

Termodinamica

- Energia interna E
- Calore specifico $C_v = \left. \frac{\partial E}{\partial T} \right|_v$

$$E(T) = E(T_0) + \int_{T_0}^T C_v(T) dT \quad \left\{ \begin{array}{l} \text{gas perfetto} \\ \text{solido amorfo} \end{array} \right.$$

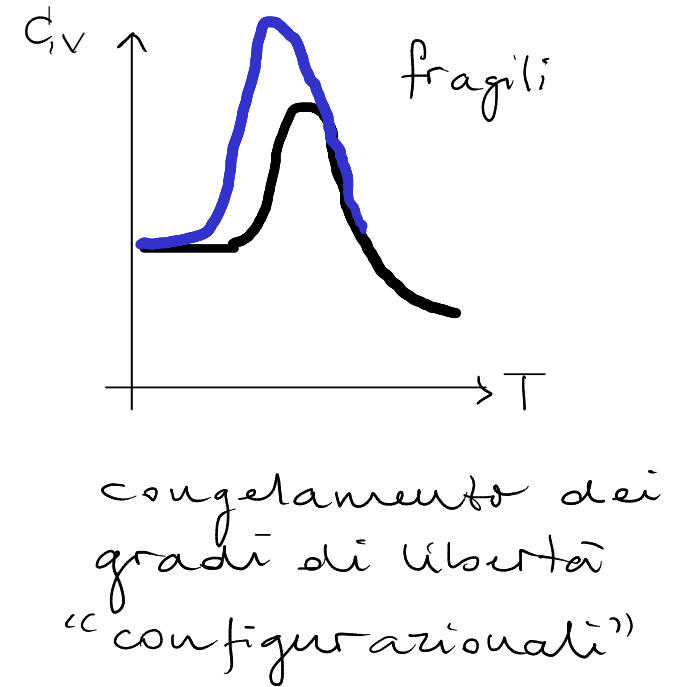
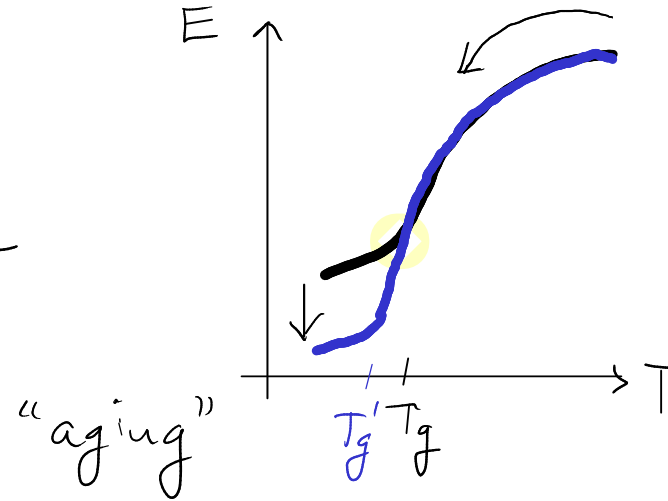
- Entropia S

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \quad V = \text{cost}$$

$$dS = \frac{1}{T} C_v dT \rightarrow S(T) = S(T_0) + \int_{T_0}^T \frac{C_v}{T} dT \quad \left\{ \begin{array}{l} \text{gp.} \\ \text{sol. am.} \end{array} \right.$$

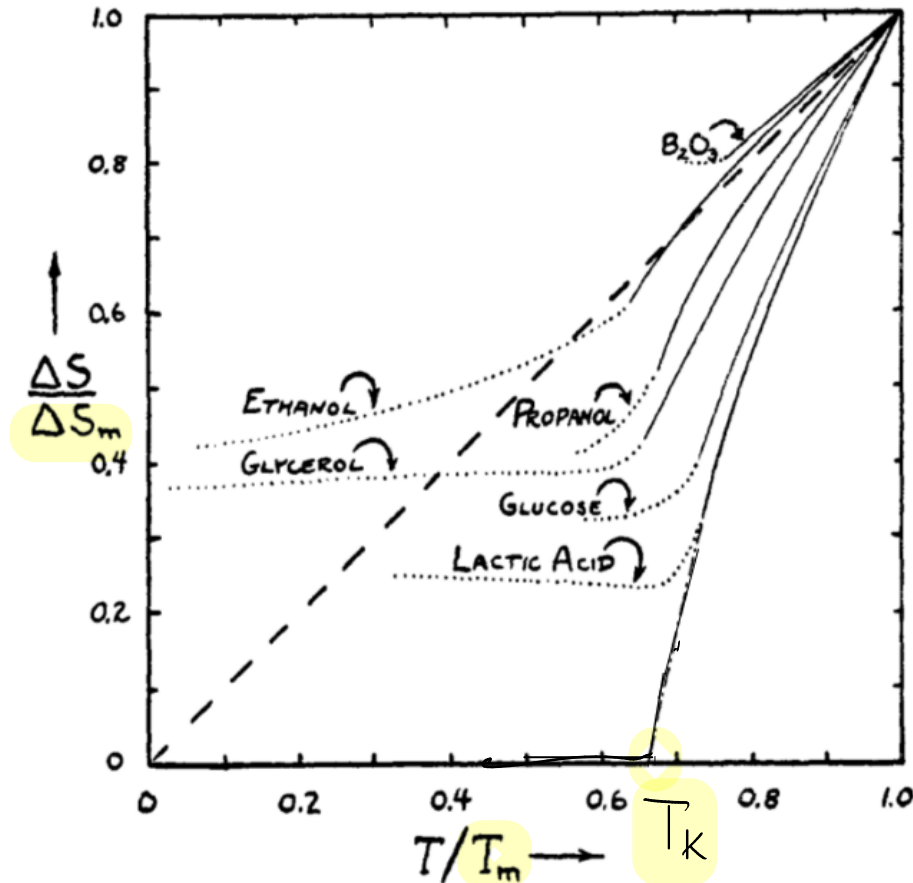
- Entropia configurazionale S_c

- cristallo perfetto: $S = S_{\text{vib}} \quad (S_c = 0)$
- liquido: ?
- liquido sottoraffreddati: $S = S_c + S_{\text{vib}}$



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

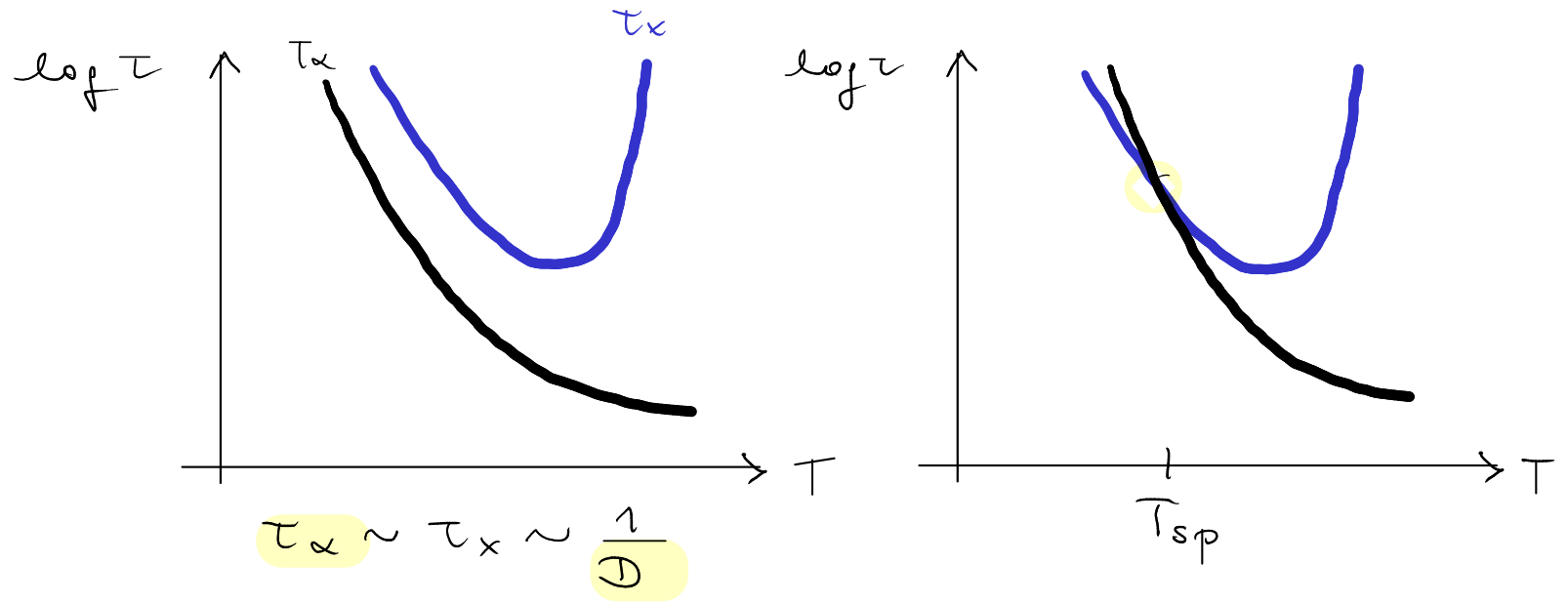
paradosso di Kauzmann \rightarrow entropy crisis



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.

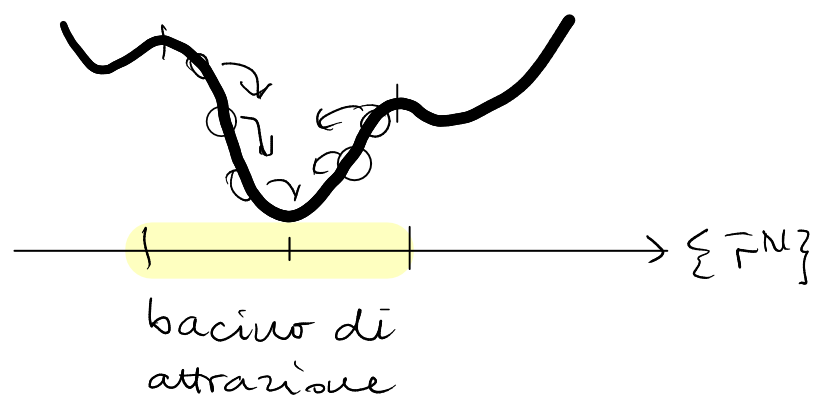
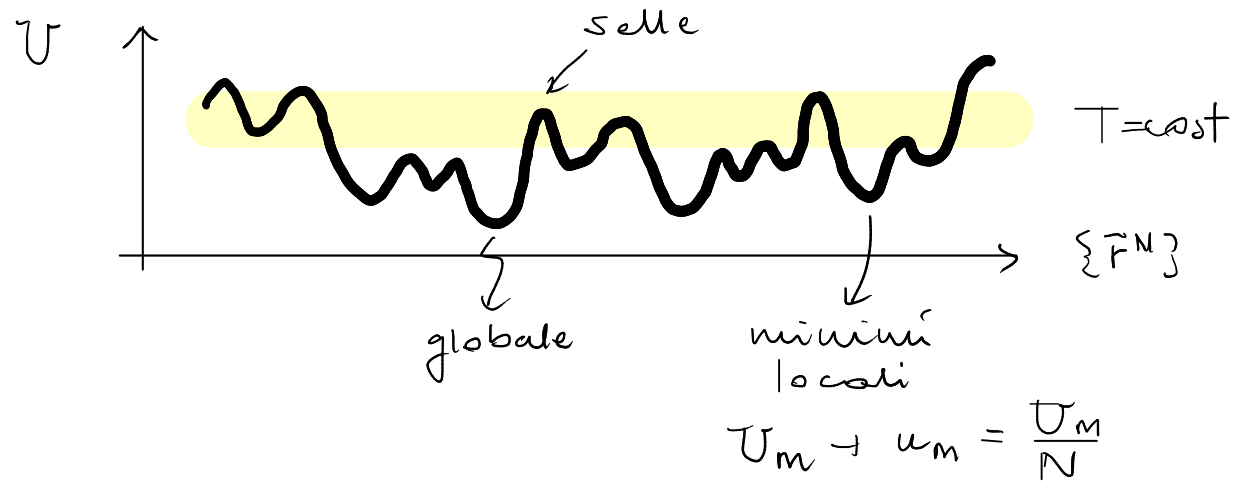


② Transizione di fase a vetro ideale $S_c(T_K) = 0$

① Spius data cinetica
 $T < T_{sp} \rightarrow$ cristallizza

TEORIE E MODELLI DELLA TRANSIZIONE VETROSA

Energy landscape



$$U = U(\{F^N\})$$

Strutture inerti
(IS) Stillinger &
Weber

N, V, T canonico

$$Z(T) = \text{Tr} [e^{-\beta U(\{F^N\})}] = \int du_m \Omega(u_m) e^{-\beta N u_m} Z(u_m, T)$$

$\Omega(u_m) du_m$ n. di minimi u_m e $u_m + du_m$ densità degli stati

$$\left\{ \begin{aligned} F_{\text{basin}}(u_m, T) &= -k_B T \ln [Z(u_m, T)] \\ f_{\text{basin}} &= F_{\text{basin}} / N \end{aligned} \right. \quad \left\{ \begin{aligned} S_c &= k_B \ln [\Omega(u_m)] \\ s_c &= S_c / N \end{aligned} \right.$$

$$\begin{aligned} Z(T) &= \int du_m \Omega(u_m) e^{-\beta N [u_m + f_{\text{basin}}(u_m, T)]} \\ &= \int du_m e^{-\beta N [u_m + f_{\text{basin}}(u_m, T) - T s_c(u_m)]} \end{aligned}$$

1) Approssimazione armonica

$$f_{\text{baria}}(u_m, T) \approx f_{\text{vib}}(u_m, T) \quad \rightarrow \quad \frac{\partial f_{\text{vib}}}{\partial u_m} \approx 0$$

2) Approssimazione di punto sella

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

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

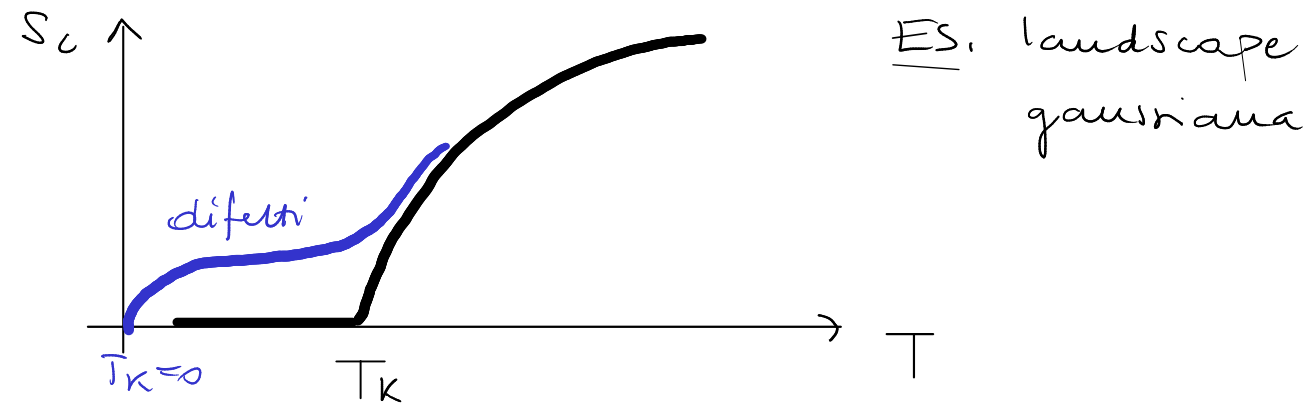
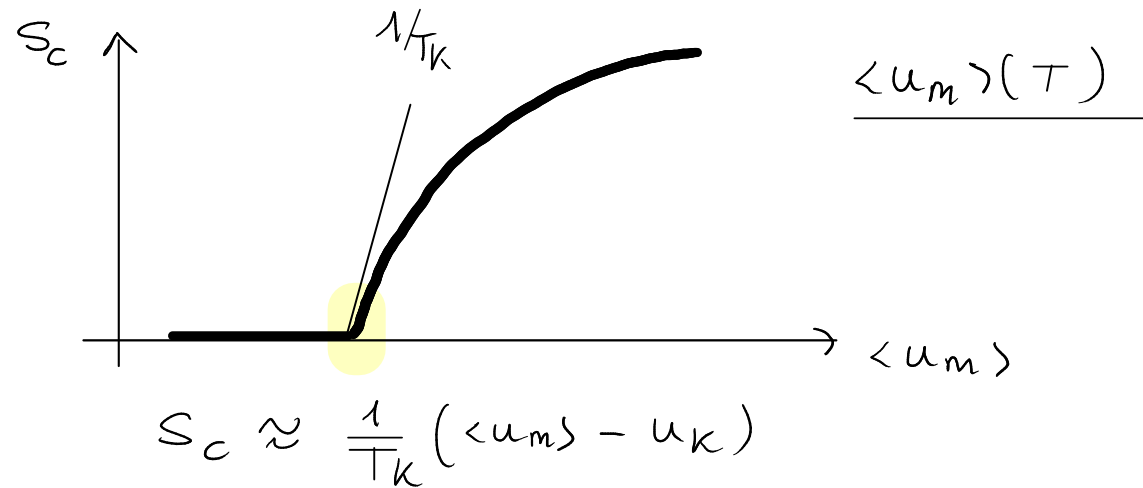
$$\approx \sqrt{\frac{2\pi}{N |f''(x_0)|}} e^{Nf(x_0)}$$

$$Z(T) \approx A(N) e^{N \left\{ -\beta \left[u_m' + f_{\text{baria}}(u_m', T) - T s_c(u_m') \right] \right\}} \quad u_m' \approx \langle u_m \rangle \quad N \rightarrow \infty$$

$$1 + \frac{\partial f_{\text{vib}}}{\partial u_m} - T \frac{\partial s_c}{\partial u_m} = 0 \quad \frac{\partial s_c}{\partial u_m} (\langle u_m \rangle) = \frac{1}{T} \quad \text{equilibrio}$$

≈ 0

$$\textcircled{1} \quad s_c(u_m) = 0, \quad u_m < u_k \quad \textcircled{2} \quad \frac{\partial s_c}{\partial u_m} (u_k) = \frac{1}{T_k} \quad N \rightarrow \infty$$



- ✓ Gibbs-Di Marzio '60 polimeri su reticolo
- ✓ spin glass campo medio '80

- ✗ Stillinger '80
- ✗ spinodale cinetica