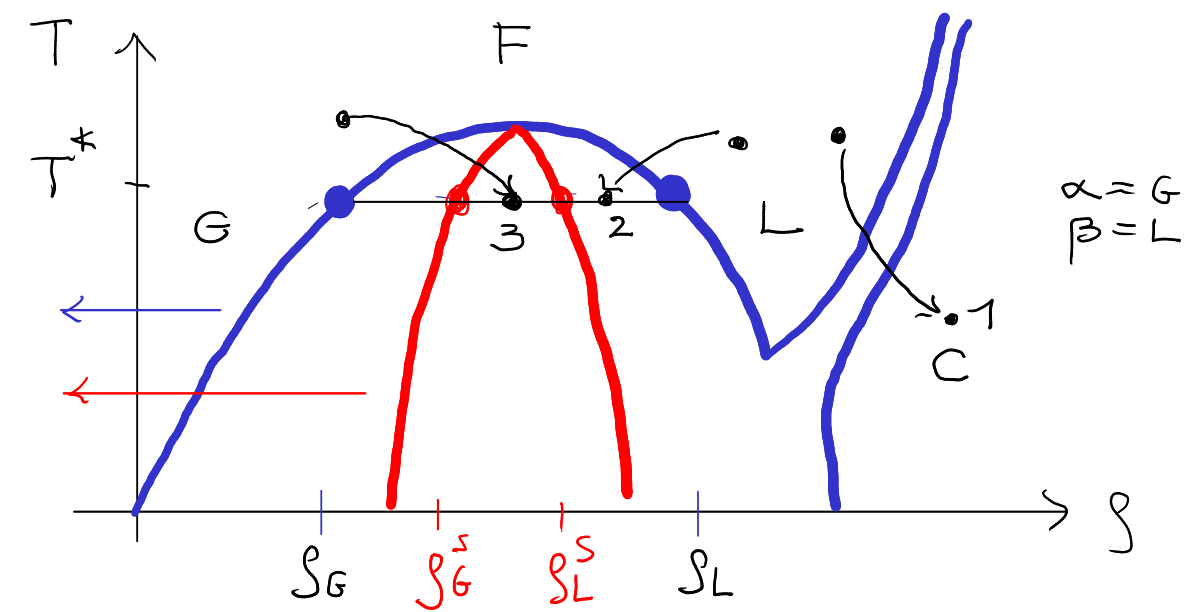
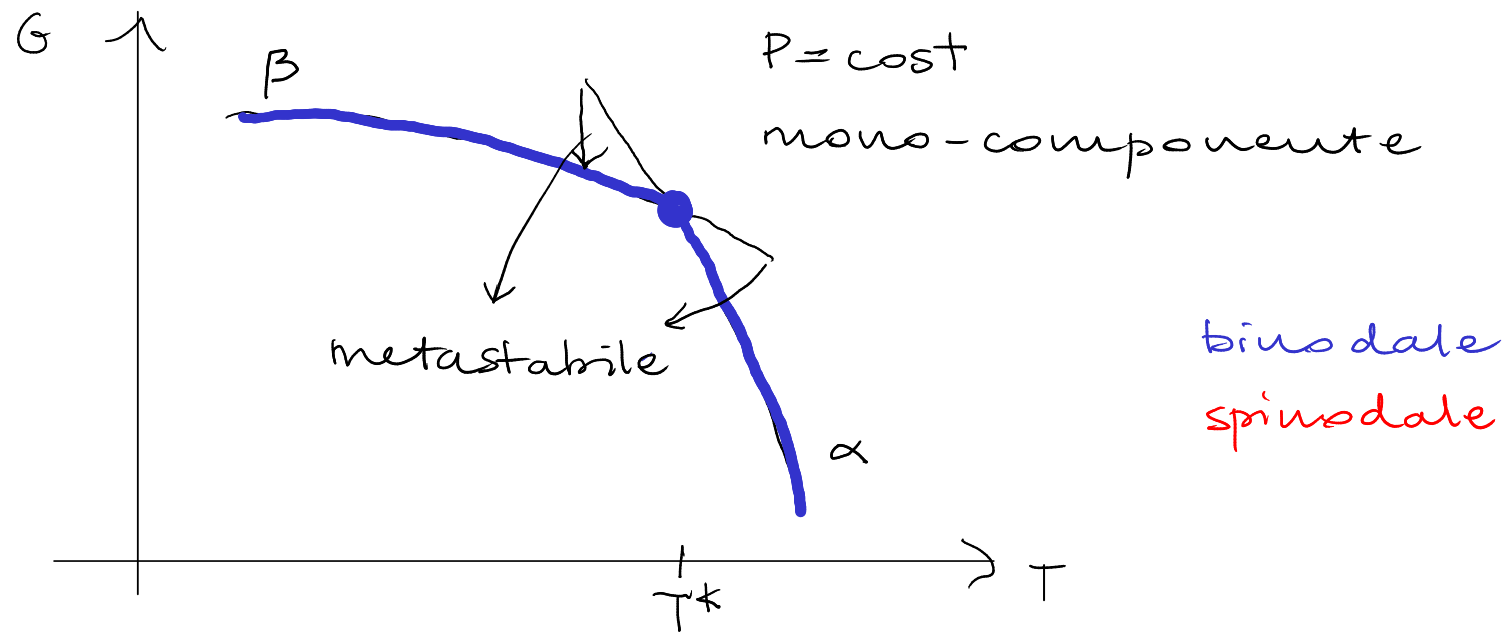


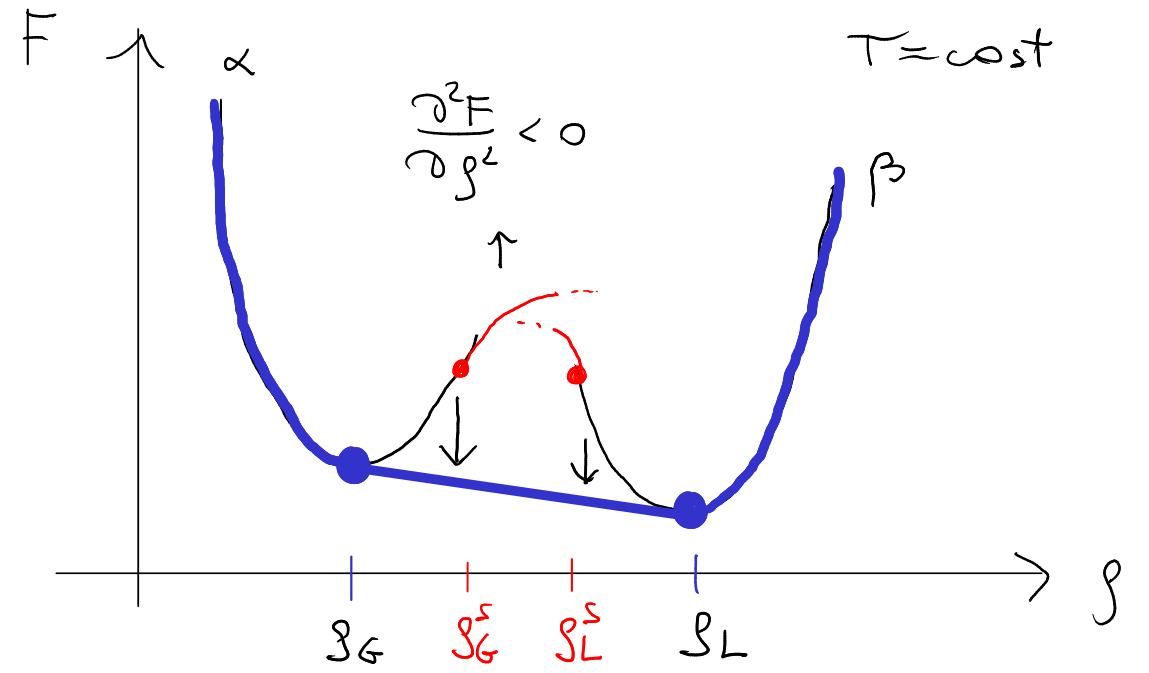
FLUIDI METASTABILI E INSTABILI



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 : fenomeno nucleologica

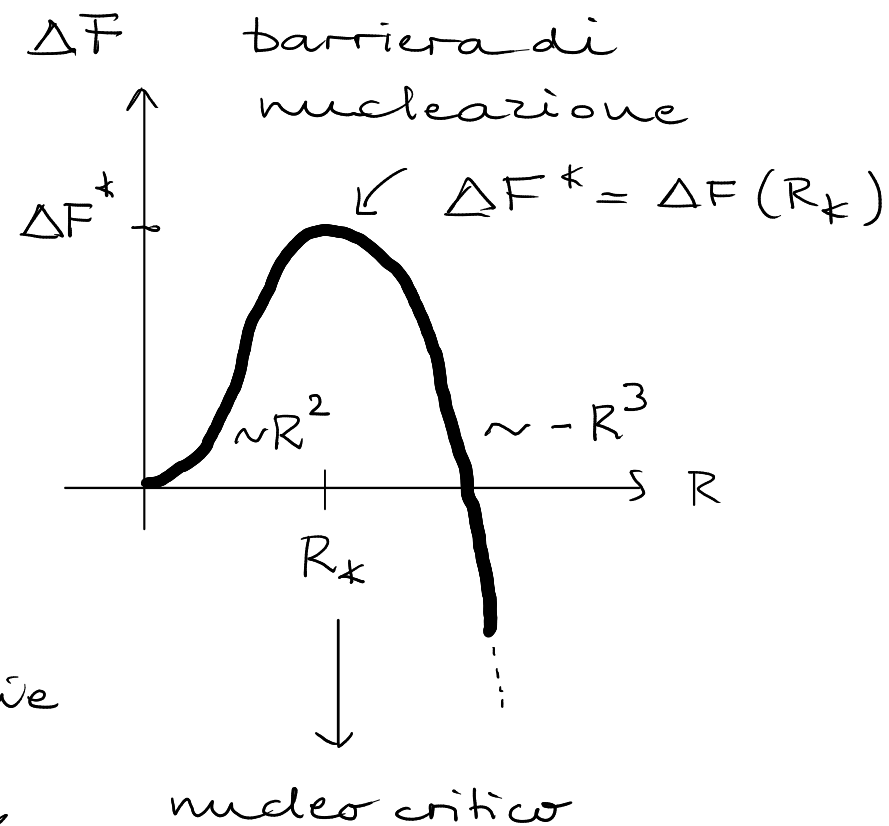
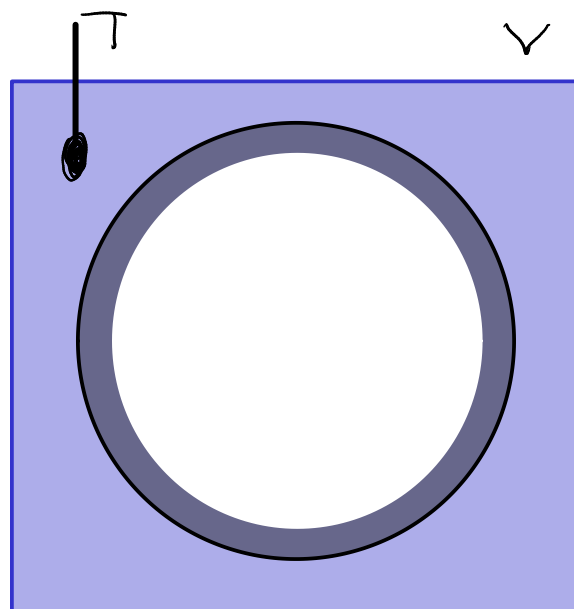
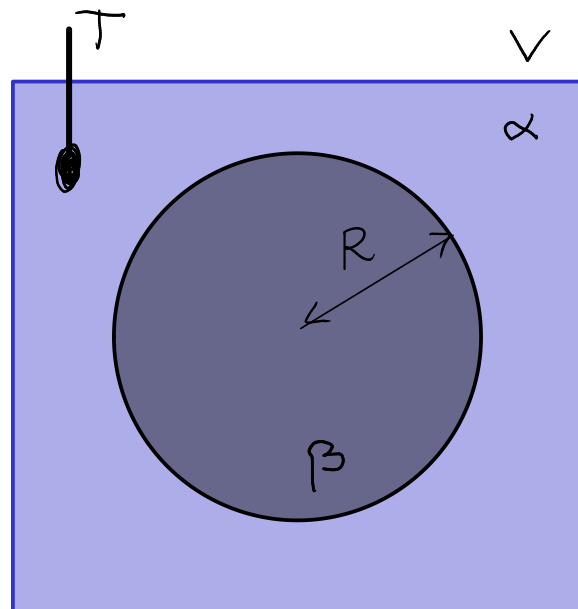
α = metastabile

β = stabile

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

$$f_{\beta} < f_{\alpha}$$

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



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

$$\frac{d\Delta F}{dR} \Big|_{R^*} = 0 : 4\pi R^2 \Delta f + 8\pi R \gamma = 0 \Rightarrow R^* = -\frac{2\gamma}{\Delta f}$$

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

Cinetica della nucleazione

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

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

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

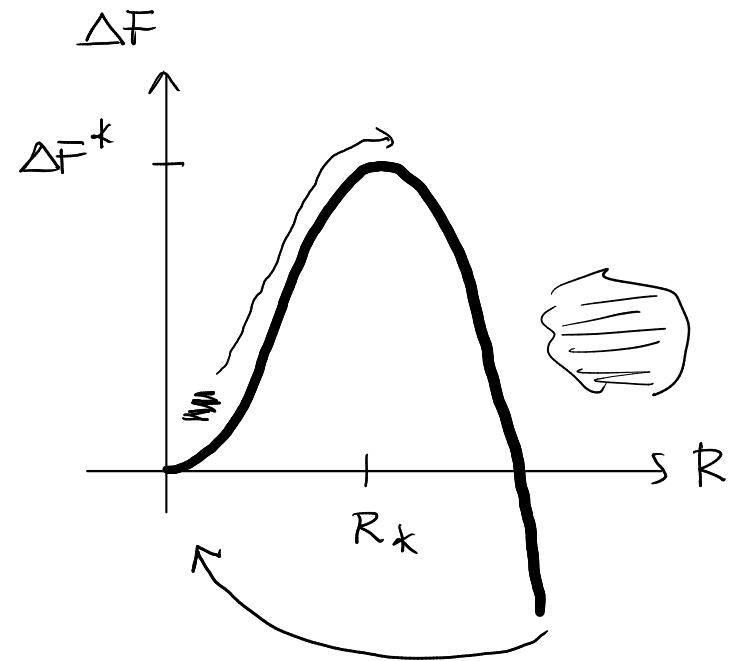
$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial R} \left[D(R) \frac{\partial p}{\partial R} + \frac{1}{\zeta} \frac{d\Delta F}{dR} p \right] \quad \Delta F^* \gg k_B T$$

Tempo di nucleazione τ_x (1 nucleo critico)

= tempo di uscita

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

\uparrow \uparrow
fattore cinetico fattore termodinamico (Zeldovich)



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

Tasso di nucleazione: nuclei / tempo / volume

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

Dipendenza di τ_x dalla temperatura

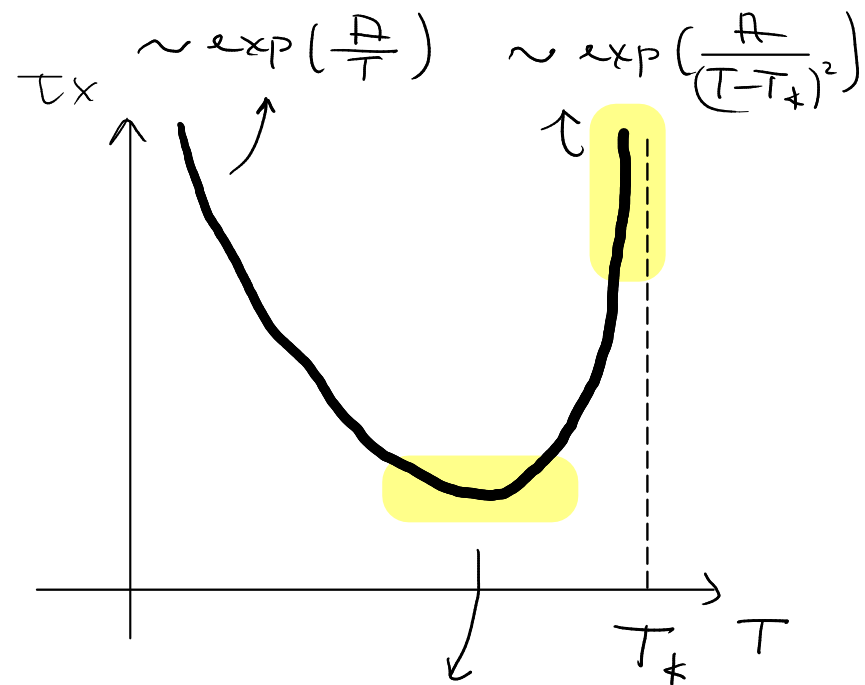
$$T \ll T_* : D(R^*) \sim \exp\left(-\frac{\Delta E_d}{k_B T}\right)$$

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

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

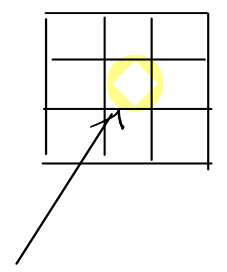
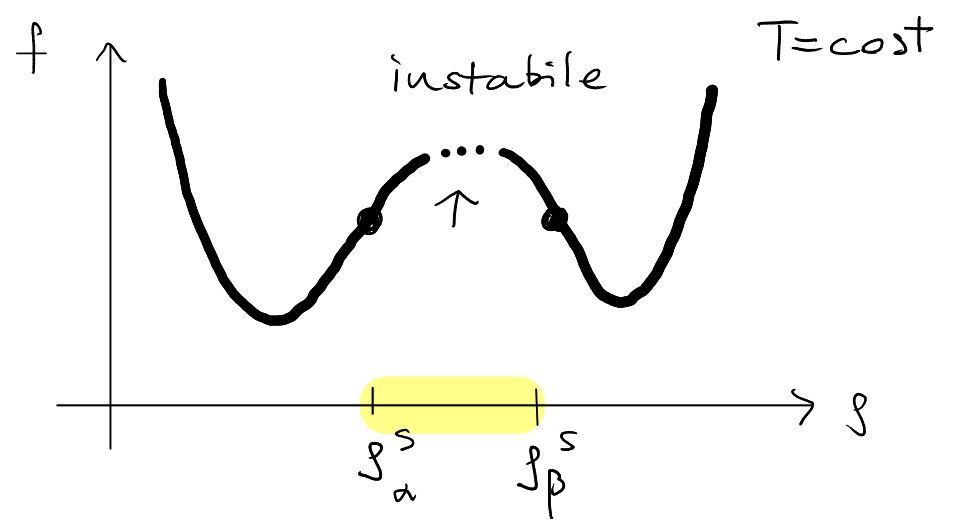
$$\Delta F^* \sim \frac{1}{\Delta f^2} \sim \frac{1}{(T - T_*)^2}$$

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



nucleazione
+ rapida
omogenea

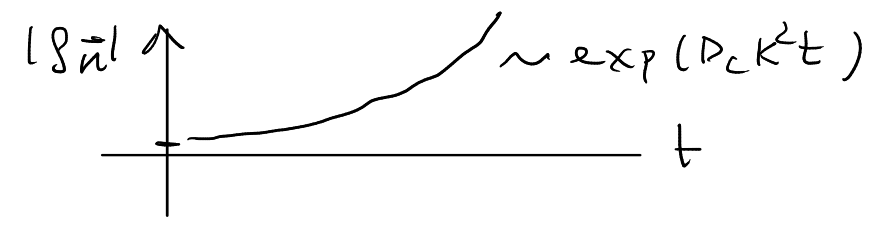
2) Decomposizione Spinozzale



$$\begin{aligned}
 g_N(\vec{F}_i, t) &= g(\vec{F}_i, t) \\
 \frac{\partial g}{\partial t} &= -\vec{\nabla} \cdot (L_{NN} \vec{\nabla} (-\frac{\mu}{T})) \\
 &= \vec{\nabla} \cdot (\frac{L_{NN}}{T} \vec{\nabla} \mu) \\
 \mu &= \mu[g(\vec{F}_i, t)] = \underbrace{\vec{\nabla} \cdot (\frac{L_{NN}}{T} \frac{\partial \mu}{\partial g} \vec{\nabla} g)}_{D_c}
 \end{aligned}$$

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

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



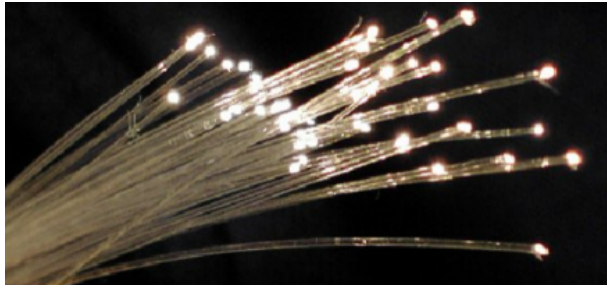
$$\frac{\partial g}{\partial t} = D_c \vec{\nabla}^2 g \Rightarrow g_{\vec{k}}(t) = g_{\vec{k}}(0) \exp(-D_c k^2 t) = g_{\vec{k}}(0) \exp(+|D_c| k^2 t)$$

Cahn-Hilliard:
$$\frac{\partial g}{\partial t} = \frac{L_{NN}}{T} \nabla^2 \left[\frac{\partial^2 f}{\partial g^2} g_N - \frac{k_B T \epsilon_0^2}{g} \nabla^2 g \right]$$

Formatori di vetro

Ossidi

Silicati : SiO_2 (silice)



B_2O_3

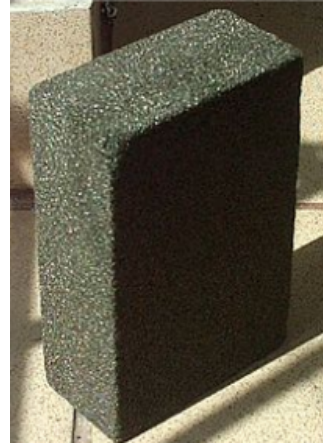


gorilla glass®

vetro da finestra

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

Polimeri



polistirene

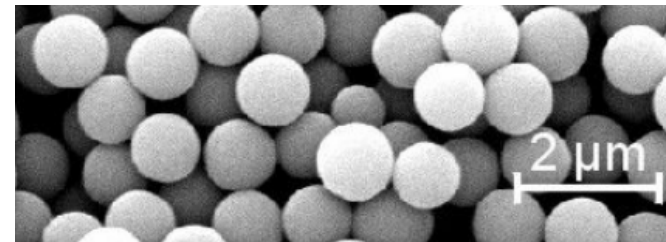


PMMA

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

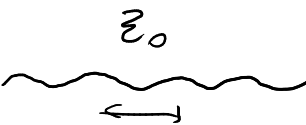
Richert & Angell JCP 1998

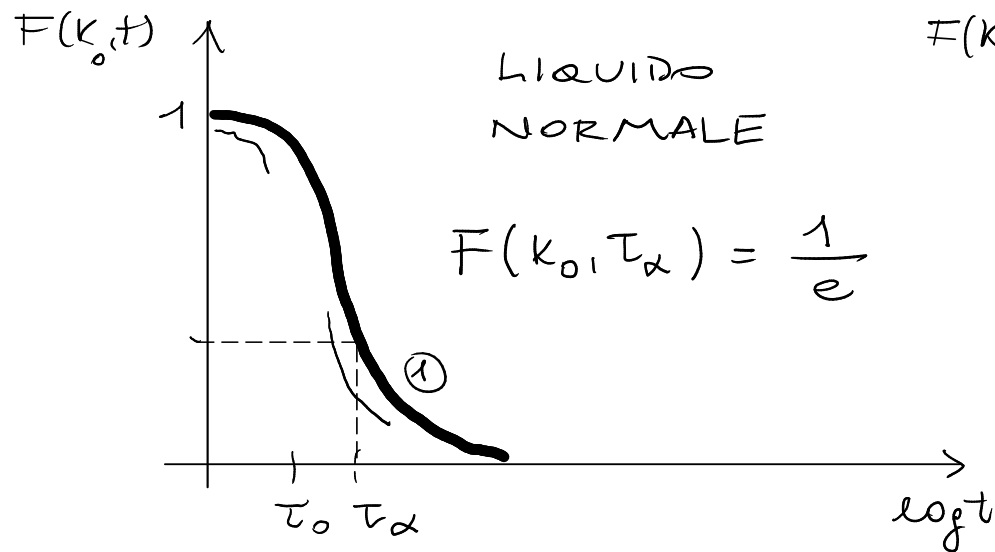
FENOMENOLOGIA DELLA TRANSIZIONE LIQUIDO - VETRO

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

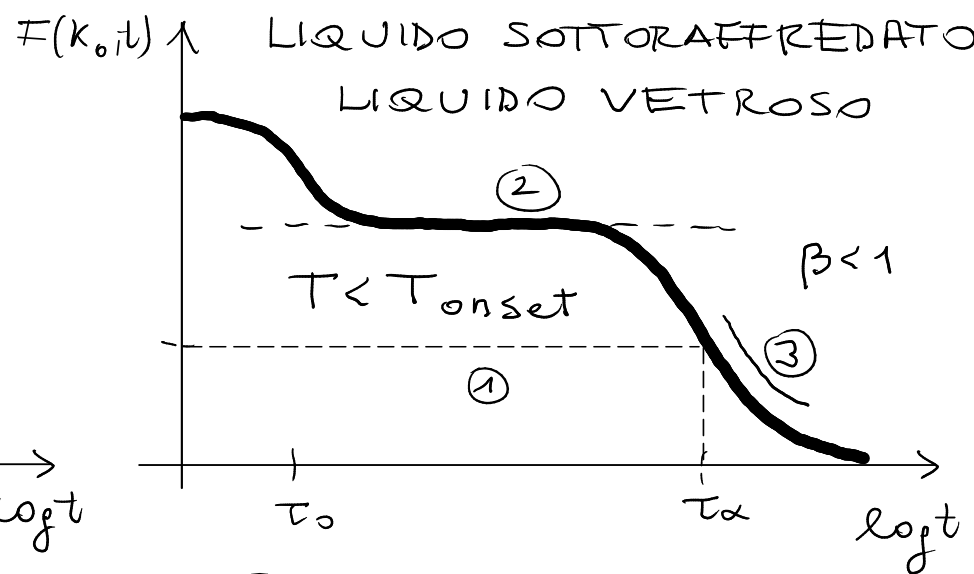
1) Tempo di rilassamento strutturale

$$F(k, t) = \frac{\langle \hat{\rho}_{\vec{k}}(t) \hat{\rho}_{-\vec{k}}(0) \rangle}{\langle \hat{\rho}_{\vec{k}}(0) \hat{\rho}_{-\vec{k}}(0) \rangle}$$

$$k_0 \approx \frac{2\pi}{\xi_0}$$




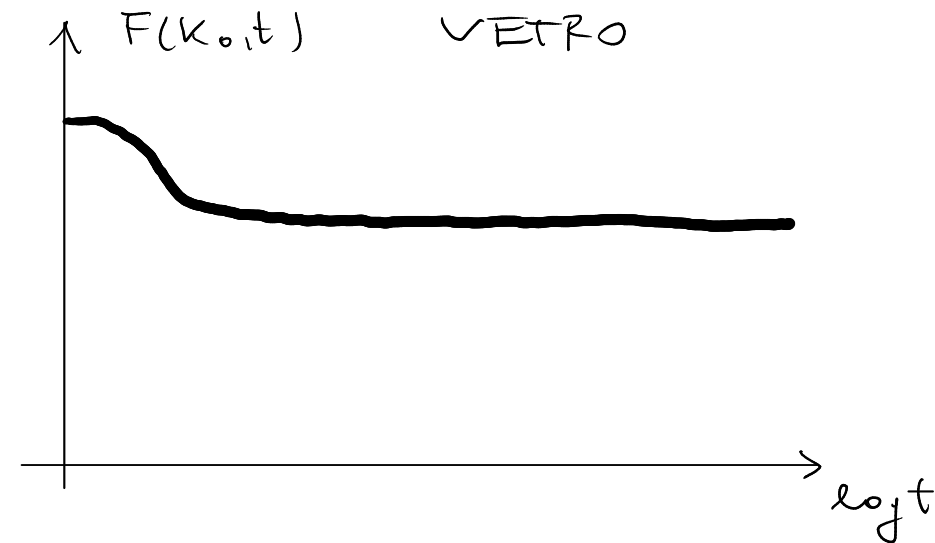
① $F(k_0, t) \sim \exp(-t/\tau_\alpha)$



① $\tau_\alpha \gg \tau_0$

② two-step

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

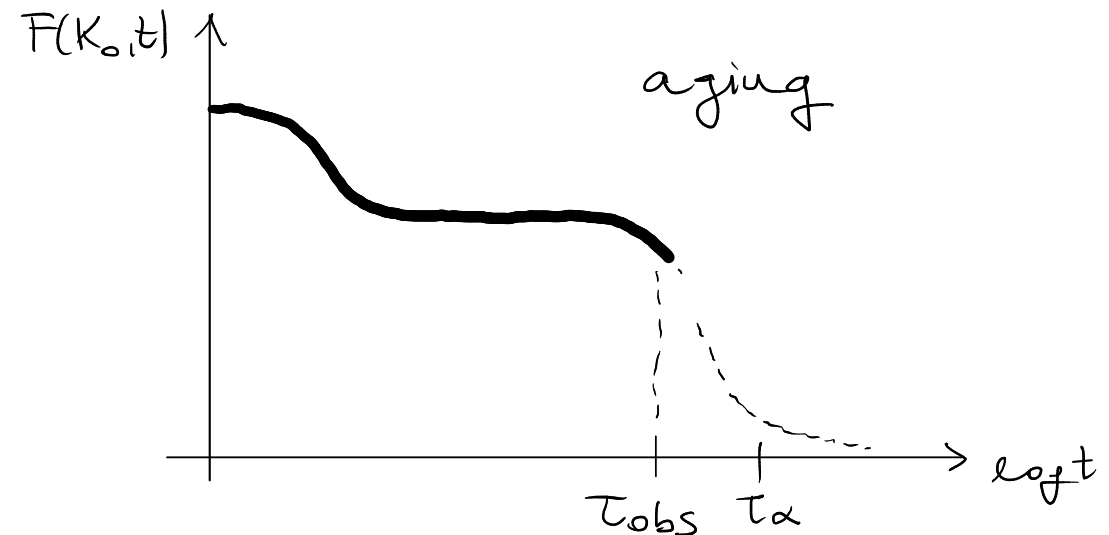
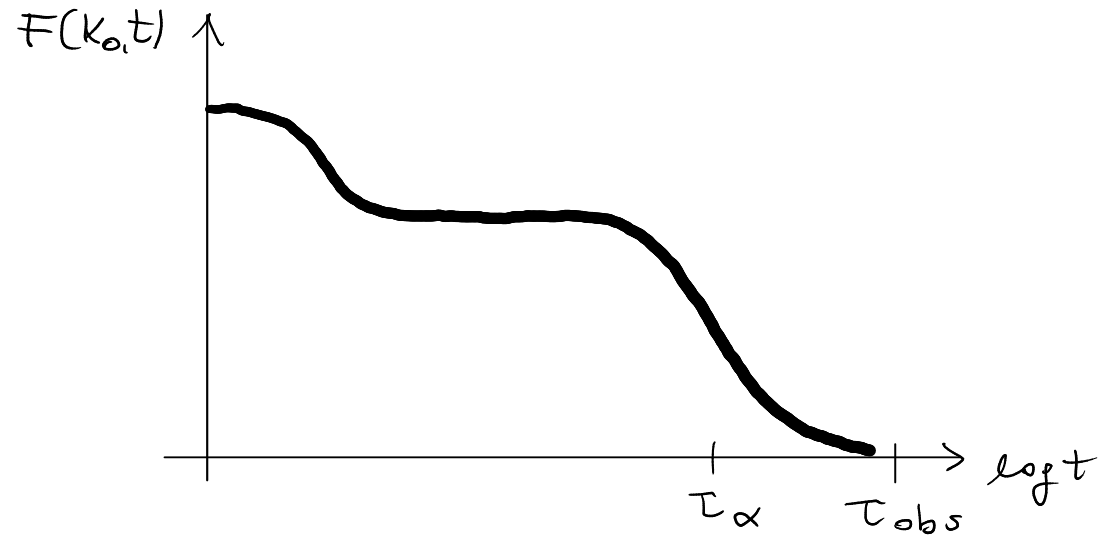


Relatione Maxwell

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

$\rightarrow 1/T$

2) Tempo di osservazione: τ_{obs}



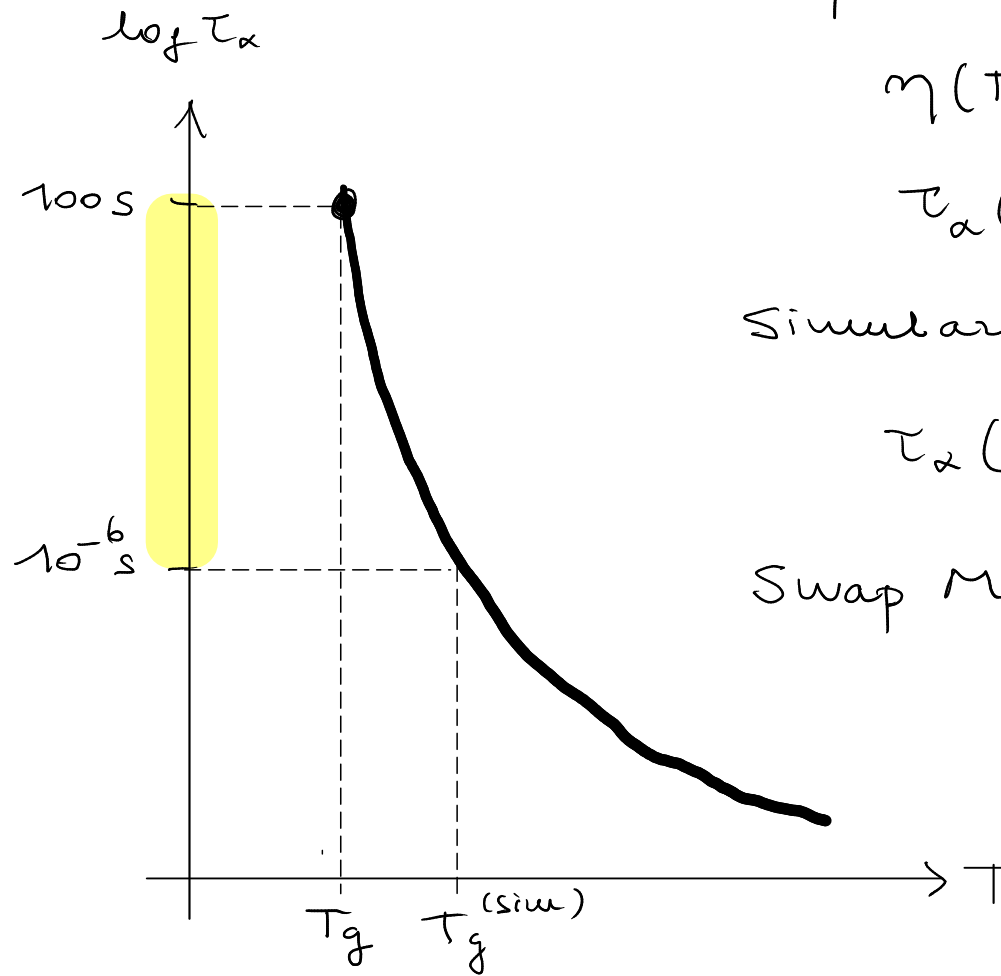
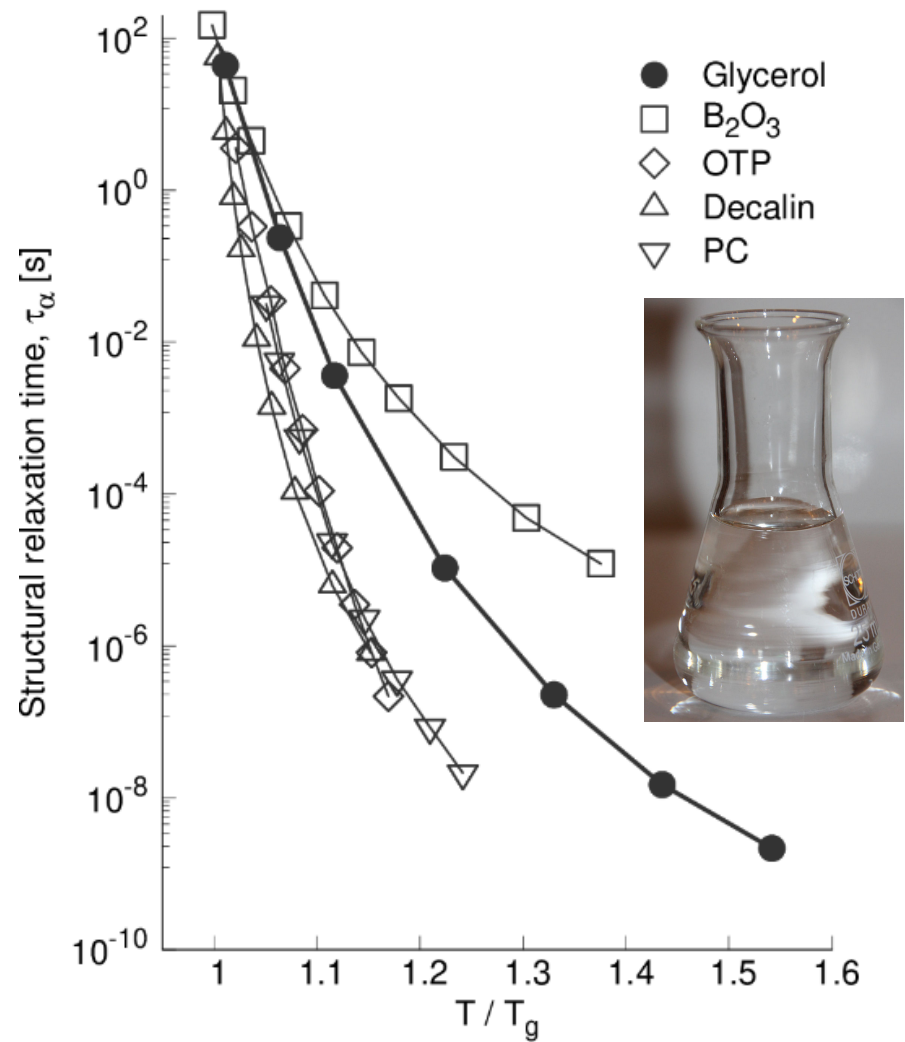
non-ergodico
fuori-equilibrio

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

Def. operativa della transizione vetrosa:

$$\tau_\alpha(\tau_g) = \tau_{obs}$$

$$\tau_\alpha = \tau_\alpha(t)$$



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

$$\text{timestep} = \frac{\tau_0}{100}$$

$$10^{-6} \frac{\text{s}}{\text{step} \cdot \text{part}}$$

$$N = 10^3$$

$$t_1 = 10^{-3} \text{ s}$$

$$\frac{t_1^{\text{reale}}}{\text{timestep}} \approx 10^{-3} \times 10^{14} = \underline{10^9}$$

$$\tau_0 \sim 10^{12} \text{ s}$$

3) tempo di cristallizzazione : τ_x

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

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

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

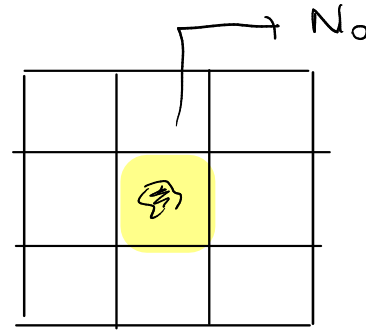
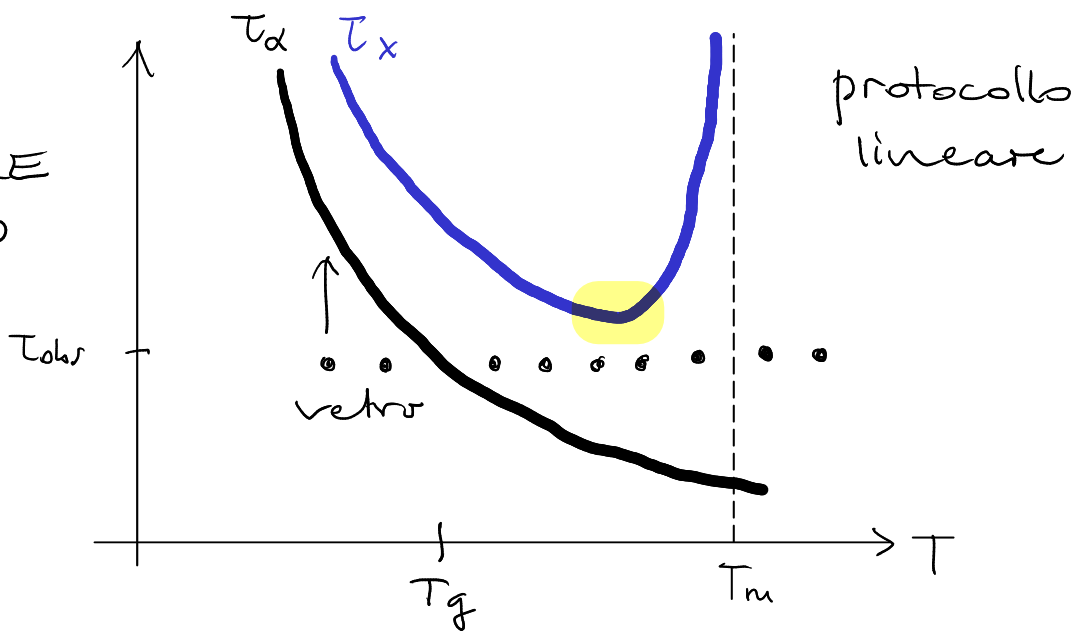


Diagramma tempo-temperatura-trasformazione (TTT)

- ① rilassare defs lenti ($\hat{\beta}_{T_0}$) ② evitare cristallo

$T_\alpha < T_{obs} < T_x$

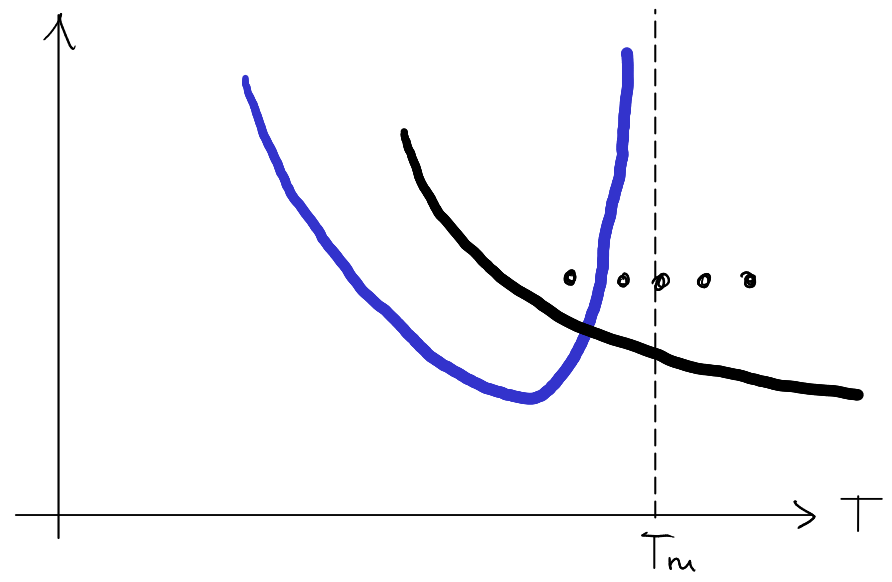
BUON
FORMATORE
DI VETRO



protocollo non-lineare

$T_{obs} \sim T_\alpha$

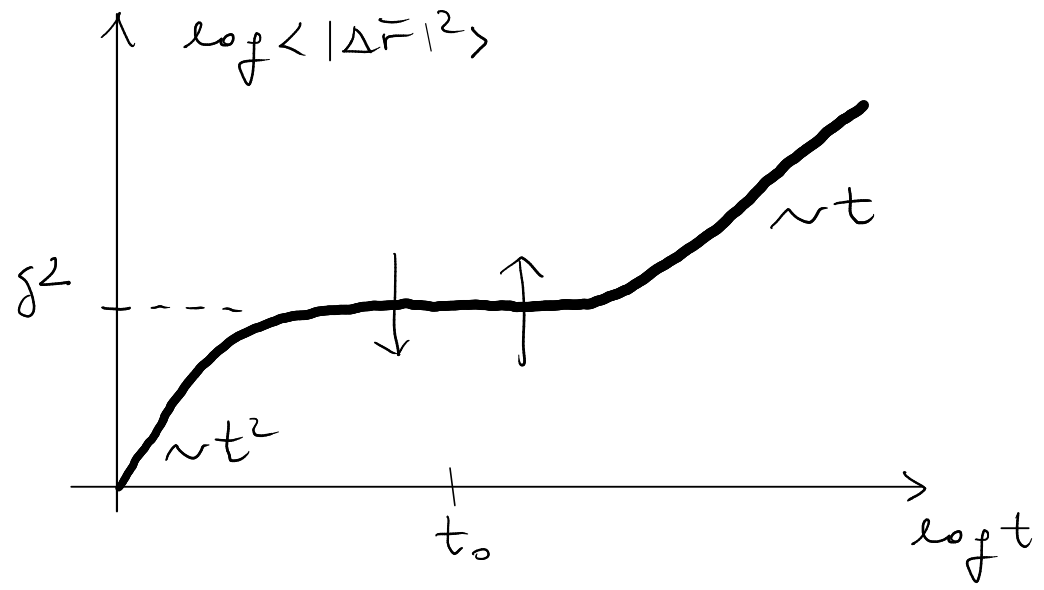
CATTIVO
FORMATORE
DI VETRO



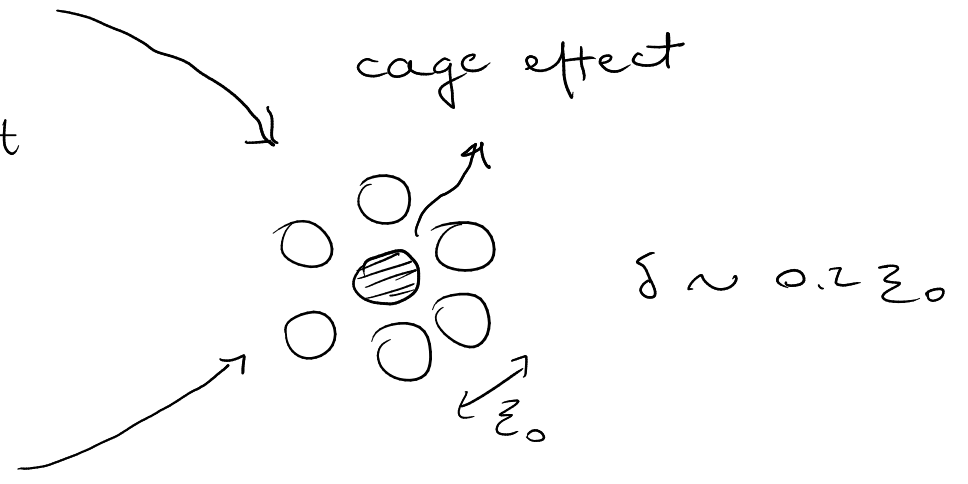
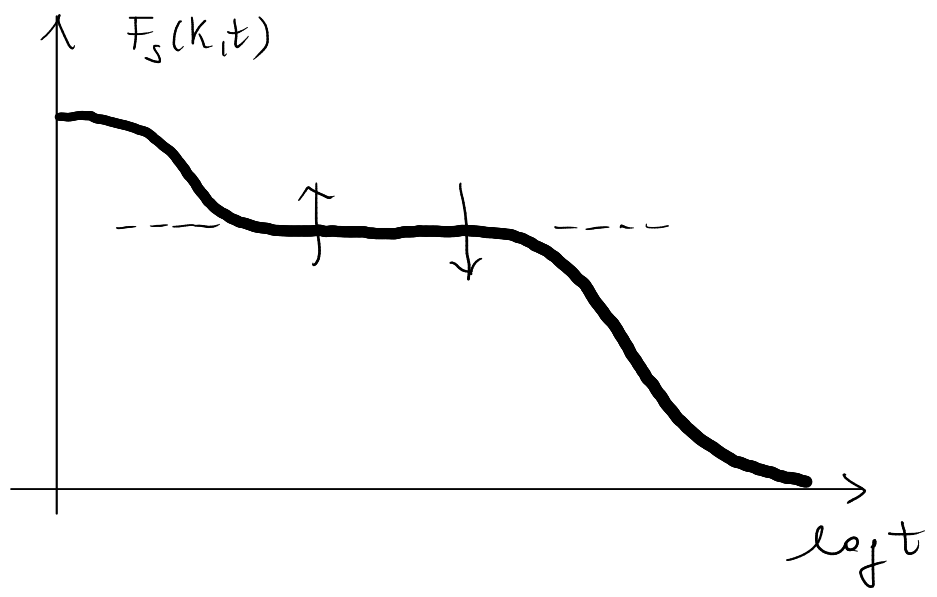
H₂O Patm
160 K - 230 K

NO MAN'S LAND

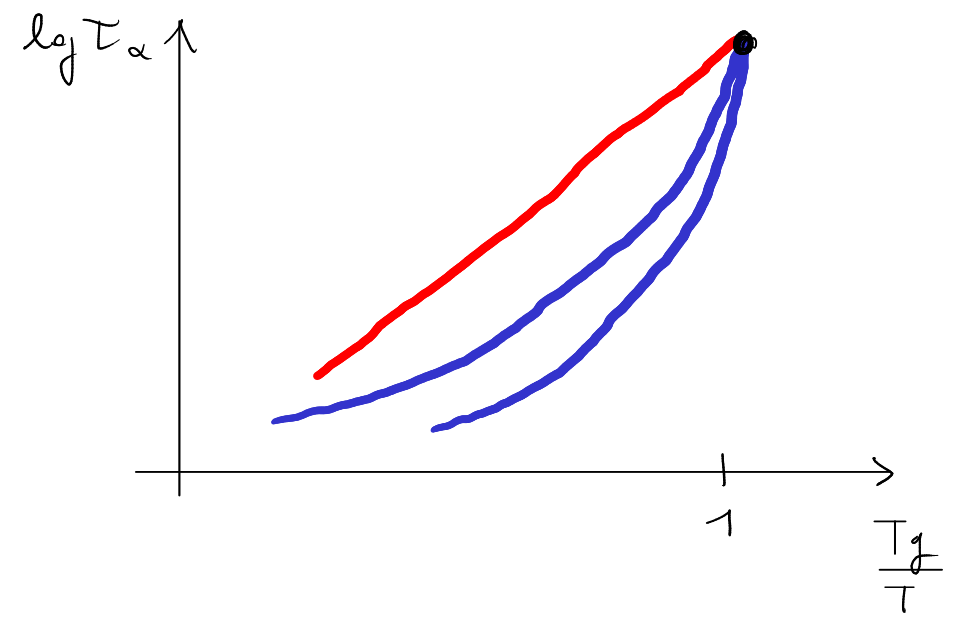
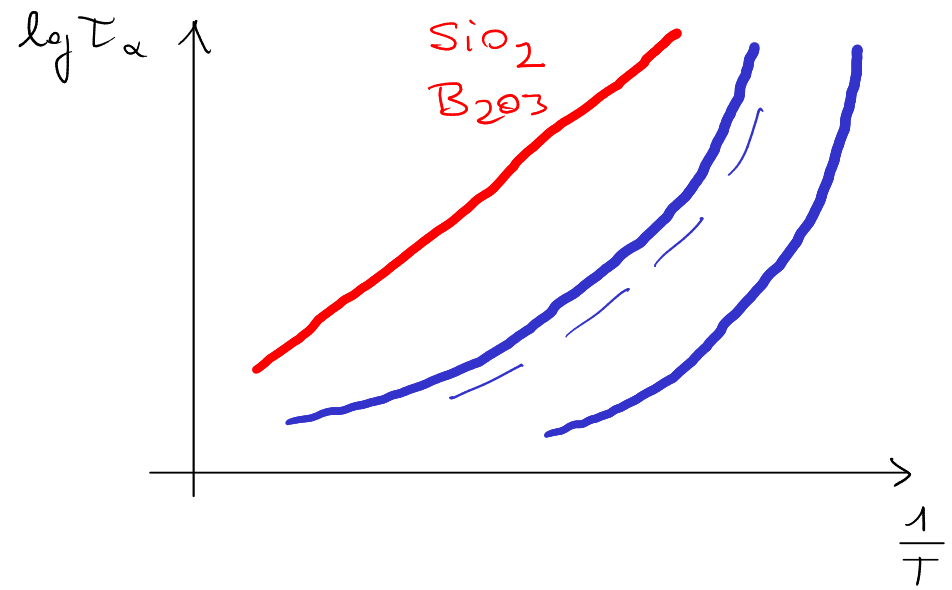
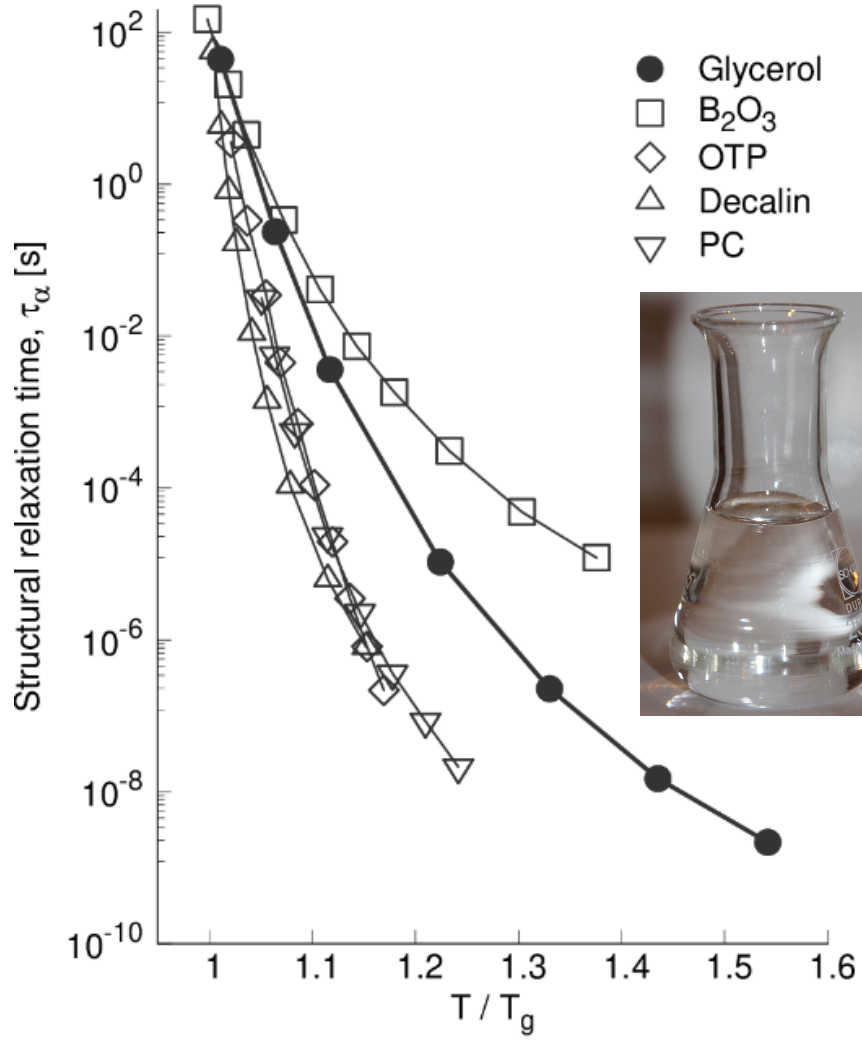
Dinamica



$\delta^2 = \langle |\Delta \vec{r}(t_0)|^2 \rangle$
 $\delta^2 \leftrightarrow T$ es.



$\delta \sim 0.2 \xi_0$



Arrhenius

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

STRONG

Super-Arrhenius

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

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

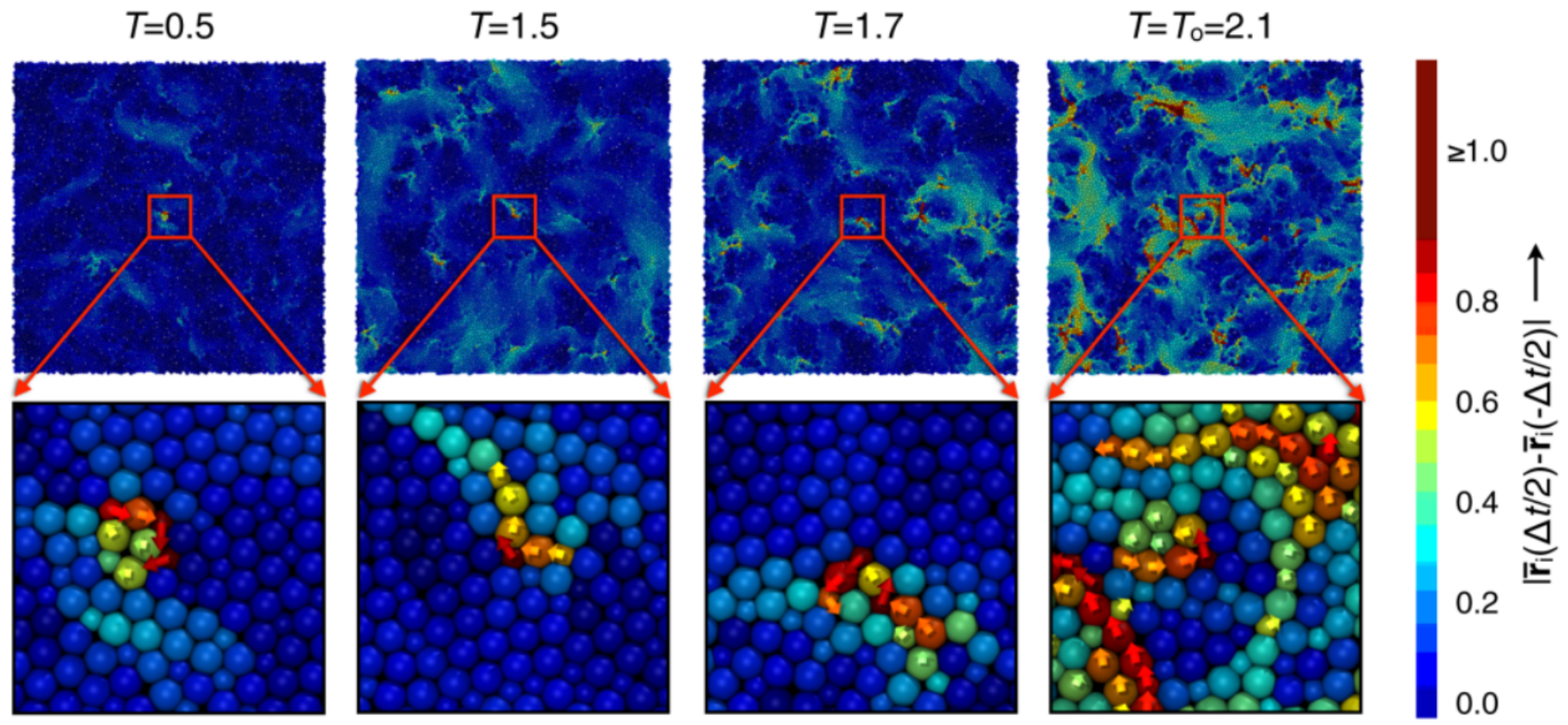
FRAGILE

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: $C_V = \left. \frac{\partial E}{\partial T} \right|_V$

Approx armonica: $E \approx 3Nk_B T$

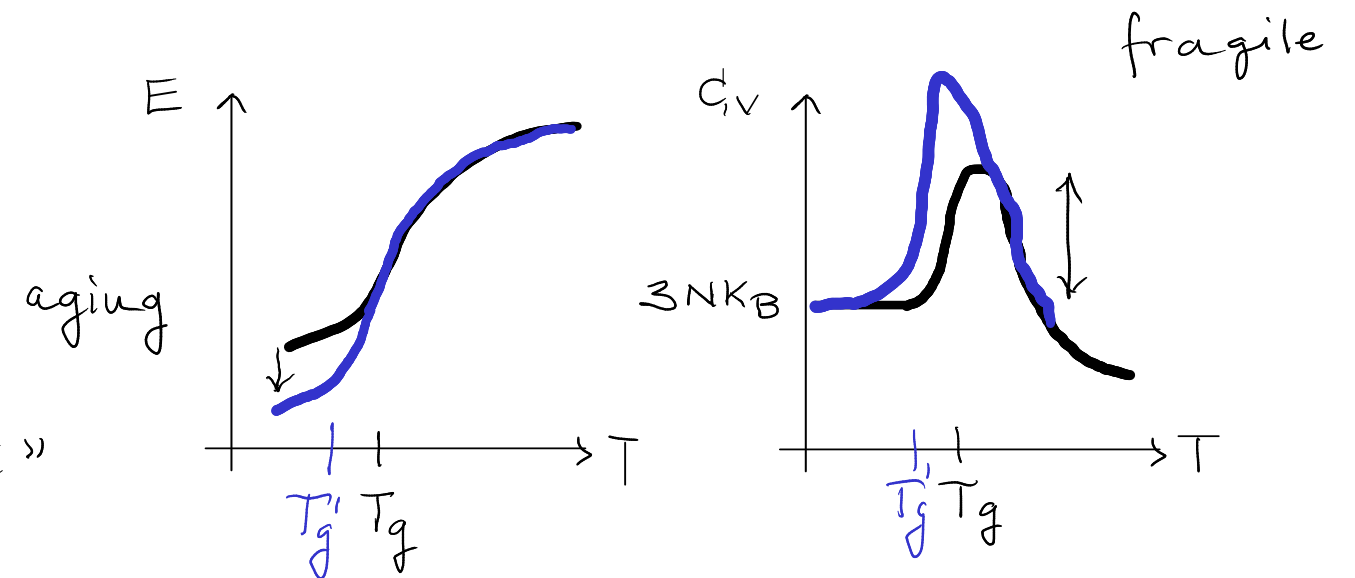
Congelamento di defs "configurazionali"

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

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

□ cristallo perfetto: $S = S_{vib}$

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



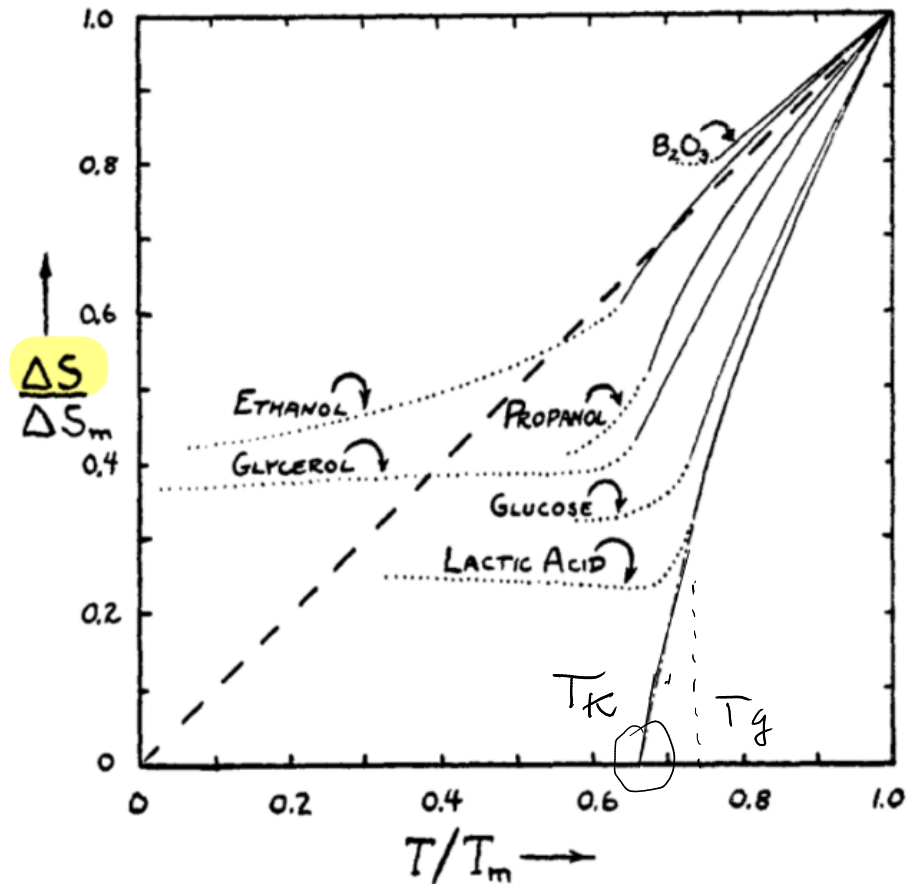
$N = \text{cost}$ $V = \text{cost}$

$\left\langle \begin{array}{ll} \text{gas perfetto} & \text{integrazione} \\ \text{solido armonico} & \text{termodinamica} \end{array} \right.$

□ liquido: S

□ liquido sotto raffreddato: $S \approx S_{vib} + S_c$

$$\Delta S = S_{\text{liq}} - S_{\text{cryst}} \approx (\underbrace{S_{\text{vib}} + S_c}_{\text{liquid}}) - (\underbrace{S_{\text{vib}}}_{\text{solid}}) \approx S_c$$

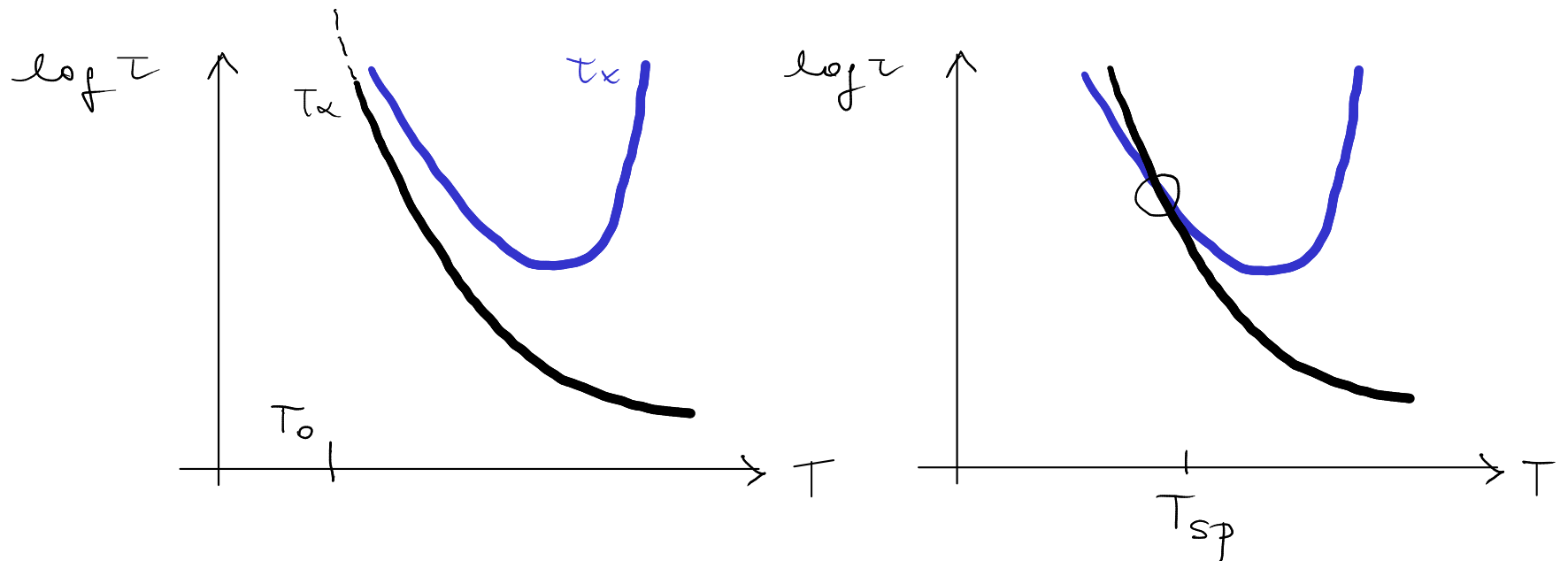


4. Differences in entropy between the supercooled liquid and crystalline ph
Kauzmann Chemical Reviews 1948

Paradosso di Kauzmann
"Entropy crisis"

Then how are these curves to be extrapolated below T_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.



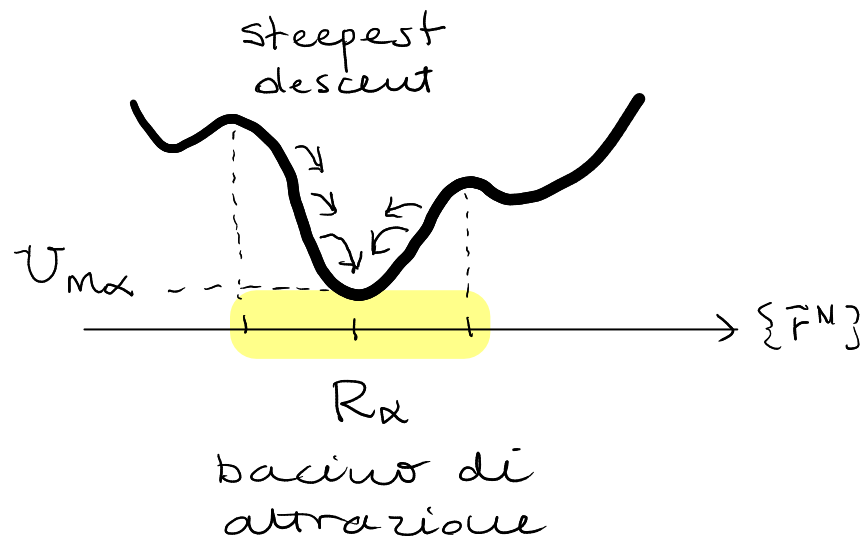
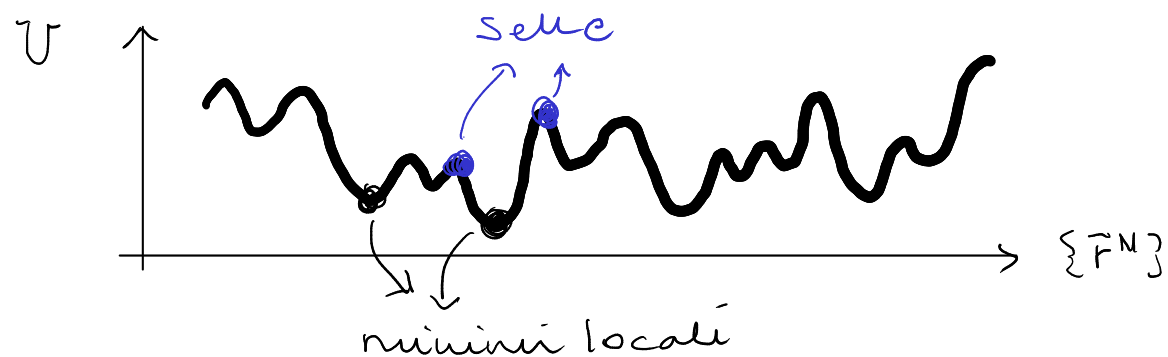
$$\tau_x \sim \exp\left(\frac{A}{T - T_0}\right) \quad \text{① vetro ideale}$$

Vogel-Fulcher

① cristallizzazione

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape (PEL)



$U = U(\{F^N\})$
 Stillinger
 Weber '80
 "struttura incoerente"

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

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

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

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

$$u_{\max} = \frac{U_{\max}}{N} \quad U(\{F^N\}) = (U(\{F^N\}) - U_{\max}) + U_{\max}$$

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

Densità di stati : $\Omega(u_m)$ $\Omega(u_m) du_m$: n. micro 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

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

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

Entropia configurazionale :

$$S_c = k_B \ln \Omega(u_m) \quad s_c = \frac{S_c}{N} \quad \triangle$$

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

1) Approx armonica:

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

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

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

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

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

← ①

$$Z(T) \approx \int du_m e^{-\beta N (u_m + f_{\text{vib}} - T s_c)} \quad N \rightarrow \infty$$

$$\left\{ \begin{array}{l} Z(T) \approx A(N) e^{-\beta N (u_m + f_{vib} - T s_c)} \quad \leftarrow \textcircled{2} \\ 1 + \frac{\partial f_{vib}}{\partial u_m} - T \frac{\partial s_c}{\partial u_m} = 0 \end{array} \right.$$

$$\uparrow \textcircled{1} \approx 0$$

$$\left\{ Z(T) \approx e^{-\beta N (u_m + f_{vib} - T s_c)} \quad \Rightarrow \text{thermodynamica} \right.$$

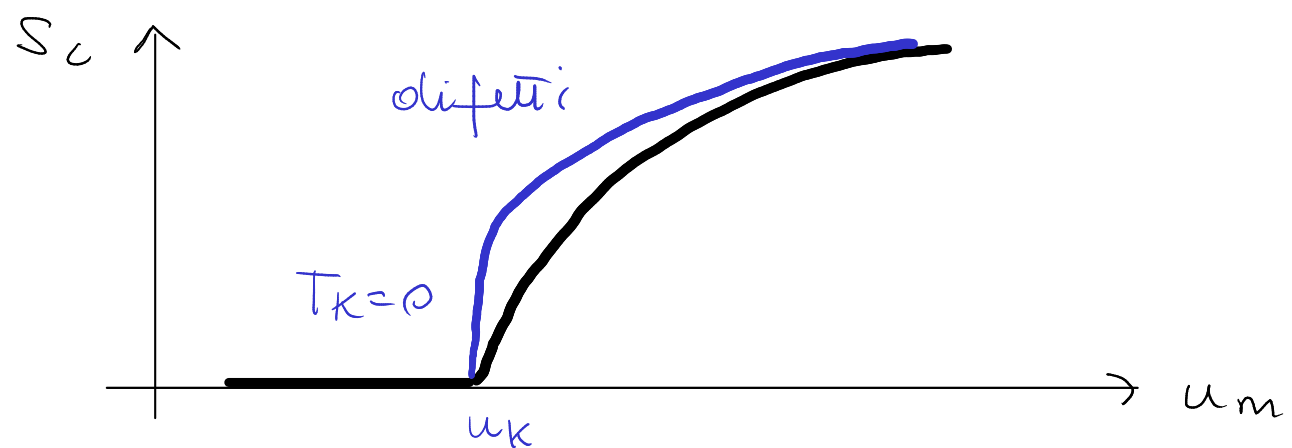
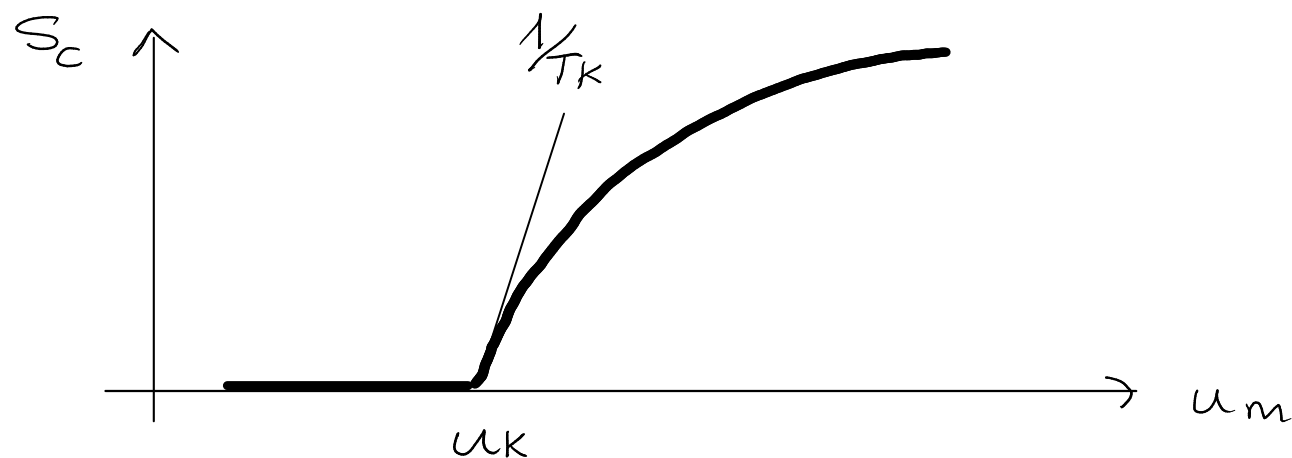
$$\left\{ \frac{\partial s_c}{\partial u_m} = \frac{1}{T} \right.$$

$$s_c = s_c(u_m)$$

Paradosso Kauzmann:

$$1) S_c = 0 \quad u_m \leq u_K$$

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



Supercooled liquids, glass transitions, and the Kauzmann paradox

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(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.

