LIQUIDI SOTTORAFFREDDATI E TRANSIZIONE VETROSA

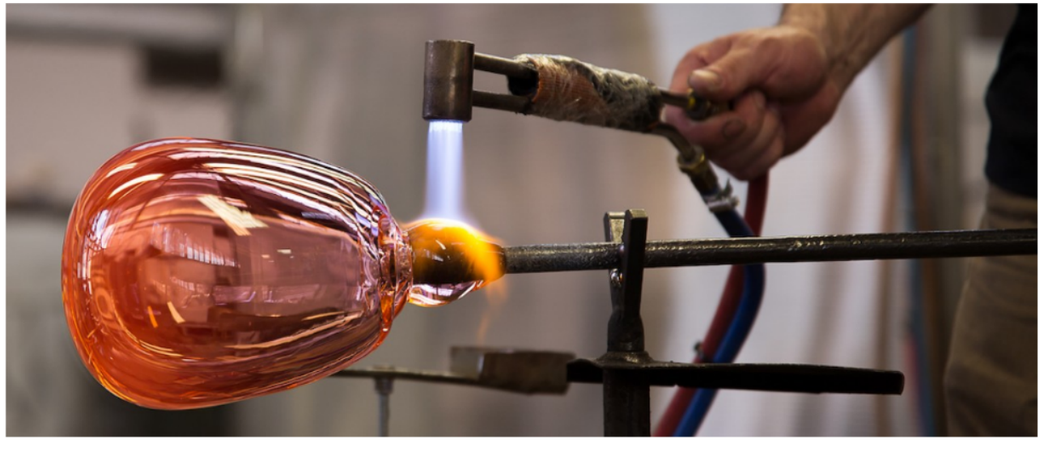
"The deepest and most interesting unsolved problem in solid state physics is probably the theory of the nature of glass and the glass transition" P.W. Anderson 1995

il POST

SCIENZA | Mercoledì 30 agosto 2023

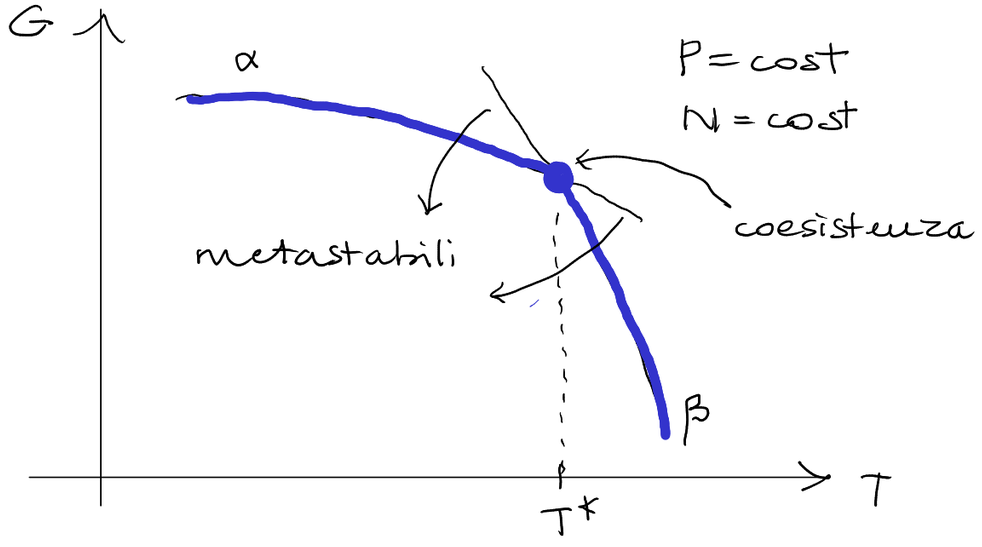
Fatichiamo ancora a spiegarci il vetro

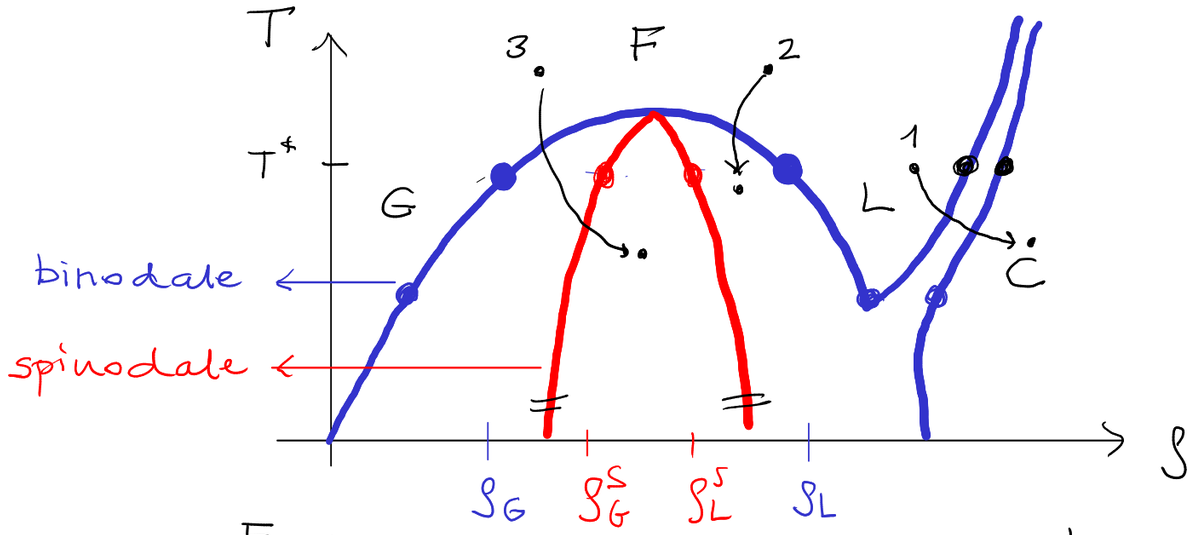
È un solido con alcune caratteristiche dei liquidi, un bel mistero per i fisici che nel tempo hanno formulato tante teorie poco convincenti



FLUIDI METASTABILI E INSTABILI

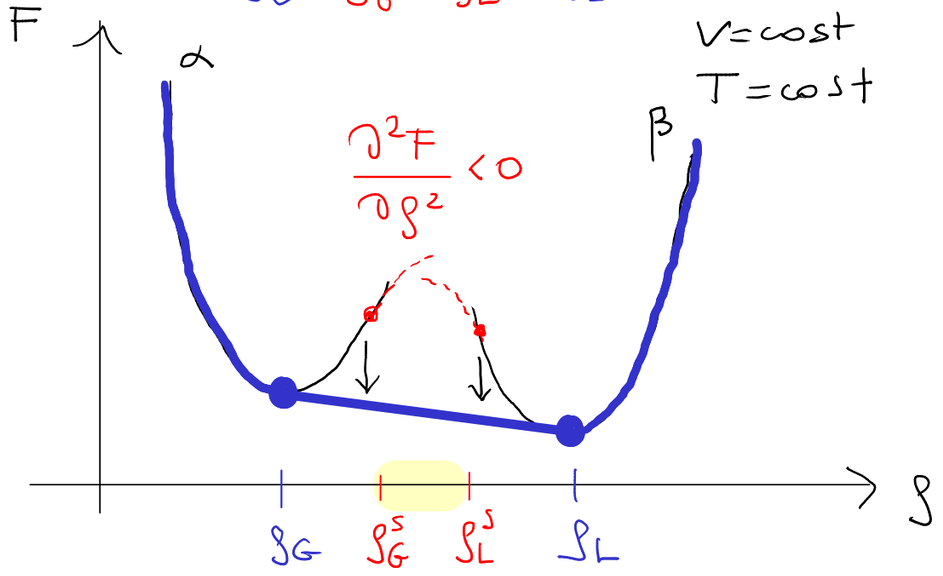
$\beta = G \quad \alpha = L$





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

} ①



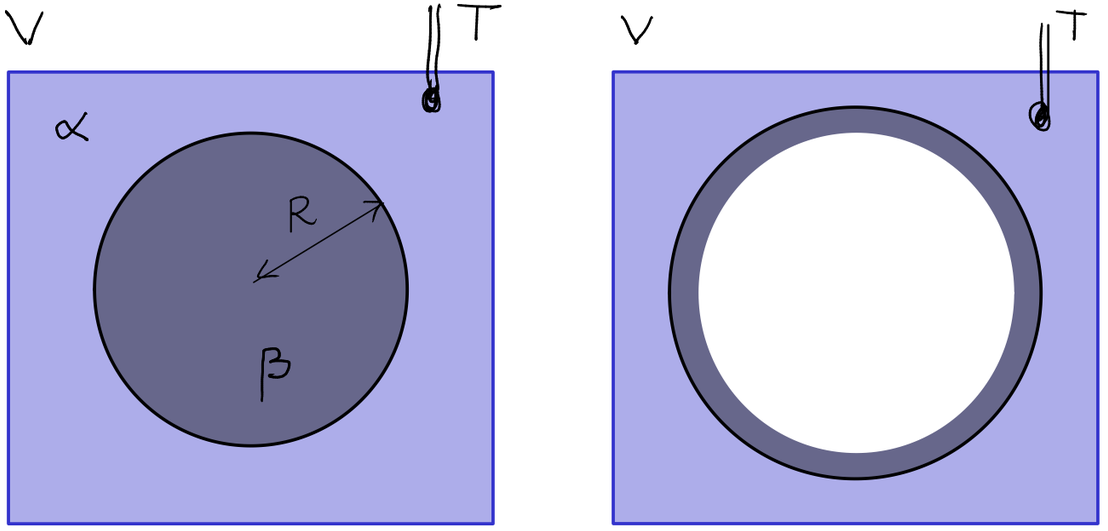
① nucleazione + crescita

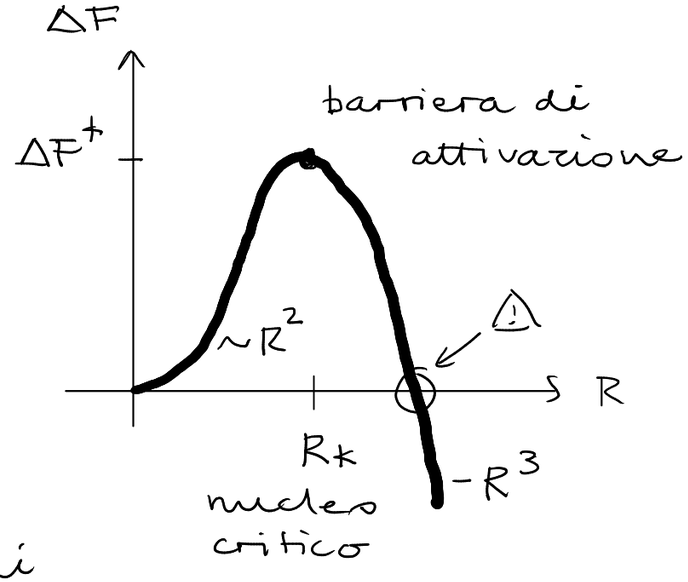
② decomposizione spinodale

1) Nucleazione

CNT: teoria fenomenologica α = metastabile β = stabile Es.: α=L β=C

$f = \frac{F}{V}$ $f_\alpha > f_\beta$ $\Delta f = f_\beta - f_\alpha < 0$





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

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

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

Cinetica della nucleazione

- ΔF : paesaggio di energia
- 1 dof: R
- particella browniana senza inerzia

$U \to \Delta F$; $x \to R$; $D = \frac{K_B T}{\xi} = D(R) \Rightarrow p(R,t)$

Smoluchowski

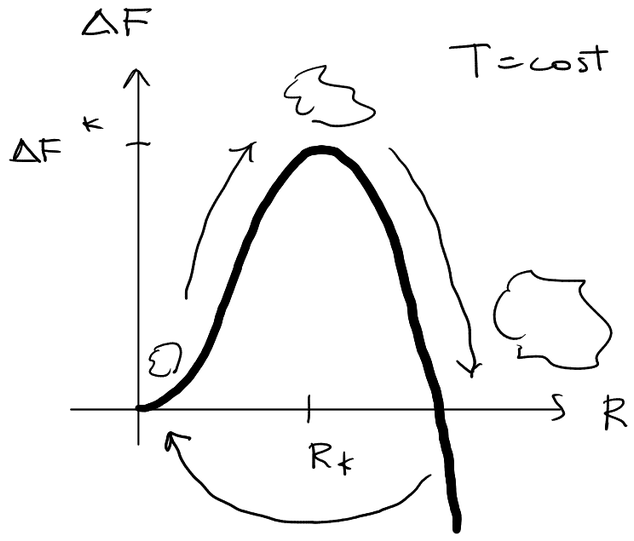
$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial R}\left[D(R)\frac{\partial p}{\partial R} + \frac{1}{\xi(R)}\frac{d\Delta F}{dR}\, p \right] \qquad \text{BH 10.6}$$

Tempo di nucleazione = tempo di uscita

$$\tau_x = \underbrace{\frac{1}{D(R_f)}}_{\text{cinetico}} \cdot \underbrace{\frac{1}{\left(-\frac{1}{2\pi K_B T}\left.\frac{d^2\Delta F}{dR^2}\right|_{R_f}\right)^{1/2}}}_{\text{Zeldovich}} \cdot \underbrace{\exp\left(\frac{\Delta F^*}{K_B T}\right)}_{\text{Arrhenius}}$$

Tasso di nucleazione : nuclei / tempo / volume

$$I = \frac{N}{\tau_x}\frac{1}{V} = \rho / \tau_x$$



problema di Kramers

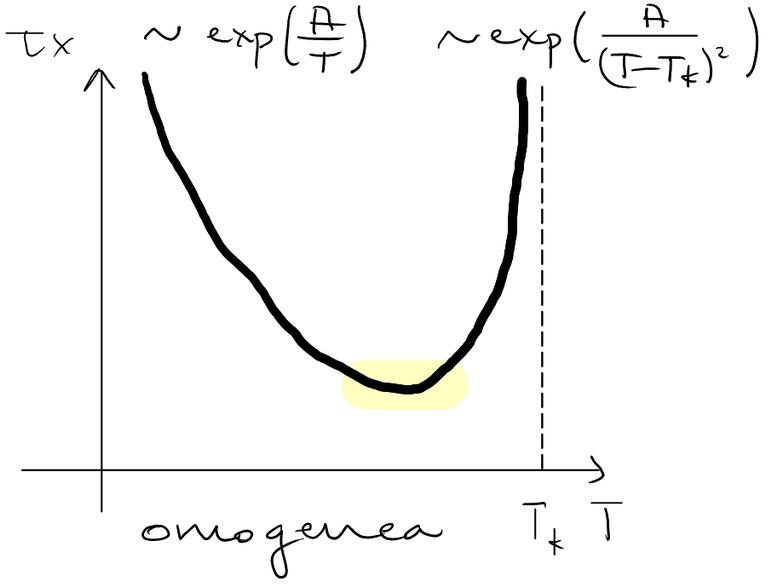
$\Delta F^* \gg K_B T$

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

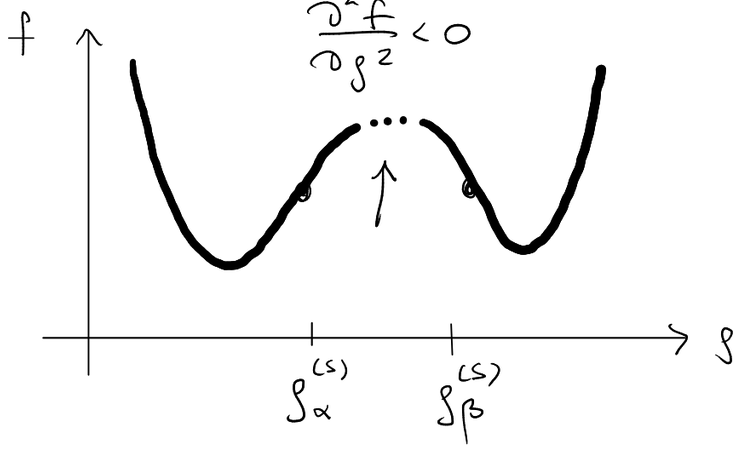
$\tau_x \sim \exp\left(\frac{\Delta E_d}{k_B T}\right) \exp\left(\frac{\Delta F^{\ddagger}}{k_B T}\right)$

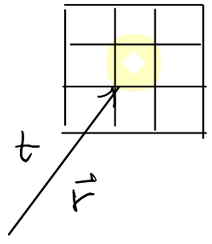
$T \approx T_k$: $\Delta f \sim (T - T_k)$ $\quad \Delta F^{\ddagger} \sim \frac{1}{\Delta f^2}$

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



2) Decomposizione Spinodale





$$\rho_N(\vec{r},t) = \rho(\vec{r},t) \qquad T = \text{cost}$$

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

LDA

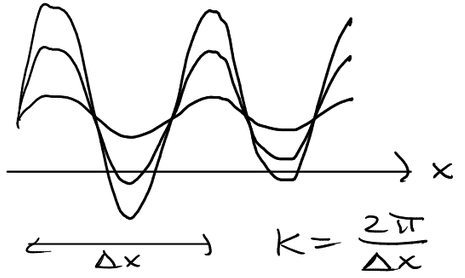
$\mu = \mu[\rho(\vec{r},t)]$

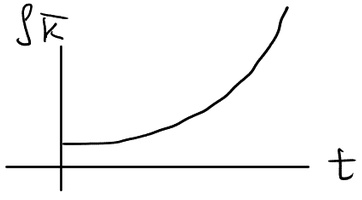
$$= \vec{\nabla}\cdot\left(\frac{L_{NN}}{T}\,\vec{\nabla}\mu\right)$$

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

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

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





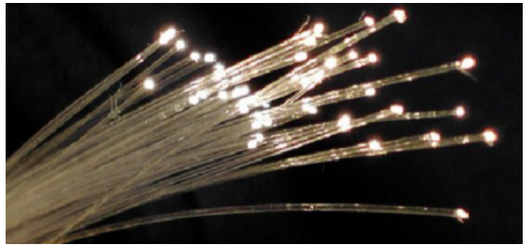
$$\frac{\partial \rho}{\partial t} = D_c \nabla^2 \rho \quad \Rightarrow \quad \rho_K(t) = \rho_K(0)\exp\left(-D_c K^2 t\right) = \rho_K(0)\exp\left(|D_c| K t^2\right)$$

$$\frac{\partial \rho}{\partial t} = \frac{L_{NN}}{T}\nabla^2\left[\frac{\partial^2 f}{\partial \rho^2}\rho_N - \frac{k_B T\,\varepsilon_0^2}{\rho}\nabla^2\rho\right]$$ Cahn – Hilliard BH 9.3

Materiali formatori di vetro

OSSIDI

Silicati (SiO_2)



B_2O_3

gorilla glass ©

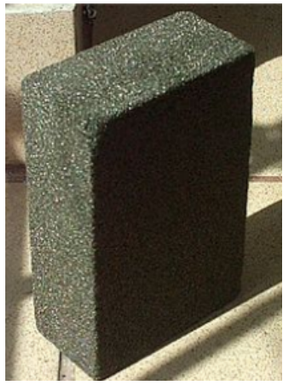
Vetro da finestra

SiO_2 : 70%

NaO_2 : 20%

CaO : 10%

POLIMERI

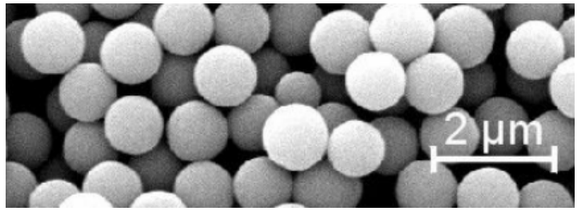


polistirene

PMMA

METALLI

COLLOIDI



ORGANICI

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

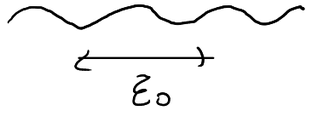
Richert & Angell JCP 1998

FENOMENOLOGIA DELLA TRANSIZIONE LIQUIDO – VETRO

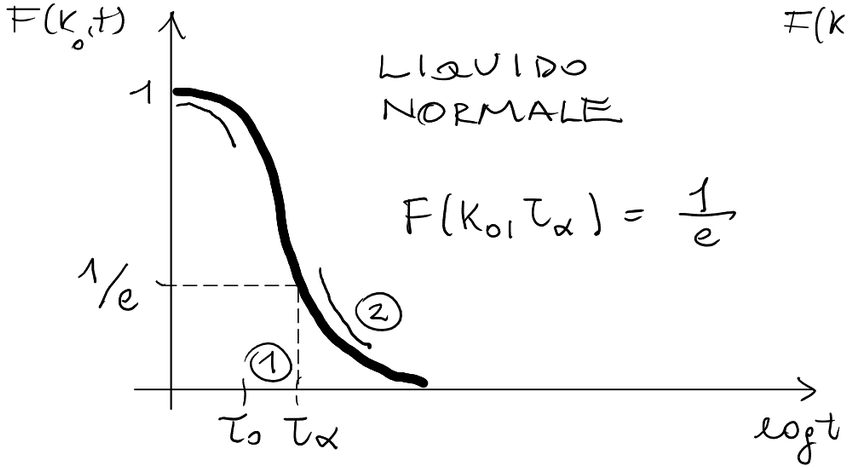
Liquido sottoraffreddato: $T < T_m$ Vetro: $T < T_g$

1) Tempo di rilassamento strutturale

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

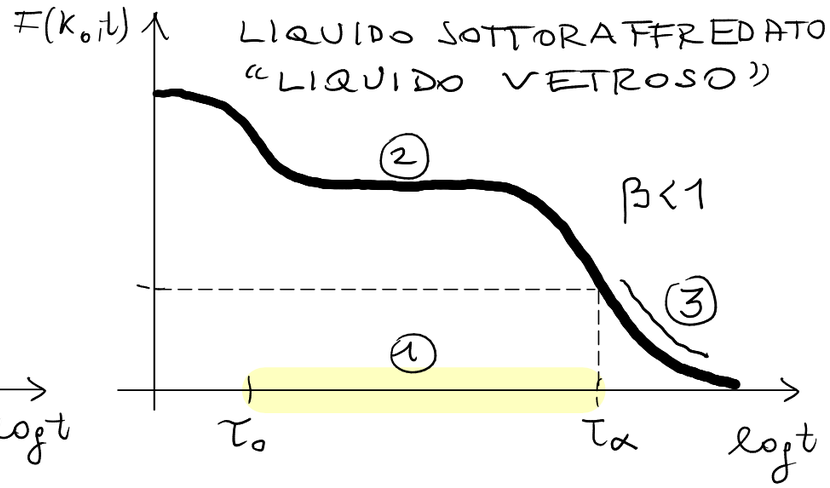
$K_0 \approx \frac{2\pi}{\xi_0}$ 

$P = P_{atm}$



① $\tau_\alpha \sim \tau_0$

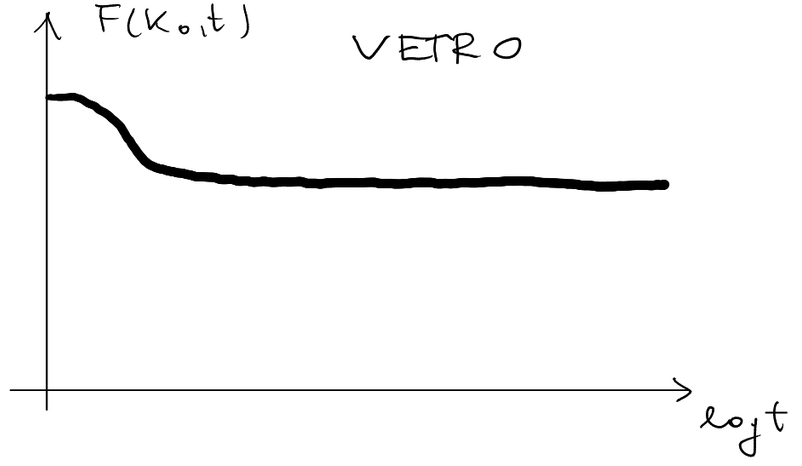
② $\sim \exp(-t/\tau_\alpha)$



① $\tau_\alpha \gg \tau_0$

② two-step relaxation

③ $\sim \exp(-(t/\tau_\alpha)^\beta)$

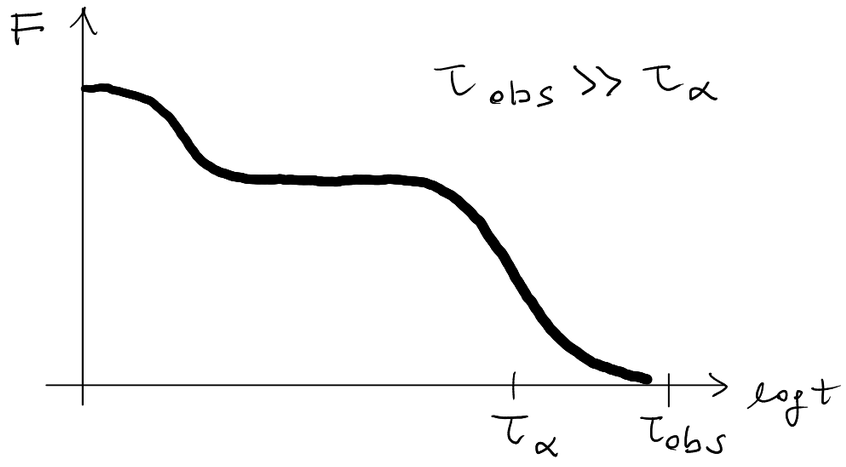


Relazione di Maxwell

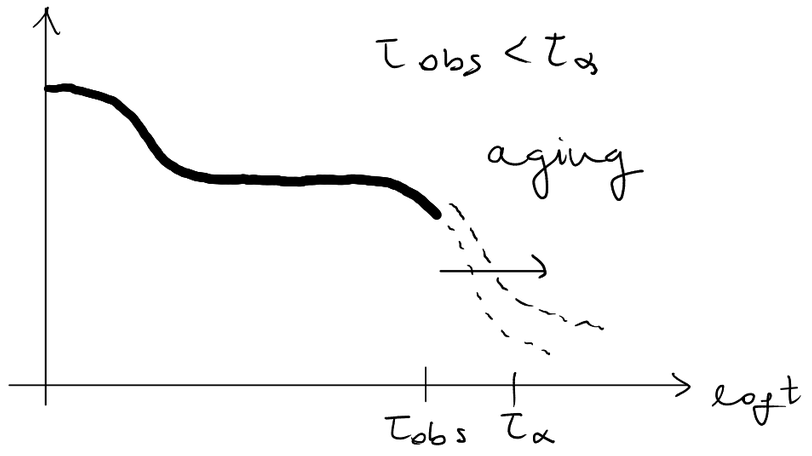
$\eta = G_0 \tau_\alpha$

onset → T_0 T_g 1/T

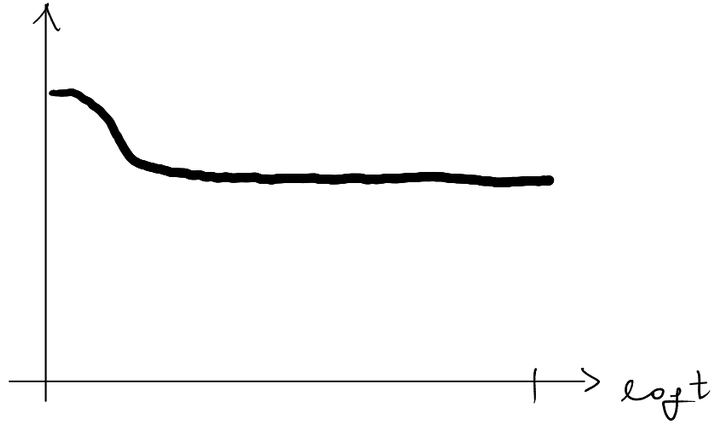
2) Tempo di osservazione: τ_{obs}



equilibrio (metastabile)



non-ergodico



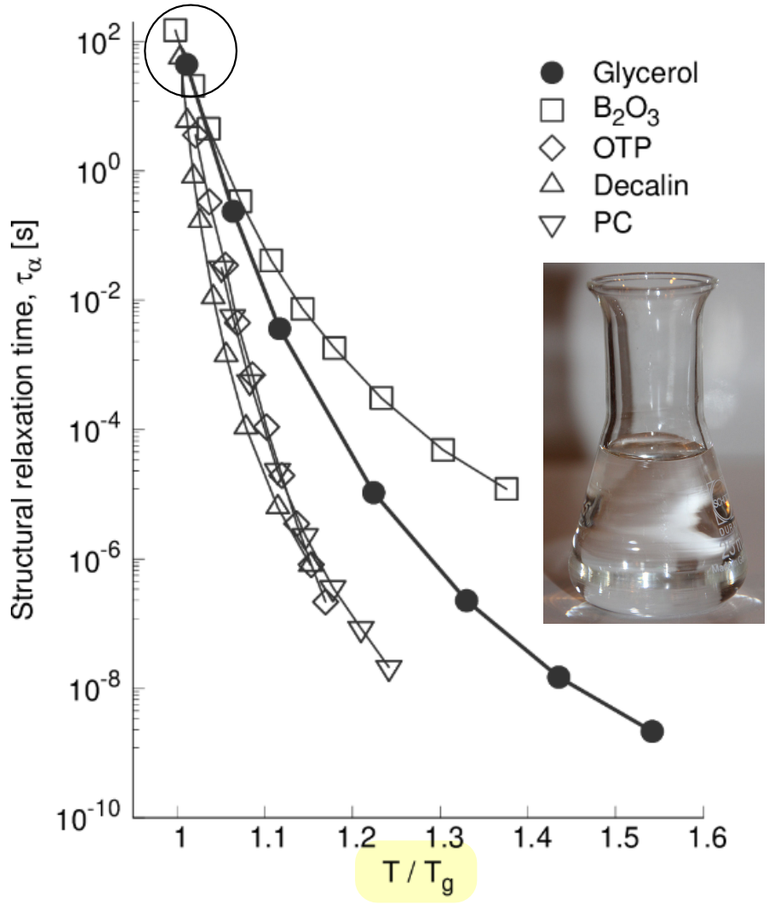
? vetro ideale ?

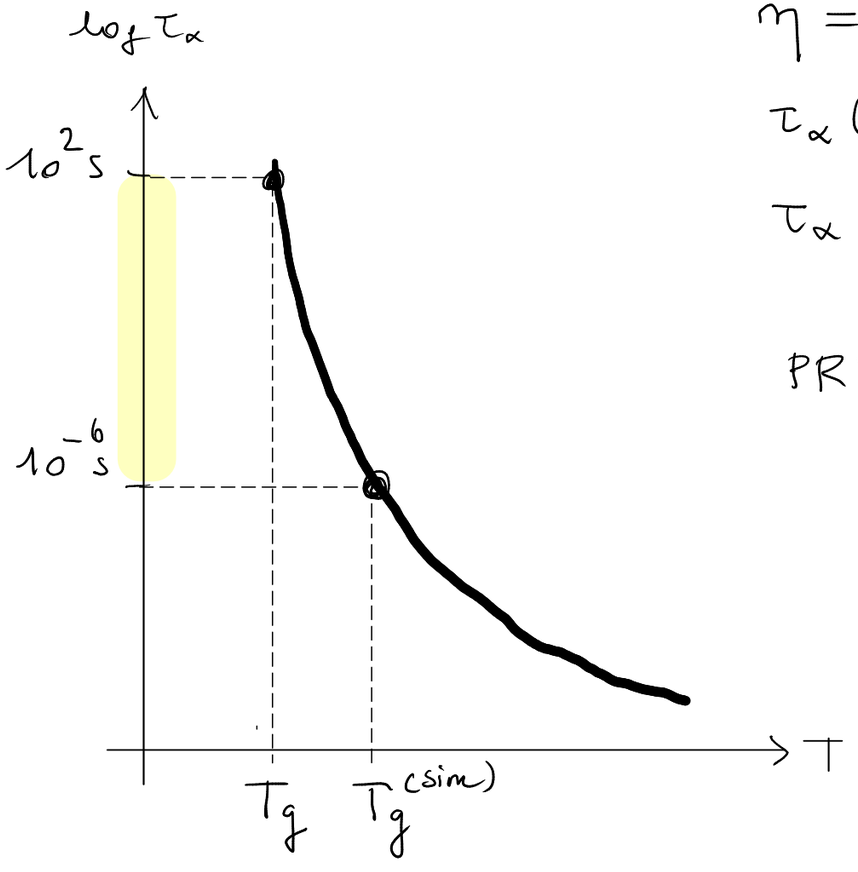
Def. di equilibrio di Feynman: "when all the fast things have happened and all the slow ones not"

Def. operativa di temperatura di transizione vetrosa T_g sperimentale

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

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





$\eta = G_0 \tau_\alpha \quad G_0 \sim 10^{10}$ Pa

$\tau_\alpha(T_g) \sim 10^{2}$ s exp.

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

PRX 2017 swap MC

$\delta t \sim \frac{\tau_0}{100}$ $\quad 10^{-6}$ s / step / particella $\quad t_1 = 10^{-3}$ s $\quad \frac{t_1}{\delta t} \sim \frac{10^{-3}}{10^{-14}} \sim 10^{11}$

step $\sim 10^{-14}$ s $\quad N = 10^{3}$ particelle

3) Tempo di cristallizzazione

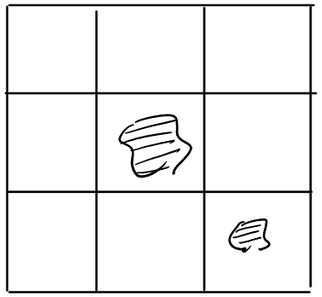
Tempo di nucleazione: CNT

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

Tempo di cristallizzazione

$$\tau_{x,N} \sim \frac{1}{N} \qquad T < T_M$$

$\exists\, N_0$ t.c. $\tau_{x,N_0} = \tau_x$



$$I = \frac{1}{\tau_x}$$

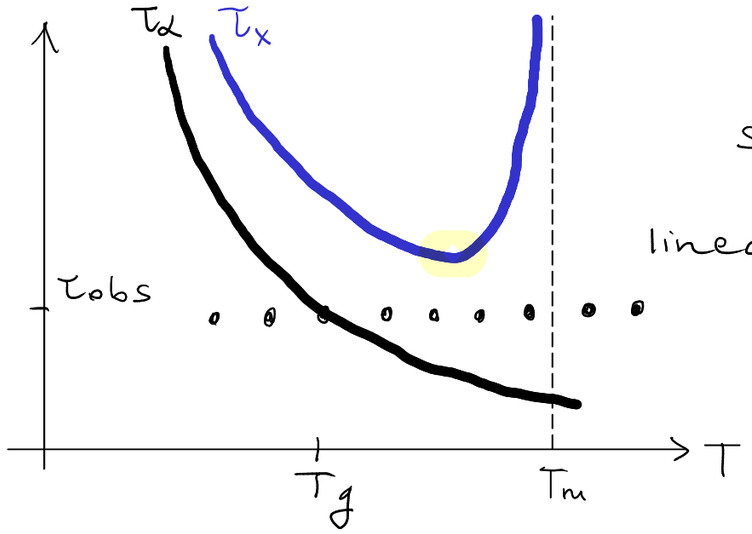
Diagramma tempo – temperatura – trasformazione (TTT)

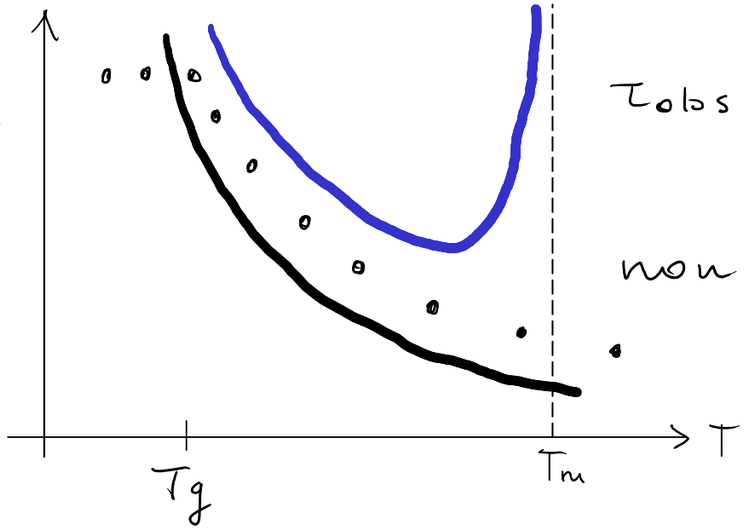
① equilibrare i dofs lenti ($\uparrow \beta_{K_0}$) $\quad \tau_\alpha < \tau_{obs} < \tau_x$ $\quad$ ② evitare cristallo

↓

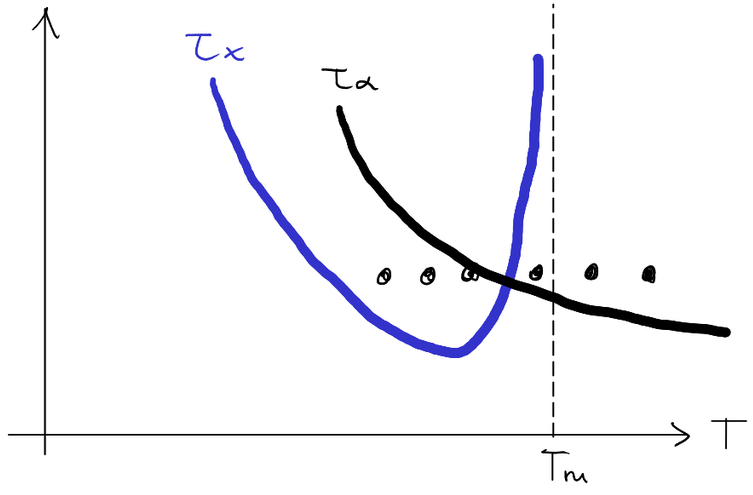
liquido sottoraffreddato

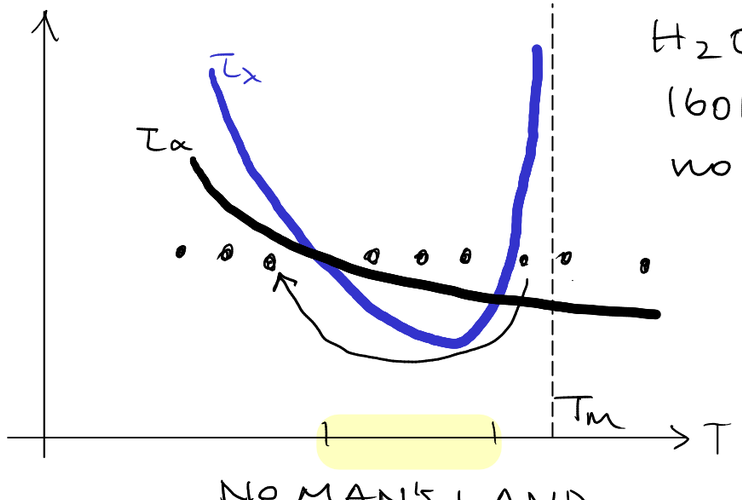
BUONI FORMATORI





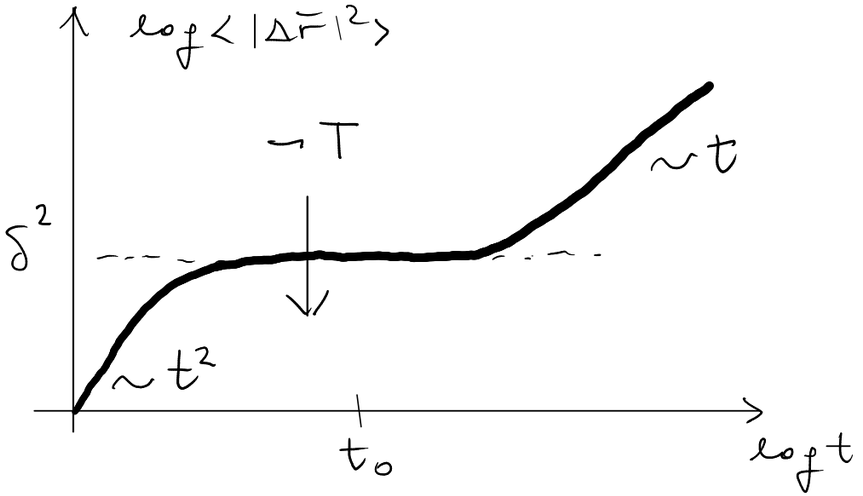
CATTIVI FORMATORI





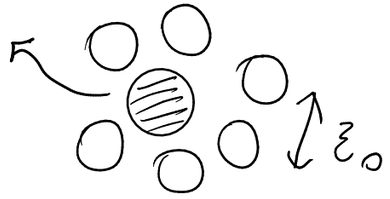
H_2O $P = P_{atm}$
160K – 230 K
no man's land

Dinamica singola particella

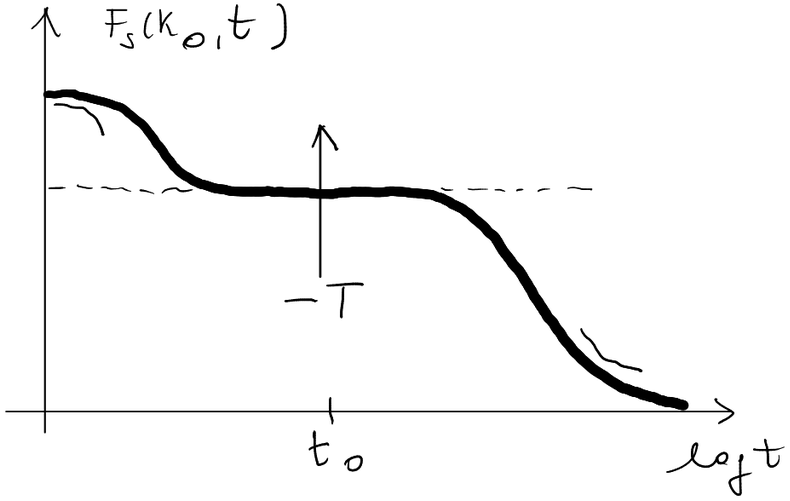


$$\delta^2 = \langle |\Delta \bar{r}(t_0)|^2 \rangle \qquad \langle \Delta x^2 \rangle \sim K_D T$$

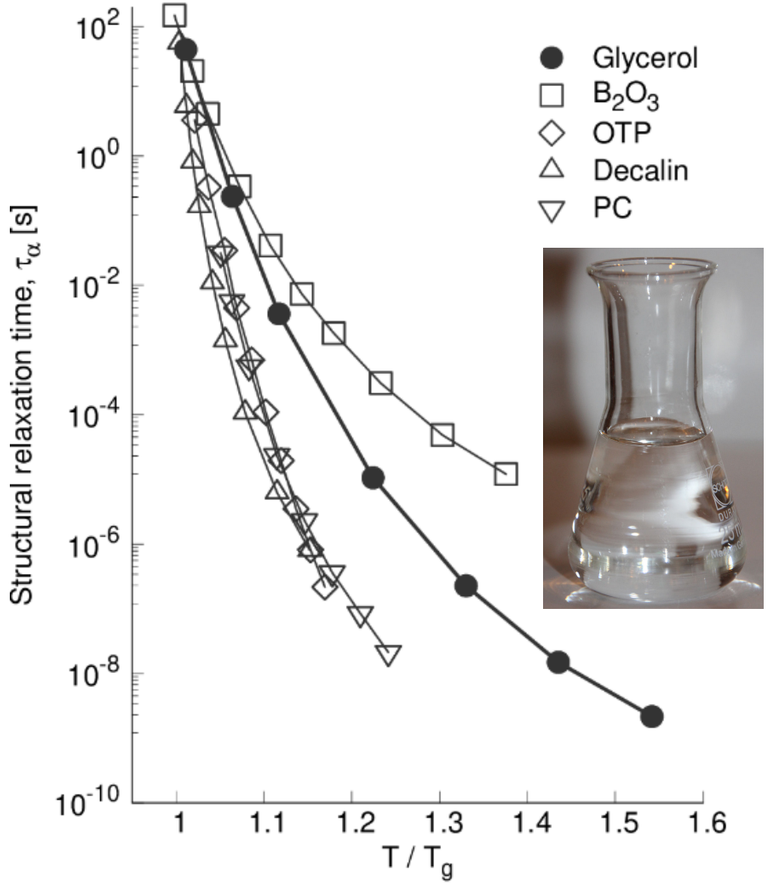
$$\delta \sim 0.2\, \xi_0 \qquad \delta^2 \sim T$$

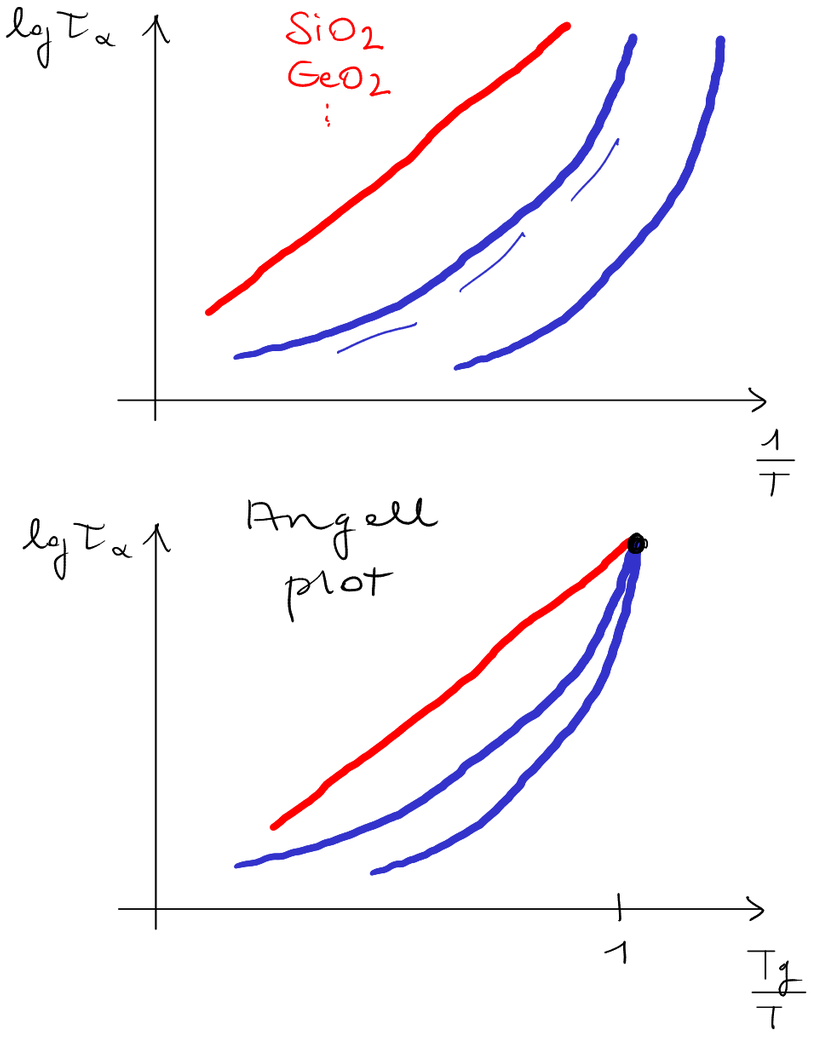


cage effect



$$F_S(k,t) \approx \exp\left(-\frac{1}{6} \langle |\Delta \bar{r}(t)|^2 \rangle k^2\right)$$





Arrhenius

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

STRONG

Super-Arrhenius

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

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

FRAGILE

Fragilità (Angell)

$$m = \frac{\partial \log \tau_\alpha}{\partial (T_g/T)}$$

Substance	T_g	T_K	$F_{1/2}$	m
SiO_2	1473[g]		0.13[g]	20[c]
B_2O_3	532[m]		0.38[m]	32[c]
nPOH	97[h]	72.2[a]	0.45[a]	35[h]
PropGlyc	167[d]	127[b]	0.45[d]	52[c]
3-MePent	77[f]	58.4[f]	0.58[j]	36[j]
3-Br-P	108[a]	82.5[a]	0.59[a]	53[a]
glycerol	190[d]	135[b]	0.62[d]	53[c]
BMPC	243[h]		0.70[h]	
salol	220[a]	175[a]	0.71[a]	63[a]
MTHF	91[a]	69.3[a]	0.73[a]	65[a]
OTP	246[h]	204[l]	0.74[h]	81[c]
PropCarb	158[i]	127[b]	0.74[i]	104[c]
triPhenPhos	203[k]	166[b]	0.75[k]	160[b,q]
CKN	333[g]		0.80[g]	

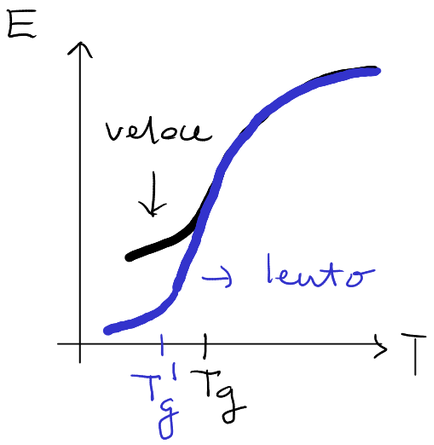
Termodinamica

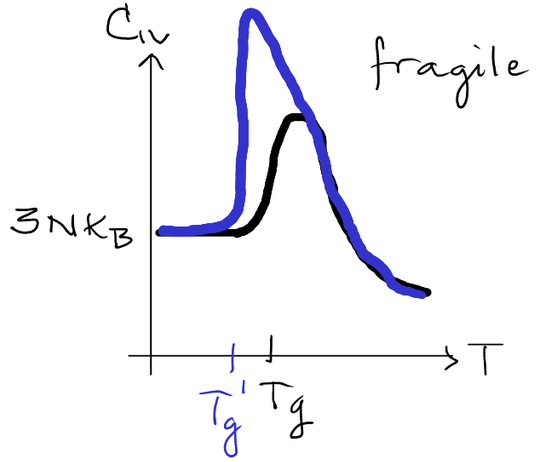
Energia interna E

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

Approx. armonica $E = 3NK_BT$

Congelamento dei defs configurazionali @ T_g





Entropia

$$dS = \frac{1}{T}dE - \frac{P}{T}dV + \frac{\mu}{T}dN \qquad N = cost \quad V = cost$$

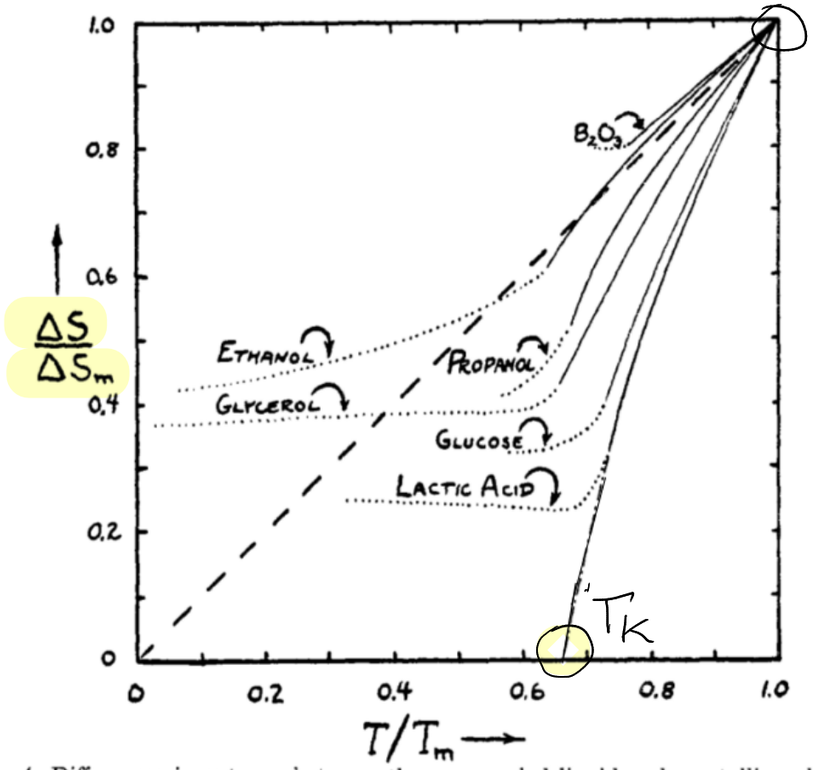
($P/T\,dV = 0$, $\mu/T\,dN = 0$)

$$S(T) = S(T_0) + \int_{T_0}^{T} \frac{1}{T}dE = S(T_0) + \int_{T_0}^{T} dT\,\frac{C_V}{T} \rightarrow \text{integrazione termodinamica}$$

$S(T_0) <$ g.p. (solido armonico)

- cristallo perfetto : $S = S_{vib}$
- liquido : S
- cristallo + defetti : $S = S_c + S_{vib}$
- liquido sottoraffreddato $S \approx S_c + S_{vib}$

$$\Delta S = S^{(liq)} - S^{(cryst)} \approx S_c^{(liq)} + S_{vib}^{(liq)} - S_{vib}^{(cryst)} \approx S_c^{(liq)}$$ empirica



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

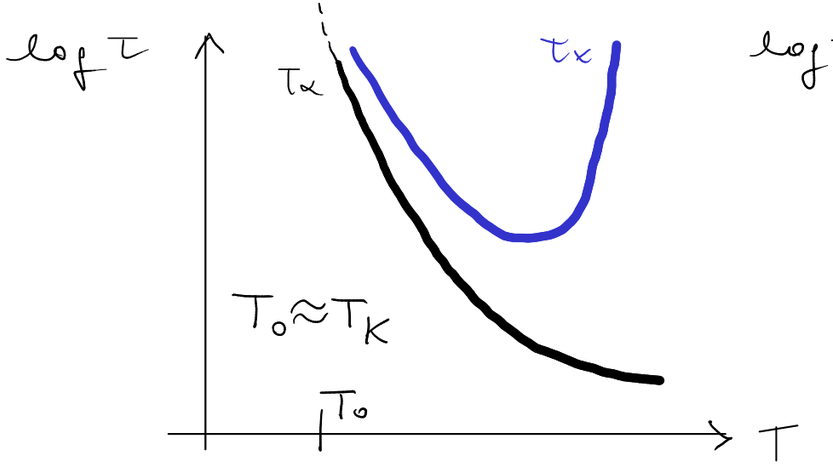
Kauzmann Chemical Reviews 1948

"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

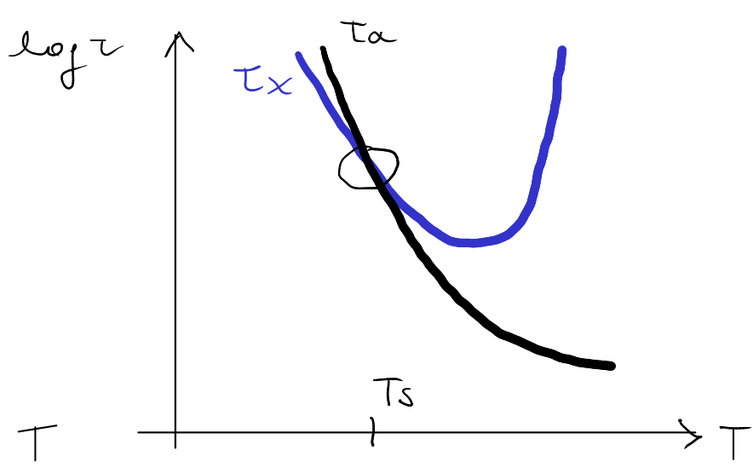
[7] It could conceivably become slightly less at finite temperatures because of a "tighter" binding of the molecule in the highly strained liquid structure, with consequent higher frequencies of vibration and a lower density of vibrational levels.



① Vetro ideale

Vogel - Fulcher - Tammann

$\tau_\alpha \sim \exp(A/(T-T_0))$

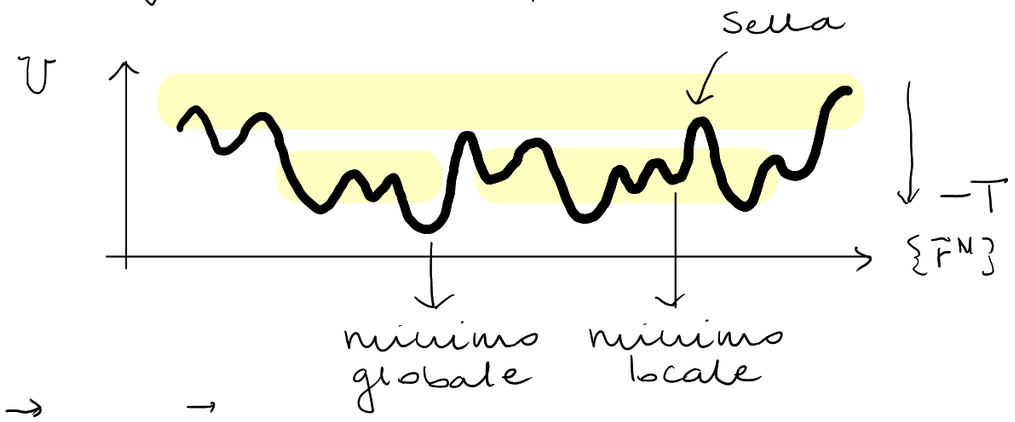


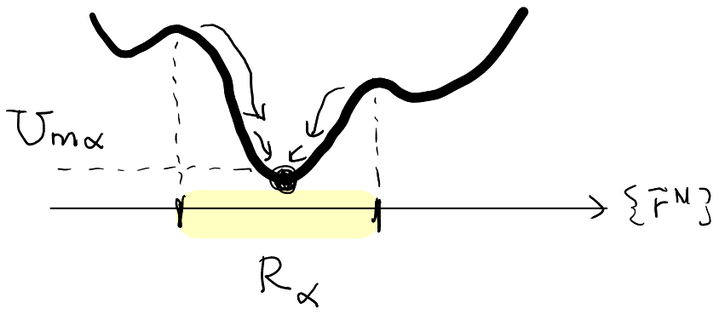
② Cristallizzazione spinodale cinetica

$T = T_S$

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape





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

Stillinger & Weber ~'80

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

bacino di attrazione di α

$$\mathcal{H} = \frac{\partial^2 U}{\partial r_{i\alpha} \partial r_{j\beta}} \qquad i,j = 1,\dots,N \quad \alpha,\beta = x,y,z$$

Hessiana $\qquad N = \text{cost} \quad V = \text{cost}$

$$Z(T) = Tr\left[e^{-\beta H(\{\vec{r}^N, \vec{p}^N\})} \right] \qquad \Lambda = \frac{h}{\sqrt{2\pi m K_B T}}$$

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

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

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

$$Z(T) = \int du_m\, \Omega(u_m)\, e^{-\beta N u_m}\, \frac{1}{\Lambda^{3N}}\, Z_c(u_m, T)$$

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

Energia libera

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

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

Entropia configurazionale

$$S_c = K_B \ln \Omega \qquad \Delta \qquad s_c = \frac{S_c}{N} \qquad \Omega = e^{N s_c / K_B}$$

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

1) Approx armonica

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

2) Approx di punto sella (metodo di Laplace)

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

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

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

$$Z(T) \approx \int du_m\, e^{-\beta N(u_m + f_{vib} - Ts_c)} \qquad N \to \infty$$

$\uparrow$

(1)

$$\begin{cases} 1 + \underbrace{\dfrac{\partial f_{vib}}{\partial u_m}}_{\approx 0} - T\dfrac{\partial s_c}{\partial u_m} = 0 \\ Z(T) \approx A(N)\, \exp\left[-\beta N (u_m + f_{vib} - T s_c)\right] \end{cases} \qquad \begin{matrix} f_{vib}(u_m) \\ \swarrow \end{matrix} \quad \begin{matrix} s_c(u_m) \\ \swarrow \end{matrix} \quad \overset{(2)}{\swarrow}$$

$$u_m = \langle u_m \rangle$$

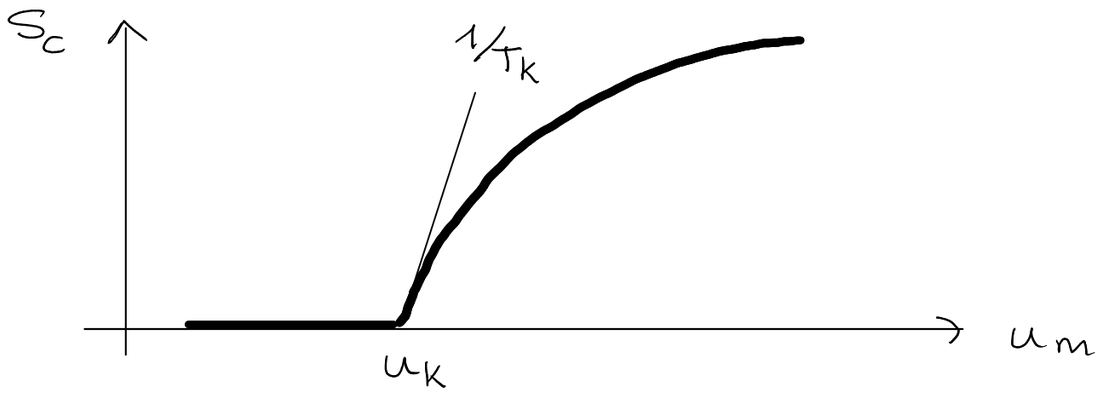
$$\frac{\partial s_c}{\partial u_m} = \frac{1}{T}$$

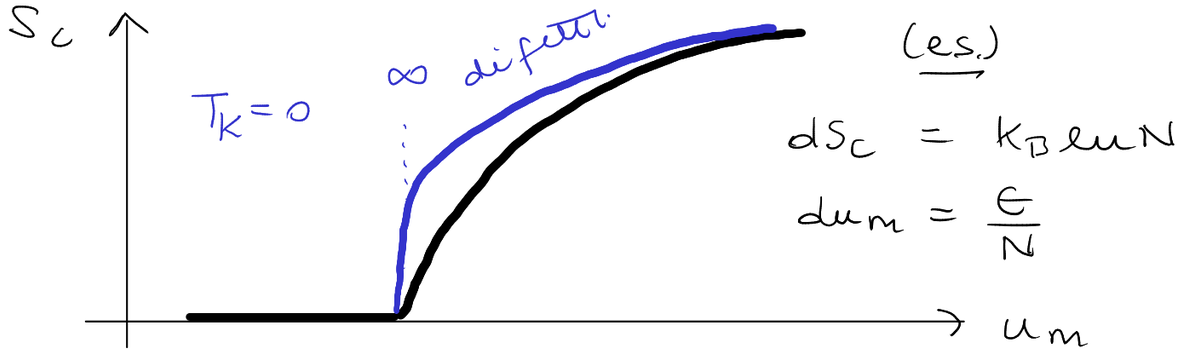
$$\Omega \sim e^{\alpha N} \qquad S_c = k_B \ln \Omega > 0 \qquad s_c = \frac{S_c}{N} \text{ finito}$$

$$\Omega \sim N \qquad \text{(sottoesponenziale)} \qquad s_c \sim \frac{\ln N}{N} \to 0 \quad \text{se } N \to \infty$$

$$s_c = s_c(u_m)$$

$$\begin{cases} s_c = 0 & u_m \le u_K \\ \left.\dfrac{\partial s_c}{\partial u_m}\right|_{u_K} = \dfrac{1}{T_K} \end{cases}$$

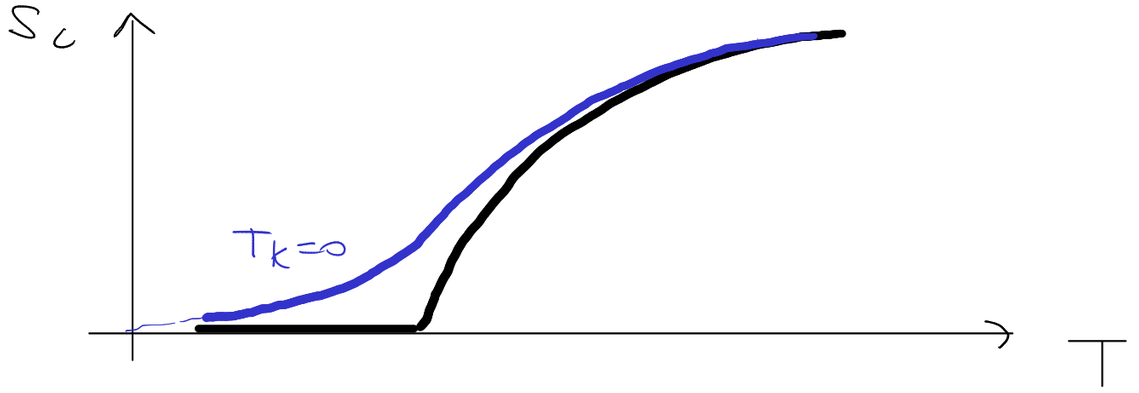




(es.)

$$ds_c = k_B \ln N$$

$$du_m = \frac{\epsilon}{N}$$



Supercooled liquids, glass transitions, and the Kauzmann paradox

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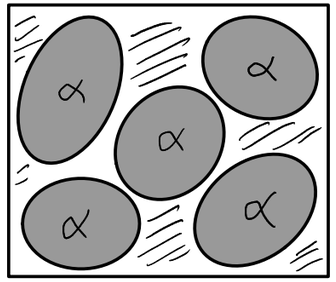
Many liquids have heat capacities that substantially exceed those of the corresponding crystal, and this discrepancy magnifies in the supercooled regime. Thus, liquid entropy declines more rapidly with temperature than does crystal entropy, and the former paradoxically seems to fall below the latter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

Modello di Adam & Gibbs (1965)

CRR = più piccolo sottosistema che può riarrangiarsi indipendentemente dal resto del sistema → non-interagenti



N = n. particelle

n = n. particelle / CRR

α = n. stati / CRR

$\alpha = 2$

Stati accessibili

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

Entropia configurazionale

$$s_c = \frac{S_c}{N} = \frac{1}{N} k_B \ln\left[\alpha^{N/n}\right] = \frac{k_B}{n} \ln\Omega \sim \frac{1}{n} \qquad n \sim \frac{1}{s_c}$$

$\xi_{CRR} \sim n^{1/3}$

$\xi_{CRR} = \left(\frac{n}{s}\right)^{1/3}$

Rilassamento termicamente attivato : $\Delta E \sim n \sim 1/s_c$

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

relazione di Adam & Gibbs

Transizione a vetro ideale T_K

Per $T \gtrsim T_K$

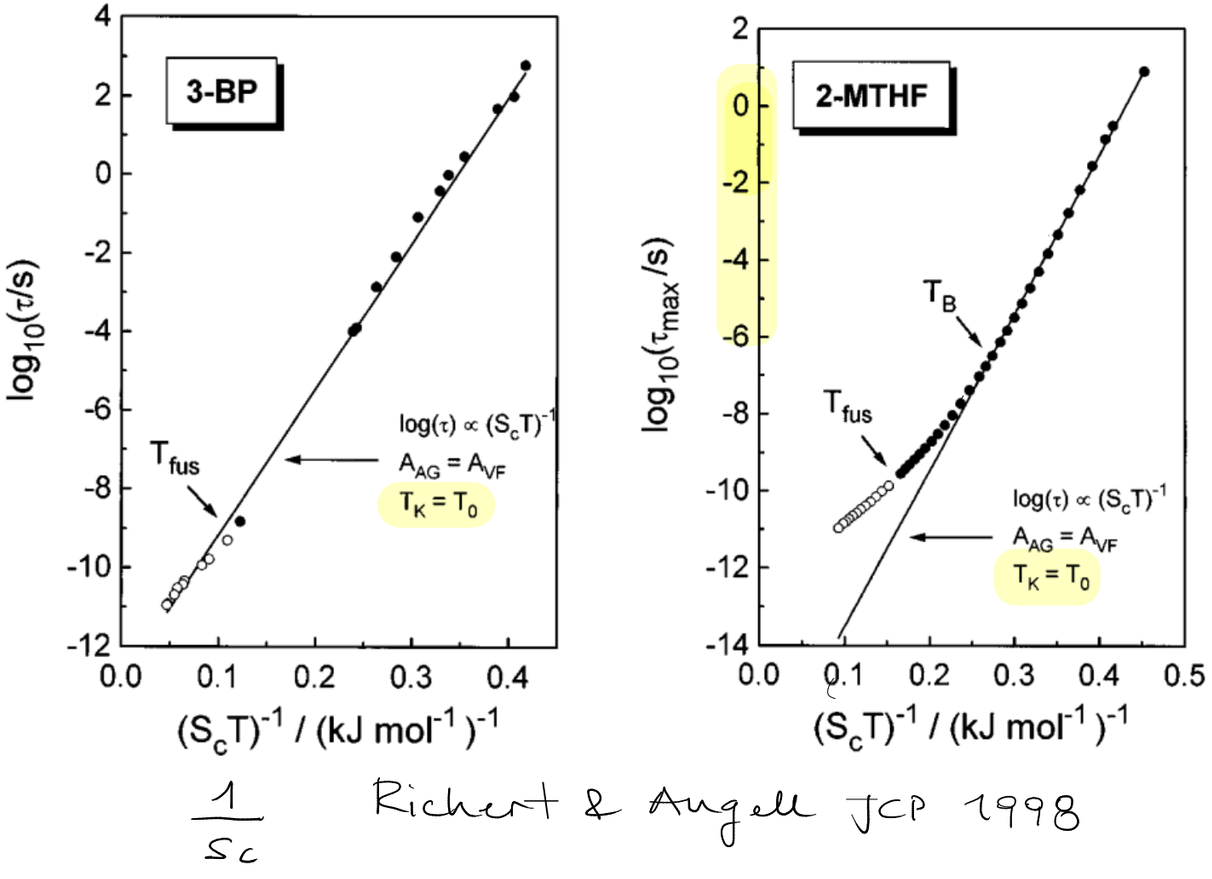
$$s_c \sim \frac{1}{T_K}(T - T_K)$$

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

$$\approx \tau_0 \exp\left(\frac{C}{T-T_K}\right)$$

→ Vogel – Fulcher – Tammann

$$T_K = T_0$$



$\frac{1}{s_c}$ Richert & Angell JCP 1998

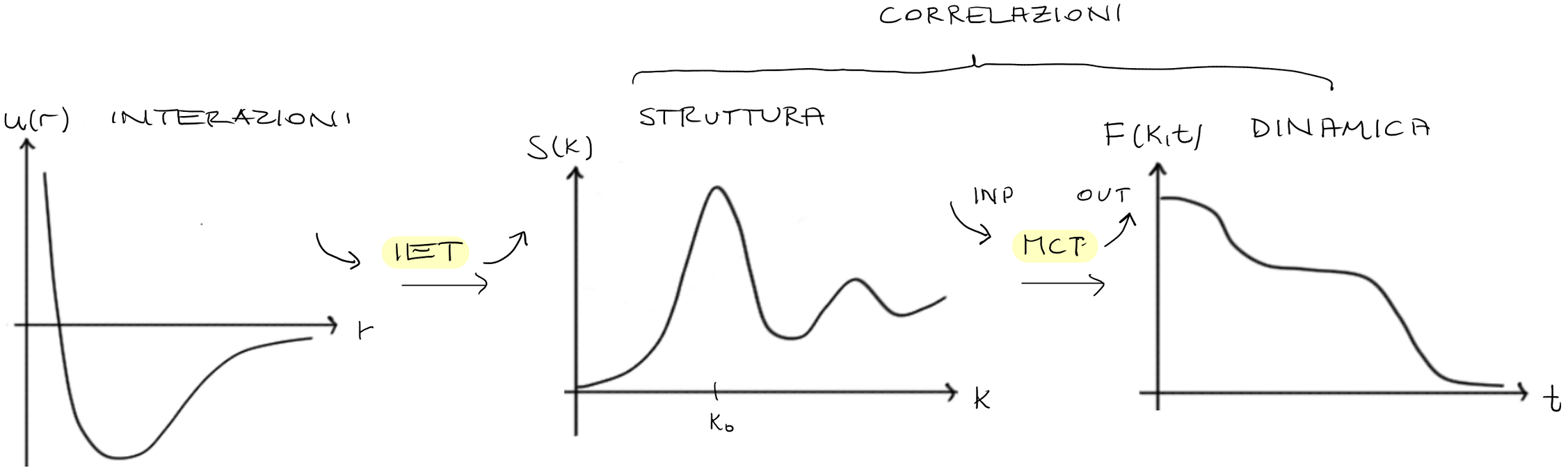
Teoria mode-coupling

Götze 1984

Formalismo dell'operatore di proiezione (Mori & Zwanzig)

① two-step relaxation + stretched exponential

② $\tau_\alpha(T)$



Formalismo dell'operatore di proiezione (Mori & Zwanzig ~ 1960)

Variabili lente

$$A(t) = A(\Gamma(t)) = \hat{A}(t)$$

$$\frac{dA}{dt} = \{A(t), H\} = i\mathcal{L}A(t)$$

$$\mathcal{L} = i\{H, \dots\} = i\sum_{i=1}^{N}\left[\frac{\partial H}{\partial \vec{r}_i}\frac{\partial \dots}{\partial \vec{p}_i} - \frac{\partial H}{\partial \vec{p}_i}\frac{\partial \dots}{\partial \vec{r}_i}\right]$$

$$i\mathcal{L} = -\{H, \dots\} = \{\dots, H\}$$

Integro formalmente

$$A(t) = \exp(i\mathcal{L}t)A(0) = \exp(i\mathcal{L}t)A \qquad \exp(i\mathcal{L}t) = \sum_{n=0}^{\infty}\frac{1}{n!}(it)^n\mathcal{L}^n$$

Prodotto scalare

$$(A, B) = (A \mid B) = \langle A \mid B\rangle = \langle B A^*\rangle = C_{BA}$$

$$A(t) = \exp(i\mathcal{L}t)A$$

Grandezze conservate: $N, E, \vec{P}$ $\qquad A(t) = A(0) = A$

$$A = \sum_{i=1}^{N} a_i$$

$$A_{\vec{k}}(t) = \sum_{i=1}^{N} a_i(t) \exp(-i\vec{k}\cdot\vec{r}_i(t)) \qquad [\text{es. } \hat{\rho}_k(t)]$$

$|\vec{k}| \ll \frac{2\pi}{\xi_0} \rightarrow$ grandezze "quasi-conservate"

$\rightarrow$ variabili lente

Operatore di proiezione

$A_1, \dots, A_n \quad n \ll N \rightarrow A \qquad [\mathbb{A}, \underline{A}]$

$$\frac{dA_\nu}{dt} = i\mathcal{L}A_\nu(t) \qquad \nu = 1, \dots, n \Rightarrow A_\nu(t) = e^{i\mathcal{L}t}A_\nu(0)$$

A linearmente indipendenti $\rightarrow$ ortogonali $\langle A_\lambda | A_\nu \rangle = 0 \quad \lambda \neq \nu$

$\rightarrow$ ortonormali $\langle A_\lambda | A_\nu \rangle = \delta_{\lambda\nu}$

$n = 1$

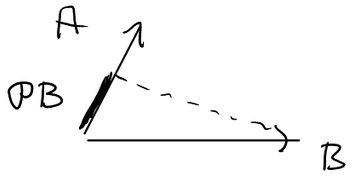
$|A\rangle = A(\Gamma)$

$\langle A| = A^*(\Gamma)$

$$\mathcal{P} = \frac{|A\rangle\langle A|\ldots\rangle}{\langle A|A\rangle} = \frac{\langle A|\ldots\rangle}{\langle A|A\rangle} A$$

$$\mathcal{P} = |A\rangle \frac{1}{\langle A|A\rangle} \langle A|$$

$\mathcal{P}A = A \qquad \mathcal{P}^2 A = A$



$n \geq 1$

$$\mathcal{P} = |A\rangle\langle A|\ldots\rangle \langle A|A\rangle^{-1} A$$

$$\mathcal{P} = \sum_\nu \sum_\lambda |A_\lambda\rangle \langle A|A\rangle^{-1}_{\lambda\nu} \langle A_\nu|$$

$A(t) = e^{i\mathcal{L}t} A(0)$

$$\frac{dA}{dt} = e^{i\mathcal{L}t} i\mathcal{L} A(0) = i e^{i\mathcal{L}t} [\mathcal{P} + (1-\mathcal{P})] \mathcal{L} A(0)$$

($\mathcal{P} + (1-\mathcal{P})$)

$$= \underbrace{i e^{i\mathcal{L}t} \mathcal{P}\mathcal{L} A(0)} + i e^{i\mathcal{L}t} (1-\mathcal{P}) \mathcal{L} A(0)$$

$$i e^{i\mathcal{L}t} P\mathcal{L} A(0) = i e^{i\mathcal{L}t} \underbrace{\langle A | \mathcal{L}A \rangle \langle A | A \rangle^{-1}} A(0)$$

Ω = matrice delle frequenze

$$= i\Omega A(t)$$

$$\frac{dA}{dt}(0) = i\mathcal{L}A(0)$$

$$i\Omega = i\langle A | \mathcal{L}A \rangle \langle A | A \rangle^{-1} = \langle A | \frac{dA}{dt} \rangle \langle A | A \rangle^{-1}$$

$\Omega_{\nu\nu} = 0$

$$\frac{dA}{dt} = i\Omega A(t) + e^{i\mathcal{L}t} i(1-P)\mathcal{L}A \qquad \frac{dA}{dt} = i\mathcal{L}A \qquad A(t) = e^{i\mathcal{L}t}A(0)$$

$$e^{i\mathcal{L}t} = e^{i\mathcal{L}t} + e^{i(1-P)\mathcal{L}t} - e^{i(1-P)\mathcal{L}t}$$

$$= e^{i\mathcal{L}t} + e^{i(1-P)\mathcal{L}t} - e^{i\mathcal{L}t} e^{-i\mathcal{L}t} e^{i(1-P)\mathcal{L}t}$$

$$= e^{i(1-P)\mathcal{L}t} + e^{i\mathcal{L}t} \underbrace{\left(1 - e^{-i\mathcal{L}t} e^{i(1-P)\mathcal{L}t}\right)}_{S(t)}$$

$$\frac{dS}{dt} = + e^{-i\mathcal{L}t}(+i\mathcal{L}) e^{i(1-P)\mathcal{L}t} - e^{-i\mathcal{L}t}(i(1-P)\mathcal{L}) e^{i(1-P)\mathcal{L}t}$$

$$= e^{-i\mathcal{L}t}(iP\mathcal{L}) e^{i(1-P)\mathcal{L}t}$$

Integro in t con $S(0) = 0$

$$S(t) = \int_0^t dt' \, e^{-i\mathcal{L}t'}(iP\mathcal{L}) e^{i(1-P)\mathcal{L}t'}$$

$$e^{i\mathcal{L}t} i(1-P)\mathcal{L}A = \underbrace{e^{i(1-P)\mathcal{L}t} i(1-P)\mathcal{L}A} + \int_0^t dt' \, e^{i\mathcal{L}(t-t')}(iP\mathcal{L}) \underbrace{e^{i(1-P)\mathcal{L}t'} i(1-P)\mathcal{L}A}$$

$$\theta(t) = \underbrace{e^{i(1-P)\mathcal{L}t}}_{\text{“propagatore anomalo”}} i(1-P)\mathcal{L}A = e^{i(1-P)\mathcal{L}t}\,\theta(0) \qquad \theta(0) = i(1-P)\mathcal{L}A$$

$$\langle A \mid \theta(t)\rangle = 0 \qquad \theta(t) = \text{“forza stocastica”}$$

$$e^{i\mathcal{L}t} i(1-P)\mathcal{L}A = \int_0^t dt'\, e^{i\mathcal{L}(t-t')}\, iP\mathcal{L}\theta(t') + \theta(t)$$

Lavoro su

$$P\mathcal{L}\theta(t) = \langle A \mid \mathcal{L}\theta(t)\rangle \langle A|A\rangle^{-1} A \qquad \mathcal{L} \text{ è Hermitiano: } \langle A \mid \mathcal{L}B\rangle = \langle \mathcal{L}A \mid B\rangle$$

$$= \langle \mathcal{L}A \mid \theta(t)\rangle \langle A|A\rangle^{-1} A$$

$$= \langle (1-P)\mathcal{L}A \mid \theta(t)\rangle \langle A|A\rangle^{-1} A \quad \leftarrow \quad \langle P\mathcal{L}A \mid \theta(t)\rangle = 0$$

$$iP\mathcal{L}\theta(t) = -\langle \theta(0) \mid \theta(t)\rangle \langle A|A\rangle^{-1} A$$

Inserisco

$$e^{i\mathcal{L}t} i(1-P)\mathcal{L}A = -\int_0^t dt' \langle \theta(0)\mid\theta(t')\rangle \langle A|A\rangle^{-1} \overbrace{e^{i\mathcal{L}(t-t')}}^{A(t-t')} A + \theta(t)$$

Equazione del moto

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t dt' \underbrace{\langle \theta | \theta(t') \rangle \langle A | A \rangle^{-1}}_{M(t)} A(t-t') + \theta(t)$$

$i\Omega A(t) \sim \langle A | \frac{dA}{dt} \rangle$ ↑

$M(t)$ = funzione di memoria $\sim \langle \theta | \theta(t) \rangle$

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t dt' M(t') A(t-t') + \theta(t)$$ eq. Langevin generalizzata

Funzioni di correlazione $C(t) = \langle A | A(t) \rangle = \langle A(t) A^*(0) \rangle$

$$\frac{dC}{dt} = i\Omega C(t) - \int_0^t dt' M(t') C(t-t')$$

$$\frac{dZ}{dt} = -\int_0^t dt' M(t-t') Z(t')$$

⇒ Approssimazioni per M !

Approssimazione mode-coupling

Variabili lente $\rightarrow$ $\{\hat{\rho}_{\vec{k}}(t), \hat{J}_{\vec{k}}(t)\}$ $\quad \hat{J}_{\vec{k}}(t) = \sum_{i=1}^{N} \vec{v}_i(t)\, e^{-i\vec{k}\cdot\vec{r}_i(t)}$ $\quad F(k,t) = \langle \rho_{\vec{k}} \mid \rho_{\vec{k}}(t) \rangle$

Mode-coupling $\quad M \sim \hat{\rho}_{\vec{k}_1} \hat{\rho}_{\vec{k}_2}$

$$\begin{cases} \dfrac{d^2F}{dt^2} + \dfrac{k_B T\, k^2}{m S(k)} F(k,t) + \displaystyle\int_0^t ds\, M(k, t-s) \dfrac{dF}{ds}(k,s) = 0 \\ M(k,t) = \dfrac{\rho\, k_B T}{16\, \pi^3 m} \displaystyle\int d\vec{k}' \, | V_{\vec{k},\vec{k}-\vec{k}'} |^2 \, F(k,t)\, F(|\vec{k}-\vec{k}'|, t) \end{cases}$$

$V_{\vec{k},\vec{k}-\vec{k}'}$ ↑ "vertici"

→ integrazione numerica

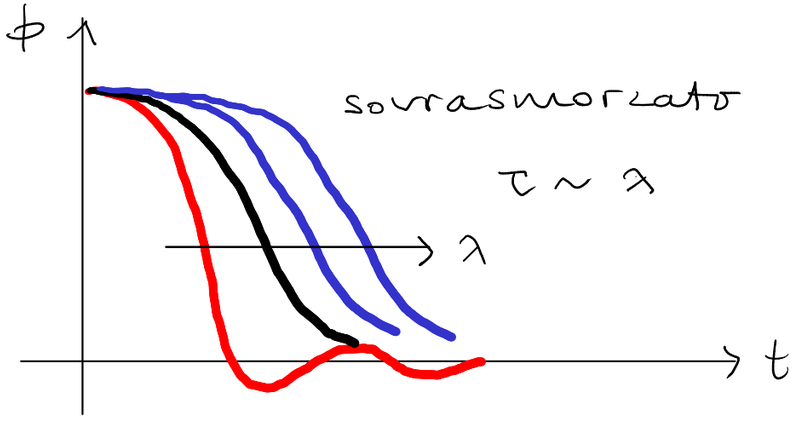
→ sviluppi asintotici

Versione schematica di MCT : $S(k) = \delta(k - k_0) \quad \Rightarrow \quad \phi(t)$

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

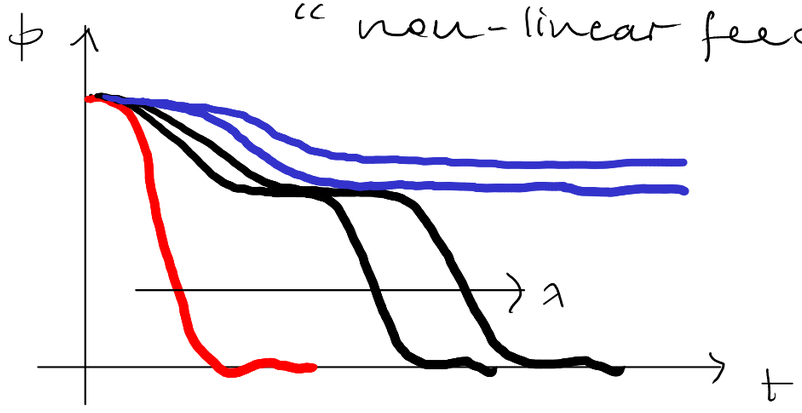
$$\ddot{\phi} + \Omega^2 \phi + \lambda \dot{\phi} = 0$$

oscillatore armonico smorzato



eq. MCT schematica

"non-linear feedback"



$\lambda < \lambda_c : \phi(\infty) = 0$

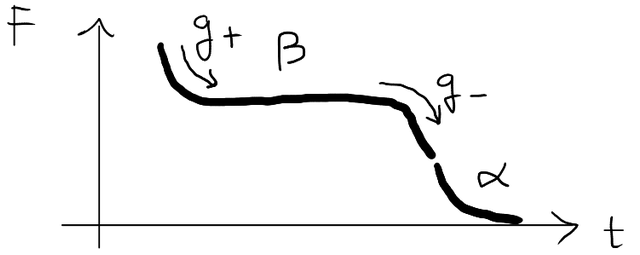
$\lambda \geq \lambda_c : \phi(\infty) > 0$

Predizioni generali della teoria

transizione ideale a $T = T_c$

Sviluppi asintotici delle $F(K,t)$ per $T \approx T_c$

① two-step + stretched relaxation



α - relaxation :

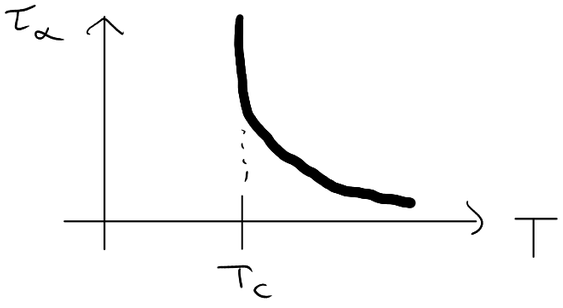
$$F(K,t) \approx \exp\left[-(t/\tau_\alpha)^\beta\right] \qquad \beta \sim 0.6 - 0.8$$

$K \to \infty$

β - relaxation : ← Debye-Waller factor

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

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



② $\tau_\alpha(T)$, $\tau_\beta(T)$ $\qquad \tau_\alpha(T) \sim \dfrac{1}{|T-T_c|^\gamma} \qquad \gamma \sim 2$

③ $F_s(K,t) \to D$, η

Verifica delle predizioni della teoria

miscela binaria LJ

Kob-Andersen

$T_{onset} \approx 0.9 - 1.0$

$T_c = 0.92$

$T_c^{(fit)} = 0.43$

$T_g^{(num)} \lesssim 0.4$

f(k)

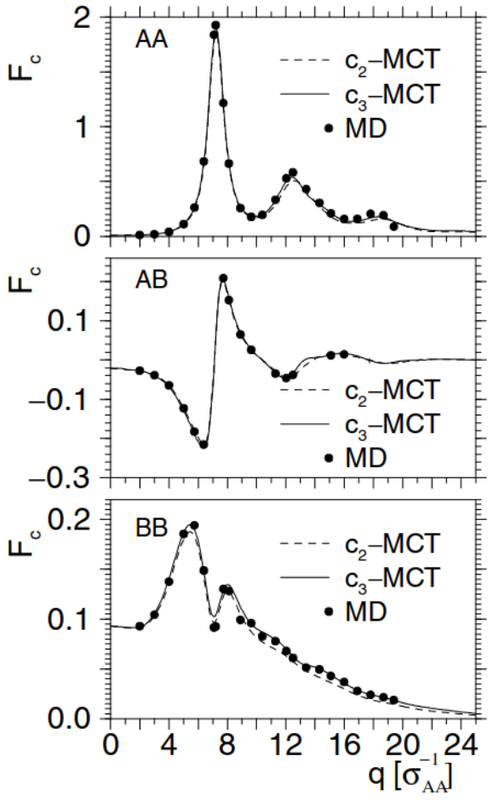


FIG. 1. Wave-vector dependence for the nonergodicity parameters for the BMLJ system. The solid and dashed curves are the theoretical predictions with and without the inclusion of the c_3 terms in Eq. (2). The circles are the MD results from [19].

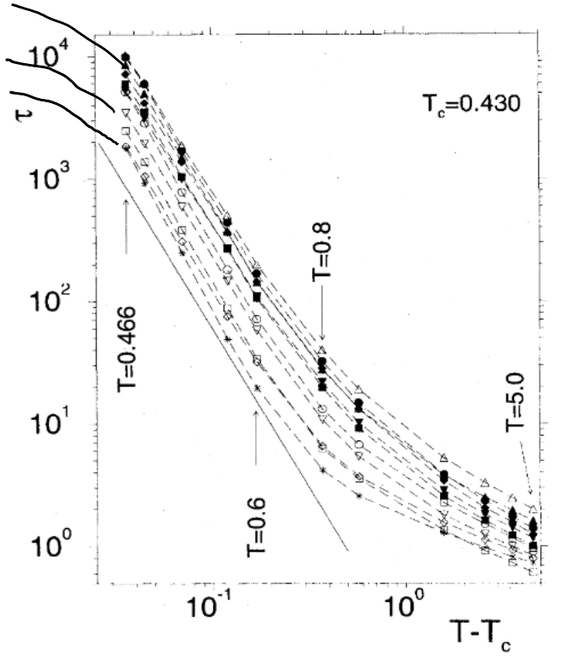


FIG. 9. Relaxation time τ versus temperature for various correlators. Squares and triangles pointing downwards: $F_s(q,t)$ for A and B particles, respectively. Circles and diamonds: $F(q,t)$ for AA and BB correlation, respectively. Triangles pointing upwards and stars: $F(q,t)$ for AB correlation. Filled and open symbols are for $q = q_{max}$ and $q = q_{min}$, respectively. Solid line: power law with exponent 2.6.