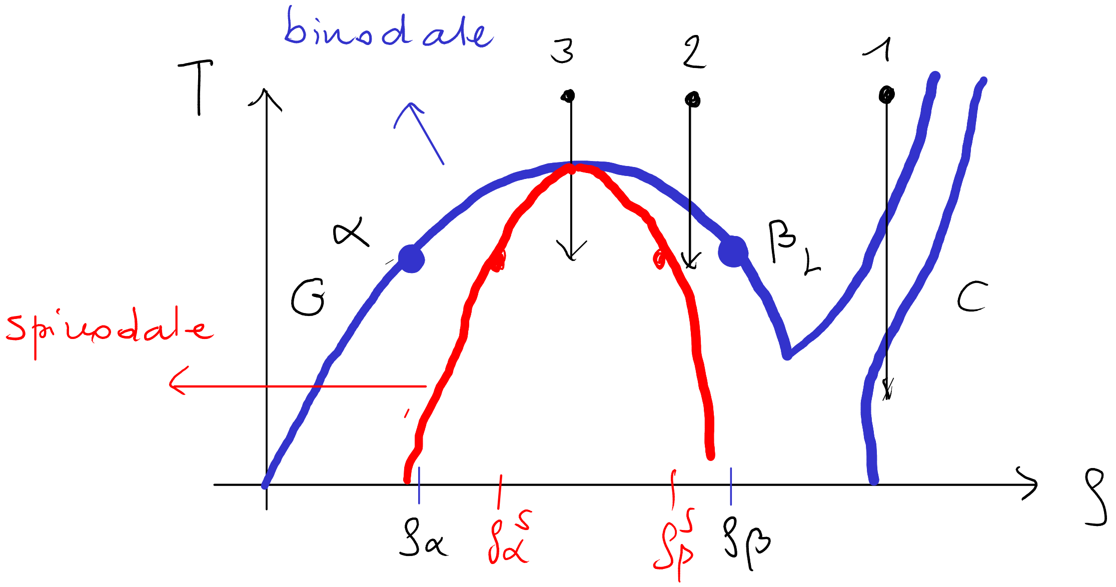
FLUIDI METASTABILI E INSTABILI

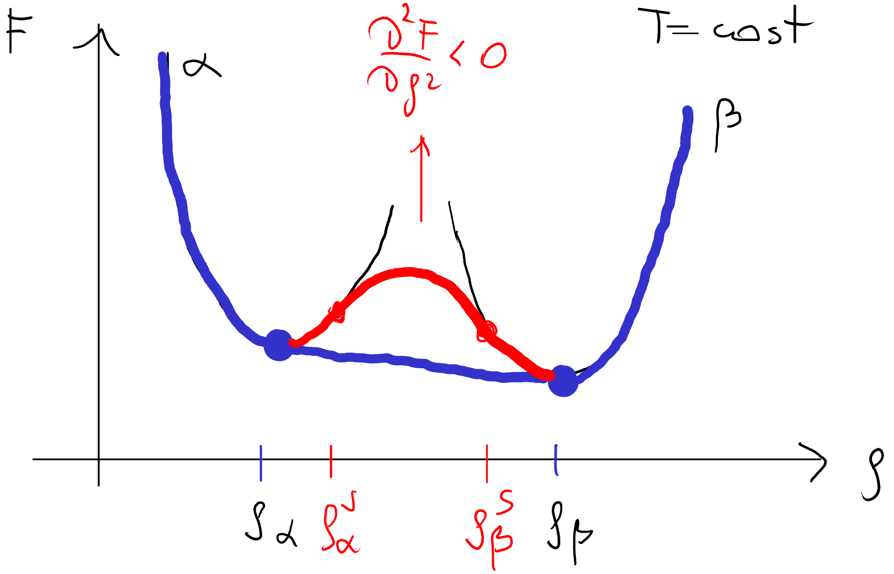


1) fluido metastabile wrt cristallo
2) fluido metastabile wrt separazione liquido - gas

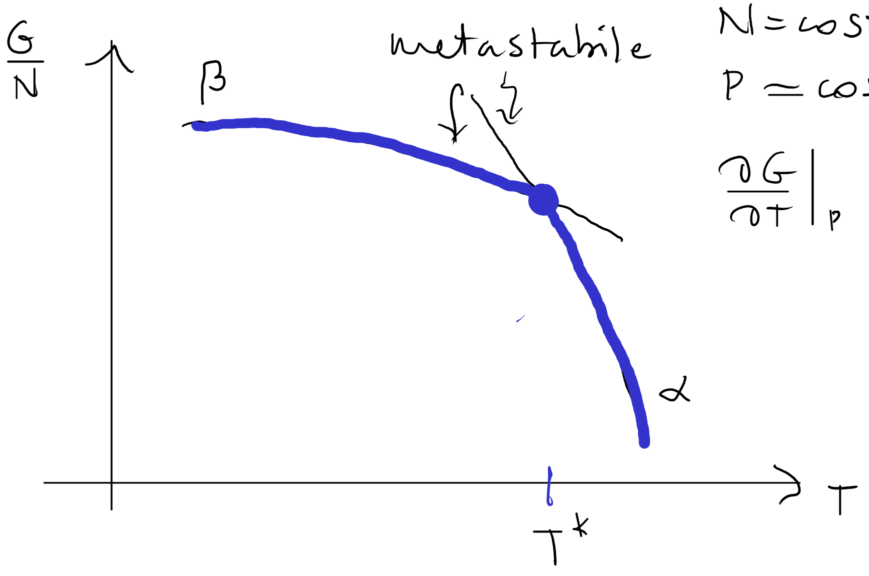
} (1) nucleazione + crescita

3) fluido instabile —//— → (2) decomposizione spinodale

Potenziale di Helmoltz



Potenziale di Gibbs



N = cost

P = cost

$$\left.\frac{\partial G}{\partial T}\right|_P = -S$$

1) Nucleazione

Teoria classica della nucleazione (CNT) → fenomenologica

α metastabile → β stabile

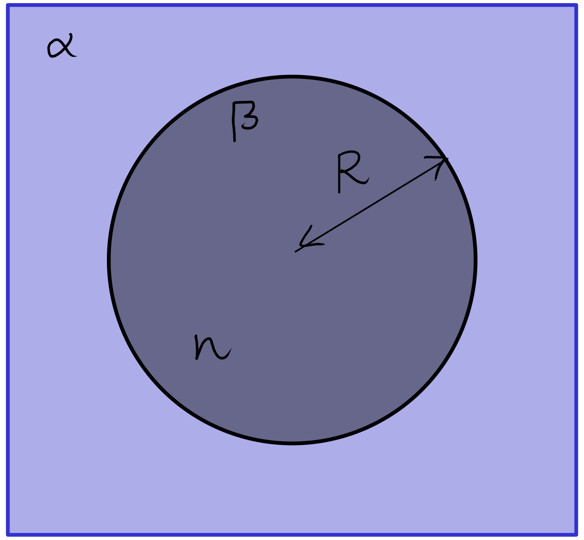
$$\Delta G(R) = \frac{4}{3}\pi R^3 \Delta g_v \quad + \quad 4\pi R^2 \cdot \gamma \leftarrow \text{tensione superficie}$$

$$n \cdot \underbrace{(g_\beta - g_\alpha)}_{\Delta g}$$

↑

$$g = \frac{G}{N}$$

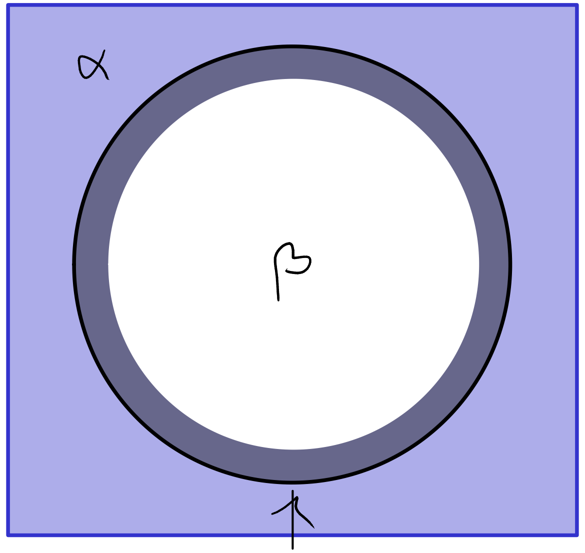
$$\Delta g_v = \rho_\beta \Delta g$$



$$n = \frac{4}{3}\pi R^3 \rho_\beta$$

↑

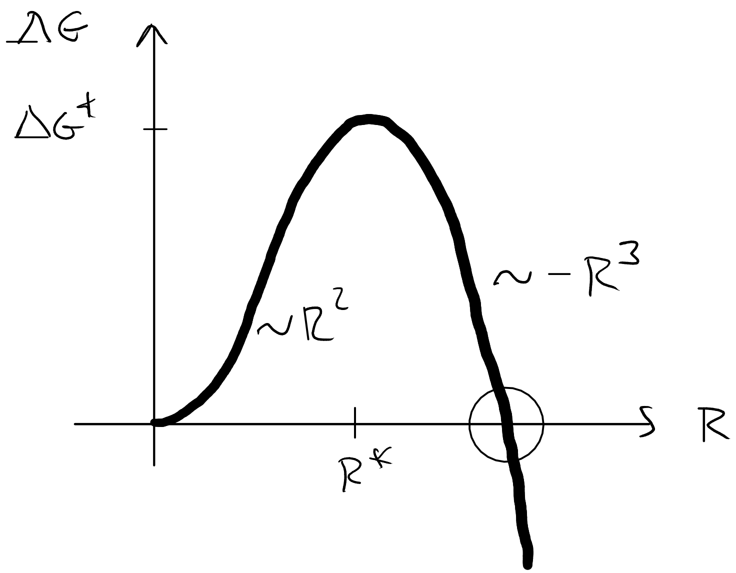
bulk



costo energetico

↑

superficie



Nucleo critico

$$\frac{d\Delta G}{dR} = 4\cancel{\pi}\Delta g_v R^{\cancel{2}} + 8\cancel{\pi}\gamma \cancel{R} = 0$$

$$R^* = -\frac{2\gamma}{\Delta g_v} > 0$$

Barriera di nucleazione

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

Cinetica della nucleazione

- ΔG è un paesaggio di energia
- n coordinata di reazione

} $\rightarrow$ $\Delta G(n)$ $\rightarrow$ n variabile continua

- particella Browniana : Langevin sovra-amortita in campo esterno
- formazione di un nucleo

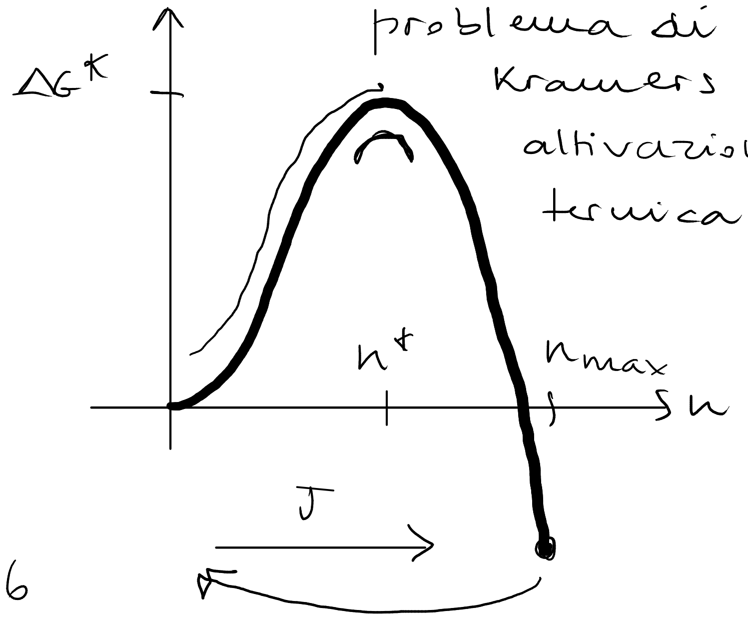
Smoluchowski : $p(x,t)$

$D = K_BT/\xi$

$$\frac{\partial p}{\partial t} = \vec\nabla\cdot\Big[\underbrace{D\vec\nabla p}_{\text{difusione}} + \underbrace{\frac{1}{\xi}\frac{\partial U}{\partial x}p}_{\text{deriva}}\Big] \simeq \frac{\partial}{\partial x}\left[D\left(\frac{\partial p}{\partial x} + \frac{1}{K_BT}\frac{\partial U}{\partial x}p\right)\right]$$

$x \to n$; $U \to \Delta G$; $D \to D(n) \sim D_{liq}$; $p(x,t) \to p(n,t)$

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial n}\left[D\left(\frac{\partial p}{\partial n} + \frac{1}{K_BT}\frac{\partial \Delta G}{\partial n}p\right)\right]$$



$\Delta G^* \gg K_BT$

problema di Kramers

attivazione termica

BH 10.6

Tempo uscita dalla buca → tempo di nucleazione τ_x

$$\tau_x = \underbrace{\frac{1}{D(n^*)}}_{\text{prefattore cinetico}} \; \underbrace{\frac{1}{\left(-\frac{1}{2\pi k_B T}\frac{d^2\Delta G}{dn^2}\Big|_{n^*}\right)^{1/2}}}_{\text{fattore di Zeldovich}} \; \underbrace{\exp\left(\frac{\Delta G^*}{k_B T}\right)}_{\text{fattore di Arrhenius}}$$

Tasso di nucleazione

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

↑ 1 nucleo

Dipendenza da T per $T \approx T_m$ ← barriera attivazione diffusiva

1) $D(n^*) \sim D_{liq} \sim \exp\left(-\frac{\Delta E_d}{k_B T}\right)$

2) $\exp\left(\frac{\Delta G^*}{k_B T}\right) \sim \exp\left(\frac{A}{T(T-T^*)^2}\right)$

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

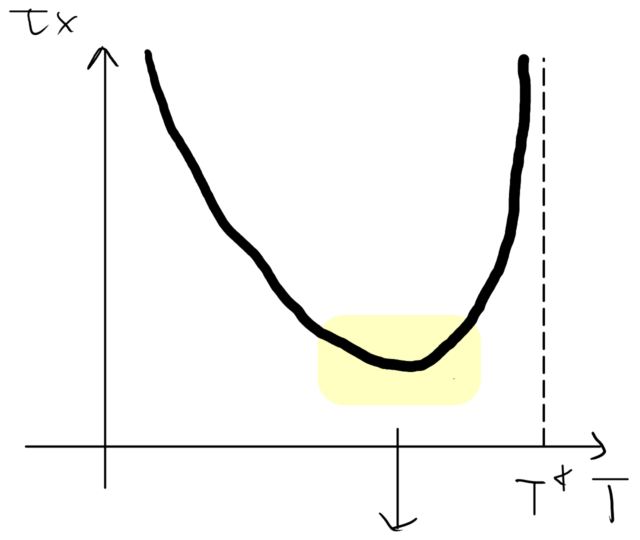
$$\Delta G^* \sim \frac{1}{\Delta g_v^2} = \frac{1}{\rho_\beta^2 \Delta g^2} \sim \frac{1}{\Delta g^2} \sim \frac{1}{(T-T^*)^2}$$

$$\Delta g = g_\beta - g_\alpha = \Delta\mu \sim (T-T^*)$$

↑ Taylor in $(T-T^*)$

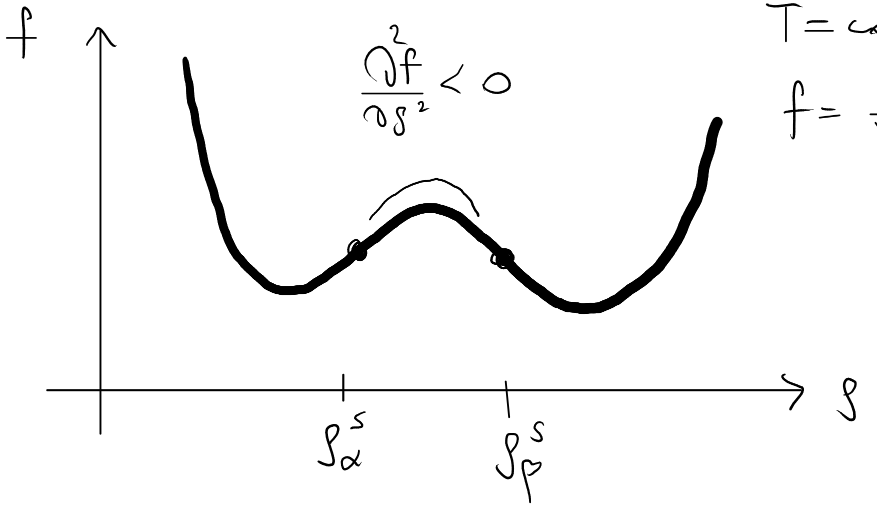
T^* coesistenza

Per $T \ll T_m$ domina il termine cinetico.



nucleazione più rapida

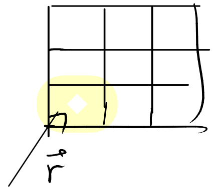
2) Decomposizione spinodale



$T = \text{cost}$

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

$\rho_N(\vec{r}, t)$



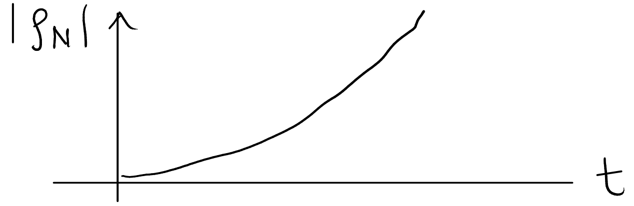
regime lineare: $\displaystyle \frac{\partial \rho_N}{\partial t} \overset{T=\text{cost}}{=} - \vec{\nabla} \cdot \left(- L_{NN} \vec{\nabla} \left(\frac{\mu}{T} \right) \right)$

$$\underset{\mu = \mu(\rho_N(\vec{r}))}{\simeq} \vec{\nabla} \cdot \Big(\underbrace{\frac{L_{NN}}{T} \frac{\partial \mu}{\partial \rho_N}\Big|_T}_{\text{cost in } \vec{r}} \vec{\nabla} \rho_N \Big) = \underbrace{\frac{L_{NN}}{T} \frac{\partial \mu}{\partial \rho_N}\Big|_T}_{D_c \neq D} \nabla^2 \rho_N$$

Regime diluito: $\displaystyle \frac{\partial \rho_N}{\partial t} = D \nabla^2 \rho_N$

$$\frac{\partial \rho_N}{\partial t} = D_c \nabla^2 \rho_N \qquad \mu = \frac{\partial F}{\partial N}\Big|_T = \frac{\partial f}{\partial \rho_N}\Big|_T \rightarrow \frac{\partial \mu}{\partial \rho_N}\Big|_T = \frac{\partial^2 f}{\partial \rho_N^2}\Big|_T < 0 \Rightarrow D_c < 0$$

$$\rho_{N,\vec{k}}(0) \rightarrow \rho_{N,\vec{k}}(t) = \rho_{N,\vec{k}}(0) \exp\left(- D_c |\vec{k}|^2 t\right)$$



$\rightarrow$ decomposizione spinodale

Eq. Cahn - Hilliard

$$\frac{\partial \rho_N}{\partial t} = \frac{L_{NN}}{T} \nabla^2 \left[\frac{\partial^2 f}{\partial \rho_N^2} \rho_N - \frac{k_B T \xi_0^2}{\rho_N} \nabla^2 \rho_N \right]$$