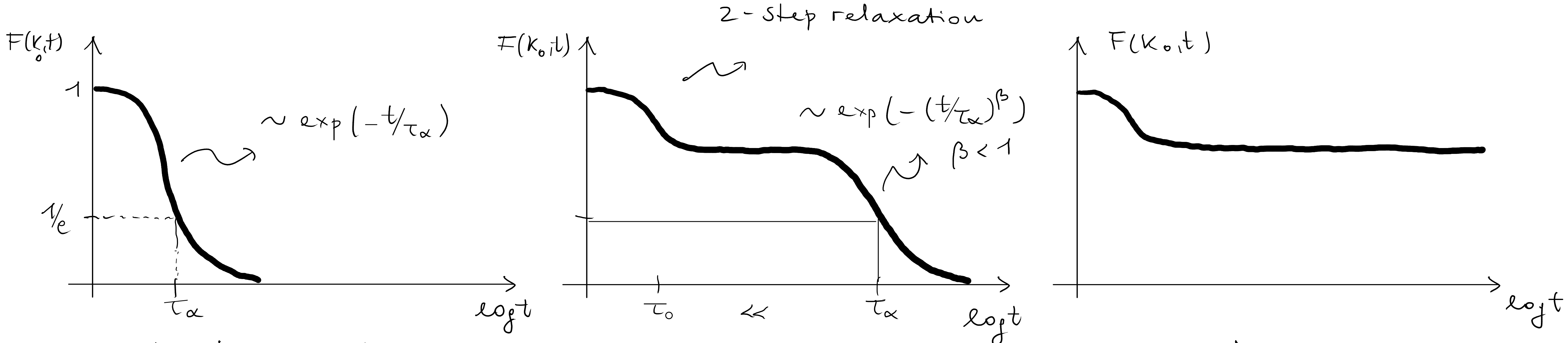
FENOMENOLOGIA DELLA TRANSIZIONE LIQUIDO - VETRO

Termodinamica: sottoraffreddato se $T < T_m$

Dinamica: vetro se $T < T_g$

1) **Tempo di rilassamento strutturale** : τ_α

$$F(k,t) = \frac{1}{N} \langle \rho_{\bar{k}}(t)\, \rho_{-\bar{k}}(0) \rangle \qquad k_0 \approx \frac{2\pi}{\varepsilon_0}$$



liquido normale — liquido sottoraffreddato — vetro

$$\frac{F(k_0, \tau_\alpha)}{F(k_0, 0)} = \frac{1}{e} \qquad \tau_\alpha \approx \tau_0 \sim 10^{-12}\,s$$

$T \gtrsim T_{onset}$

$\tau_\alpha \gg \tau_0$

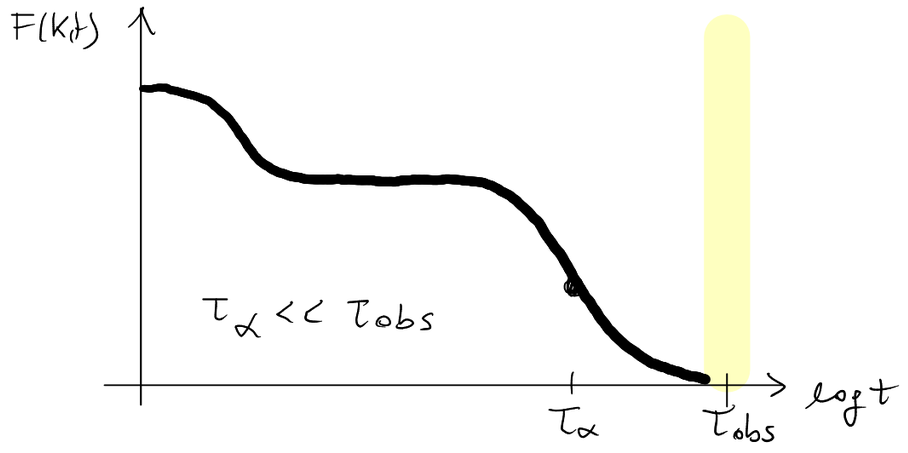
$T \lesssim T_{onset}$

modello di Maxwell

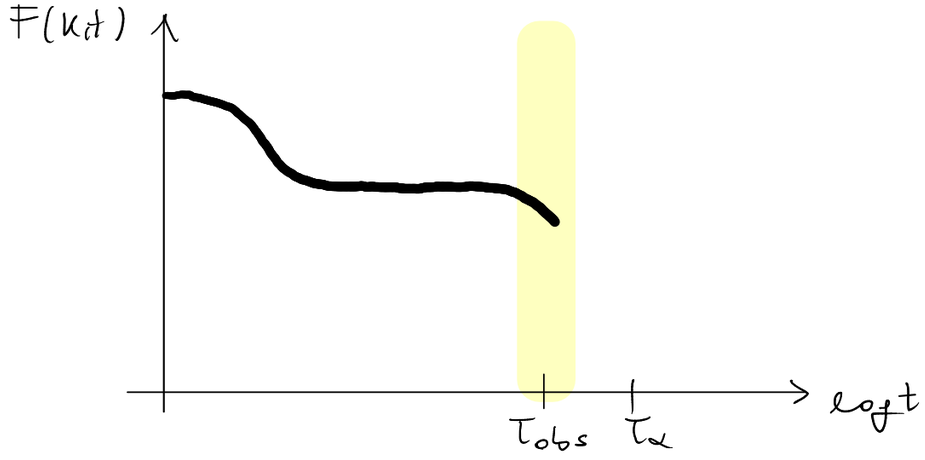
$\eta = G_\infty \tau \leftarrow \tau_\alpha$

$\longrightarrow 1/T$

2) Tempo di osservazione τ_{obs}



liquido sottoraffreddato
equilibrio metastabile



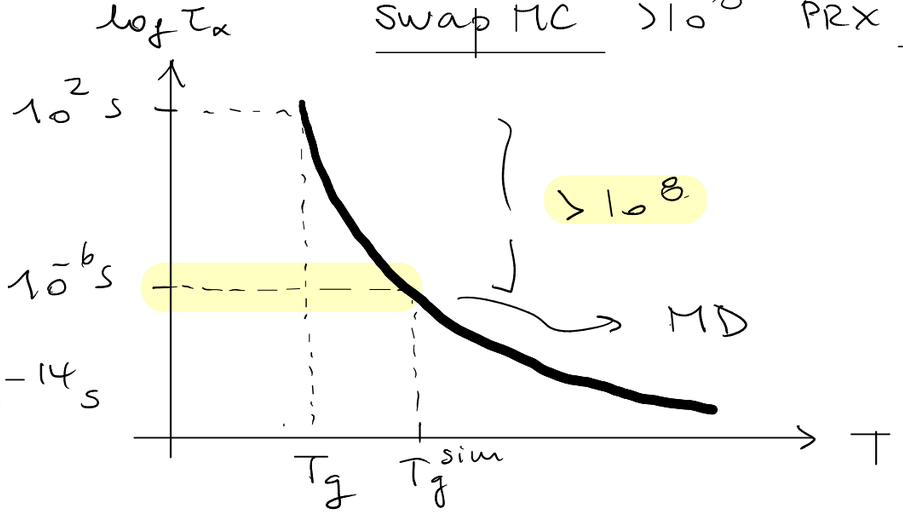
fuori equilibrio
~ vetro

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

Def. operativa della transizione vetrosa

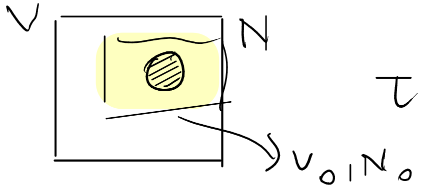
$\tau_{obs} \approx \tau_\alpha(T_g) \approx 10^2 s$ $\quad \eta(T_g) = 10^{12}$ Pa·s

$10^{-6} \frac{s}{\text{step} \times \text{particelle}}$; $N \sim 10^3$; $\delta t \to 10^{-3} s$; $\delta t \sim 10^{-2} \tau_0 \sim 10^{-14} s$

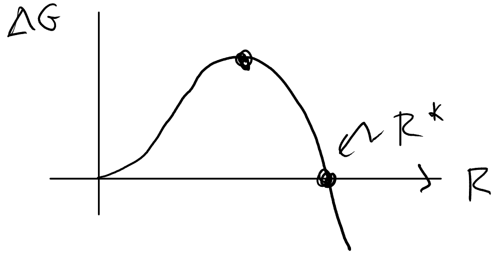


Swap MC > 10^8 PRX 2017

3) Tempo di nucleazione: τ_x



$\tau_x(N)$:
- $\sim N$ ①
- cost ② V
- $\sim \frac{1}{N}$ ③ V V V



Cavagna 3.2

$$\tau_x(N) \sim \frac{1}{N} \exp\left(\frac{\Delta G^*}{k_B T}\right) \to \tau_x = \tau_x(N_0)$$

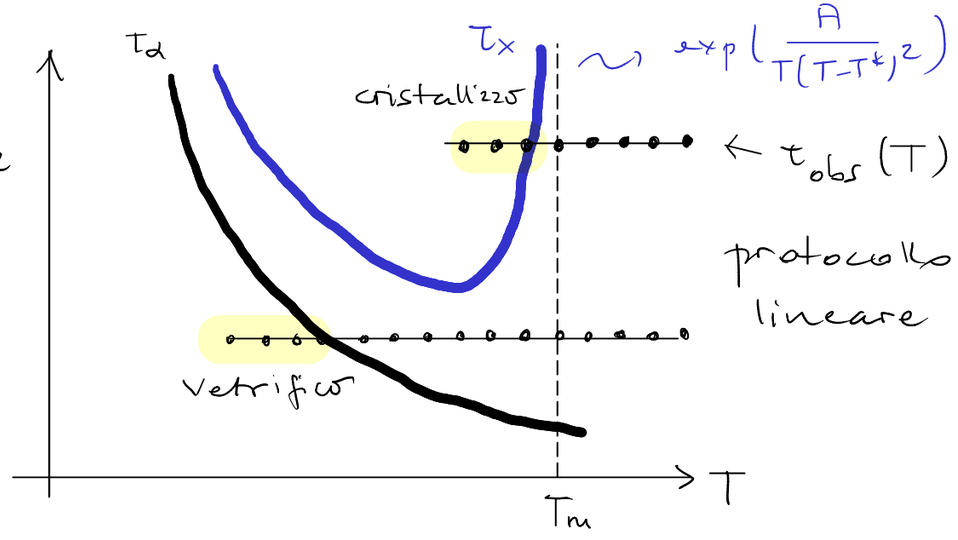
Diagramma tempo – temperatura – trasformazione (TTT)

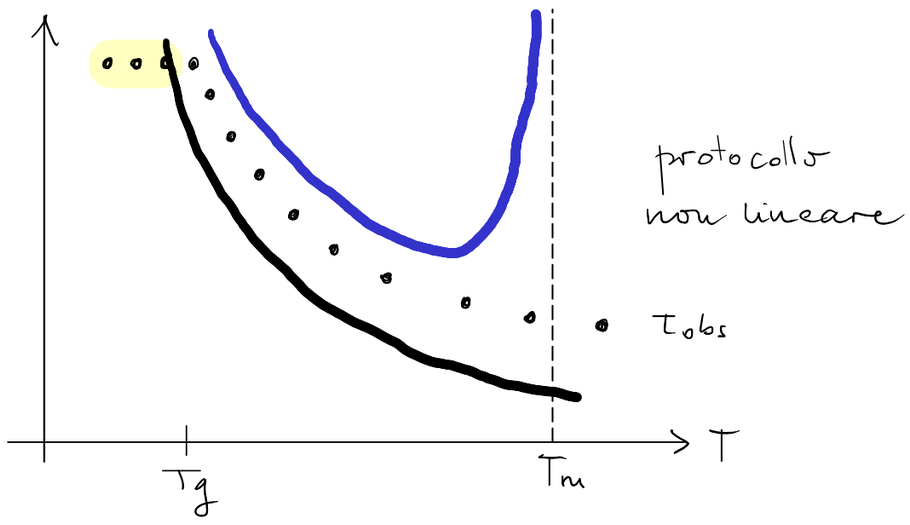
* rilassare fluttuazioni di densità * evitare il cristallo ⇒ sottoraffreddato $\tau_\alpha \ll \tau_{obs} \ll \tau_x$

$\tau_{obs} > \tau_x$

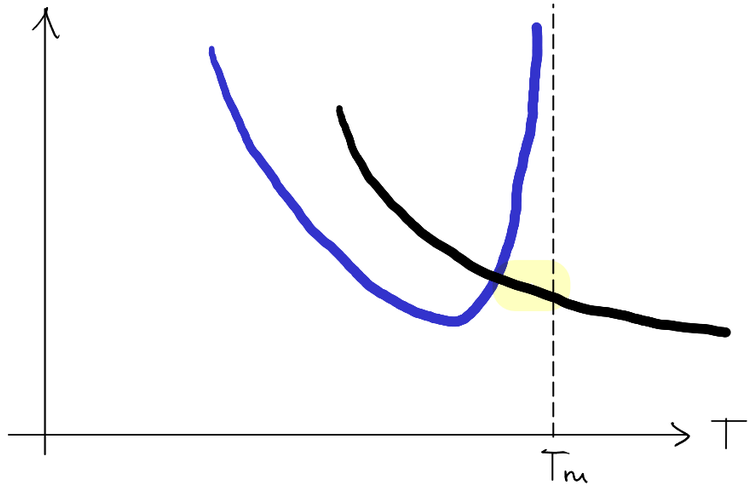
buon formatore di vetro

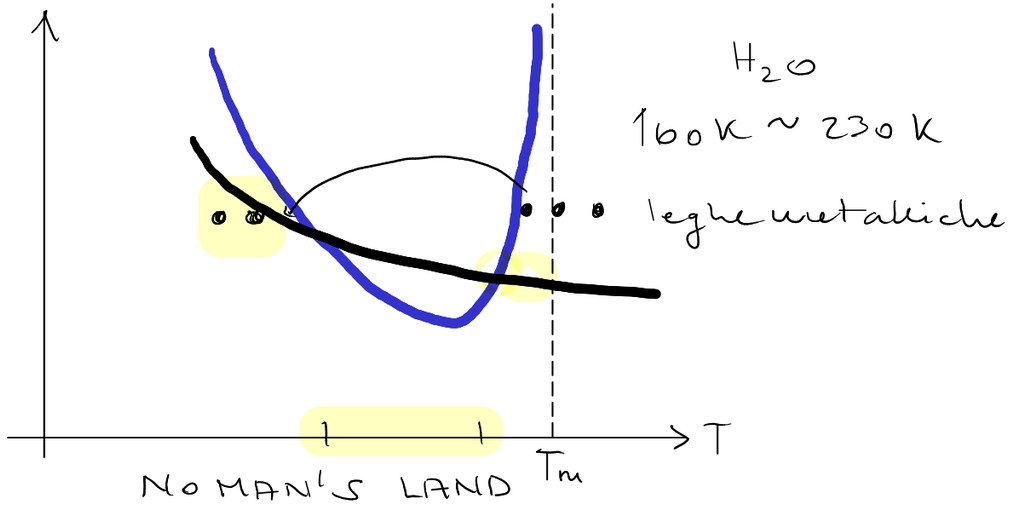
$\tau_{obs} < \tau_x$





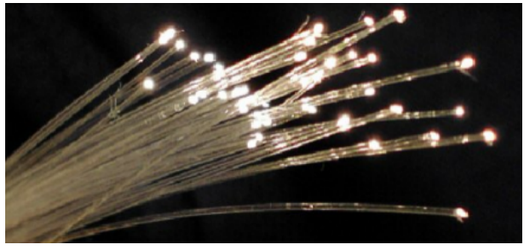
cattivo formatore di vetro





Formatori di vetro

Silicati : SiO_2 (silice)



B_2O_3

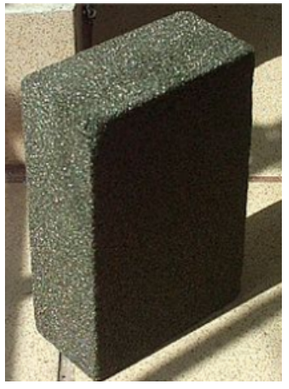
Vetro da finestra

SiO_2 : 70%

NaO_2 : 20%

CaO : 10%

Polimeri

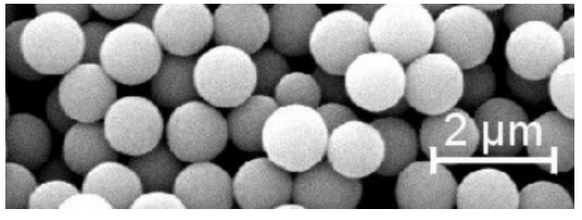


polistirene

PMMA

Metalli

Colloidi



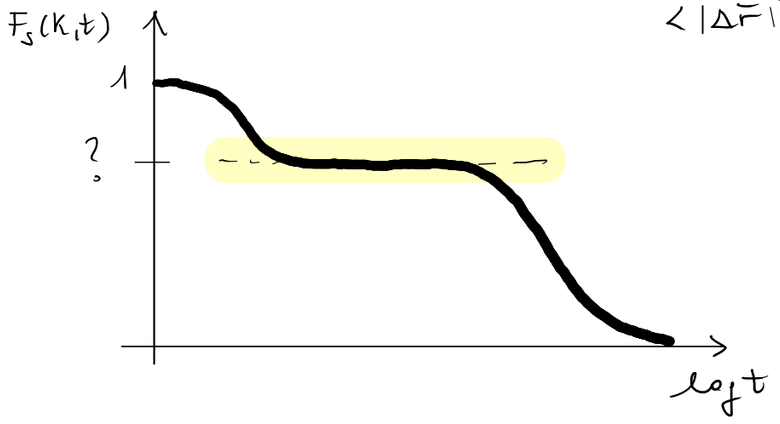
Vetri organici

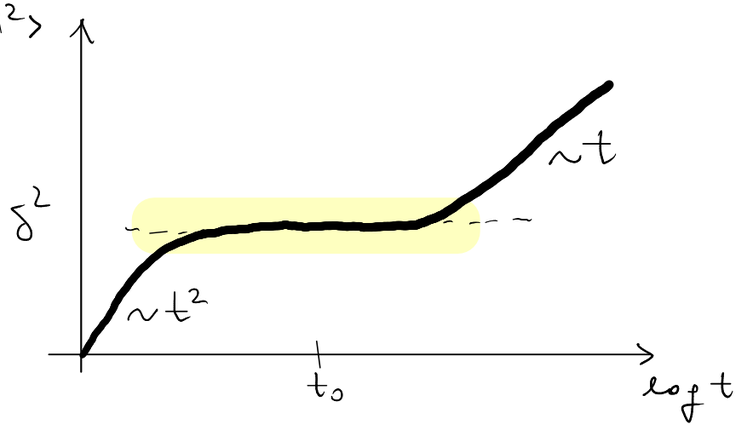
Substance	T_g
SiO_2	1473[g]
B_2O_3	532[m]
nPOH	97[h]
PropGlyc	167[d]
3-MePent	77[f]
3-Br-P	108[a]
glycerol	190[d]
BMPC	243[h]
salol	220[a]
MTHF	91[a]
OTP	246[h]
PropCarb	158[i]
triPhenPhos	203[k]
CKN	333[g]

Richert & Angell JCP 1998

Dinamica

$T < T_{onset}$





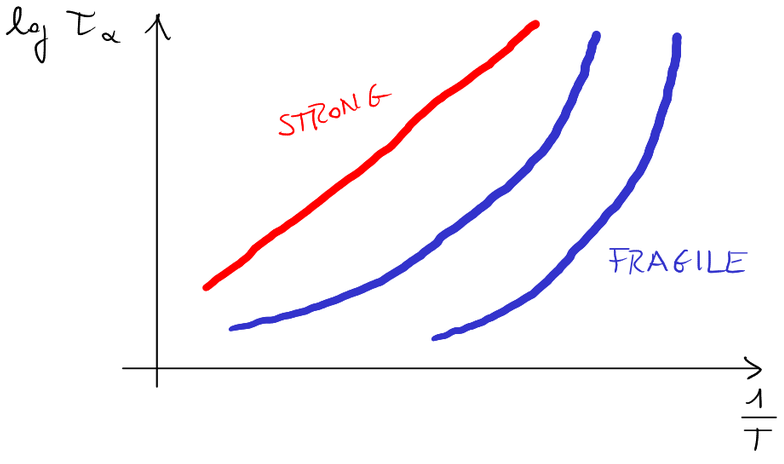
(es.)

$\langle|\Delta r(t_0)|^2\rangle \sim T$?

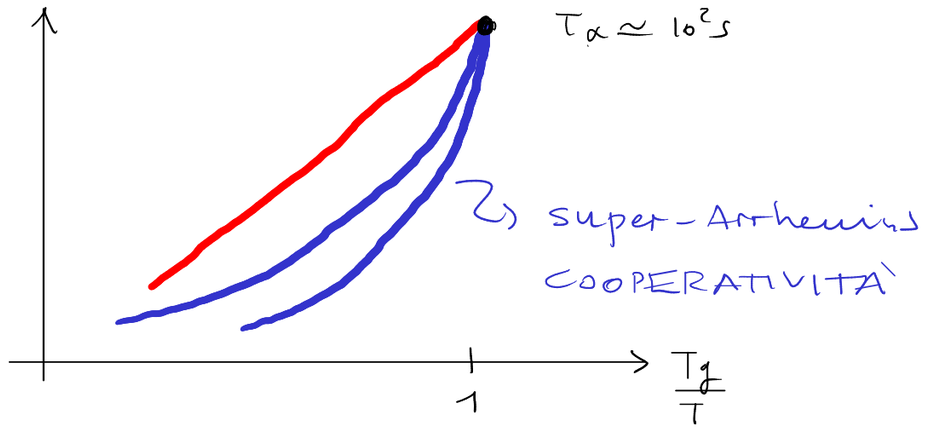
(es.)

$F_s(k,t_0) \rightarrow \delta^2$?

Classificazione di Angell



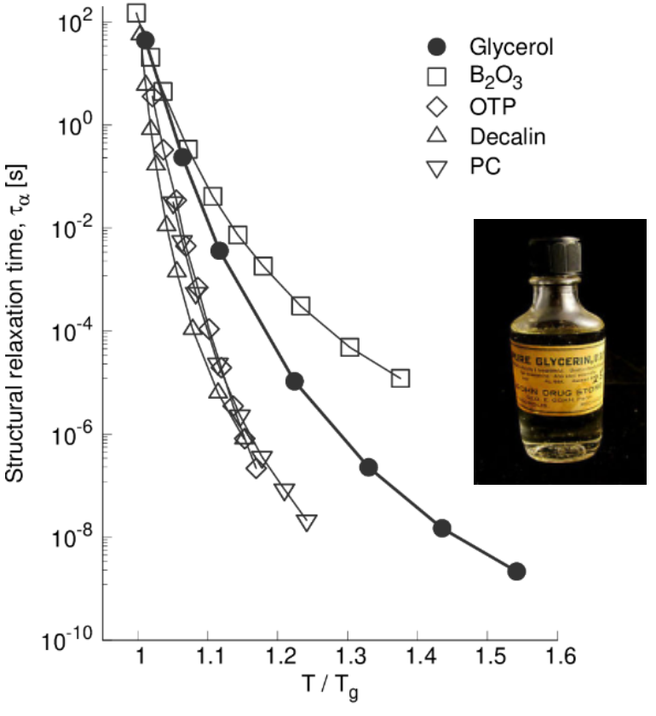
Angell plot

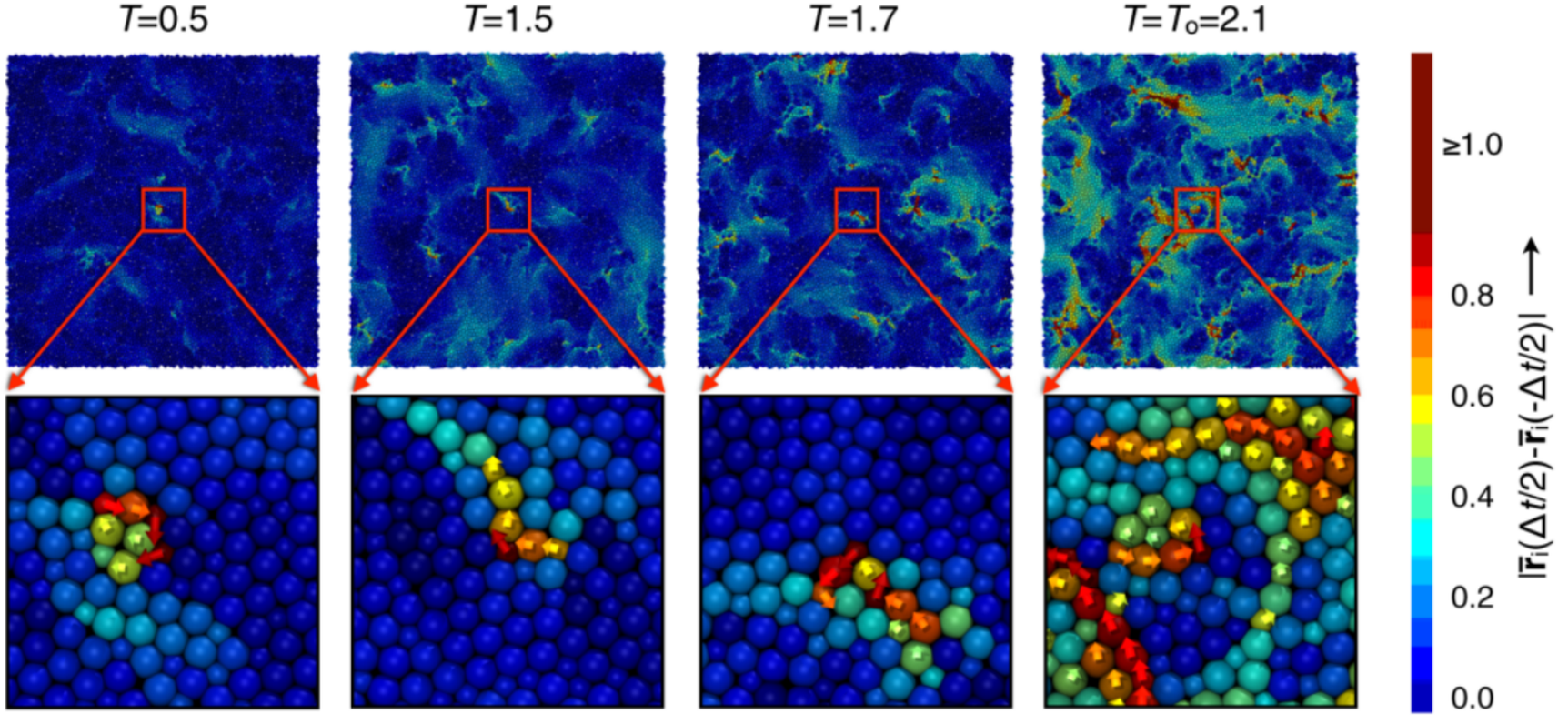


$\tau_\alpha(T) \sim \exp\left(\frac{\Delta E}{K_B T}\right)$ <

ΔE = cost SiO_2, GeO_2 STRONG

$\Delta E \nearrow$ $T \searrow$ FRAGILI





Keys et al. PRX 2011