

Phase transitions

- Gas-liquid, liquid-solid, liquid-liquid etc.
- Polymer solution-gel
- Glass-crystal
- Separation of liquids
- Nematic-smectic liquid crystal transition
- Self assembly
- Denaturation of proteins

Origin of a phase transition: (at least one)

- **order parameter**

1st order p.t. order parameter changes discontinuously on a continuous change of **interaction parameter**

2nd order continuous change

A phase transition involves a decrease of the free energy:

Helmholtz's free energy F :

$$F = U - TS \quad \leftarrow \text{entropy} \quad \text{Constant } T \text{ and } V$$

↑
internal energy

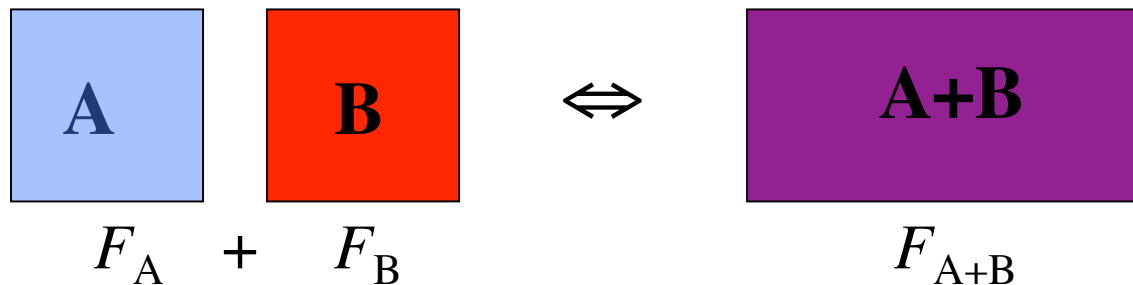
Gibb's free energy G :

$$G = H - TS \quad \text{Constant } T \text{ and } P$$

↑
enthalpy

The regular solution model

Very simple model - used in a variety of problems in physics



Free energy of mixing $F_{mix} = F_{A+B} - (F_A + F_B)$

Volume fraction ϕ $\phi_A = \frac{V_{A-molecules}}{V_{system}}$

Incompressible liquid $\phi_A + \phi_B = 1$

Liquid-liquid unmixing regular solution model

Assumptions:

- Molecules occupy lattice sites (z nearest neighbours)
- Probability that site is occupied with A or B molecules is independent on what occupies the neighbours

-Mean field assumption

- Energy is pairwise additive - molecular interaction only between nearest neighbours

$$\epsilon_{AA}, \quad \epsilon_{BB}, \quad \epsilon_{AB}$$

Entropy of mixing (per lattice site)

$$S = -k_B \sum_i p_i \ln p_i$$

In the mixed liquid there are only two states for each site.
The probabilities are ϕ_A and ϕ_B .

$$S_{mix} = S_{A+B} - (S_A + S_B) = -k_B (\phi_A \ln \phi_A + \phi_B \ln \phi_B)$$

S_A and S_B are naturally =0

Energy of mixing (per lattice site)

$$\begin{aligned} U_{mix} &= \frac{1}{2} \left(z\phi_A^2 \varepsilon_{AA} + z\phi_B^2 \varepsilon_{BB} + 2z\phi_A \phi_B \varepsilon_{AB} \right) - \frac{1}{2} \left(z\phi_A \varepsilon_{AA} + z\phi_B \varepsilon_{BB} \right) = \\ &= \frac{z}{2} \left[\left(\phi_A^2 - \phi_A \right) \varepsilon_{AA} + \left(\phi_B^2 - \phi_B \right) \varepsilon_{BB} + 2\phi_A \phi_B \varepsilon_{AB} \right] \end{aligned}$$

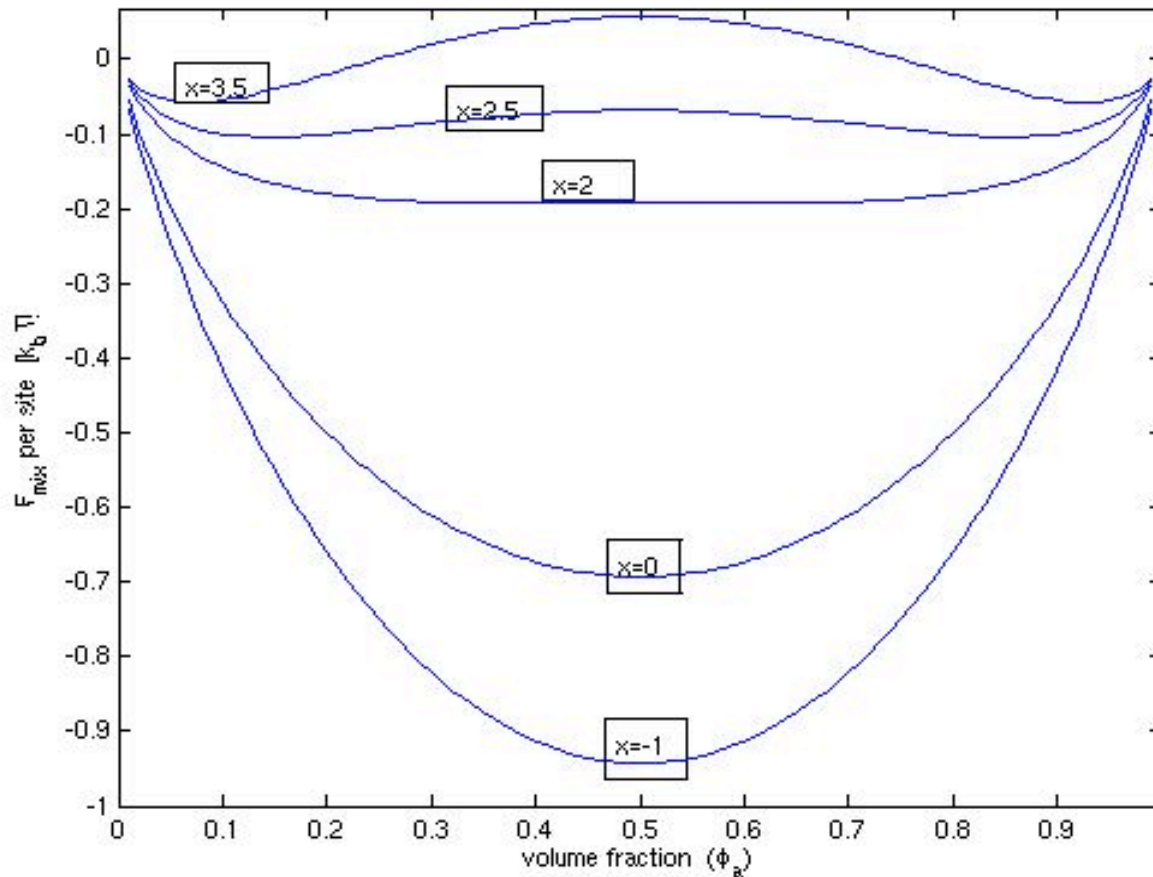
Writing: $\chi = \frac{z}{2k_B T} (2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB})$

Interaction parameter

we get: $U_{mix} = \chi \phi_A \phi_B$

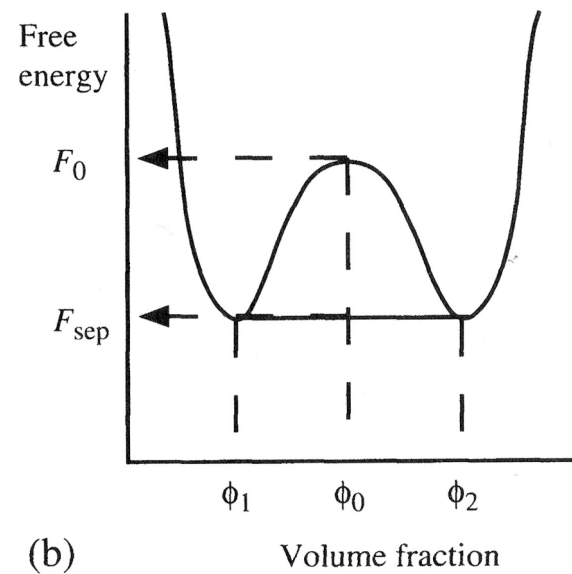
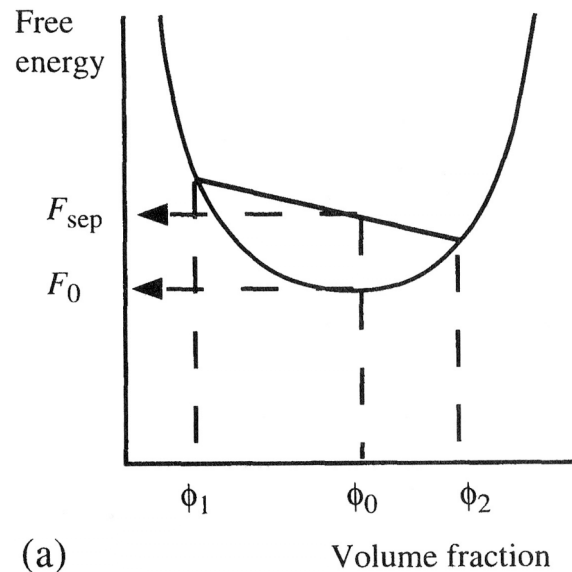
Free energy of mixing (per lattice site, in units of $k_B T$)

$$\frac{F_{mix}}{k_B T} = U_{mix} - \frac{S_{mix} T}{k_B T} = \phi_A \ln \phi_A + \phi_B \ln \phi_B + \chi \phi_A \phi_B$$

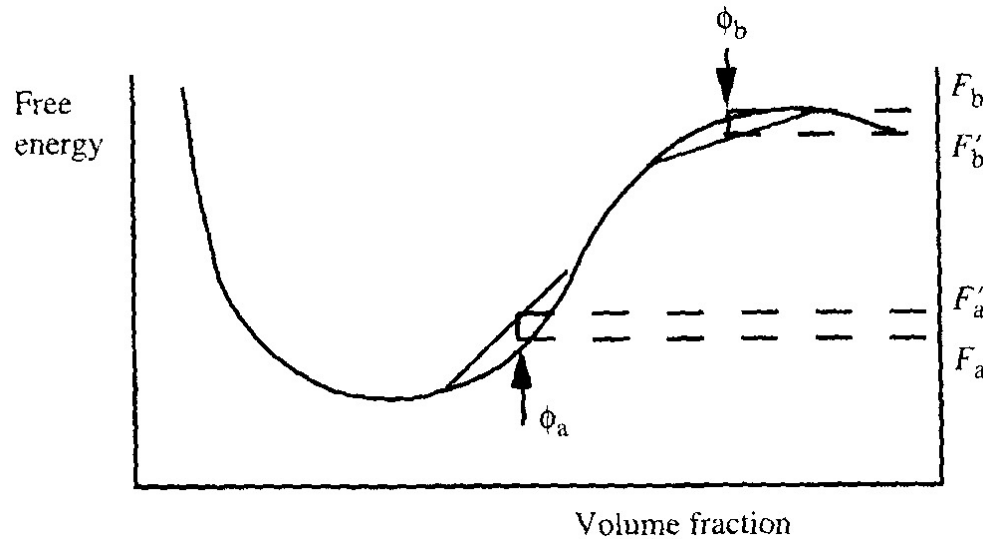


$\chi < 2$ min @ $\phi = 0.5$

$\chi > 2$ max @ $\phi = 0.5$



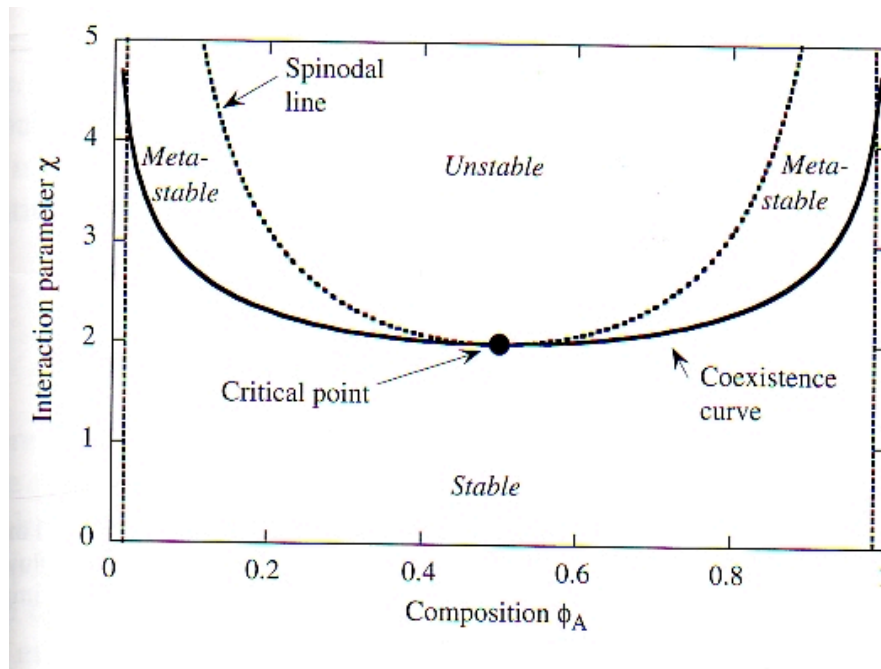
- In (a) the initial composition is **stable**. Any phase separation leads to increase of F .
- In (b) compositions between ϕ_1 and ϕ_2 will lower their F by separating into these compositions.
- Compositions joined by a common tangent minimise F . These are called coexisting compositions.
- The locus of these compositions (when χ is changed) is called the **coexisting curve** or **binodal**.



- ϕ_a is stable to small fluctuations, even if not globally stable. ϕ_a is a **metastable** composition.
- ϕ_b is **unstable** to small fluctuations. Phase separates immediately.

A composition is metastable when $\frac{\partial^2 F}{\partial \phi^2} > 0$
 The locus of this composition as χ is varied is called the **spinodal**.

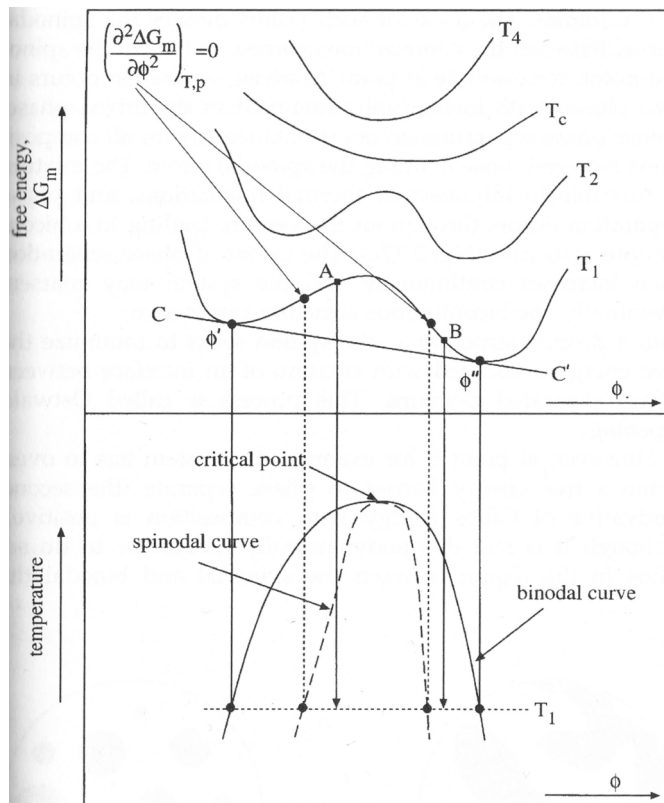
We can now construct a **phase diagram**



There is a critical temperature, T_c (or χ_c) between temperatures where all compositions are stable and T where there exist compositions which will phase separate. This is where the spinodal meets the binodal.

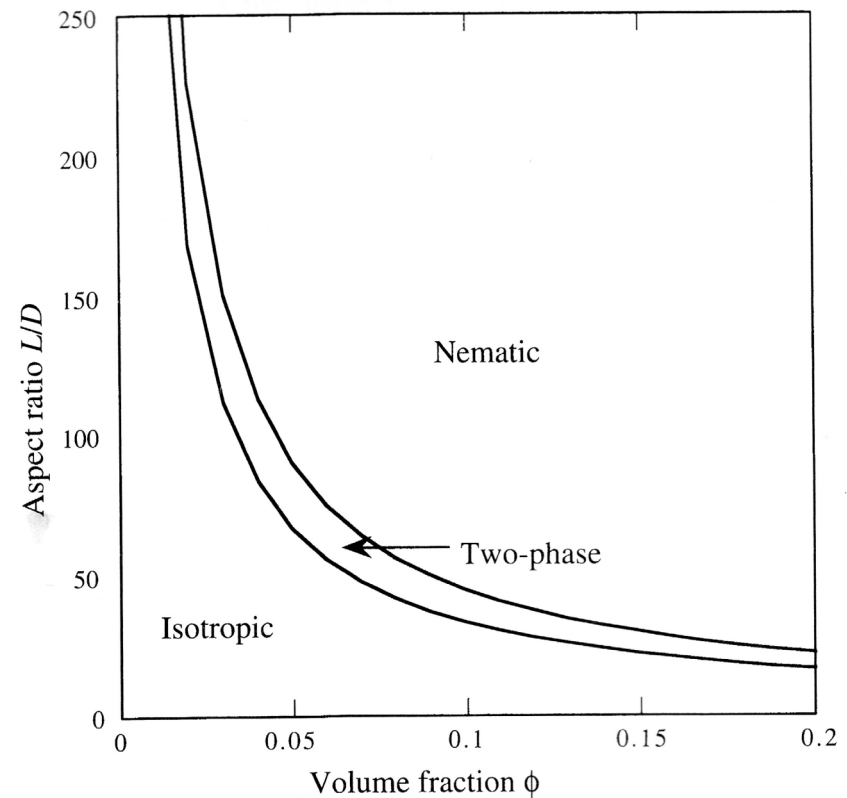
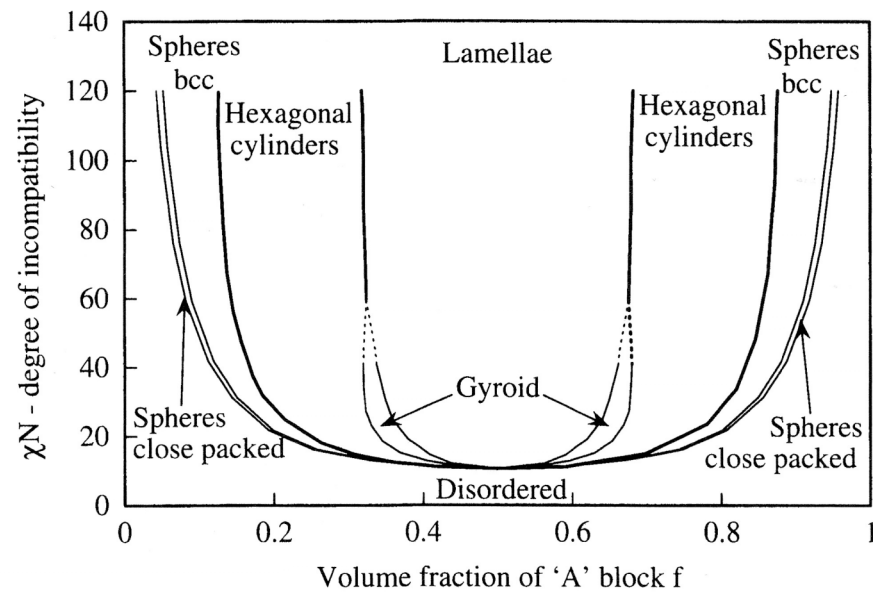
Defined by:
$$\frac{\partial^3 F}{\partial \phi^3} = 0$$

For polymer-solvent mixing use Flory-Huggins theory



- Asymmetric free energy curve.
- Restrictions due to the connectivity of the polymer.
- Internally inconsistent
- See Hamley, "Introduction to soft matter"

Examples of phase diagram



Examples are
from Jones

Kinetics of phase separation

Unstable



Spinodal decomposition

Metastable

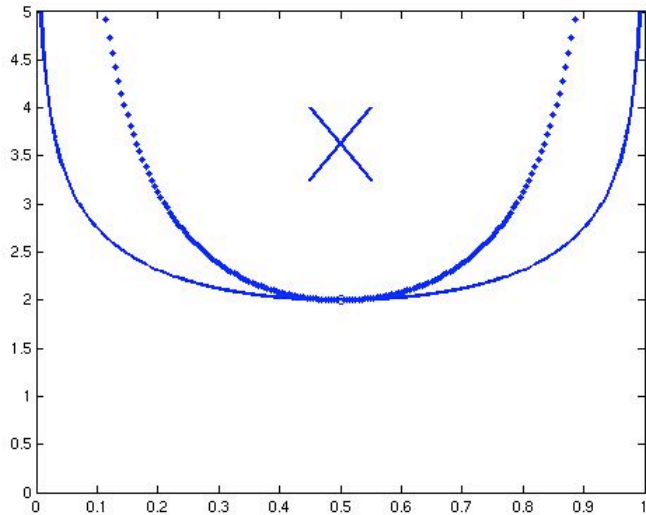


Homogeneous
nucleation



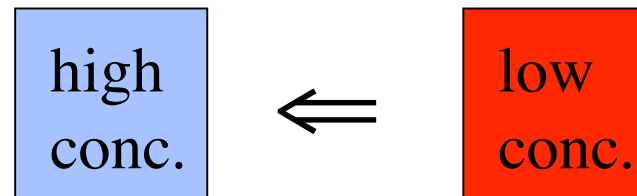
Heterogeneous
nucleation

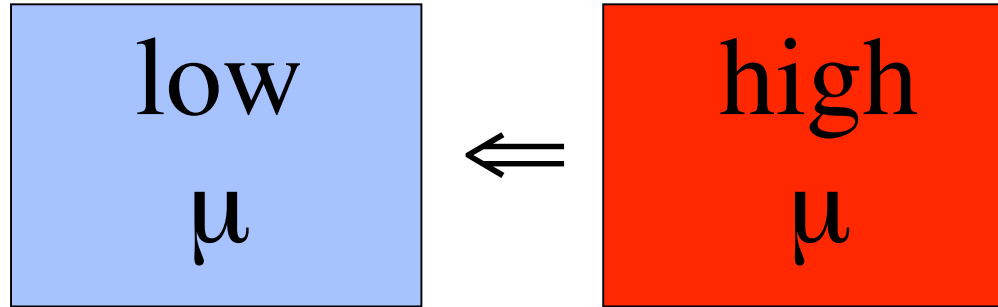
Kinetics of phase separation



Spinodal
decomposition

- Any fluctuation amplifies continuously.
- Material flow from regions of low concentration to regions of high in contrast to normal diffusion.



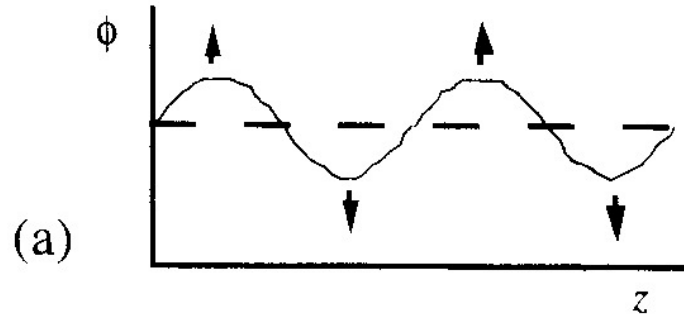


In equilibrium the **chemical potential** $\mu \propto \frac{\partial F}{\partial \phi}$ has to be uniform.

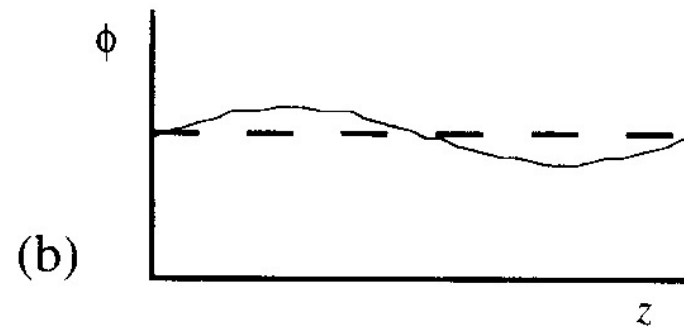
In metastable region: $\frac{\partial^2 F}{\partial \phi^2} > 0 \Rightarrow \frac{\partial \mu}{\partial \phi} > 0$ Corresponding to normal diffusion

In unstable region: $\frac{\partial^2 F}{\partial \phi^2} < 0 \Rightarrow \frac{\partial \mu}{\partial \phi} < 0$

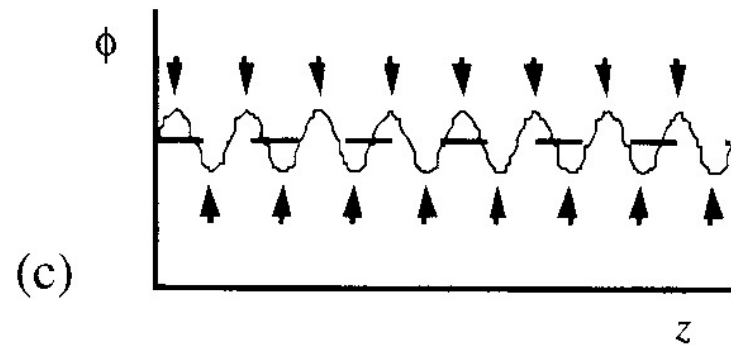
Uphill diffusion



Characteristic length
scale of fluctuation



Too long wave length is
slow due to diffusion over
long distances



Too short wave length yields
a high cost in surface energy

Quantative analysis: Cahn-Hilliard

Kinetics of phase separation - metastable compounds

- Metastable compounds undergoes the transition through an activated process called **nucleation**.
- Compounds are stable to small fluctuations but are not in global minima.
- A drop of the coexisting compound must be created by thermal fluctuations even if this increases the free energy.
- This drop, or **nucleus**, must thereafter grow until the free energy change is negative.

Kinetics of phase separation - metastable compounds

Homogeneous nucleation

- The activation is due to the creation of an interface with a characteristic **surface tension**, γ associated with a **surface energy**.
- There is both a **positive** and a **negative** contribution to F

$$\Delta F(r) = \frac{4}{3}\pi r^3 \Delta F_v + 4\pi r^2 \gamma$$

Energy change per
unit volume on
complete separation

Surface energy
due to interface

Kinetics of phase separation - metastable compounds

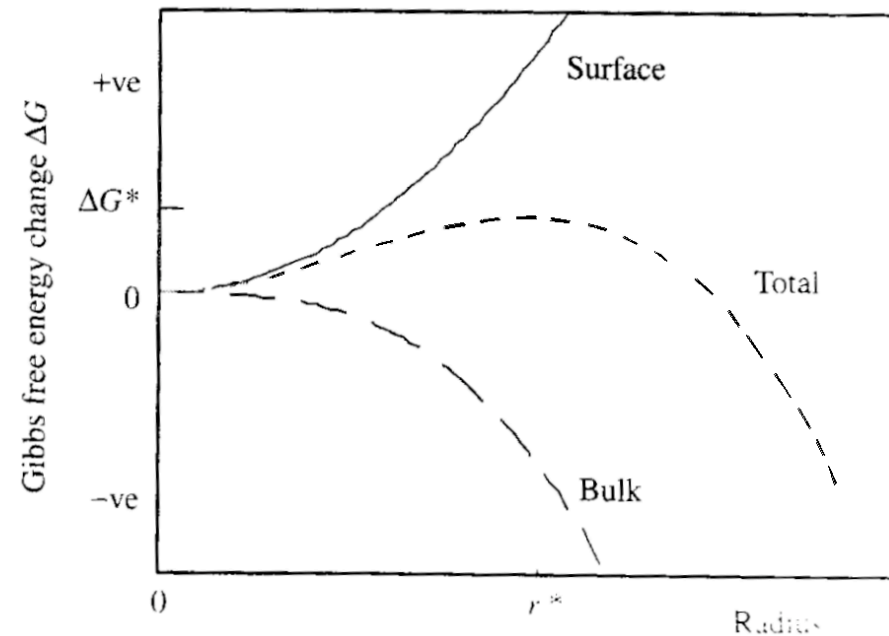
Homogeneous nucleation

$$\frac{\partial}{\partial r} \Delta F = 0 \quad \Rightarrow \quad r = r^*$$

$$r^* = -\frac{2\gamma}{\Delta F_v}$$

$$\Delta F(r^*) = \Delta F^* =$$

$$= \frac{16\pi\gamma^3}{3\Delta F_v^2}$$



Kinetics of phase separation - metastable compounds

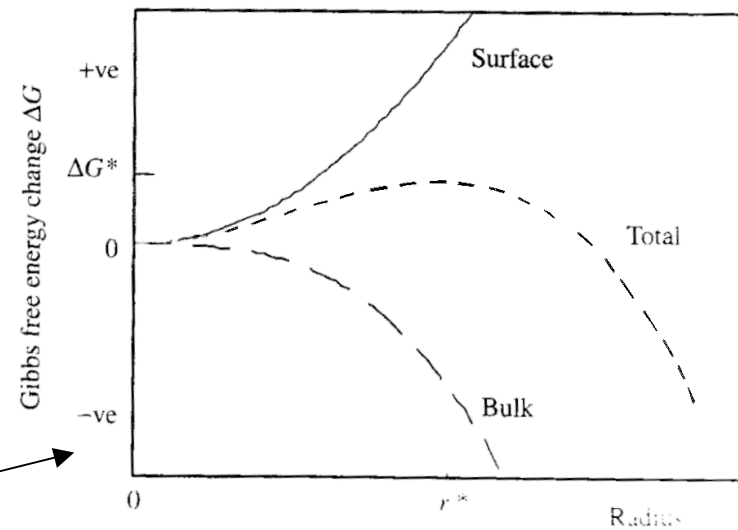
Homogeneous nucleation

Probability of forming a nucleus which can grow is:

$$P = \exp(-\Delta F^* / k_B T)$$

typical values gives significant
nucleation growth ~ 10 K below T_m
Usually we see crystallisation just
Below T_m **Why?**

Example is from Jones.
Gibbs free energy of
liquid-solid transition.
same principles apply



Kinetics of phase separation - metastable compounds

heterogeneous nucleation

ΔF^* is decreased by the presence of an interface.
Container edge, dust particle (airplanes...) etc.

$$\Delta F_{he}^* = \Delta F_{ho}^* \frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{4}$$

