \text{cost}$$

es. SiO_2, GeO_2

Super - Arrhenius

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

$$\Delta E \uparrow \quad T \downarrow$$

Fragilità

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

STRONG

FRAGILE

Eterogeneità dinamica

→ funzioni di correlazione a 4 punti
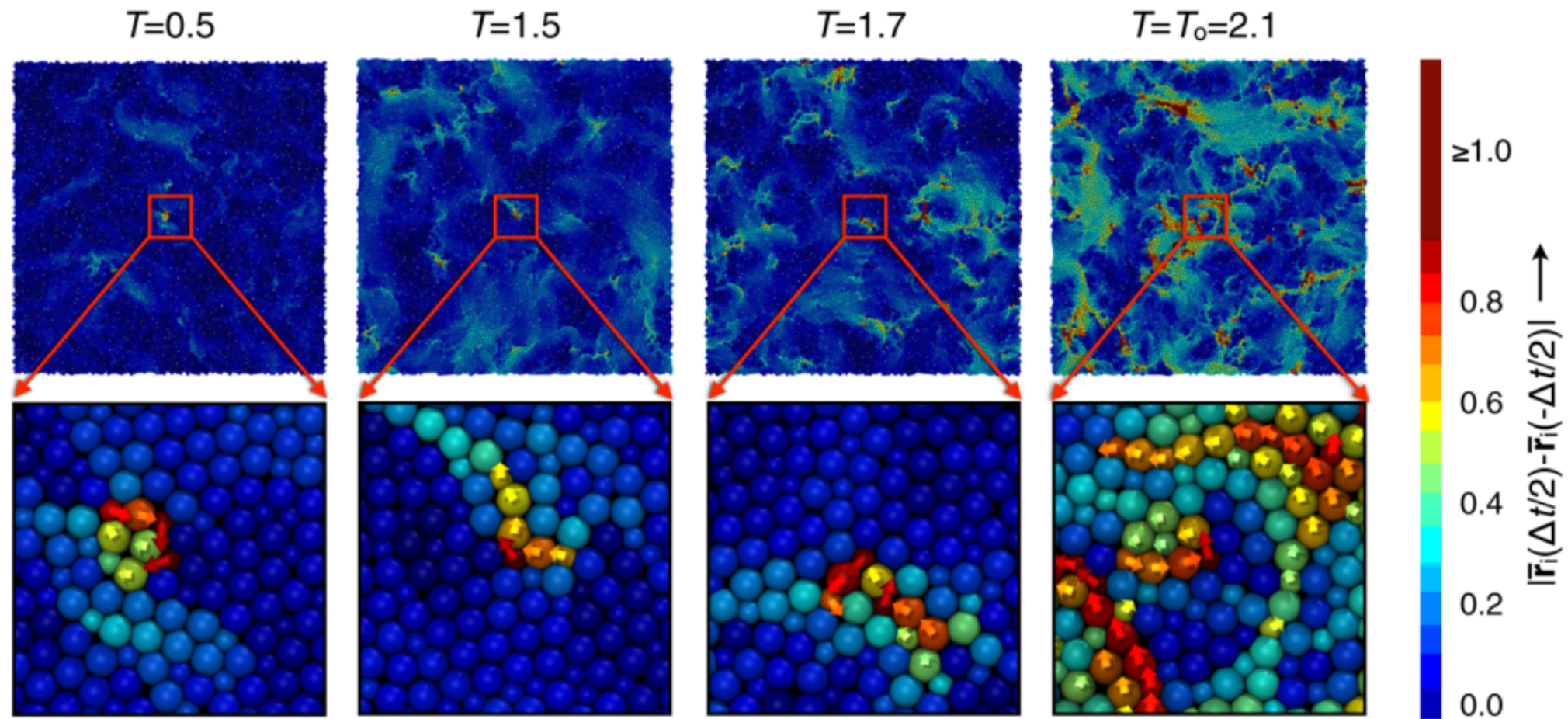
keys et al. PRX 2011

Termodinamica

Energia interna : E

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

Approx armonica : $E = 3 N K_B T$

Entropia : $S(T) = ?$ $V = cost$ $N = cost$

"aging"

$3 N K_B$ vetro

"congelamento" dei dofs
configurazionali

$dS = \frac{1}{T} dE + \underset{=0}{\frac{P}{T} dV} - \underset{=0}{\frac{\mu}{T} dN} = \frac{1}{T} dE$

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

              ↑

integrazione termodinamica $<$ g.p.
                        solido armonico

Entropia configurazionale :

▱ cristallo perfetto : $S = S_{vib}$ □ cristallo : $S = S_{vib} + S_c$ ← difetti

□ liquido ← $S = ?$ ▱ liquido sottoraffreddato : $S \approx S_{vib} + S_c$
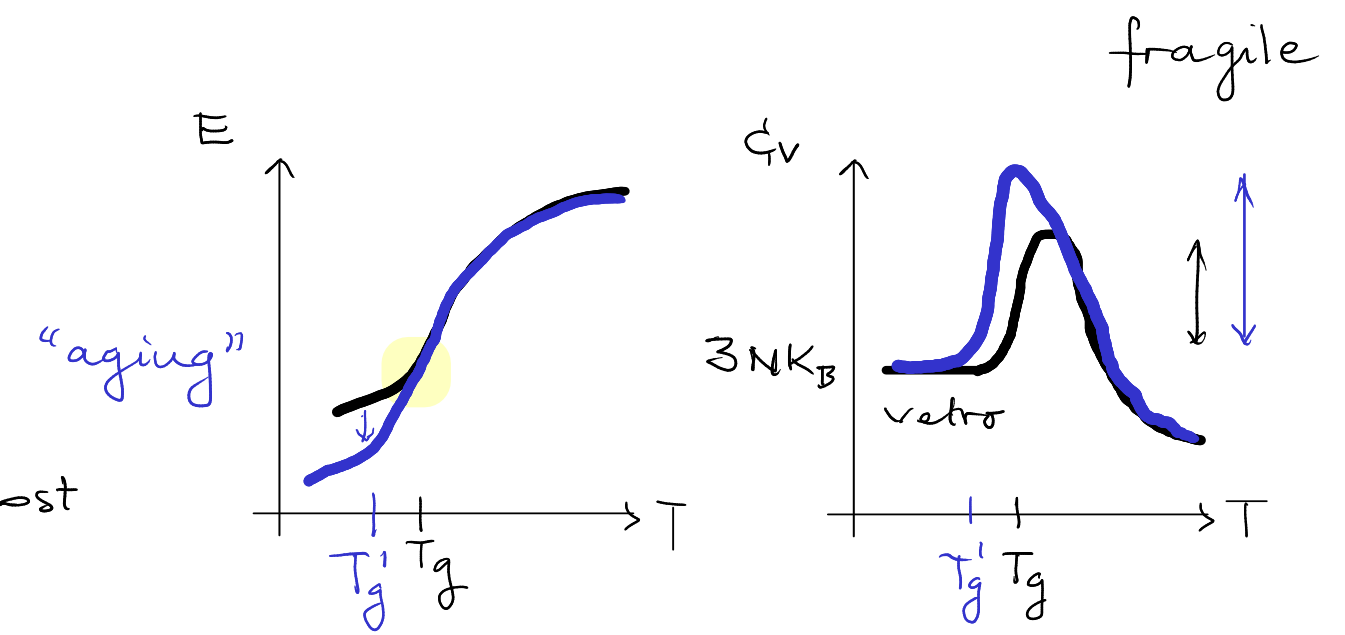
1948 Kauzmann $\Delta S = S_{liq} - S_{crist} = S_{vib} + S_c - S_{vib} \approx S_c$

Paradosso di Kauzmann

$\frac{\Delta S}{\Delta S_m}$

ETHANOL
GLYCEROL
PROPANOL
GLUCOSE
LACTIC ACID

B_2O_3

T_K

$T/T_m \longrightarrow$
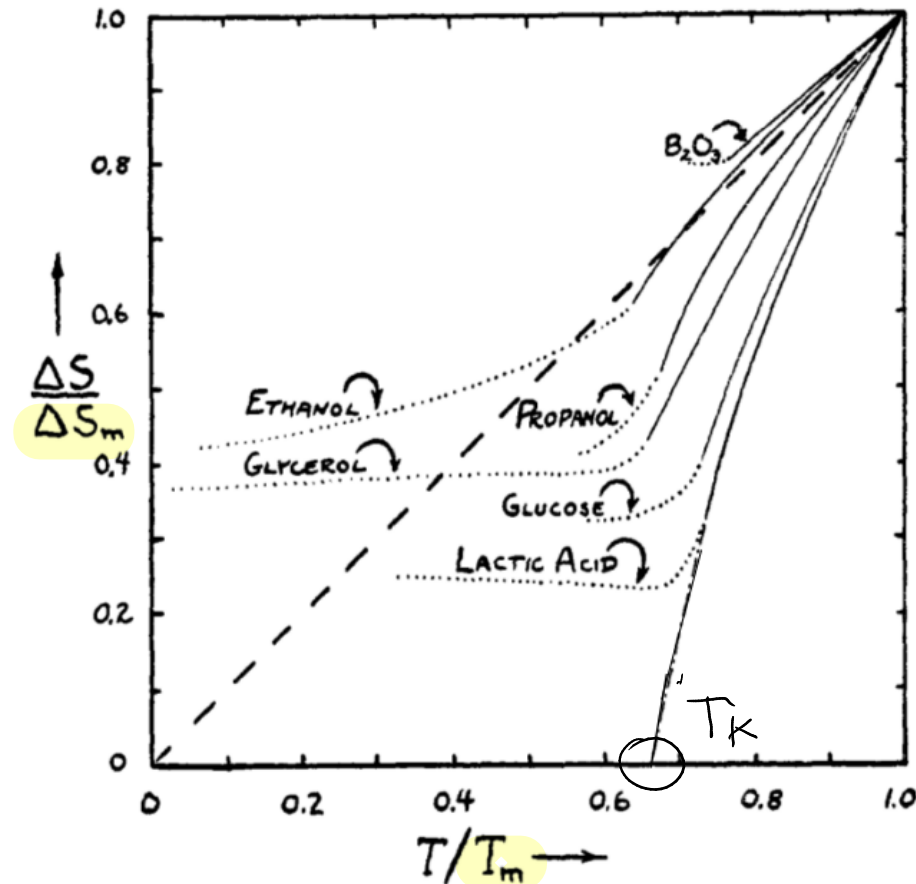
4. Differences in entropy between the supercooled liquid and crystalline ph

Kauzmann Chemical Reviews 1948

Then how are these curves to be extrapolated below T_0? 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.

$\log \tau$

T_α

τ_x

$\tau_x \sim \tau_\alpha$

① vetro ideale ?

$\log \tau$

τ_x

spinodale cinetica

T_{sp}
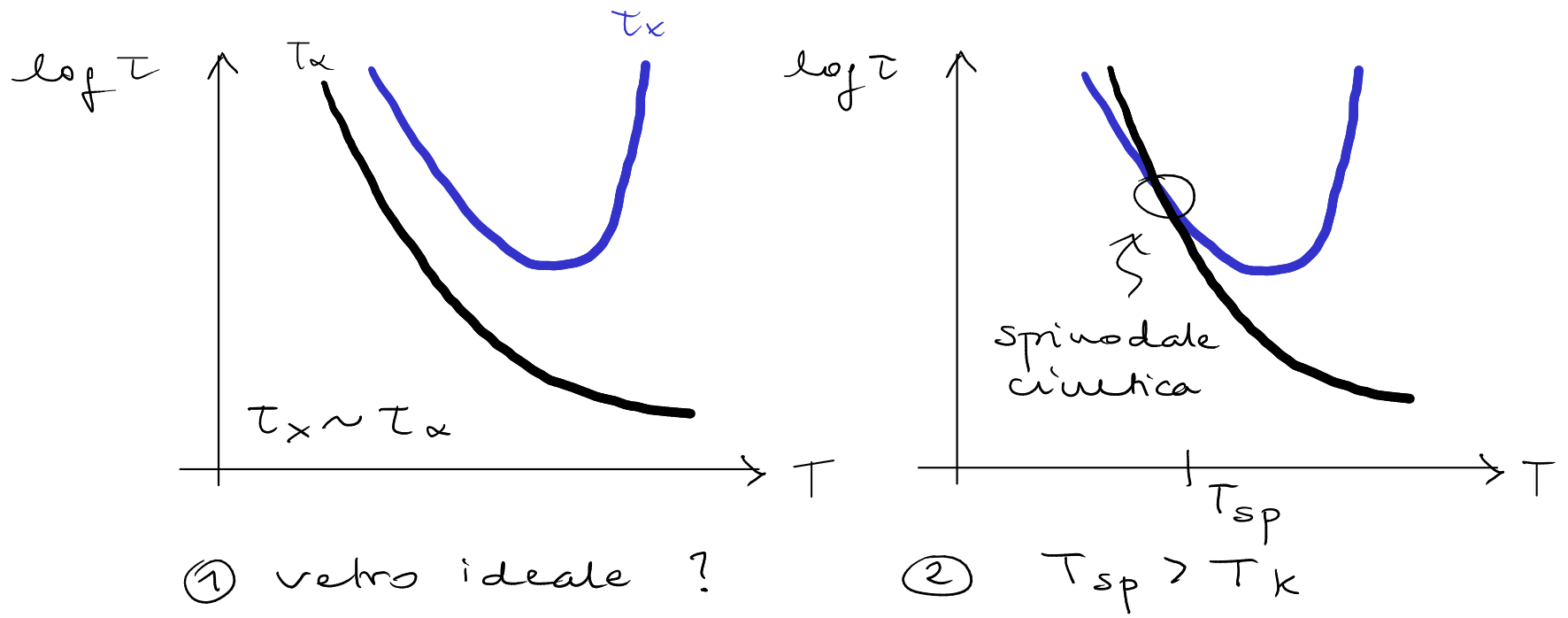
② $T_{sp} > T_k$

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape   (PEL / PES) $N = \text{cost}$, $V = \text{cost}$
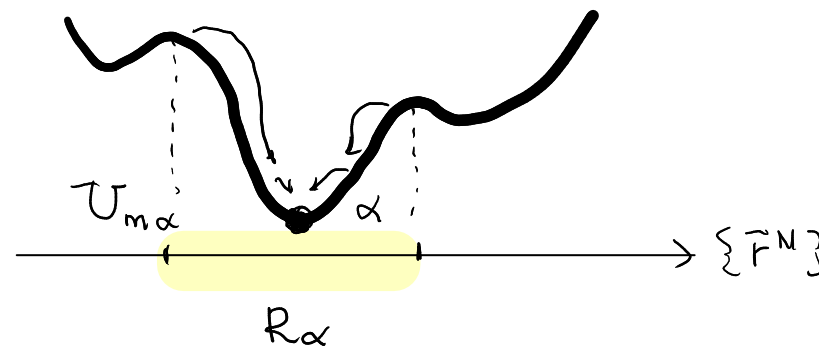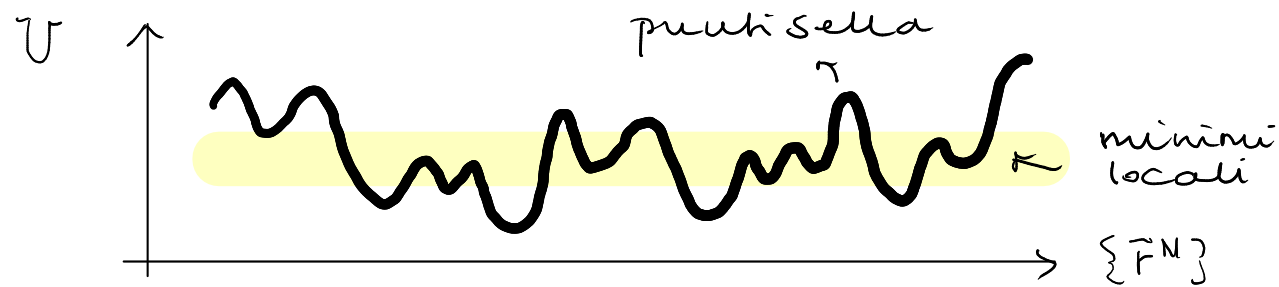
$\widetilde{U} = U(\{\vec{r}^N\})$

180 Stillinger
Weber

Strutture inerenti

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

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

bacino di attrazione

$N \to \infty$ $u_{m\alpha} = \dfrac{U_{m\alpha}}{N}$

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

$\qquad = \sum_{\alpha} e^{-\beta U_{\alpha m}} \dfrac{1}{\Lambda^{3N}} \int_{R_\alpha} d\vec{r}^N \, e^{-\beta(U - U_{m\alpha})}$

Densità degli stati : $\Omega(u_m) = \sum_{\alpha} \delta(u_m - u_{m\alpha})$ $\Omega(u_m)\, du_m$: n. minimi

$$= \int du_m \, \Omega(u_m) \, e^{-\beta N u_m} \, Z(u_m, T) \quad \leftarrow \text{funzione di partizione vincolata}$$

$$\Omega(u_m) \sim \exp(N) \quad \Rightarrow \quad \boxed{S_c = k_B \ln \Omega(u_m)} \quad \rightarrow \quad s_c = \frac{S_c}{N}$$

$$\underline{\text{entropia configurazionale}}$$

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

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

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

1) Approssimazione armonica

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

2) Approssimazione di punto sella (metodo di Laplace)

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

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

$$\approx \sqrt{\frac{2\pi}{N|f''(x_o)|}} \; e^{Nf(x_o)} \qquad\qquad N \to \infty$$

$$Z(T) = \int du_m \, e^{-\beta N(u_m - Ts_c + f_{basin})} \quad \overset{①}{\underset{\approx}{\downarrow}} \quad \int du_m \, e^{-\beta N(u_m - Ts_c + f_{vib})}$$

$$\begin{cases} Z(T) \approx A(N) \exp\left[-\beta N\left(u_m - T s_c + f_{vib}\right)\right] & \xleftarrow{\textcircled{2}} \quad \triangle \\ 1 - T \dfrac{\partial s_c}{\partial u_m} + \underbrace{\dfrac{\partial f_{vib}}{\partial u_m}}_{\approx 0} = 0 \end{cases}$$

u_m massimizza integrando

$$\Rightarrow \quad \frac{\partial s_c}{\partial u_m} = \frac{1}{T}$$

Es.: landscape gaussiano

Transizione a vetro ideale

① $\quad S_c = 0 \qquad u_m \lesssim u_k$

② $\quad \dfrac{\partial S_c}{\partial u_m} = \dfrac{1}{T_K}$
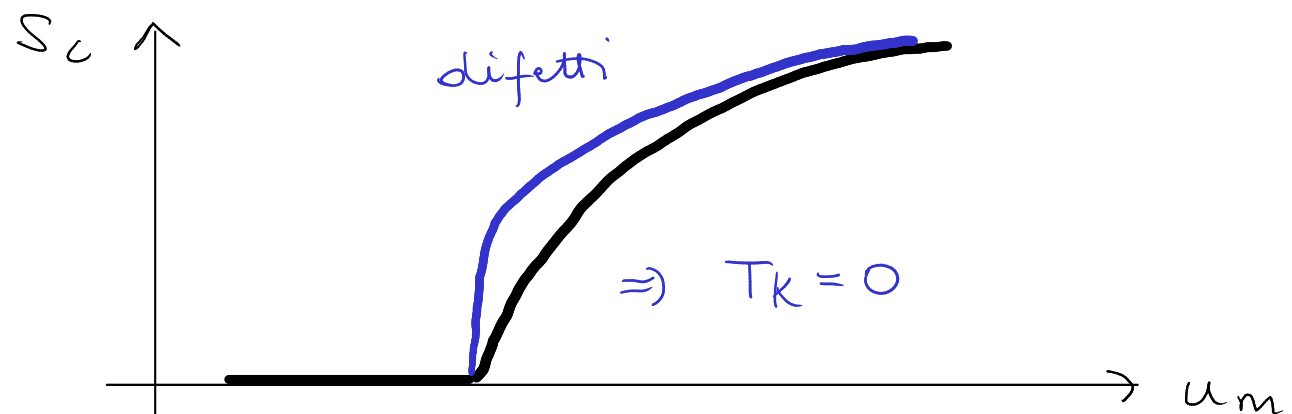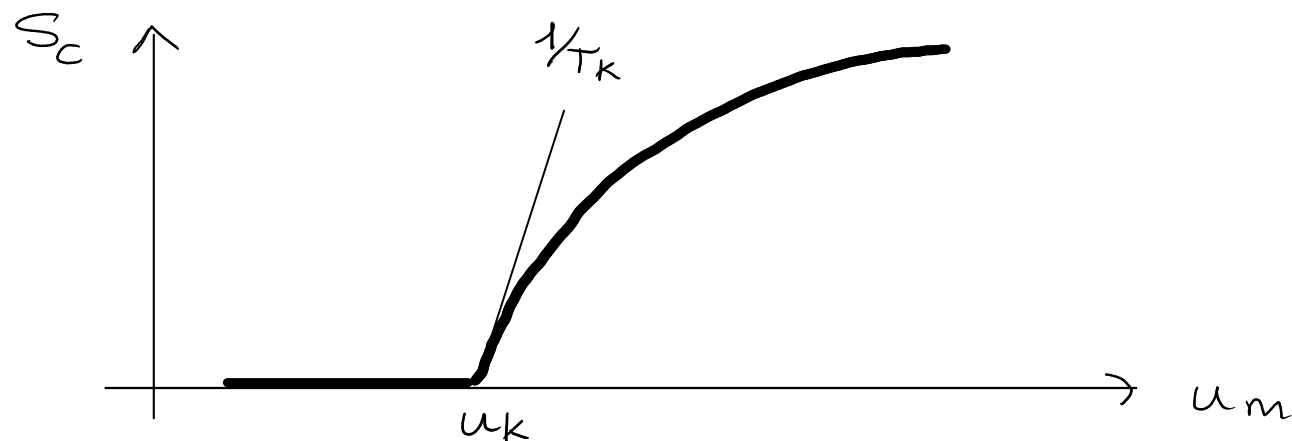
Supercooled liquids, glass transitions, and the Kauzmann paradox

Frank H. Stillinger

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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.
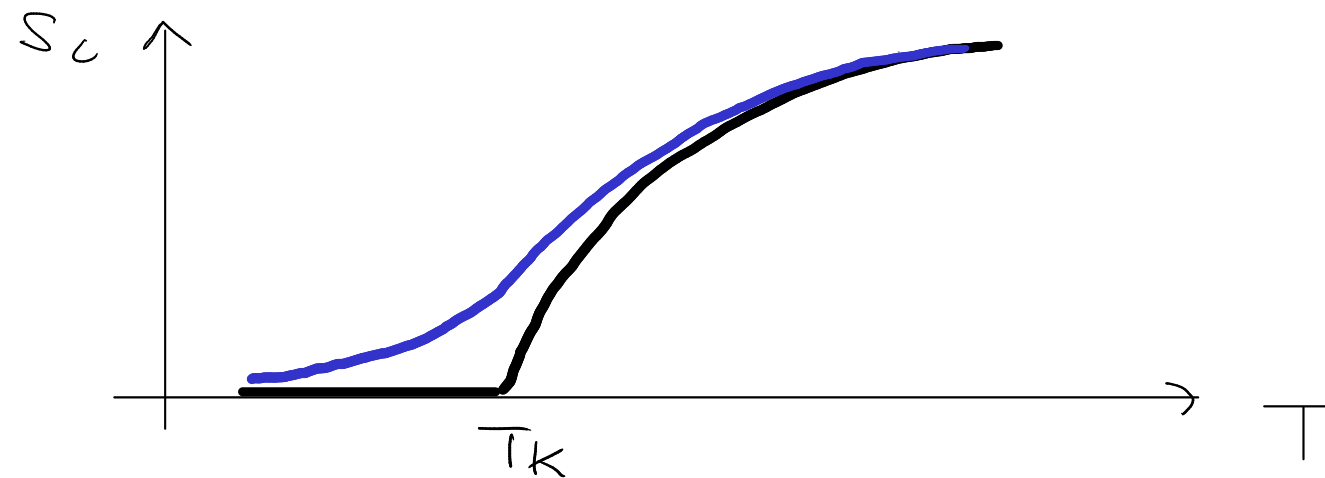
Modello di Adam e Gibbs (1965)

Cooperatively rearranging regions = CRR
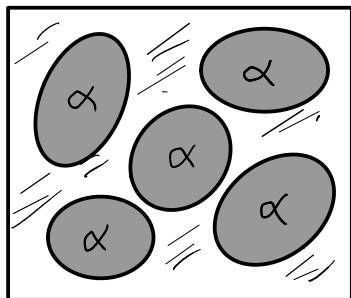
N particelle

n particelle / CRR

α n·stati / CRR

Stati accessibili

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

Entropia configurazionale

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

Dinamica attivata   con $\Delta E \sim n$

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

relazione Adam-Gibbs

3-BP

$\log(\tau) \propto (S_c T)^{-1}$

$A_{AG} = A_{VF}$

$T_K = T_0$

T_{fus}

2-MTHF

T_B

T_{fus}

$\log(\tau) \propto (S_c T)^{-1}$

$A_{AG} = A_{VF}$

$T_K = T_0$
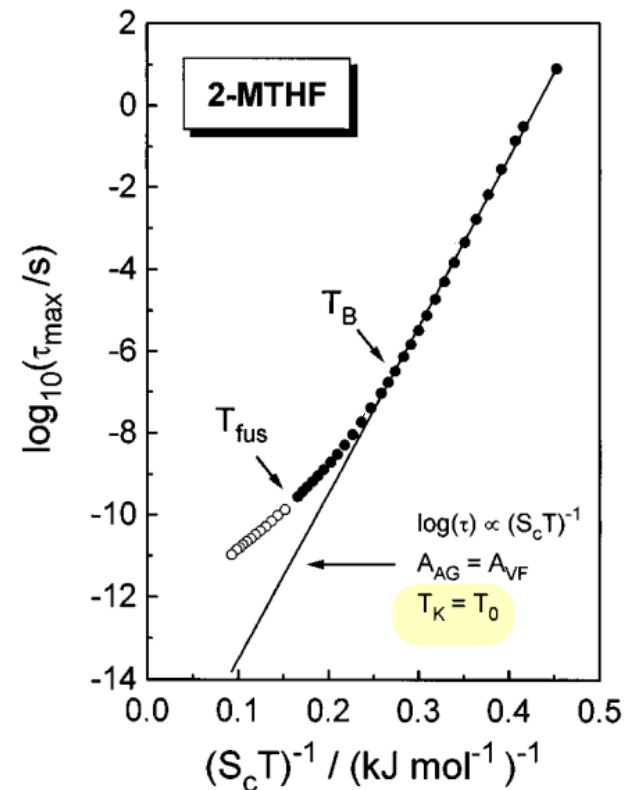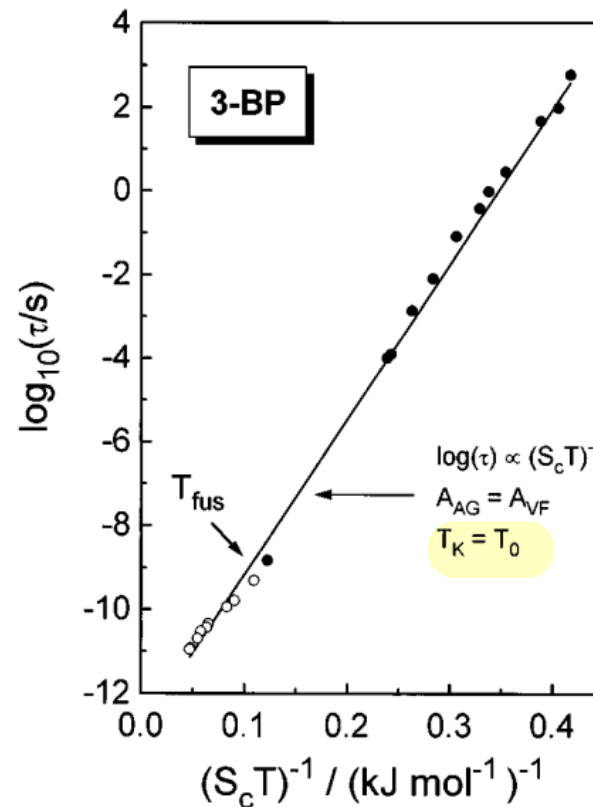
Richert & Angell JCP 1998

Transizione a vetro ideale

$$s_c \sim \frac{1}{T_K}(T - T_K) \qquad T \approx T_K$$

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

$$\approx \tau_0 \exp\left(\frac{B}{T - T_K}\right) \qquad \begin{array}{c}\text{legge di}\\ \text{Vogel-Fulcher}\end{array}$$

(MCT)

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

1984 Götze + co. $\Rightarrow$ transizione vetrosa

1) 2-step relaxation + stretched exponential

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

INTERAZIONI

u

r

IET

STRUTTURA

$S(k)$

k^+

k

MCT

DINAMICA

$F(k,t)$

t
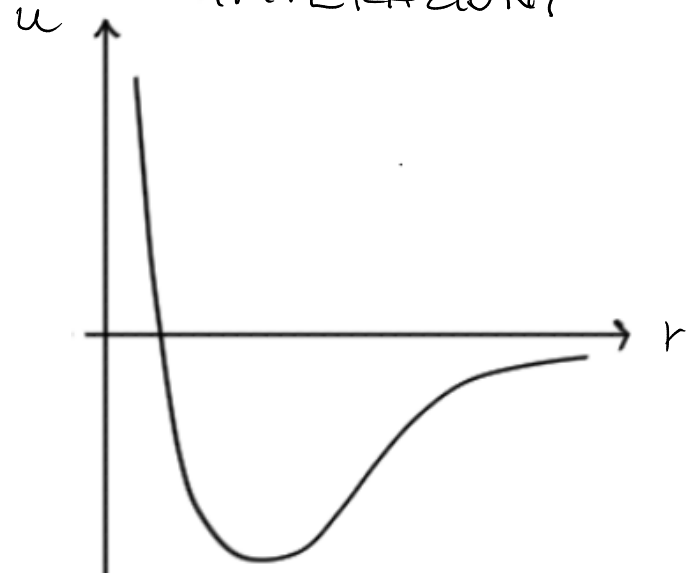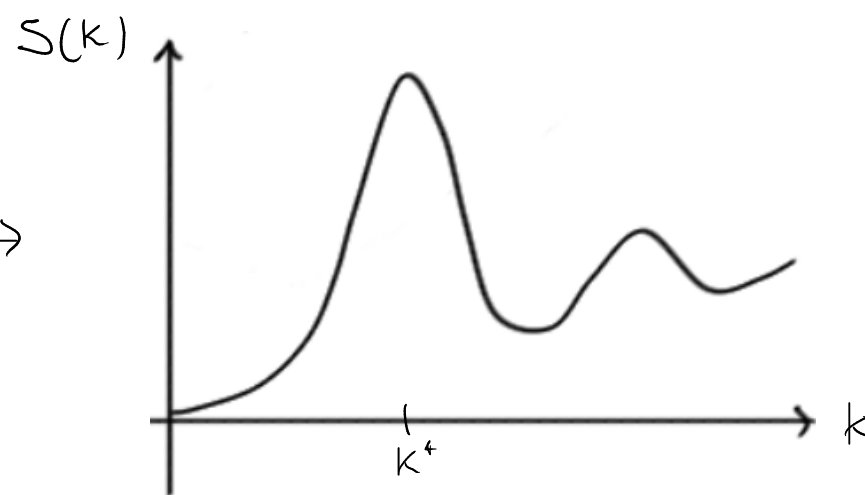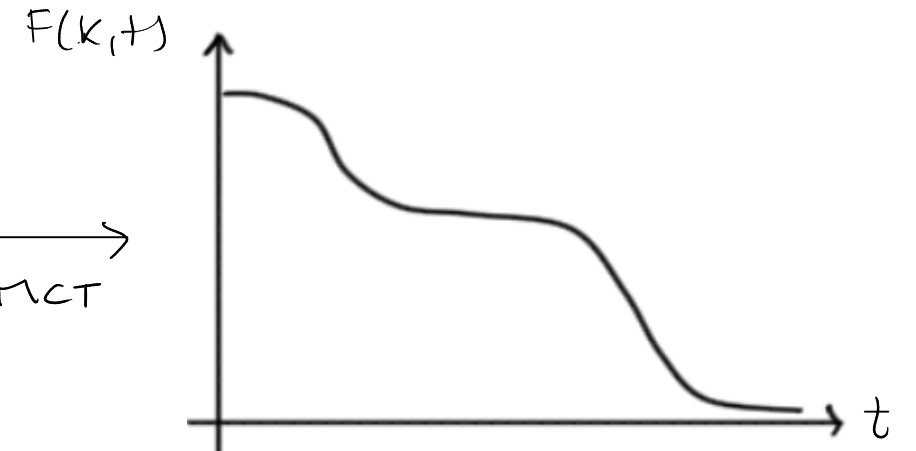
Osservabile "rilevante" $A(t)$ $(\{A_1, ..., A_M\})$

$\nearrow$ lente : $\hat{S}_{\vec{k}}(t)$, $\vec{J}_{\vec{k}}(t)$

$\searrow$ veloci : tutte le altre

Operatore di proiezione $\rightarrow$ prodotto scalare

$$(B \mid A) = \langle A B^* \rangle \qquad \{ \langle \delta A \, \delta B^* \rangle \,]$$

Eq. del moto per A $\longrightarrow$ <mark>eq. di Langevin generalizzata</mark>

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t ds \, M(t-s) A(s) + \theta(t) \quad \leftarrow \text{<mark>forza stocastica</mark>} \quad (A, \theta(t)) = 0$$

<mark>matrice di frequenze</mark>

$$\frac{(A, \dot{A})}{(A, A)}$$

<mark>funzione di memoria</mark>

$$\frac{(R \mid R(t))}{(A, A)}$$

Funzione di correlazione

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

$$= (A \mid A(t))$$

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

F. intermedia di scattering : $F(k,t) = \frac{1}{N} \langle \hat{\rho}_k(t) \hat{\rho}_{-k}(0) \rangle$

Approssimazione mode-coupling : $\theta \sim \rho_{\bar{k}_1}(t) \, \rho_{\bar{k}_2}(t)$

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

$$M(k,t) = \frac{\rho \, k_B T}{16 \, \pi^3 m} \int d\bar{k}' \, |V_{\bar{k}, \bar{k}-\bar{k}'}|^2 \, \underbrace{F(k,t)} \, \underbrace{F(|\bar{k}-\bar{k}'|, t)}$$

$\uparrow$ vertici $\rightarrow$ $S(k)$

Versione schematica di MCT : $\phi(t) = F(k_0, t)$ k_0 primo picco di $S(k)$

$$\frac{d^2 \phi}{dt^2} + \Omega^2 \phi(t) + \lambda \int_0^t ds \, \phi^2(t) \frac{d\phi}{ds} = 0$$ oscillatore armonico smorzato con memoria

$\uparrow$ parametro di controllo

oscillatore armonico smorzato

$$\frac{d^2 \phi}{dt^2} + \Omega^2 \phi(t) + \lambda \frac{d\phi}{ds} = 0$$

oscillatore armonico smorzato

Sovramorzato

$\tau \sim \lambda$

Sottosmorzato

oscillatore armonico smorzato con memoria

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

λ_c

$\begin{cases} \lambda < \lambda_c : f = 0 \\ \lambda \geq \lambda_c : f > 0 \end{cases} \Rightarrow$ transizione vetrosa ideale
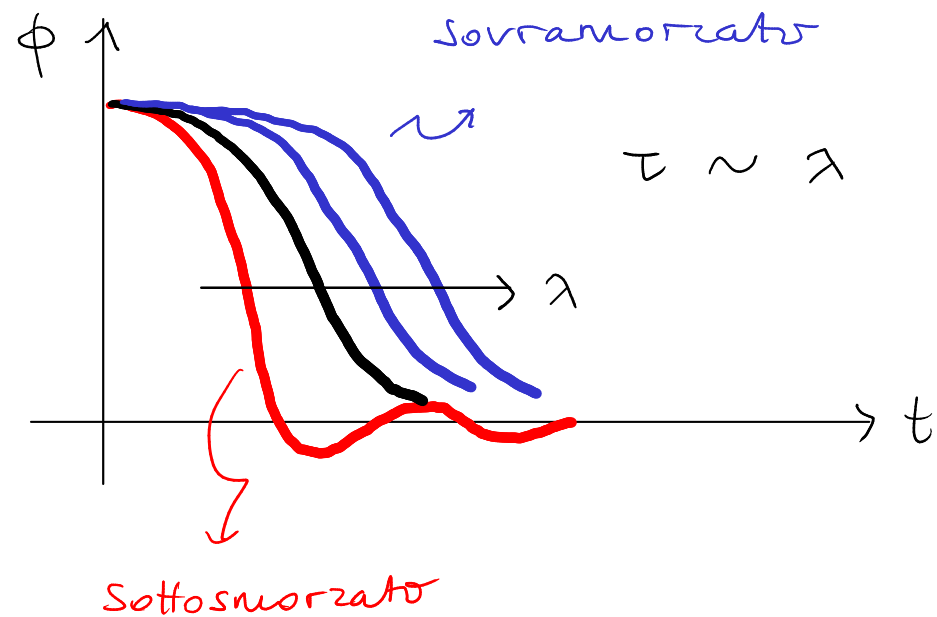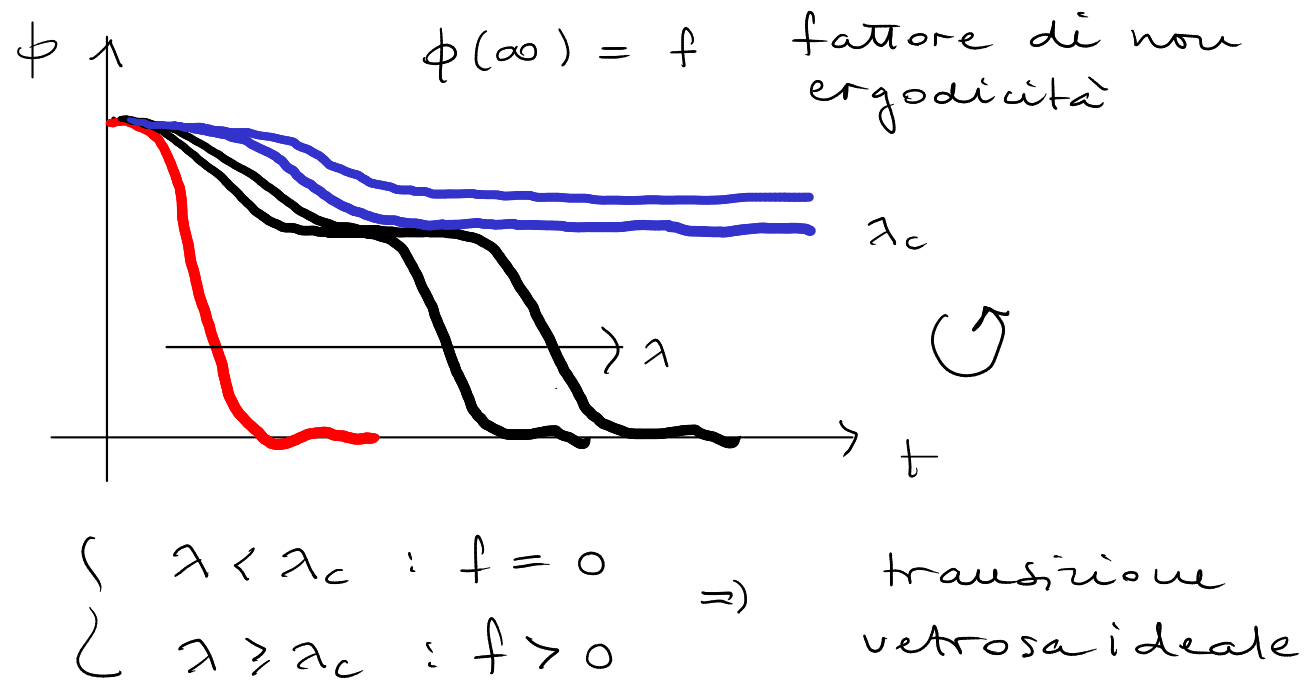
Predizioni generali della MCT

1) **2- step relaxation**

- **β - relaxation**

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

$$g < \begin{array}{l} (t/\tau_\beta)^{-a} \\ (t/\tau_\beta)^{b} \end{array}$$

- **α - relaxation**

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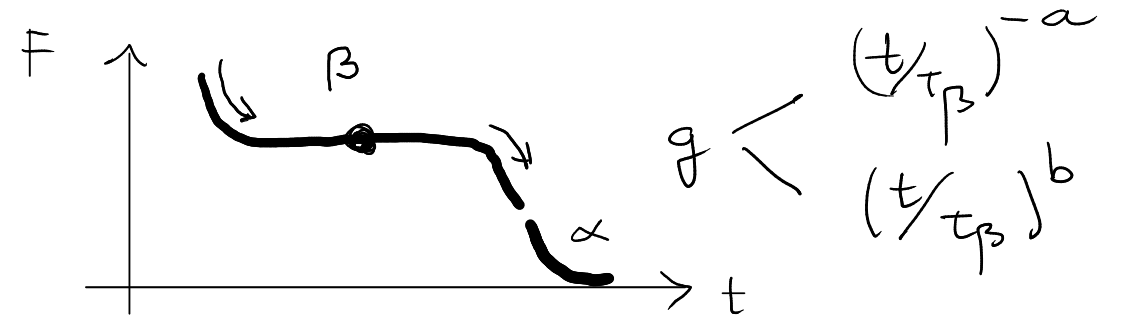
2) **$\tau_\alpha(T)$**

- $$\tau_\alpha \sim \frac{1}{|T-Tc|^\gamma} \qquad \gamma \sim 2$$
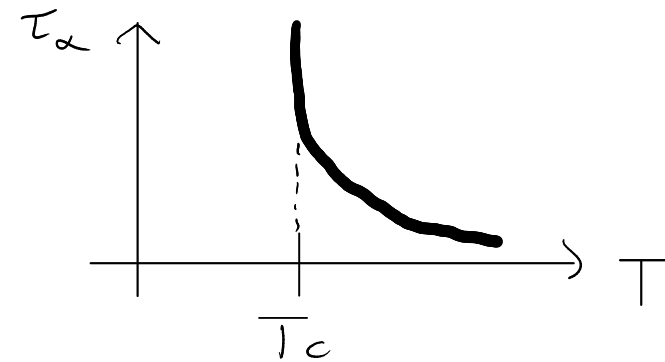
3) **$D, \eta, \ldots$**

Verifica predizioni della MCT

1) "Principi primi" : $S(K) \to F(K,t)$

2) "Fit" $\to$ a, b, γ, T_c parametri liberi

$T_{onset} \sim 1.0$

$T_c^{(pp)} = 0.92$

$T_g^{(sim)} = 0.4$

$T_c^{(fit)} = 0.435$

processi
attivati

$\nearrow$ difetti

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

$\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$

crossover   evitata   convenzionale   evitata
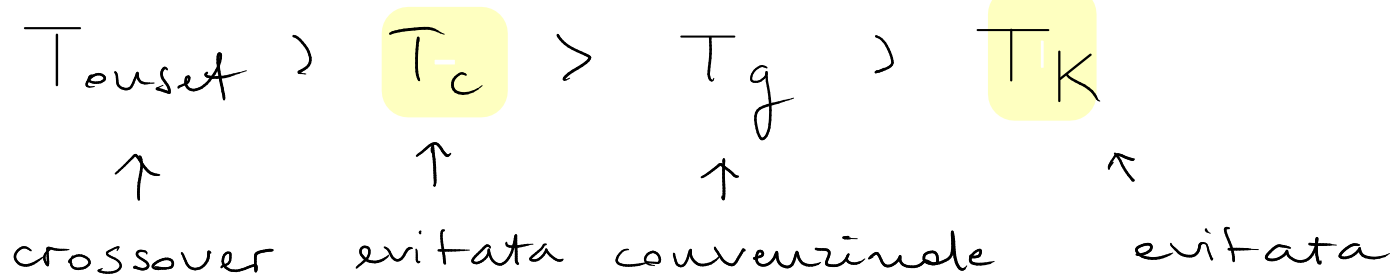
cf. Cavagna
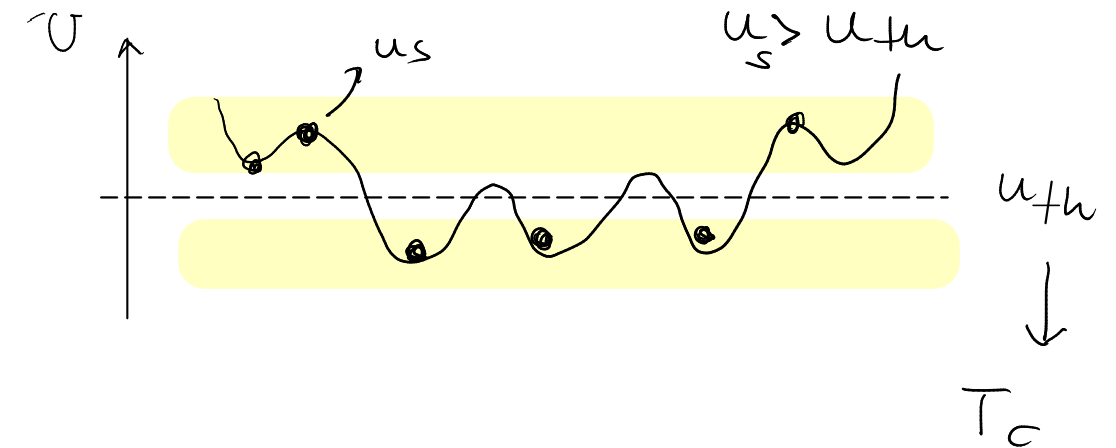
THE ATOMIC ARRANGEMENT IN GLASS

By W. H. Zachariasen

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   →   ossidi (silicati), calcogenidi

- close - packed glasses   →   metalli, colloidi, polimeri

Periodic Table of the Elements

Legend box:
Atomic Number — Atomic Mass
Symbol
Name
Electron Shells
Electron Configuration

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

Group headers:

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	10 VIII	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A

Period 1
- 1, 1.008, H, Hydrogen, 1, 1s¹ → $1s^1$
- 2, 4.003, He, Helium, 2, $1s^2$

Period 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, $[He]2s^2 2p^6$

Period 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, $[Ne]3s^2 3p^6$

Period 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, $[Ar]3d^{10} 4s^2 4p^6$

Period 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, $[Kr]4d^{10} 5s^2 5p^6$

Period 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 (Lanthanides)
- 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, $[Xe]4f^{14} 5d^{10} 6s^2 6p^6$

Period 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 (Actinides)
- 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 17 1, $[Rn]5f^{14} 6d^8 7s^{2*}$
- 111, [272], Rg, Roentgenium, 2 8 18 32 32 18 1, $[Rn]5f^{14} 6d^9 7s^{2*}$
- 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 9 2, $[Xe]5d^1 6s^2$
- 58, 140.116, Ce, Cerium, 2 8 20 8 2, $[Xe]4f^1 5d^1 6s^2$
- 59, 140.908, Pr, Praseodymium, 2 8 21 8 2, $[Xe]4f^3 6s^2$
- 60, 144.243, Nd, Neodymium, 2 8 22 8 2, $[Xe]4f^4 6s^2$
- 61, 144.913, Pm, Promethium, 2 8 23 8 2, $[Xe]4f^5 6s^2$
- 62, 150.36, Sm, Samarium, 2 8 24 8 2, $[Xe]4f^6 6s^2$
- 63, 151.964, Eu, Europium, 2 8 25 8 2, $[Xe]4f^7 6s^2$
- 64, 157.25, Gd, Gadolinium, 2 8 25 9 2, $[Xe]4f^7 5d^1 6s^2$
- 65, 158.925, Tb, Terbium, 2 8 27 8 2, $[Xe]4f^9 6s^2$
- 66, 162.500, Dy, Dysprosium, 2 8 28 8 2, $[Xe]4f^{10} 6s^2$
- 67, 164.930, Ho, Holmium, 2 8 29 8 2, $[Xe]4f^{11} 6s^2$
- 68, 167.259, Er, Erbium, 2 8 30 8 2, $[Xe]4f^{12} 6s^2$
- 69, 168.934, Tm, Thulium, 2 8 31 8 2, $[Xe]4f^{13} 6s^2$
- 70, 173.055, Yb, Ytterbium, 2 8 32 8 2, $[Xe]4f^{14} 6s^2$
- 71, 174.967, Lu, Lutetium, 2 8 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 22 9 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, $[Rn]5f^{14} 6d^1 7s^2$

Legend (categories):
Alkali Metal · Alkaline Earth · Transition Metal · Basic Metal · Metalloid · Nonmetal · Halogen · Noble Gas · Lanthanide · Actinide

Network-forming glasses

Ossidi : $A_m O_n$

Calcogenidi : S, Se, Te + $Ge, As, ...$

$Si O_2, Ge O_2$
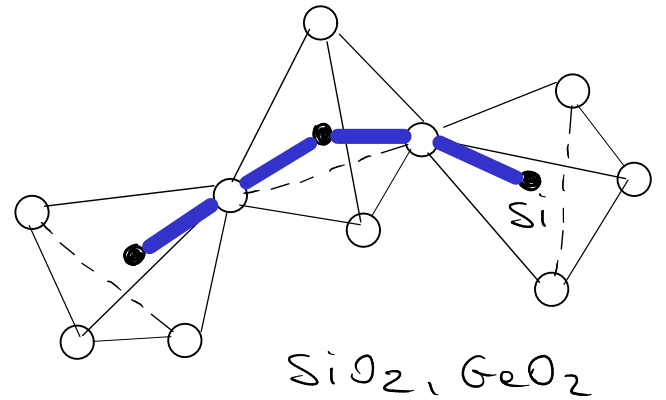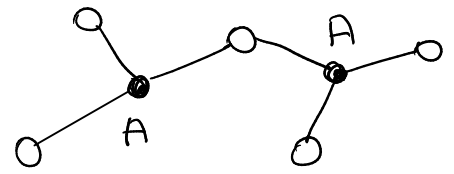
continuous random network

$\left. \begin{array}{c} z_A \\ z_O \end{array} \right\}$ numeri di coordinazione

$\left. \begin{array}{c} x_A = N_A/N \\ x_O = N_O/N \end{array} \right\}$ concentrazioni chimiche

<u>ES.</u> : saturazione dei legami ?

$$z_A, z_O \Rightarrow x_A, x_O ?$$

$z_{Si} = 4 \; ; \; z_O = 2$

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

$x_A z_A = (1 - x_A) z_O$

$x_A (z_A + z_O) = z_O$

es: $x_{Si} = \dfrac{1}{3}$ $x_O = \dfrac{2}{3}$ $x_A = \dfrac{z_O}{z_A + z_O}$
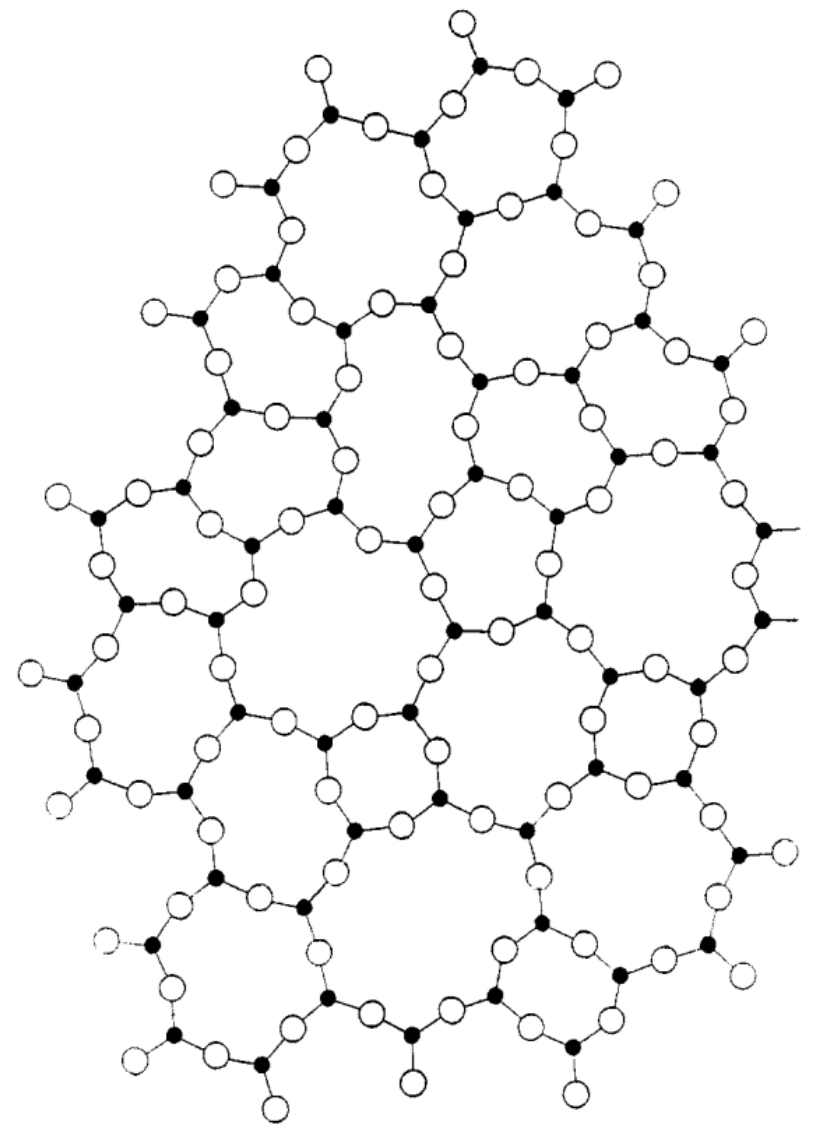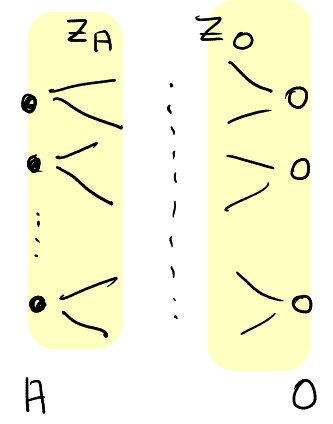
Fig. 1b.

Zachariasen 1932

ES: $Ge + Se$

$As + Se ...$

Silice 2d

$$z_{Si} \simeq 3 \qquad z_0 = 2$$
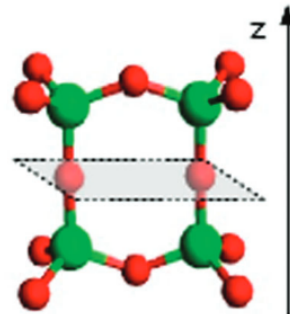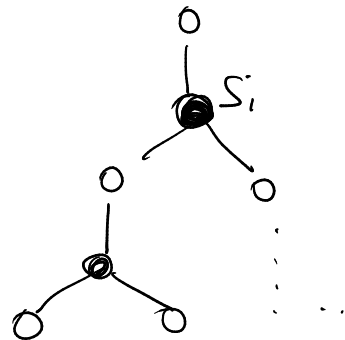
Teorie della rigidità

1) Gupta - Cooper (>1978)

2) Phillips - Thorpe (>1979) $\rightarrow$ $T = 0$

Stabilità marginale / isostaticità

Maxwell (1864)

$$N_{dof} = N_v \leftarrow \text{vincoli}$$

$T = 0$; x_α, z_α fissati
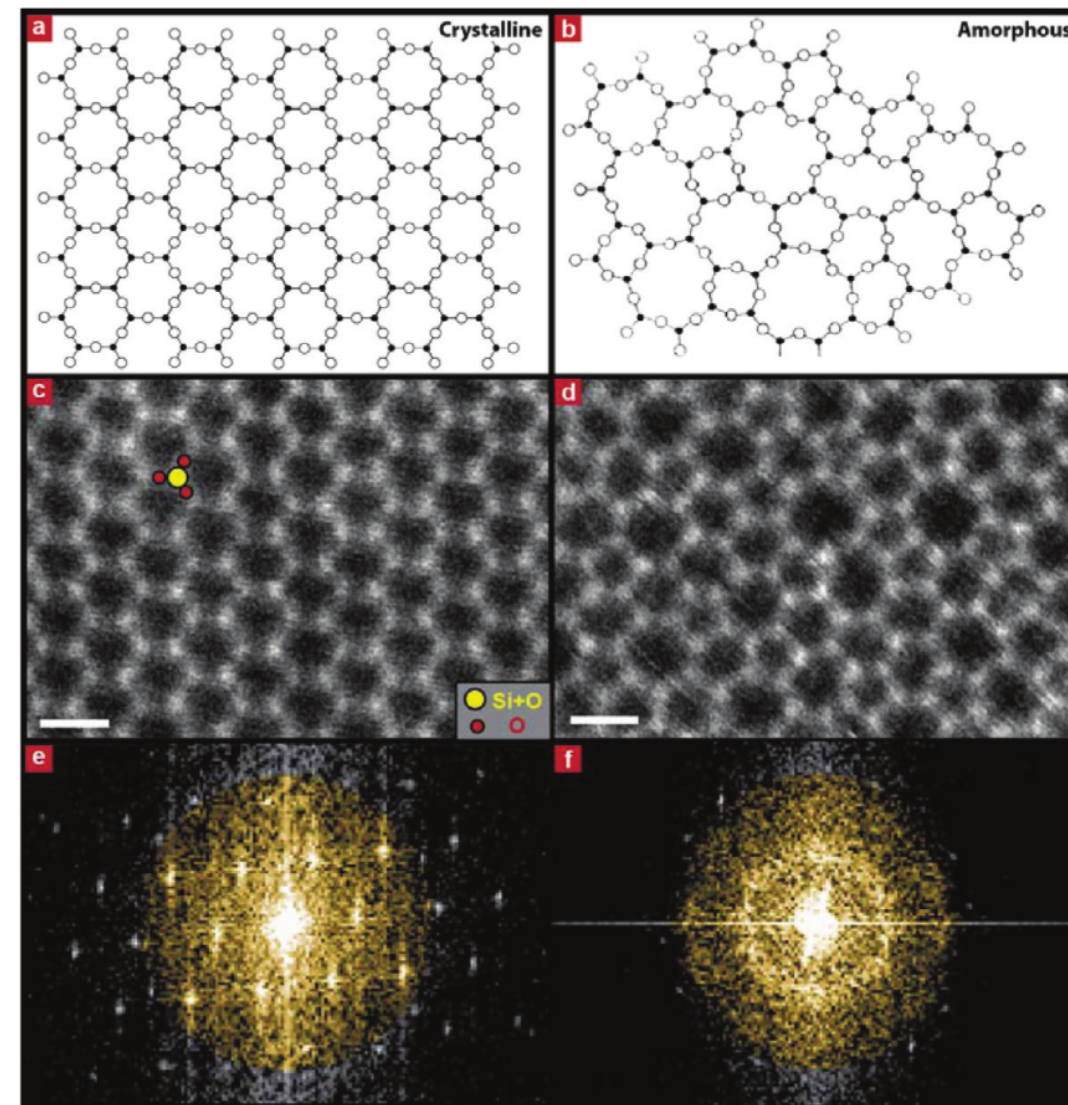
$$N_v \simeq \sum_\alpha \left[N_\alpha \frac{z_\alpha}{2} + N_\alpha \left(2 z_\alpha - 3 \right) \right]$$

$\uparrow$ $\uparrow$

legami   angoli

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

$$3 N = N \left(\frac{5}{2} \langle z \rangle - 3 \right) \implies \langle z \rangle = \frac{12}{5} = 2.4$$

$$\text{ES}: \quad \langle z \rangle \simeq z_{Si} x_{Si} + z_0 x_0 = 4 \cdot \frac{1}{3} + 2 \cdot \frac{2}{3} = \frac{8}{3} = 2.\overline{6} \gtrsim 2.4$$

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.
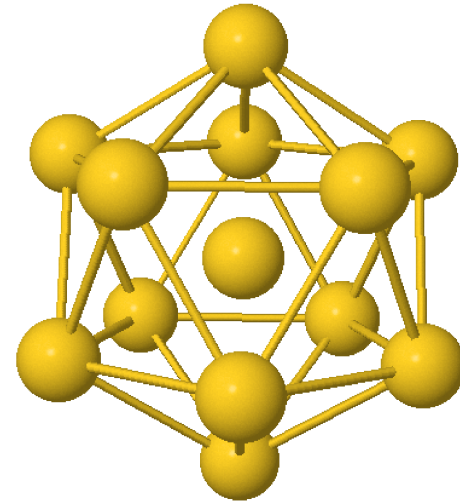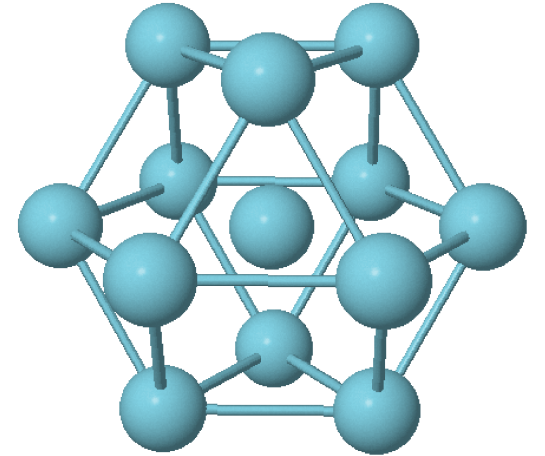
ICOSAEDRO   FCC

$$U_{ICO} < U_{FCC} \quad LJ$$

$$(8\%)$$

$$\downarrow$$

FRUSTRAZIONE GEOMETRICA
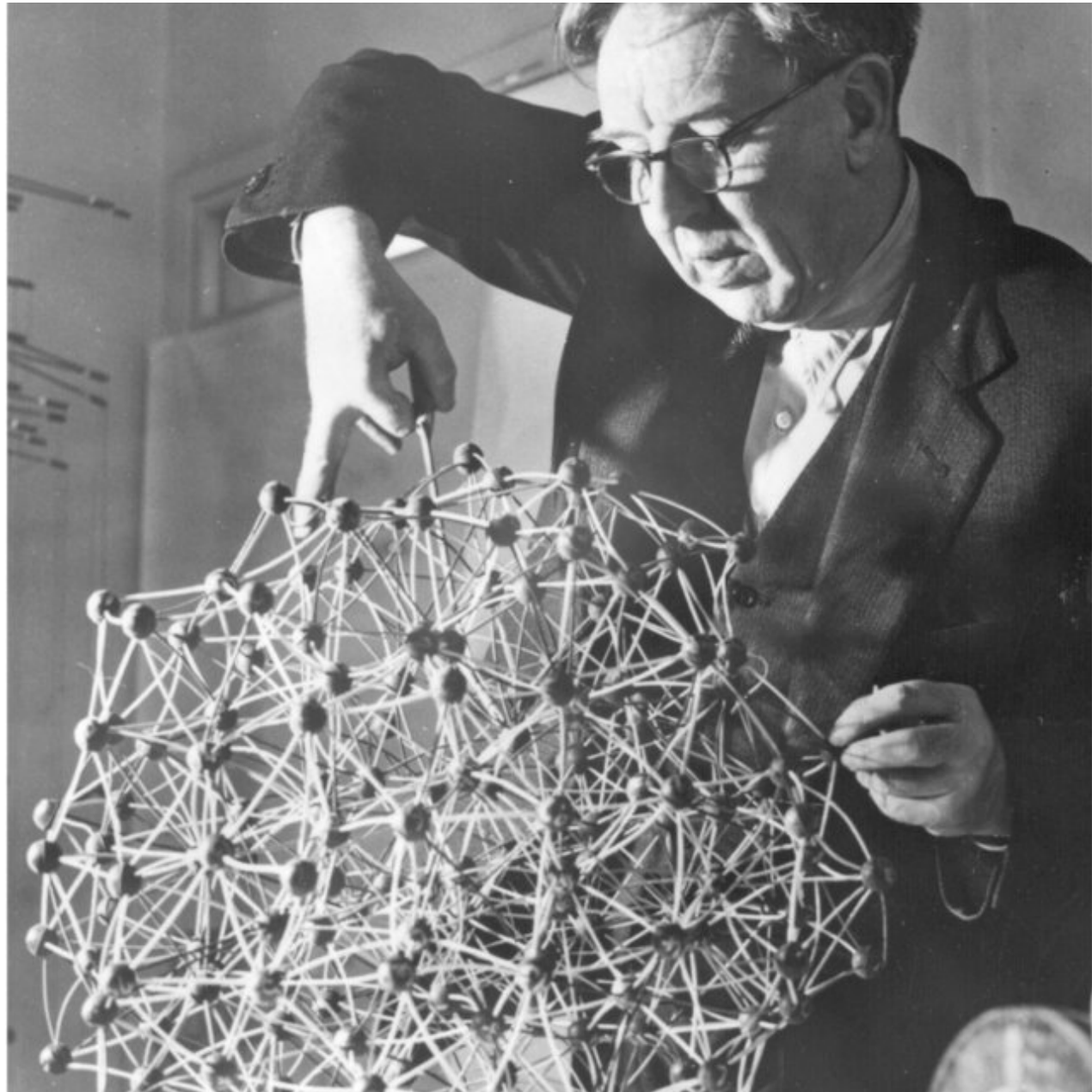
Bernal 1964

Tassellazione di Voronoi

→ Wigner – Seitz

Celle di Voronoi

- f : n. di facce

- p : n. vertici di ogni faccia

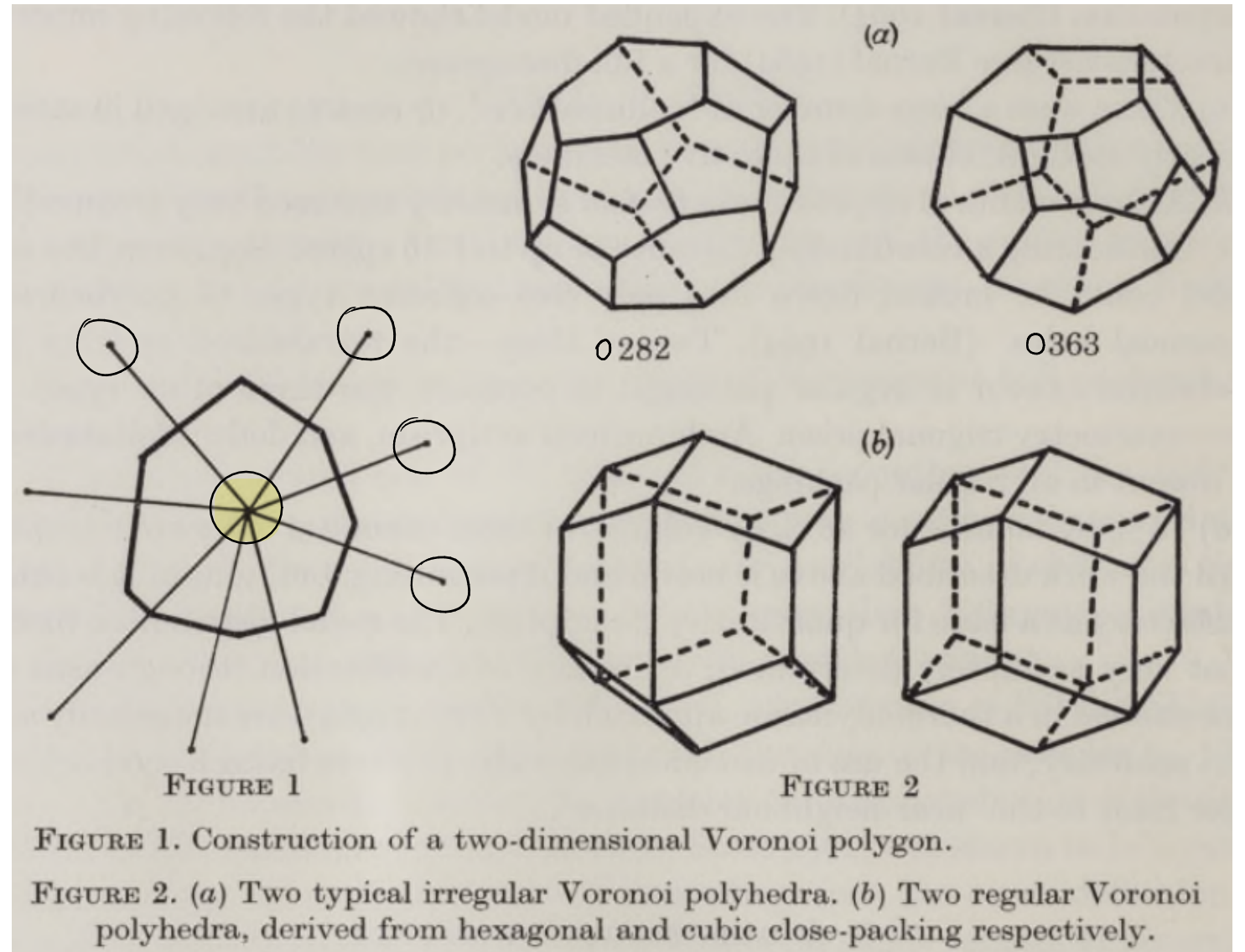$$\langle f \rangle = \frac{12}{6 - \langle p \rangle}$$

"Segnatura" : $\{ f_3, f_4, f_5, \dots \}$

Icosaedri : $\{0, 0, 12\}$

Close - packing : $\phi_{FCC} = 0.74$

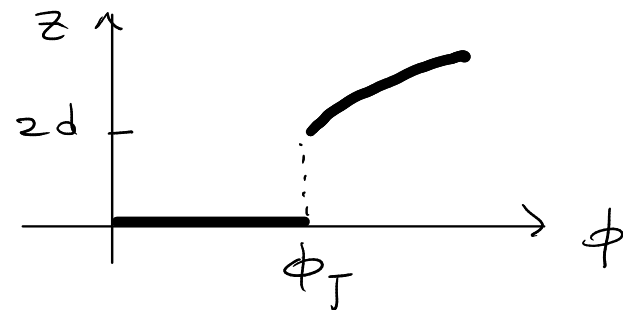Random close - packing : $\phi_{RCP} \sim 0.64 - 0.68$
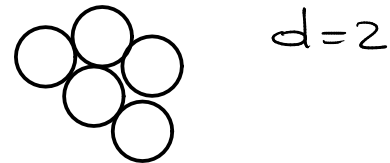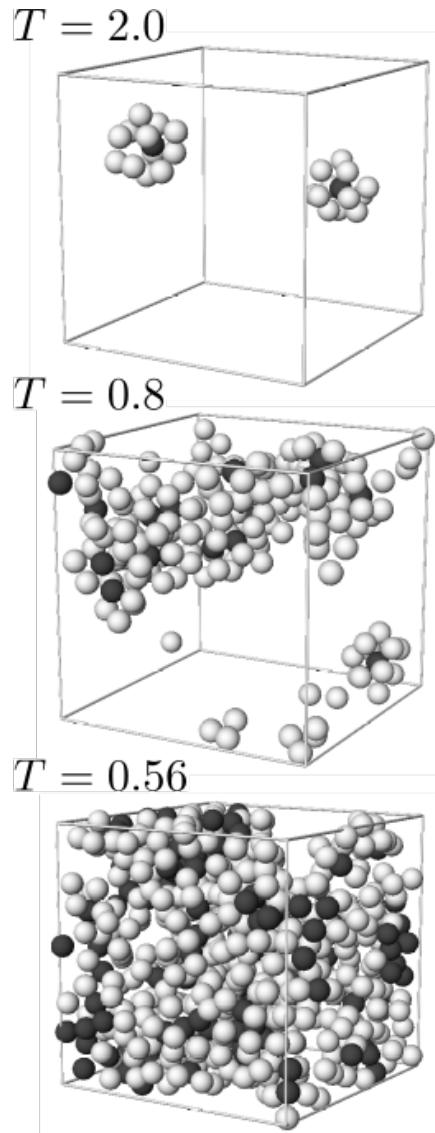
Maxwell : $N_{dof} = N_v$

0282   0363

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

$$dN = N \frac{z}{2} \quad \Rightarrow \quad z_c = 2d$$

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

JAMMING

$d=2$

$T = 2.0$

$T = 0.8$

$T = 0.56$

Coslovich Pastore JCP 2007

Miscela binaria di
WAHNSTRÖM

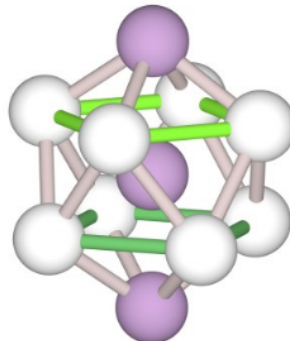$T_{onset} \approx 1.0$

$T_c \approx 0.55$

ICO
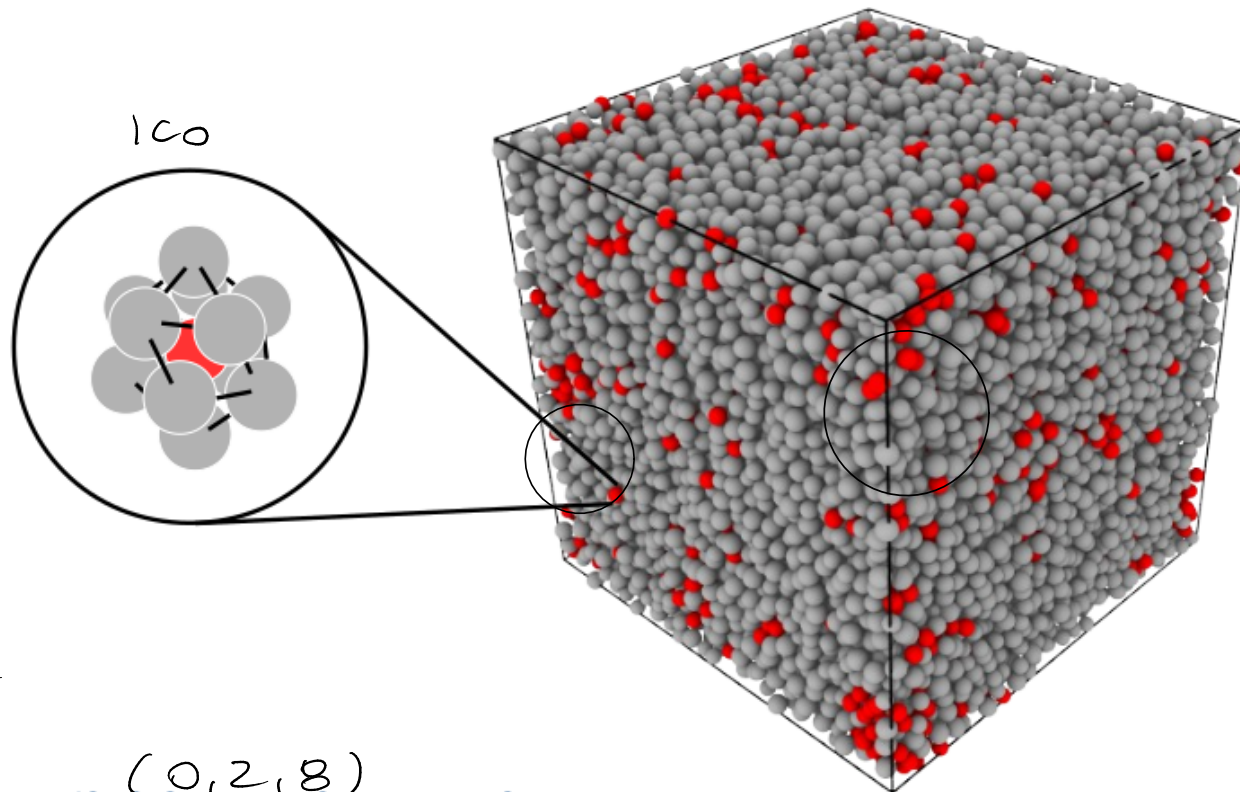
LFS

$(6,0,12)$
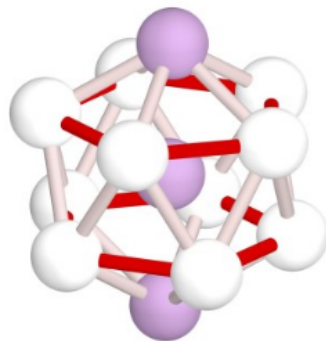
Wahnström
mixture

$(0,2,8)$

Kob-Andersen
mixture
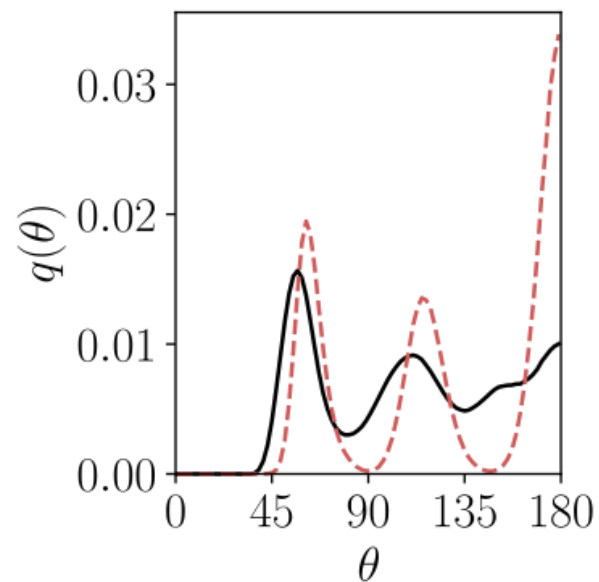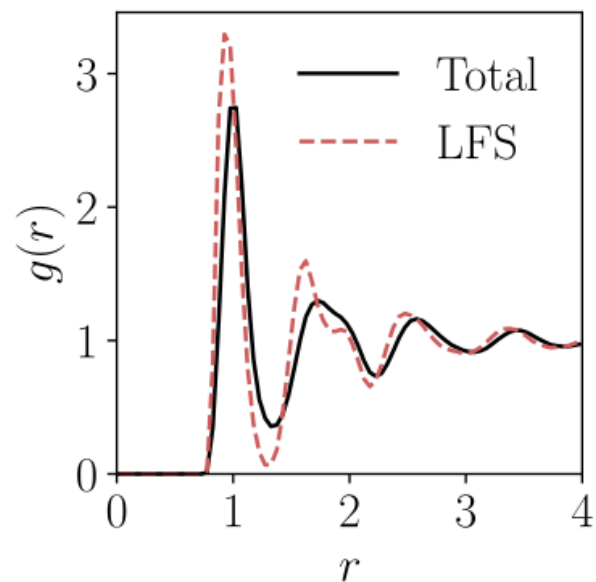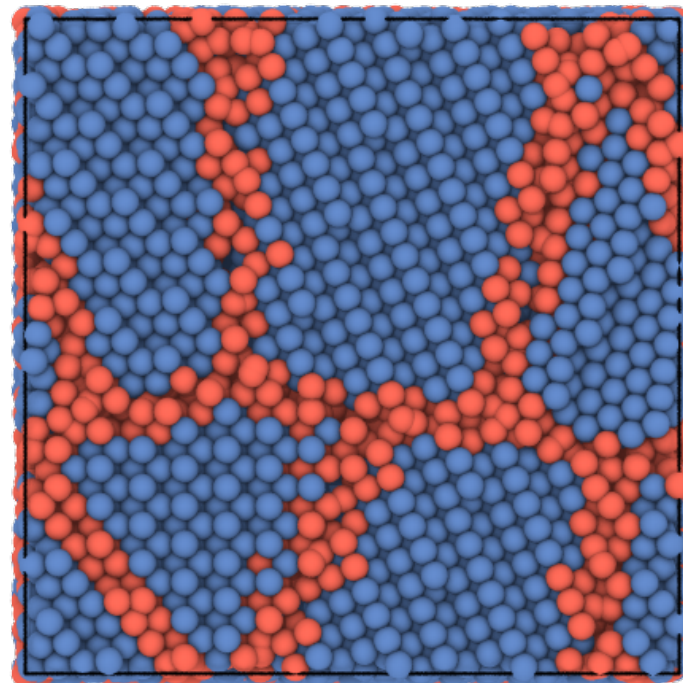
Paret, Jack, Coslovich JCP 2019

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