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## 02. Fundamentals II

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# Free Energy of Solutions [p1n26]

Two-component incompressible fluid system: solute (p) and solvent (s).

Terms of specification:

- $N_p, N_s$ ;  $m_p, m_s$ : numbers and masses of molecules,
- $v_p, v_s$ ;  $\rho_p \doteq m_p/v_p, \rho_s \doteq m_s/v_s$ : specific volumes<sup>1</sup> and mass densities,
- $V = N_p v_p + N_s v_s$ : volume,
- $c \doteq \frac{N_p m_p}{V}$ : weight concentration of solute,
- $x_m \doteq \frac{N_p}{N_p + N_s}$ : molar fraction of solute,
- $\phi_m \doteq \frac{N_p m_p}{N_p m_p + N_s m_s}$ : mass fraction of solute,
- $\phi \doteq \frac{N_p v_p}{N_p v_p + N_s v_s} = \frac{N_p v_p}{V}$ : volume fraction of solute.

Relation :  $c = \rho_p \phi$ .

**Helmholtz free energy:**  $F(T, N_p, N_s) = U - TS$ ,

- ▷ internal energy  $U$  to be constructed from interactions,
- ▷ entropy  $S$  to be derived from combinatorics,
- ▷ volume  $V$  via  $N_p, N_s$  (see above).

Extensivity:  $F(T, \alpha N_p, \alpha N_s) = \alpha F(T, N_p, N_s)$ .

$$\text{Set } \alpha = v_p/V \Rightarrow F\left(T, \frac{N_p v_p}{V}, \frac{N_s v_p}{V}\right) = \frac{v_p}{V} F(T, N_p, N_s).$$

$$\Rightarrow F(T, N_p, N_s) = \frac{V}{v_p} F\left(T, \phi, \frac{v_p}{v_s}(1 - \phi)\right) \doteq V f(T, \phi).$$

**Gibbs free energy:**  $G(T, p, N_p, N_s) = F + pV = V[p + f(T, \phi)]$ .

The function  $f(T, \phi)$  has yet to be determined from molecular interactions and the combinatorics of molecular configurations.

---

<sup>1</sup>In the fluids considered here all volume is taken up by either solute or solvent particles. In gases the specific volume,  $V/N$ , is unrelated to the size of the particles.

# Homogeneous State vs Phase-Separated State [p1n27]

When we mix solutions of the same solute and solvent materials in different amounts and concentrations the system equilibrates either in a *homogeneous* state or in a *phase-separated* state.

Initial state:  $(V_1, \phi_1), (V_2, \phi_2)$  with  $\phi_1 < \phi_2$ .

Amounts expressed by  $x \doteq \frac{V_1}{V_1 + V_2}, \quad 1 - x = \frac{V_2}{V_1 + V_2}$ .

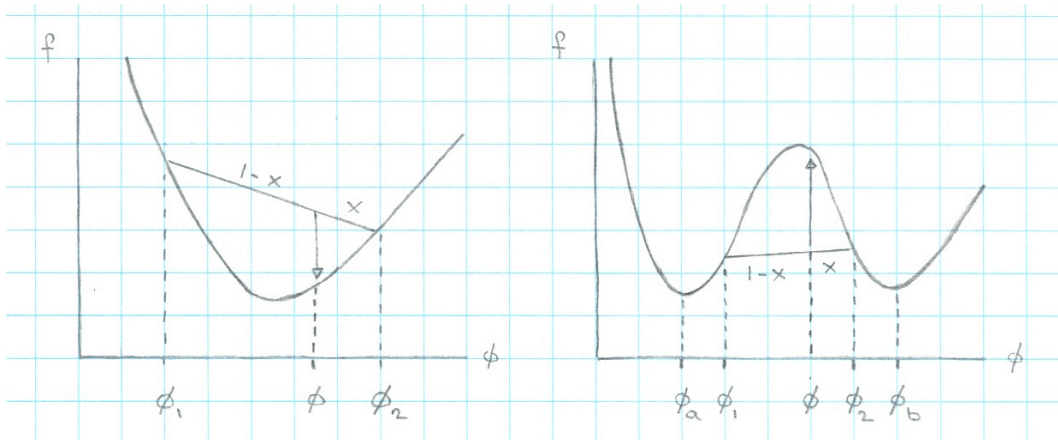
Concentrations expressed by volume fractions of solute:  $\phi_1, \phi_2$ .

**Homogeneous state:**  $(V, \phi)$  with  $V = V_1 + V_2$  and  $\phi = x\phi_1 + (1 - x)\phi_2$ .

Stability criterion for homogeneous state:

$$\begin{aligned} (V_1 + V_2)f(T, \phi) &< V_1f(T, \phi_1) + V_2f(T, \phi_2) \\ \Rightarrow f(T, x\phi_1 + (1 - x)\phi_2) &< xf(T, \phi_1) + (1 - x)f(T, \phi_2) \\ &\Rightarrow \frac{\partial^2 f}{\partial \phi^2} > 0, \quad \phi_1 < \phi < \phi_2. \end{aligned}$$

Free energy minimized at  $F = Vf(T, \phi)$ .



**Phase-separated state:**  $(V_a, \phi_a), (V_b, \phi_b)$  with  $V = V_a + V_b$  and  $\phi_a < \phi_b$ .

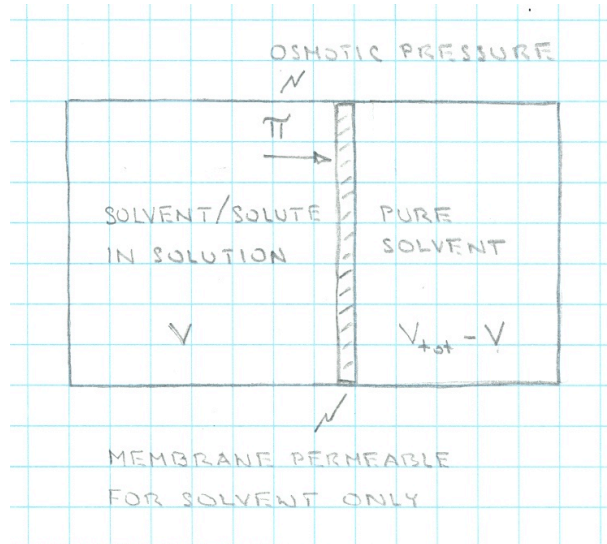
$$\phi(V_a + V_b) = \phi_a V_a + \phi_b V_b \quad \Rightarrow \quad V_a = V \frac{\phi_b - \phi}{\phi_b - \phi_a}, \quad V_b = V \frac{\phi - \phi_a}{\phi_b - \phi_a}.$$

Free energy minimized at  $F = V_a f(T, \phi_a) + V_b f(T, \phi_b)$ .

# Osmotic Pressure [pln28]

Mixing solute and solvent raises the entropy  $S$ . If molecular interactions make the internal energy  $U$  either increase by an amount smaller than  $TS$  or decrease then the free energy  $F = U - TS$  decreases.

Mixing is thermodynamically favorable in these conditions. This tendency can be converted into a thermodynamic force that acts, for example, on a semi-permeable wall.



Helmholtz free energy:  $F_{\text{tot}} = Vf(T, \phi) + (V_{\text{tot}} - V)f(T, 0)$ ,

Definition of osmotic pressure:  $\pi \doteq - \left( \frac{\partial F_{\text{tot}}}{\partial V} \right)_T$ .

Use  $\phi = \frac{N_{\text{p}}v_{\text{p}}}{V}$  from [pln26] and infer  $\frac{\partial \phi}{\partial V} = -\frac{\phi}{V}$ .

General expression for osmotic pressure:

$$\pi(T, \phi) = -f(T, \phi) + \phi f'(T, \phi) + f(T, 0), \quad f' \doteq \frac{\partial f}{\partial \phi}.$$

# Chemical Potential [pln29]

Gibbs free energy (from [pln26]):  $G(T, p, N_p, N_s) = V[p + f(T, \phi)]$ .

Thermodynamic functions from first derivatives:

- entropy and volume:  $S \doteq - \left( \frac{\partial G}{\partial T} \right)_{p, N_p, N_s}$ ,  $V \doteq \left( \frac{\partial G}{\partial p} \right)_{T, N_p, N_s}$ ,
- chemical potentials:  $\underbrace{\mu_p \doteq \left( \frac{\partial G}{\partial N_p} \right)_{T, p, N_s}}_{\text{solute}}$ ,  $\underbrace{\mu_s \doteq \left( \frac{\partial G}{\partial N_s} \right)_{T, p, N_p}}_{\text{solvent}}$

- ▷ Heat tends to flow, diffuse, or radiate from regions of high  $T$  to regions of low  $T$ .
- ▷ Fluid tends to flow from regions of high  $p$  to regions of low  $p$ .
- ▷ Solute (solvent) tends to migrate from regions of high  $\mu_p$  ( $\mu_s$ ) to regions of low  $\mu_p$  ( $\mu_s$ ).

Expressions for the chemical potentials from part (a) of [pex46].

- solute:  $\mu_p(T, p, \phi) = v_p[p + f(T, \phi) + (1 - \phi)f'(T, \phi)]$ ,
- solvent:  $\mu_s(T, p, \phi) = v_s[p + f(T, \phi) - \phi f'(T, \phi)]$ ,

where  $\phi = N_p v_p / V$ ,  $V = N_p v_p + N_s v_s$ .

Chemical potential of solvent depends on osmotic pressure (from [pln28]):

$$\mu_s(T, p, \phi) = \mu_s^{(0)}(T) + v_s[p - \pi(T, \phi)], \quad \mu_s^{(0)}(T) \doteq v_s f(T, 0).$$

Dependence of chemical potentials on volume fraction of solute:

$$\frac{\partial \mu_p}{\partial \phi} = v_p(1 - \phi)f''(T, \phi), \quad \frac{\partial \mu_s}{\partial \phi} = -v_s \phi f''(T, \phi).$$

- ▷  $f''(T, \phi) > 0 \Rightarrow \frac{\partial \mu_p}{\partial \phi} > 0, \quad \frac{\partial \mu_s}{\partial \phi} < 0,$   
 $\Rightarrow$  solute migrates from high to low  $\phi$  and solvent from low to high  $\phi$ ,  
 $\Rightarrow$  homogeneous state favored.
- ▷  $f''(T, \phi) < 0 \Rightarrow \frac{\partial \mu_p}{\partial \phi} < 0, \quad \frac{\partial \mu_s}{\partial \phi} > 0,$   
 $\Rightarrow$  solute migrates from low to high  $\phi$  and solvent from high to low  $\phi$ ,  
 $\Rightarrow$  phase-separated state favored.

# Dilute Solutions [pln30]

Criterion:  $\phi \ll 1$ .

Expansion of osmotic pressure in powers of volume fraction:

$$\pi(T, \phi) = \frac{k_B T}{v_p} \phi + A_2 \phi^2 + A_3 \phi^3 + \dots \quad (1)$$

- ▷  $A_2, A_3$ : virial coefficients.
- ▷ Leading *van't Hoff* term,  $n k_B T$ , with number density,  $n \doteq N_p/V = \phi/v_p$ , is independent of molecular interactions.
- ▷  $A_2 > 0$  is realized for repulsive solute interaction;  $A_2 < 0$  is possible if solute interaction is attractive.

Consistent expansion of free energy function  $f(T, \phi)$  (from [pln26]):

$$f(T, \phi) = f(T, 0) + k_0 \phi + \frac{k_B T}{v_p} \phi \ln \phi + A_2 \phi^2 + \frac{1}{2} A_3 \phi^3 + \dots \quad (2)$$

with  $T$ -dependent  $k_0, A_2, A_3$ .

To prove consistency use  $\pi(\phi) = f(0) + \phi f'(\phi) - f(\phi)$  from [pln28] and convert the rhs into  $f(0) + \phi^2 [f(\phi)/\phi]'$ .

Chemical potentials inferred from (2):

- solvent

$$\mu_s(T, \phi) = \mu_s^{(0)}(T) + v_s p - \frac{v_s}{v_p} k_B T \phi - v_s [A_2 \phi^2 + A_3 \phi^3 + \dots],$$

- solute

$$\begin{aligned} \mu_p(T, \phi) &= \mu_p^{(0)}(T) + v_p p + k_B T \ln \phi \\ &+ v_p \left[ \left( 2A_2 - \frac{k_B T}{v_p} \right) \phi + \left( \frac{3}{2} A_3 - A_2 \right) \phi^2 + \dots \right]. \end{aligned}$$

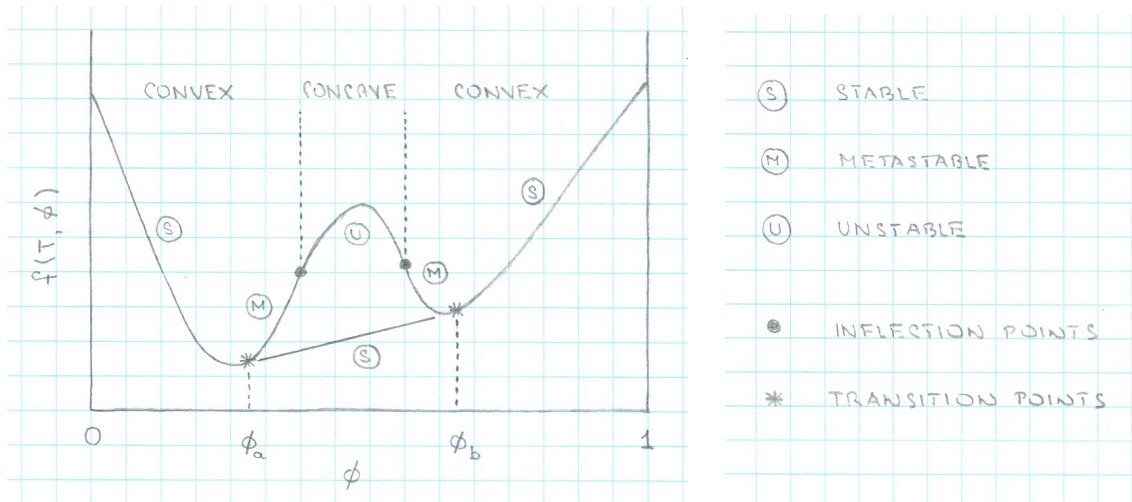
# Two-Phase Coexistence [pln31]

Coexistence of two phases with  $\phi_a < \phi_b$ .

Conservation of volume and solute volume:  $V = V_a + V_b$ ,  $\phi V = \phi_a V_a + \phi_b V_b$ .

$$\Rightarrow V_a = \frac{\phi_b - \phi}{\phi_b - \phi_a} V, \quad V_b = \frac{\phi - \phi_a}{\phi_b - \phi_a} V, \quad \phi_a \leq \phi \leq \phi_b.$$

Profile of  $f(T, \phi)$  that accommodates phase separation:



Helmholtz free energy of (i) homogeneous and (ii) phase-separated states:

$$(i) F = V f(T, \phi),$$

$$(ii) F = V_a f(T, \phi_a) + V_b f(T, \phi_b) = V \left[ \frac{\phi_b - \phi}{\phi_b - \phi_a} f(T, \phi_a) + \frac{\phi - \phi_a}{\phi_b - \phi_a} f(T, \phi_b) \right].$$

Minimum free energy of states (i) and (ii) in comparison (see graph).

Transition points  $\phi_a, \phi_b$  from geometric criteria:

$$f'(T, \phi_a) = f'(T, \phi_b), \quad f(T, \phi_a) + f'(T, \phi_a)[\phi_b - \phi_a] = f(T, \phi_b).$$

Consequences for chemical potential and osmotic pressure [pex46]:

- $\mu_p(T, \phi_a) = \mu_p(T, \phi_b), \quad \mu_s(T, \phi_a) = \mu_s(T, \phi_b),$
- $\pi(T, \phi_a) = \pi(T, \phi_b).$

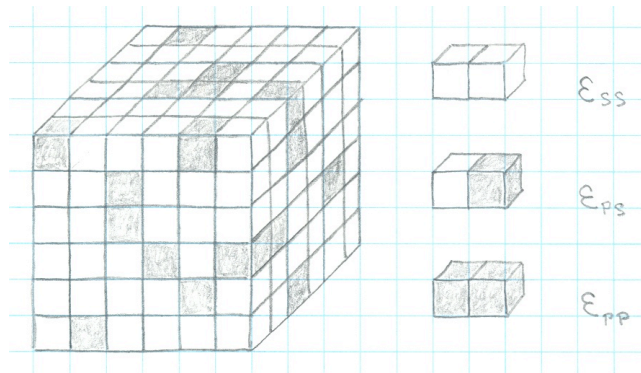
[extracted from Doi 2013]



# Model Free-Energy Density [p1n32]

Lattice-gas model of two-component incompressible fluid with *internal energy* determined in mean-field approximation and *entropy* by maximum randomness in configuration space. The calculation of both ingredients ignores spatial correlations between solute particles (p) and solvent particles (s).

- Number of cells:  $N = N_p + N_s = \phi N + (1 - \phi)N$ .
- Cell volume:  $v_p = v_s \doteq v_c$ .
- Total volume:  $V = Nv_c$ .
- Volume fraction of solute:  $\phi = N_p/N$ .
- Hardcore repulsion implied by single occupancy of all cells.
- VDW attraction via nearest-neighbor cell coupling:  $\epsilon_{pp}, \epsilon_{ss}, \epsilon_{ps}$ .
- Coordination number:  $z$  ( $z = 6$  in cubic lattice shown).



Statistical mechanical task:

- Energy of microstate:  $E_i = N_i^{(pp)}\epsilon_{pp} + N_i^{(ss)}\epsilon_{ss} + N_i^{(ps)}\epsilon_{ps}$ .
- Canonical partition function:  $Z_N = \sum_i e^{-E_i/k_B T}$ .
- Helmholtz free energy:  $F = -k_B T \ln Z_N = U - TS$ .
- Task here carried out by approximating  $U$  and  $S$ .

Average numbers of nearest-neighbor pairs (ignoring correlations):

- $\bar{N}_{pp} = \frac{1}{2}N_p z \phi = \frac{1}{2}N z \phi^2$ ,
- $\bar{N}_{ss} = \frac{1}{2}N_s z (1 - \phi) = \frac{1}{2}N z (1 - \phi)^2$ ,
- $\bar{N}_{ps} = N_p z (1 - \phi) = N z \phi (1 - \phi)$ .

Internal energy (relative to unmixed state):

$$\begin{aligned}
 U &= \frac{1}{2}zN \left\{ [\epsilon_{pp}\phi^2 + \epsilon_{ss}(1-\phi)^2 + 2\epsilon_{ps}\phi(1-\phi)] - [\epsilon_{pp}\phi + \epsilon_{ss}(1-\phi)] \right\} \\
 &= -\frac{1}{2}zN \underbrace{[\epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}]}_{\Delta\epsilon} \phi(1-\phi).
 \end{aligned}$$

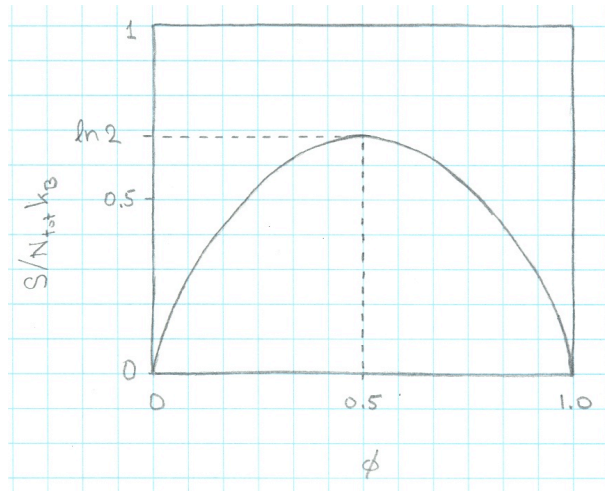
Energetically,  $\Delta\epsilon > 0$  favors mixing and  $\Delta\epsilon < 0$  favors unmixing.

Multiplicity of microstates:  $W = \binom{N}{N_p} = \frac{N!}{N_p!(N-N_p)!}$ .

Entropy of mixing (ignoring correlations):  $S = k_B \ln W$ .

Use Stirling approx.,  $\ln N! \simeq N \ln N - N$ , and volume fraction,  $\phi = N_p/N$ .

$$\begin{aligned}
 S &= Nk_B [\ln N - 1 - \phi \ln N_p + \phi - (1-\phi) \ln(N-N_p) + 1 - \phi] \\
 &= Nk_B [-\phi \ln \phi - (1-\phi) \ln(1-\phi)].
 \end{aligned}$$



Helmholtz free-energy density,  $f(T, \phi) \doteq [U - TS]/V$ :

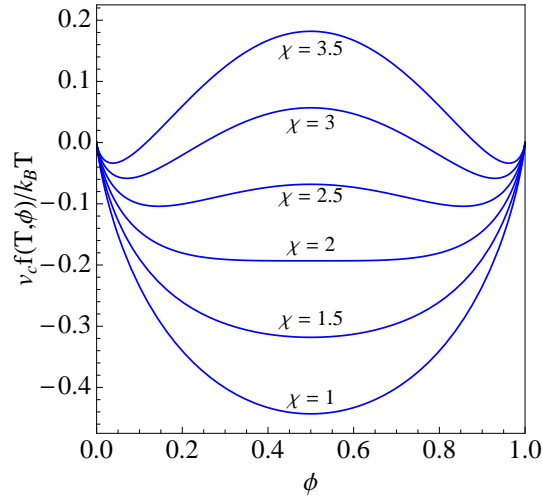
$$f(T, \phi) = \frac{k_B T}{v_c} [\phi \ln \phi + (1-\phi) \ln(1-\phi) + \chi \phi(1-\phi)], \quad \chi \doteq -\frac{z}{2k_B T} \Delta\epsilon.$$

Typically,  $\chi > 0$  is realized. Overall then (energetically and entropically), low  $\chi$  (high  $T$ ) favors mixing and high  $\chi$  (low  $T$ ) favors unmixing.

[extracted from Doi 2013]

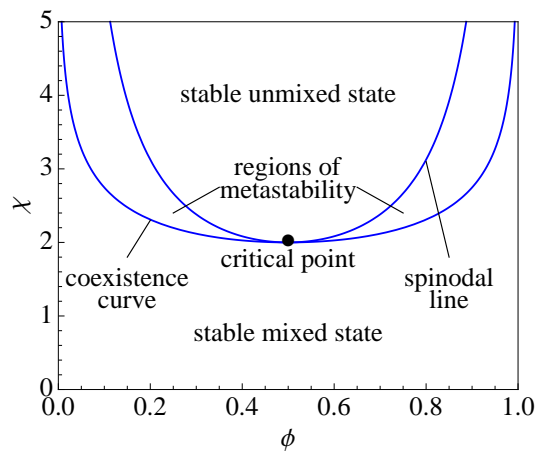
# Mixing-Unmixing Transition [ps14]

**Helmholtz free energy density** (scaled) versus volume fraction  $\phi$  for selected values of interaction parameter  $\chi$ :



- $\chi \leq 2$ : convex function with zero slope at  $\phi = \frac{1}{2}$ ,
- $\chi = 2$ : zero curvature at  $\phi = \frac{1}{2}$  in addition to zero slope,
- $\chi > 2$ : concave portion centered at  $\phi = \frac{1}{2}$  gradually grows.

**Phase diagram** in the  $(\phi, \chi)$ -plane:



**Critical point:** Lowest value of  $\chi$  for which phase separation exists.

- ▷ Criterion:  $f'(\phi) = f''(\phi) = 0$ .
- ▷ Solution:  $\phi_c = \frac{1}{2}$ ,  $\chi_c = 2$ .

**Spinodal line:** Boundary of region of stable phase-separated states.

▷ Criterion:  $f''(\phi) = 0$  at  $\phi \neq \frac{1}{2}$  (inflection points).

▷ Solution:  $\chi_{\text{sp}} = \frac{1}{2\phi(1-\phi)}$  [pex47].

**Coexistence line:** Boundary of region of stable mixed states.

▷ Criterion:  $f'(\phi) = 0$  at  $\phi \neq \frac{1}{2}$  (local minima).

▷ Solution:  $\chi_{\text{co}} = \frac{1}{1-2\phi} \ln \frac{1-\phi}{\phi}$  [pex47].

**Osmotic pressure:**

General expression from [pln28]:

$$\pi(T, \phi) = -f(T, \phi) + \phi f'(T, \phi) + f(T, 0).$$

Prediction of mean-field model [pex48]:

$$\pi(T, \phi) = \frac{k_{\text{B}}T}{v_{\text{c}}} [-\ln(1-\phi) - \chi\phi^2] \overset{\phi \ll 1}{\rightsquigarrow} \frac{k_{\text{B}}T}{v_{\text{c}}} [\phi + (\frac{1}{2} - \chi)\phi^2].$$

Interpretation of last expression:

- ▷ First term represents van't Hoff osmotic pressure,
- ▷ Second term with 2<sup>nd</sup> virial coefficient  $A_2 = \frac{1}{2} - \chi$  represents correction with opposite trends due to hardcore repulsion ( $\frac{1}{2}$ ) and nearest-neighbor coupling ( $\chi$ ).

Stability criterion for osmotic pressure:  $\pi'(T, \phi) > 0$ .

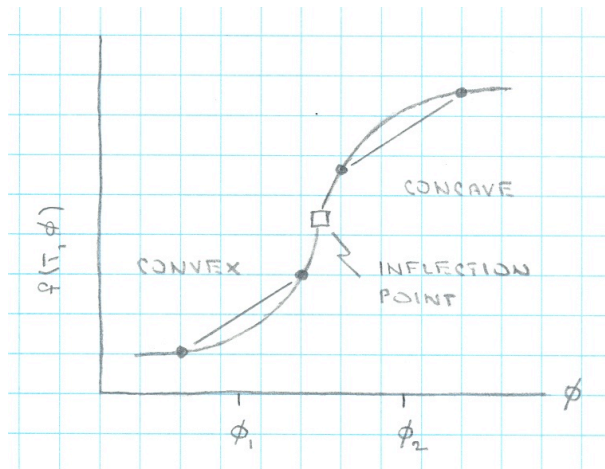
- ▷  $\chi < \chi_{\text{c}}$ :  $\pi$  is stable for exactly one value of  $\phi$ ,
- ▷  $\chi > \chi_{\text{c}}$ :  $\pi$  is stable for two distinct values of  $\phi$ .

[extracted in part from Doi 2013]

# Stability – Metastability – Instability [pln33]

Examine local stability of mixed (homogeneous) state in two regions.

- $\phi = \phi_1$  in region of global metastability:  $\chi_{co}(\phi) < \chi < \chi_{sp}(\phi)$ ;  
convex segment of function  $f(T, \phi)$ ;  
curve segment falls below straight-line segment;  
mixed state is stable against local fluctuations.
- $\phi = \phi_2$  in region of global instability:  $\chi > \chi_{sp}(\phi)$  (see [psl4]);  
concave segment of function  $f(T, \phi)$ ;  
curve segment lies above straight-line segment;  
mixed state is unstable against local fluctuations.



Kinetics of unmixing is different in the two regions:

- $\chi_{co}(\phi) < \chi < \chi_{sp}(\phi)$ : unmixing requires fluctuations of wide range; energy barriers present; (slow) *nucleation* process.
- $\chi > \chi_{sp}(\phi)$ : unmixing initiated by small fluctuations; energy barriers absent; (fast) *spinodal decomposition* process.

Distinguish two types of nucleation processes:

- *homogeneous* nucleation involves high barriers and thus entails longer time scales;
- *heterogeneous* nucleation relies on presence of impurities/interfaces, which lower the barriers and thus shorten the time scales.

### [pex48] Osmotic pressure in two-component fluid system

Consider a two-component fluid system with Helmholtz free energy,

$$F = Vf(T, \phi) + (V_{tot} - V)f(T, 0),$$

where  $V = N_p v_p + N_s v_s$  is the volume of the solution on one side of a semi-permeable membrane and  $V_{tot} - V$  the volume of the pure solvent on the other side. The numbers of solute and solvent particles in the solution are  $N_p$  and  $N_s$ , respectively. Their specific volumes are  $v_p$  and  $v_s$ , respectively. The free-energy density  $f(T, \phi)$  is an unspecified function of temperature  $T$  and volume fraction  $\phi = N_p v_p / V$  of solute particles.

(a) Derive, via the standard thermodynamic relation  $\pi = -(\partial F / \partial V)_T$ , the following general expression of the osmotic pressure in a two-component fluid:

$$\pi(T, \phi) = -f(T, \phi) + \phi f'(T, \phi) + f(T, 0), \quad f' \doteq \partial f / \partial \phi.$$

(b) Apply this expression to the explicit free-energy density  $f(T, \phi)$  used in [pex47] for a two-component fluid in a single compartment (no membrane). Plot  $\pi(T, \phi)$  thus obtained in explicit form versus  $\phi$  for three parameter values  $\chi > \chi_c$ ,  $\chi = \chi_c$ , and  $\chi < \chi_c$ . Identify the number of coexisting phases and their volume fractions  $\phi$  in each case. Expand the expression to second order in powers of  $\phi$  and interpret the physical significance of the first two terms.

**Solution:**

### [pex46] Chemical potential in two-component system

Consider a two-component fluid system with Gibbs free energy,

$$G = V[p + f(T, \phi)],$$

where  $V = N_p v_p + N_s v_s$  is the volume and  $p$  the pressure. The numbers of solute and solvent particles are  $N_p$  and  $N_s$ , respectively. Their specific volumes are  $v_p$  and  $v_s$ , respectively. The free-energy density  $f(T, \phi)$  is an unspecified function of temperature  $T$  and volume fraction  $\phi = N_p v_p / V$  of solute particles.

(a) Derive, via standard thermodynamic relations  $\mu_p = (\partial G / \partial N_p)_{T,p,N_s}$  and  $\mu_s = (\partial G / \partial N_s)_{T,p,N_p}$ , the following general expressions for the chemical potentials of the solute and solvent particles:

$$\mu_p(T, p, \phi) = v_p [p + f(T, \phi) + (1 - \phi) f'(T, \phi)], \quad \mu_s(T, p, \phi) = v_s [p + f(T, \phi) - \phi f'(T, \phi)],$$

where we use the convention  $f' \doteq \partial f / \partial \phi$ .

(b) If the profile of  $f(T, \phi)$  permits the coexistence of two phases with volume fractions  $\phi_a < \phi_b$  then the common-tangent conditions must be satisfied:  $f'(T, \phi_a) = f'(T, \phi_b)$  and  $f(T, \phi_a) + f'(T, \phi_a)[\phi_b - \phi_a] = f(T, \phi_b)$ . Show that it follows that the chemical potentials must be the same in both phases:  $\mu_p(T, \phi_a) = \mu_p(T, \phi_b)$  for the solute and  $\mu_s(T, \phi_a) = \mu_s(T, \phi_b)$  for the solvent.

**Solution:**

## [pex47] Phase diagram of two-component fluid

The free-energy density describing the phase separation of a two-component fluid as derived in a mean-field lattice model has the form

$$f(T, \phi) = \frac{k_B T}{v_c} \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right], \quad \chi = -\frac{z \Delta \epsilon}{2k_B T} > 0,$$

where  $\phi$  is the volume fraction of the solute,  $v_c$  is the specific volume of solute and solvent particles,  $z$  is the coordination number, and  $\Delta \epsilon$  is a measure of the (attractive) interaction between solute particles and between solvent particles.

- (a) Derive explicit expressions for the spinodal line  $\chi_{sp}(\phi)$  as the locations of inflection points and the coexistence curve  $\chi_{co}(\phi)$  as the locations of local minima.
- (b) Plot the phase diagram in the  $(\phi, \chi)$  plane with proper labels and the proper identifications of regions where the mixed macrostate is stable, unstable, or metastable.
- (c) For a certain realization of this model the energy parameter assumes the value  $\chi = 600/T$ , where  $T$  is the temperature measured in units of Kelvin. What is the highest temperature for which phase separation is a possibility? In the phase-separated state at temperature 273K what are the solute volume fractions  $\phi_{co}$  on the coexistence curve and  $\phi_{sp}$  on the spinodal line?

**Solution:**



### [pex45] Water solubility of hydrocarbons

The hydrophobicity of some linear hydrocarbons is expected and observed to increase with carbon content. This attribute is incorporated into the model free-energy density

$$f(T, \phi) = \frac{k_B T}{v_c} \left[ \phi \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right]$$

by an interaction-energy parameter (at room temperature) that depends on the number  $n_C$  of carbon atoms in a hydrocarbon as follows:

$$\chi = 3.04 + 1.37n_C.$$

Find the solubilities in water thus predicted by this model for hexane ( $C_6H_{14}$ ), octane ( $C_8H_{18}$ ), and decane ( $C_{10}H_{22}$ ).

[adapted from Jones 2002]

**Solution:**

[pex49] Osmotic weight lifting

Consider a cylinder of cross-sectional area  $A$ . The space between two pistons, a distance  $2h$  apart, is divided into two compartments by an immobile semi-permeable membrane. In the initial state both compartments have equal size and are filled with a solution of equal solute volume fraction  $\phi_0 = 0.4$ . The pistons are stabilized by ambient air pressure. A reservoir of volume equal to either initial compartment contains a more highly concentrated solution ( $\phi_r = 0.9$ ).

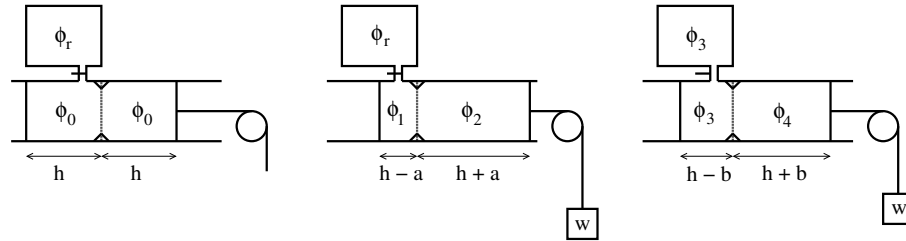
When a force  $w$  is applied to one piston as shown, some solvent is forced through the membrane. This changes the solute concentrations in the two compartments until the difference in osmotic pressure,  $\Delta\pi$ , balances the applied force.

When the valve is opened, the solutions in the reservoir and in the compartment on the left are allowed to mix. This changes  $\Delta\pi$  and lifts the weight  $w$  to a new balance of forces.

Use the expression  $\pi(\phi) = p_0[-\ln(1 - \phi) - \chi\phi^2]$  derived in [pex48] for the osmotic pressure and set  $\chi = 1$ , indicating strong solubility.

(a) Plot  $\Delta\pi/p_0$  as a function of the relative displacement  $x/h$  (i) with the valve still closed and (ii) with the valve open. In both cases  $x$  is the displacement of both pistons from their initial position.

(b) Assuming that the weight is  $w = p_0A$  calculate the equilibrium displacement  $x = a$  before the valve has been opened and  $x = b$  after the valve has been opened.



**Solution:**

# Spinodal Decomposition Process [p1n34]

Unmixing process from unstable mixed macrostate initiated by local fluctuations unimpeded by energy barriers.

**Normal diffusion** (in 1D) as benchmark. It is realized in stable solutions: solute particles migrate from regions of high to regions of low concentration.

- ▷  $\phi(x, t)$ : volume fraction of solute,
- ▷  $J(x, t)$ : flux of solute particles,
- ▷  $D$ : diffusion constant.

(1) Fick's law:  $J = -D \frac{\partial \phi}{\partial x}$  (constitutive equation)

(2) continuity equation:  $\frac{\partial \phi}{\partial t} = -\frac{\partial J}{\partial x}$  (conservation law)

(3) diffusion equation: (1) & (2)  $\Rightarrow \frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$ .

**Reverse diffusion**: solute particles spontaneously migrate from regions of low to regions of high concentration.

General direction of particle migration: from regions of high to regions of low chemical potential. Inside spinodal region, where mixing is unstable, gradient of chemical potential is opposite to gradient of concentration.

**Phenomenological model** of reverse diffusion:

(4) Exchange chemical potential:  $\mu \doteq \mu_p - \mu_s$ .

(5) Transport equation:  $J_p = -M \frac{\partial \mu}{\partial x}$ .

(6) Free-energy functional:  $F = A \int dx \left[ f_0(\phi) + \kappa \left( \frac{d\phi}{dx} \right)^2 \right]$ .

- ▷  $J_p$ : flux of solute particles relative to solvent,
- ▷  $M > 0$ : Onsager transport coefficient,
- ▷  $A$ : cross sectional area perpendicular to gradient,
- ▷  $f_0(\phi)$ : free-energy density of homogeneous macrostate,
- ▷  $f_0''(\phi) < 0$  inside spinodal region,
- ▷  $\kappa$ : gradient energy coefficient with  $\kappa > 0$  favoring homogeneity.

Exchange chemical potential (4) from (6) via variational derivative:

$$(7) \quad \mu = f'_0(\phi) - 2\kappa \frac{d^2\phi}{dx^2} \quad (\text{first term consistent with [pex46]}).$$

Resulting transport equation (5):

$$(8) \quad J_p = -M f''_0(\phi) \frac{\partial\phi}{\partial x} + 2M\kappa \frac{\partial^3\phi}{\partial x^3} \quad (\text{constitutive law}).$$

Continuity equation:

$$(9) \quad \frac{\partial\phi}{\partial t} = -\frac{\partial J_p}{\partial x} \quad (\text{conservation law}).$$

*Cahn-Hilliard equation* for reverse diffusion:

$$(8) \quad \frac{\partial\phi}{\partial t} = M f''_0(\phi) \frac{\partial^2\phi}{\partial x^2} - 2M\kappa \frac{\partial^4\phi}{\partial x^4}, \quad D_{\text{eff}} = M f''_0 < 0.$$

Linearizing assumptions:  $M$ ,  $f''_0$ ,  $\kappa$  are treated as constants.

Solution of linearized Cahn-Hilliard equation from [pex20]:

$$\phi(x, t) = \phi_0 + a \cos(qx) \exp(R(q)t), \quad R(q) \doteq M(|f''_0|q^2 - 2\kappa q^4),$$

- ▷  $R(q)$ : amplification factor,
- ▷  $|f''_0|$ : measure for instability of mixed macrostate,
- ▷  $q$ : wave number of emerging morphological pattern,
- ▷  $q_0$ : wave number with maximum amplification.

Amplification at  $q < q_0$  (longer wavelengths) suppressed owing to the need of longer-distance transport.

Amplification at  $q > q_0$  (shorter wavelengths) suppressed due to the higher cost of interfacial energy (encoded in  $\kappa$ ).

**Experimental evidence:** [psl5]

- microscopy → random patterns emerge with characteristic pixel size (encoded in  $q_0$ ).
- light scattering → observation of pattern coarsening (nonlinear effect).

[extracted in part from Jones 2002]

# Spinodal decomposition: coarsening of morphological patterns

[ps15]

Computation: nonlinear Cahn-Hilliard kinetics

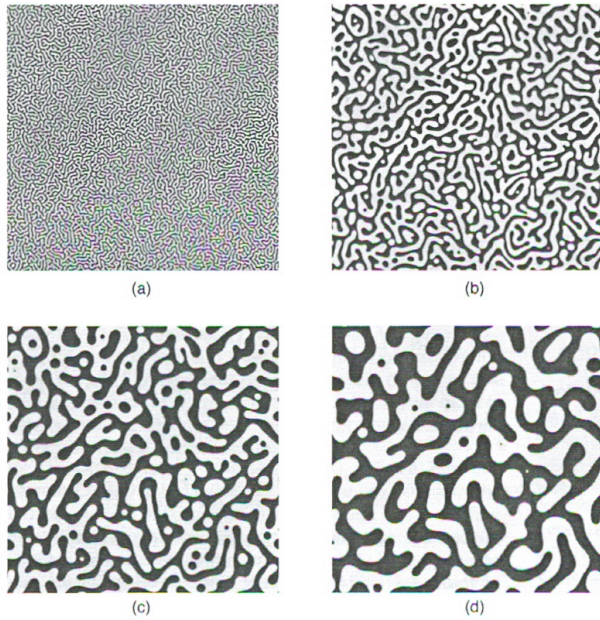


FIG. 1. Morphological patterns during spinodal decomposition and subsequent coarsening for bulk-diffusion-controlled dynamics: (a)  $t = 100$ , (b)  $t = 2000$ , (c)  $t = 10\,000$ , (d)  $t = 30\,000$ .

[from J. Zhu et al. Phys. Rev. E **60**, 3564 (1999)]

Experiment: Light scattering on polymer mixture

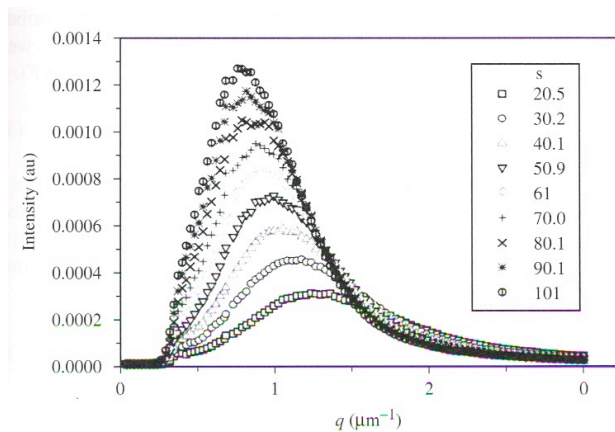


Fig. 3.10 Light-scattering curves from a polymer mixture quenched into the unstable region of the phase diagram, showing the maximum in intensity at  $q_{\max}$  characteristic of spinodal decomposition.  $q_{\max}$  moves to smaller values at longer annealing times, owing to non-linear coarsening effects. Graph courtesy of B. Jung.

[from Jones 2002]

## [pex20] Solution of linearized Cahn-Hilliard equation

The unmixing process of two liquids from an unstable macrostate, spinodal decomposition, is initiated by small local fluctuations in concentration. A quantitative analysis of this process leads, under certain assumptions, to a nonlinear partial differential equation for the concentration  $\phi(\vec{r})$  of one or the other liquid: the Cahn-Hilliard equation. One characteristic attribute of the morphological patterns emerging during the unmixing process can be found already in the linearized Cahn-Hilliard equation for a single space coordinate,

$$\frac{\partial \phi}{\partial t} = -Mc \frac{\partial^2 \phi}{\partial x^2} - 2M\kappa \frac{\partial^4 \phi}{\partial x^4},$$

where  $M > 0$  is a transport coefficient,  $\kappa > 0$  is an energy coefficient associated with inhomogeneities, and  $c > 0$  is a measure for the instability of the mixed macrostate.

(a) Show that the concentration profile with characteristic wave number  $q$ ,

$$\phi(x, t) = \phi_0 + a \cos(qx) \exp(R(q)t), \quad R(q) \doteq M(cq^2 - 2\kappa q^4)$$

is an exact solution of the linearized Cahn-Hilliard equation.

(b) Visualize the amplification factor  $R(q)$  in a scaled plot of universal shape.

(c) Morphological patterns with different wave numbers  $q$  are amplified or suppressed at different rates. Find the wave number  $q_0$  for which morphological patterns are amplified most.

[adapted from Jones 2002]

**Solution:**

# Nucleation and Growth of Domains [p1n35]

Unmixing process from metastable mixed macrostate initiated by local fluctuations impeded by energy barrier.

Consider spontaneously formed, small droplets of unmixed liquids in the otherwise homogeneous mixed bulk state.

Free energy of droplets with radius  $r$  relative to mixed reference state:

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

- $\Delta f_V$ : bulk difference in free-energy density,
- $\gamma$ : interface free-energy density.

The graph of  $\Delta F(r)$  versus  $r$  first rises quadratically, reaches a smooth maximum, then goes negative as the cubic term becomes dominant.

Threshold radius:  $r^* = \frac{2\gamma}{\Delta f_V}$  (location of energy-barrier maximum).

Activation energy:  $\Delta F(r^*) = \frac{16\pi\gamma^3}{3\Delta f_V^2}$  (height of energy barrier).

Nucleation probability:  $P \propto \exp\left(-\frac{\Delta F(r)}{k_B T}\right)$ ,

- nucleated droplets of radius  $r < r^*$  tend to shrink and disappear,
- nucleated droplets of radius  $r > r^*$  tend to continue growing.

Distinguish *homogeneous* nucleation (in bulk) and *heterogeneous* nucleation (from walls or impurities) with significantly reduced energy barriers.

Growth of phase-separated domains driven by reduction in interfacial energy:

- initiation: via spinodal decomposition (from unstable mixed state) or via nucleation (from metastable mixed state),
- early stage of growth: domain size and interface width both grow (fluctuations slow down as their wavelengths increase),
- intermediate stage of growth: domain size grows and interface width shrinks (toward energetically optimized value),
- late stage of growth: domain size continues to grow at roughly constant interface width,
- Ostwald ripening: smaller domains are absorbed in larger domains.

# Gibbs Free Energy Near Freezing/Melting [pln36]

First-order phase transition at  $p = \text{const.}$

Control variables:  $T, p, N.$

Gibbs free energy:  $G(T, p, N) = U - TS + pV = \mu N.$

Differential:  $dG = -SdT + Vdp + \mu dN.$

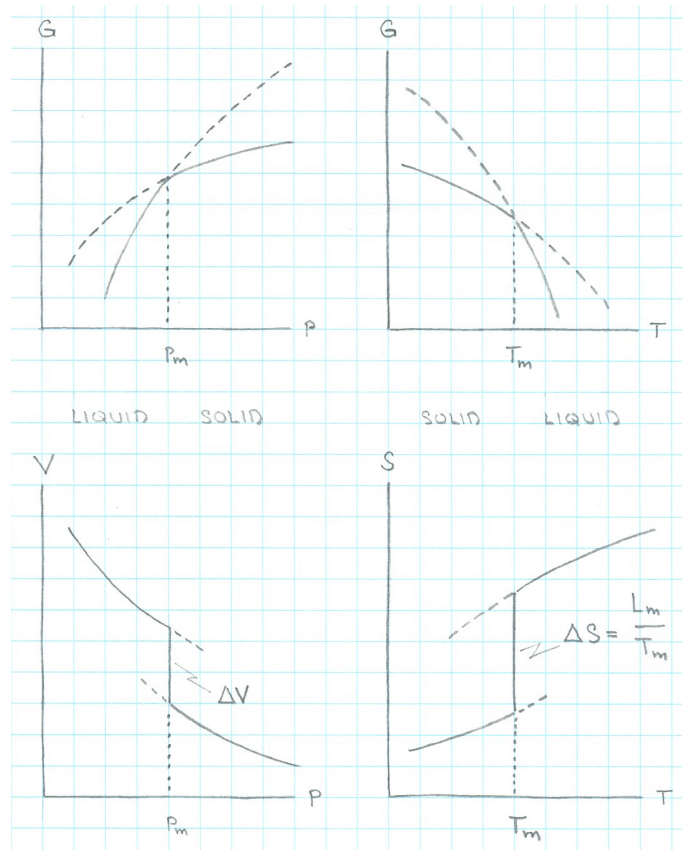
Volume:  $V = \left( \frac{\partial G}{\partial p} \right)_{T, N}.$

Entropy:  $S = - \left( \frac{\partial G}{\partial T} \right)_{V, N}.$

Chemical potential:  $\mu = \left( \frac{\partial G}{\partial N} \right)_{T, p} = \frac{G}{N}.$

Freezing/melting point at  $(T_m, p_m)$  for  $N \rightarrow \infty.$

Latent heat of melting:  $L_m = T_m \Delta S.$





# Freezing by Nucleation [pln37]

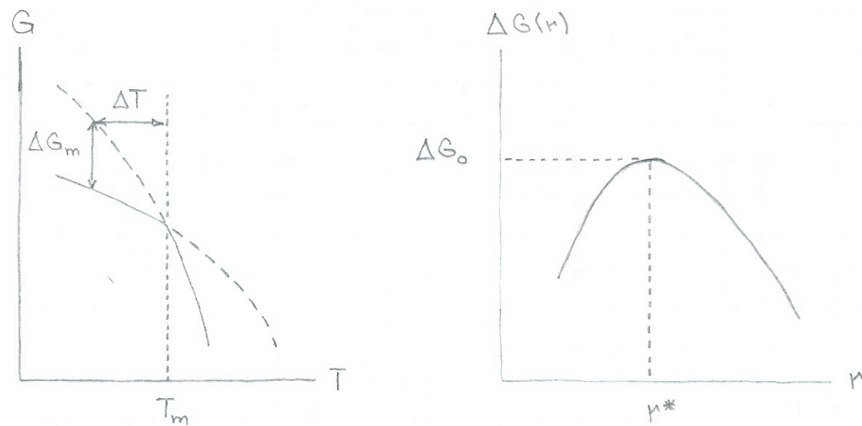
## Homogeneous nucleation:

Spontaneous formation of crystal nuclei of radius  $r$  in undercooled melt:

Gibbs free energy relative to undercooled liquid state:

$$\Delta G(r) = \underbrace{-\frac{4\pi}{3}r^3 \frac{L_m}{T_m} \Delta T}_{\text{volume}} + \underbrace{4\pi r^2 \gamma_{sl}}_{\text{interface}}$$

- $T_m$ : melting temperature,
- $L_m$ : latent heat of melting (per volume),
- $\Delta T \doteq T_m - T > 0$ : undercooling temperature,
- $S_m = -\frac{L_m}{T_m}$ : drop in entropy (per volume) during freezing,
- $\Delta G_m = -S_m(-\Delta T) = -\frac{L_m}{T_m} \Delta T$ : change in free energy (per volume),
- $\gamma_{sl}$ : liquid-solid interfacial tension.



Find location and height of free-energy barrier:

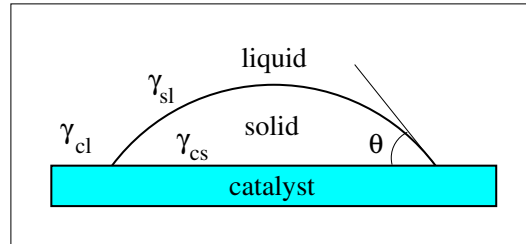
$$\left. \frac{d\Delta G(r)}{dr} \right|_{r^*} = 0 \quad \Rightarrow \quad r^* = \frac{2\gamma_{sl}T_m}{L_m\Delta T}, \quad \Delta G_0 = \frac{16\pi}{3}\gamma_{sl}^3 \left( \frac{T_m}{L_m\Delta T} \right)^2.$$

- Spontaneously created crystal nuclei with  $r < r^*$  ( $r > r^*$ ) tend to shrink (grow).
- Probability of nucleation is  $\propto \exp(-\Delta G_0/k_B T)$ .
- Homogeneous nucleation typically requires  $\Delta T \gtrsim 10^\circ$ .

## Heterogeneous nucleation:

Container walls or contaminant particles provide sites of nucleation with lower activation barriers. They become catalysts for crystallization.

Example worked out in [pex21]: spherical cap nucleated at planar catalyst surface.



The angle  $\theta$  depends on the interfacial tensions between liquid (l), solid (s), and catalyst (c) via Young's equation,  $\gamma_{sl} \cos \theta = \gamma_{cl} - \gamma_{cs}$ .

The free-energy depends on the radius  $r$  of the cap and has a maximum at  $r_c$ :

$$r_c = \frac{2\gamma_{sl}T_m}{L_m\Delta T}, \quad \Delta G(r_c) = \frac{1}{4} \underbrace{(1 - \cos \theta)^2(2 + \cos \theta)}_{g(\theta)} \Delta G_0.$$

- $0 < g(\theta) < 1$ : geometric factor,
- $g(\pi) = 1$ : limit of homogeneous nucleation,
- $\Delta G_0$ : energy barrier for homogeneous nucleation.

[extracted in part from Jones 2002]

## [pex21] Catalytic freezing of spherical cap

Container walls provide sites of nucleation for the freezing process with lower activation barriers compared to nucleation from pure liquid (homogeneous nucleation). Consider a solid spherical cap heterogeneously nucleated against a flat catalyst surface. The radius of the completed sphere is  $r$ . The angle  $\theta$  remains constant during the nucleation process. Its value is dictated by the balance of interfacial tensions between liquid (l), solid (s), and catalyst (c):

$$\gamma_{sl} \cos \theta = \gamma_{cl} - \gamma_{cs} \quad (\text{Young's equation}).$$

If the melting temperature is  $T_m$  and the latent heat is  $L_m$  then the change in Gibbs free energy when the liquid is undercooled by  $\Delta T \doteq T_m - T$  has three terms that depend on  $r$  as follows:

$$\Delta G(r) = -\frac{L_m \Delta T}{T_m} V_s(r) + \gamma_{sl} A_{sl}(r) + (\gamma_{cs} - \gamma_{cl}) A_{cs}(r),$$

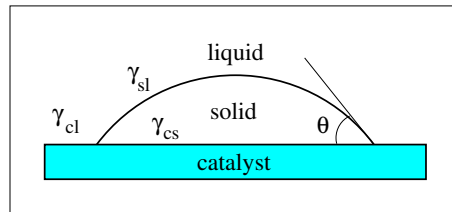
where  $V_s(r)$ ,  $A_{sl}(r)$ , and  $A_{cs}(r)$  are the volume, the curved surface, and the flat surface of the cap, respectively.

(a) Show that  $\Delta G(r)$  has a maximum at  $r_c = 2\gamma_{sl}T_m/L_m\Delta T$ , which means that caps with  $r > r_c$  grow spontaneously.

(b) Show that the energy barrier for this kind of heterogeneous nucleation is

$$\Delta G(r_c) = \frac{1}{4}(1 - \cos \theta)^2(2 + \cos \theta)\Delta G_0, \quad \Delta G_0 = \frac{16\pi}{3}\gamma_{sl}^3 \left( \frac{T_m}{L_m\Delta T} \right)^2.$$

The quantity  $\Delta G_0$  is the energy barrier for homogeneous nucleation, represented by the case  $\theta = \pi$ .



[adapted from Jones 2002]

**Solution:**

# Advancing Front of Solidification [pln38]

Consider a flat portion of solid-liquid interface during the freezing process.

Front of solid phase advances as molecules in liquid phase are being immobilized and incorporated into crystal structure.

Immobilization and binding entail release of energy (latent heat) at interface.

Continued freezing depends on transport of latent heat away from interface into liquid.

Transport of latent heat is dominated by conduction (thermal diffusion).

Heat flux is proportional to temperature gradient (Fourier's law).

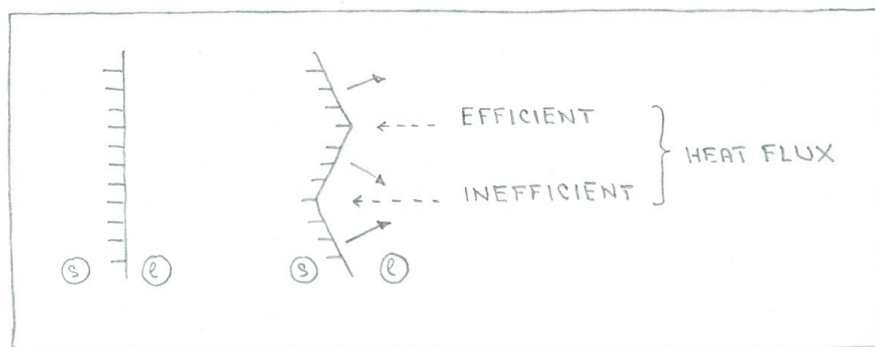
Local deviations from flat interface produce regions where temperature gradient is suppressed and regions where it is enhanced.

In the former regions the heat transport is slowed down, in the latter regions it is accelerated.

Positive feedback renders flat surface unstable against random structures of growing amplitude.

Dominant counteracting force: interfacial tension, favoring a flat interface.

Competing tendencies in balance: profile with a characteristic wavelength.



[extracted in part from Jones 2002]