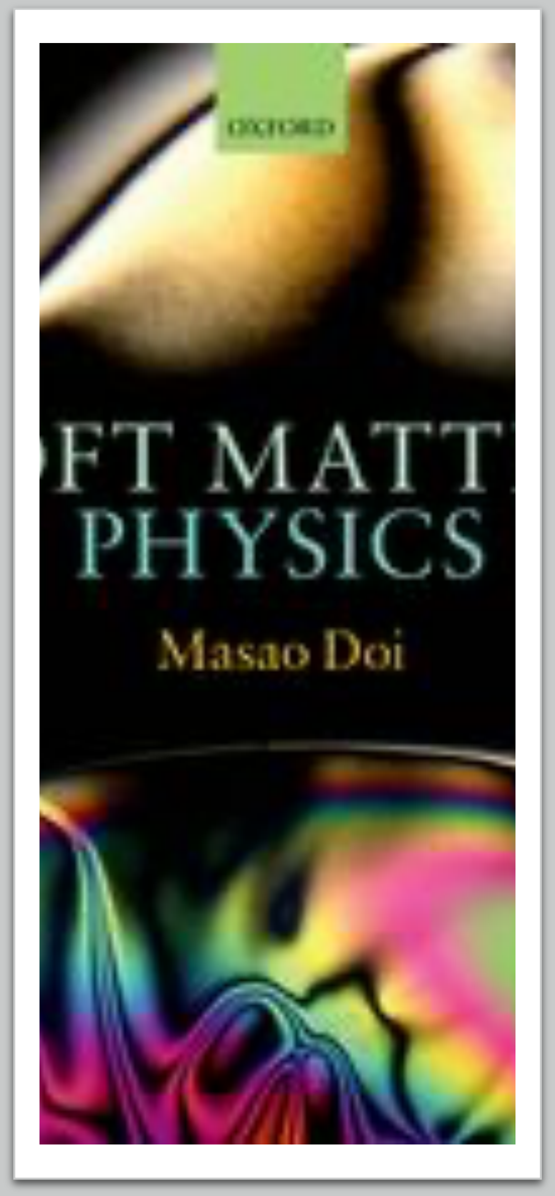
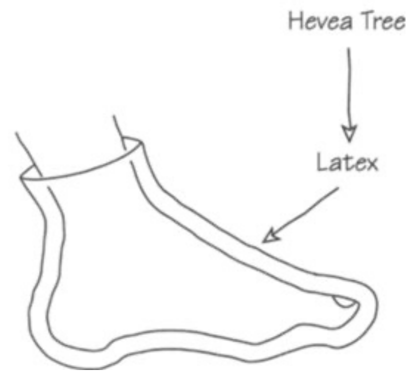


Soft Matter Solutions

Characteristics of soft matter

Figure I



Large responses cannot be described by linear relations between the force and the response. For example, rubbers can be elongated by several hundred percent of their initial length and their mechanical responses cannot be described by a linear relation between the stress and strain. The nonlinear response is quite important in soft matter.

Slow and non-equilibrium response. The collectivity of soft matter slows down their dynamics. The response time of simple liquids is of the order of 10^{-9} [s], while it can be billions or more times longer (1 [s] to 10^4 [s]) in solutions of polymers and colloids.

Consequently, the properties of the non-equilibrium state, or the dynamics in the non-equilibrium state, are quite important in soft matter.

Thermo review

1. Zeroth law. There is a T

T is the same in thermal equilibrium.

2. First law.   dU = dW + dQ

U is conserved in isolated systems.

3. Second law. It is impossible to transform completely Q in W.

S cannot diminish in na isolated system.

4. Third law. T=0 cannot be achievied in a finite number of processes.
$\Delta S \rightarrow 0$ as $T \rightarrow 0$

Thermodynamic potentials

Closed system: $F(T, V)$ minimal at eqln

$F = U - TS$

$dF = -SdT - pdV$

Open system: $F(T, V, N)$

$dF = -SdT - pdV + \mu dN$

More than one species: $F(T, V, N_1, N_2)$

$dF = -SdT - pdV + \mu_1 dN_1 + \mu_2 dN_2$

$\mu_i = \frac{\partial F}{\partial Ni}$, keeping T, V and all the other N_j constant

Solutions

Solutions are made by dissolving a material in a liquid. The dissolved material is called the solute and the liquid is called the solvent. The main player in solutions is the solute, but the solvent also plays an important role.

The effective interaction between solute molecules can be controlled by the solvent: solute molecules attract or repel each other depending on the solvent.

By properly changing the solvent conditions (e.g., by changing the temperature or composition of the solvent), one can induce various orderings (crystallization, phase separation) of solute molecules.

Thermodynamics

The essential characteristic of these solutions is that the size of solute molecule is much larger than that of the solvent molecule. The main theme here is how the size affects the solution properties.

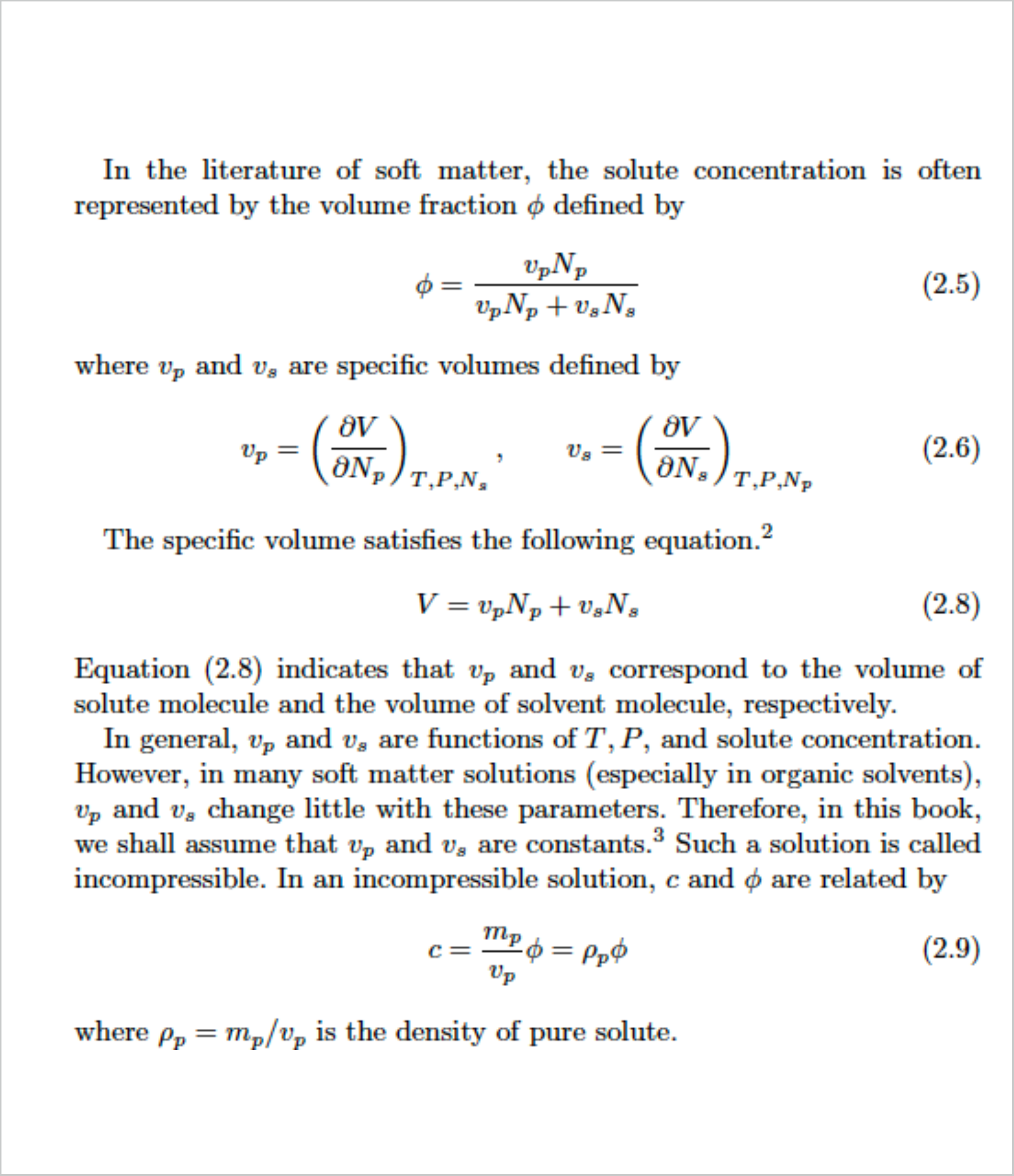
The thermodynamic state of a two-component solution can be specified by four parameters: temperature T, pressure P, and two other parameters which specify the amount of solute and solvent in the solution.

A natural choice for these parameters is Np and Ns, the number of solute and solvent molecules, respectively.

Then the Gibbs free energy of the solution is written as

G = G (Np, Ns, T, P)

Incompressibility



In the literature of soft matter, the solute concentration is often represented by the volume fraction ϕ defined by

$$\phi = \frac{v_p N_p}{v_p N_p + v_s N_s} \tag{2.5}$$

where v_p and v_s are specific volumes defined by

$$v_p = \left(\frac{\partial V}{\partial N_p}\right)_{T,P,N_s}, \qquad v_s = \left(\frac{\partial V}{\partial N_s}\right)_{T,P,N_p} \tag{2.6}$$

The specific volume satisfies the following equation.[2]

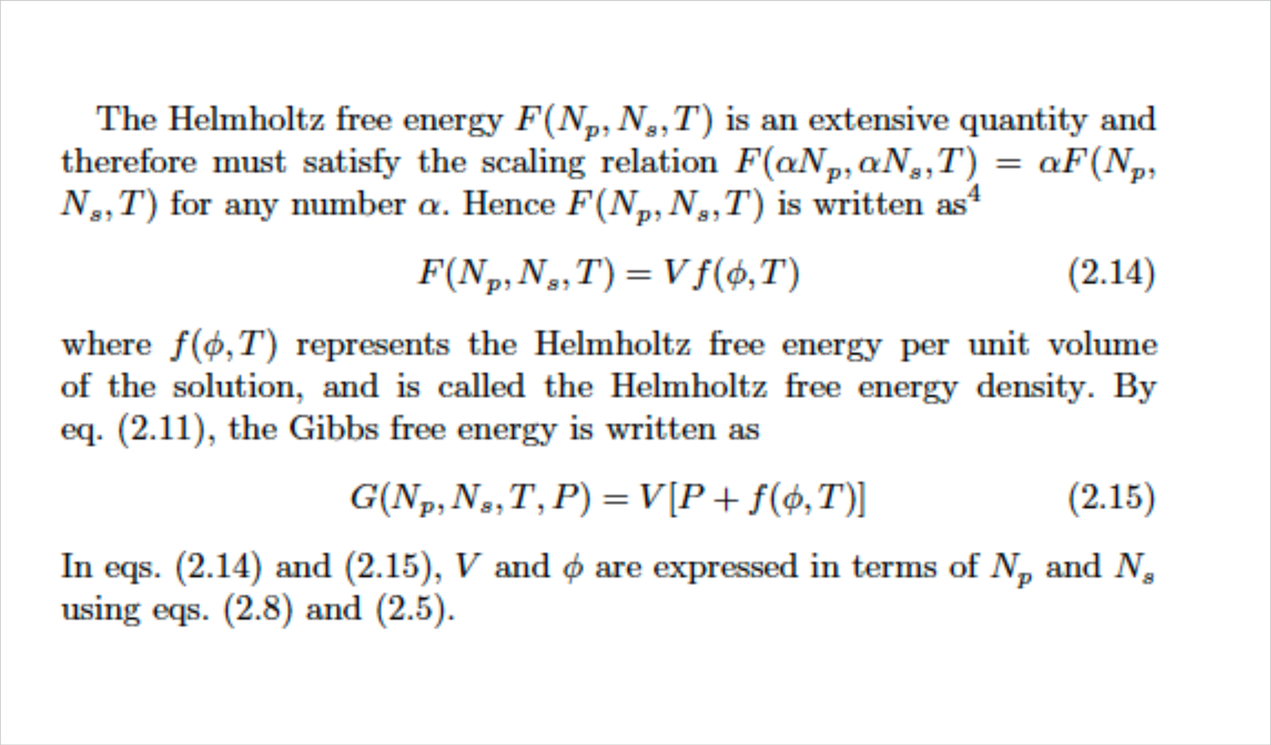
$$V = v_p N_p + v_s N_s \tag{2.8}$$

Equation (2.8) indicates that v_p and v_s correspond to the volume of solute molecule and the volume of solvent molecule, respectively.

In general, v_p and v_s are functions of T, P, and solute concentration. However, in many soft matter solutions (especially in organic solvents), v_p and v_s change little with these parameters. Therefore, in this book, we shall assume that v_p and v_s are constants.[3] Such a solution is called incompressible. In an incompressible solution, c and ϕ are related by

$$c = \frac{m_p}{v_p}\phi = \rho_p \phi \tag{2.9}$$

where $\rho_p = m_p/v_p$ is the density of pure solute.



The Helmholtz free energy $F(N_p, N_s, T)$ is an extensive quantity and therefore must satisfy the scaling relation $F(\alpha N_p, \alpha N_s, T) = \alpha F(N_p, N_s, T)$ for any number α. Hence $F(N_p, N_s, T)$ is written as[4]

$$F(N_p, N_s, T) = V f(\phi, T) \tag{2.14}$$

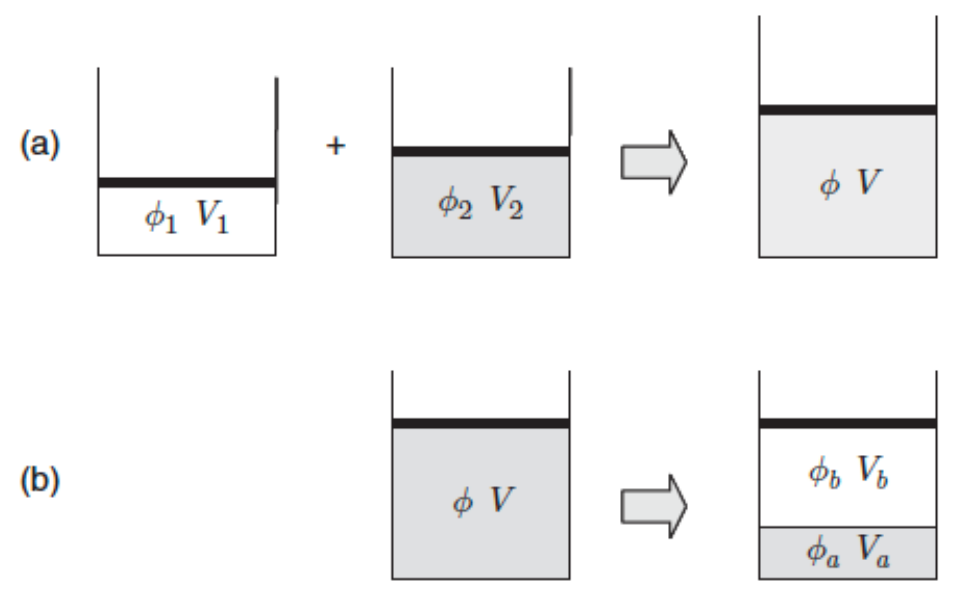
where $f(\phi, T)$ represents the Helmholtz free energy per unit volume of the solution, and is called the Helmholtz free energy density. By eq. (2.11), the Gibbs free energy is written as

$$G(N_p, N_s, T, P) = V[P + f(\phi, T)] \tag{2.15}$$

In eqs. (2.14) and (2.15), V and ϕ are expressed in terms of N_p and N_s using eqs. (2.8) and (2.5).

The Helmholtz free energy

Mixing and demixing

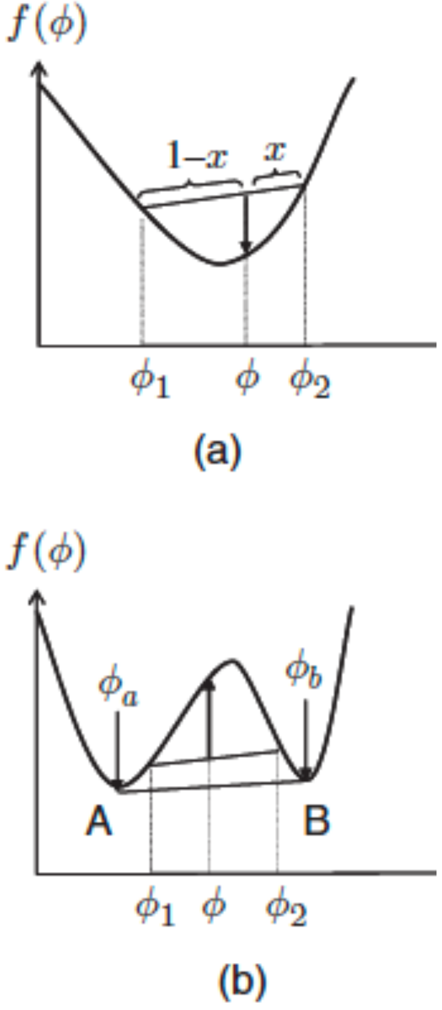


$$\phi = \frac{\phi_1 V_1 + \phi_2 V_2}{V_1 + V_2} = x\phi_1 + (1 - x)\phi_2$$

(a) Mixing:
two solutions having concentration ϕ1 and ϕ2 are mixed and produce a homogeneous solution of concentration ϕ.

(b) Demixing:
a homogeneous solution of concentration ϕ separates into two solutions of concentration ϕa and ϕb.

Mixing



(a)

(b)

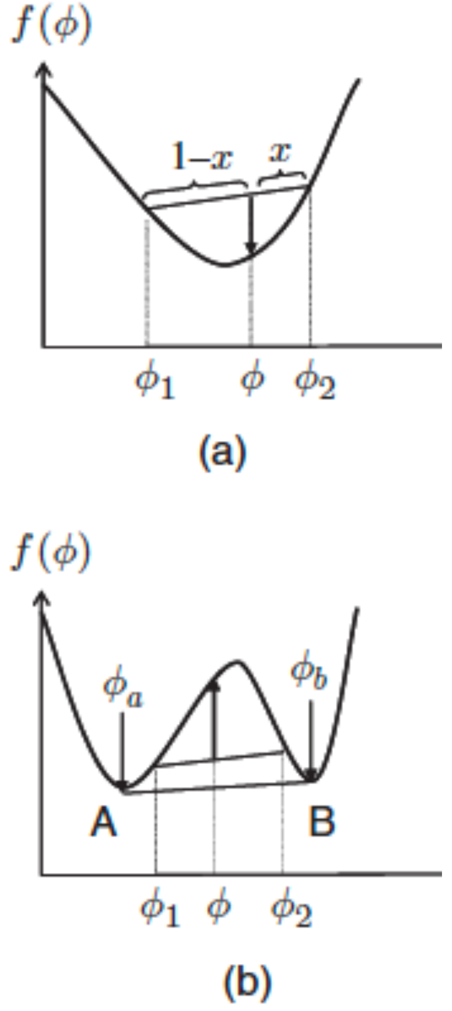
$$(V_1 + V_2) f(\phi) < V_1 f(\phi_1) + V_2 f(\phi_2)$$

$$f(x\phi_1 + (1-x)\phi_2) < x f(\phi_1) + (1-x) f(\phi_2)$$

If the two solutions mix homogeneously at any volume ratio V1/V2, eq. has to be satisfied for any x in the region of 0 ≤ x ≤ 1. This is equivalent to the condition that f(ϕ) is upper concave in the region ϕ1 < ϕ < ϕ2.

$$\frac{\partial^2 f}{\partial \phi^2} > 0, \qquad \text{for} \quad \phi_1 < \phi < \phi_2$$

On the other hand, if f(ϕ) has an upper convex part in some region between ϕ1 and ϕ2 the solution ceases to stay homogeneous.
The system can lower its free energy by separating into two solutions with concentration ϕa and ϕb. Such phenomena are called demixing or phase separation.



(a)

(b)

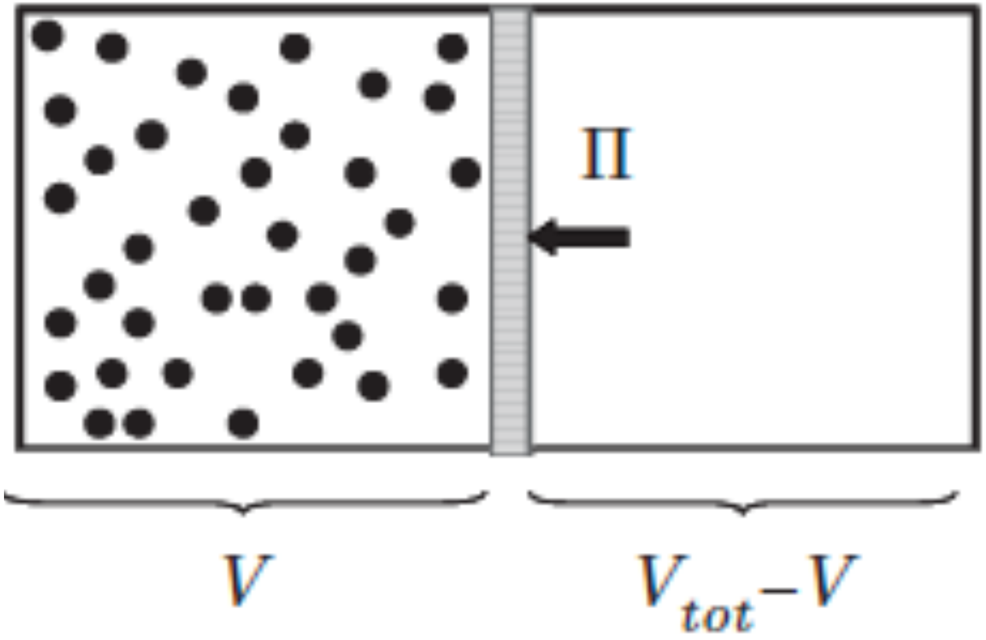
Demixing

(a) The case that the solute and solvent can mix at any composition.

(b) The case that phase separation takes place. If a solution of concentration ϕ1 is mixed with the other solution of concentration ϕ2 with the ratio x : (1 – x) and forms a homogeneous solution, the free energy of the system changes from xf(ϕ1) + (1–x)f(ϕ2) to f(xϕ1+(1–x)ϕ2).

The change of the free energy is indicated by the arrows in the figure. The free energy decreases in the case of (a), but increases in the case of (b).

Osmotic pressure



When a solution is brought into contact with pure solvent across a semipermeable membrane, the solvent tends to move into the solution and to increase the volume of the solution. In order to keep the volume of the solution at a fixed value V , a force has to be applied to the membrane. The force per unit area of the membrane is the osmotic pressure Π(V) of the solution.

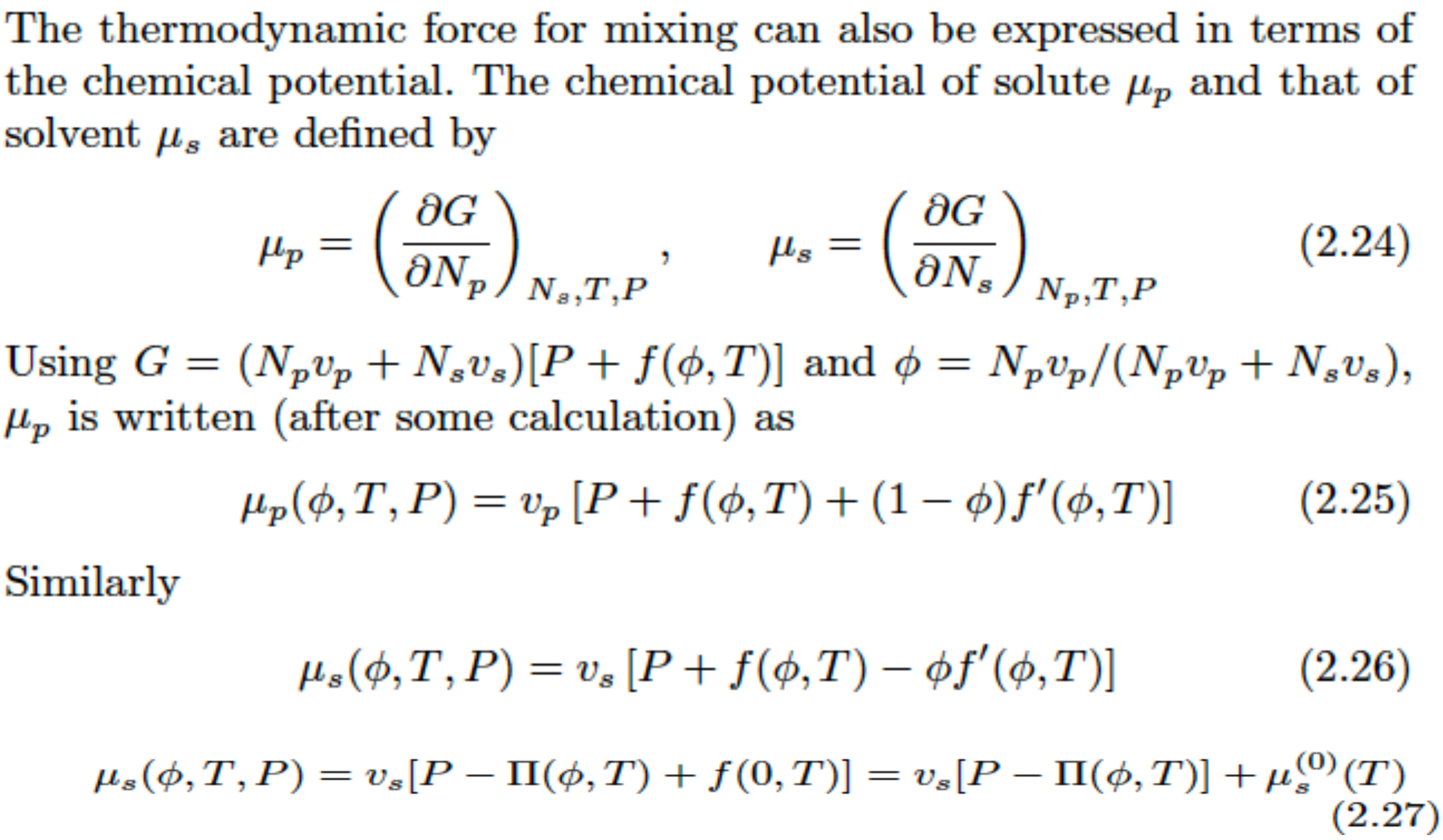
Osmotic pressure

Let $F_{tot}(V)$ be the free energy of the whole system consisting of solution (of volume V) and pure solvent (of volume $V_{tot}-V$). If we move the semi-permeable membrane and change the solution volume by dV, we do work $-\Pi dV$ to the system. This work is equal to the change of the free energy $dF_{tot}(V)$ of the whole system. Therefore Π is expressed as

$$\Pi = -\frac{\partial F_{tot}(V)}{\partial V}$$

$$\Pi(\phi) = -f(\phi) + \phi f'(\phi) + f(0)$$

Chemical potential



The thermodynamic force for mixing can also be expressed in terms of the chemical potential. The chemical potential of solute μ_p and that of solvent μ_s are defined by

$$\mu_p = \left(\frac{\partial G}{\partial N_p}\right)_{N_s,T,P}, \qquad \mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_p,T,P} \tag{2.24}$$

Using $G = (N_p v_p + N_s v_s)[P + f(\phi, T)]$ and $\phi = N_p v_p/(N_p v_p + N_s v_s)$, μ_p is written (after some calculation) as

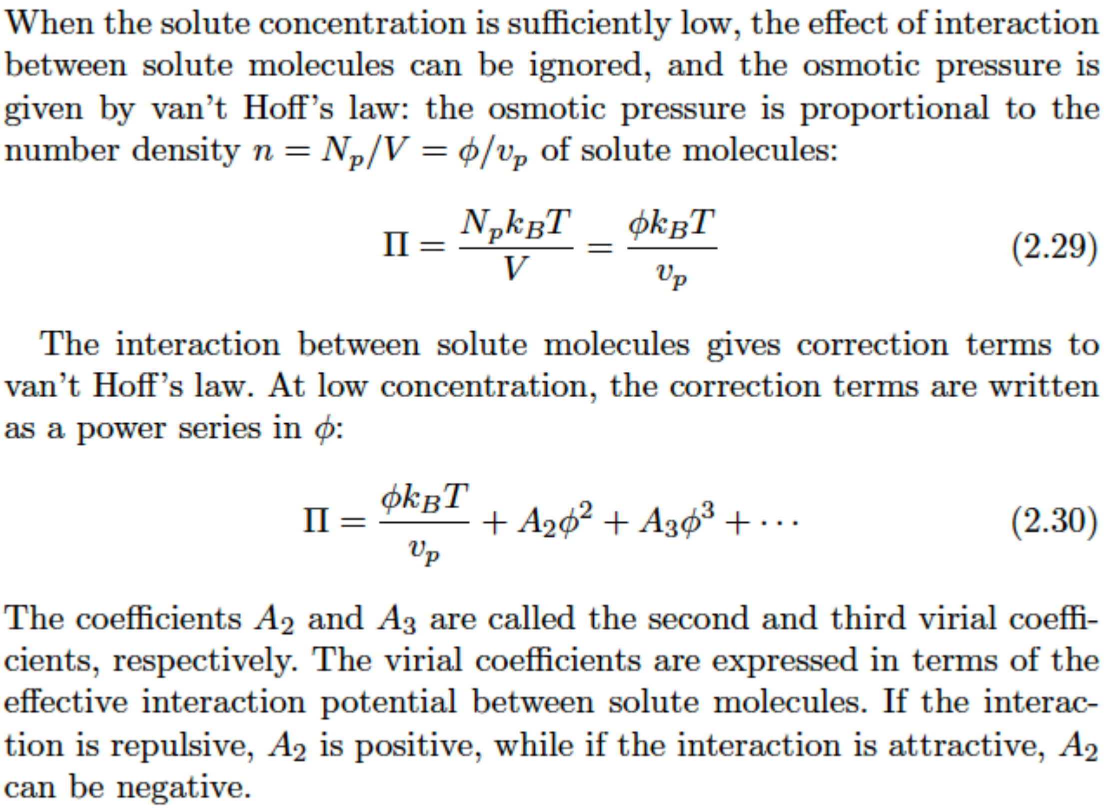
$$\mu_p(\phi, T, P) = v_p\left[P + f(\phi, T) + (1-\phi) f'(\phi, T)\right] \tag{2.25}$$

Similarly

$$\mu_s(\phi, T, P) = v_s\left[P + f(\phi, T) - \phi f'(\phi, T)\right] \tag{2.26}$$

$$\mu_s(\phi, T, P) = v_s[P - \Pi(\phi, T) + f(0, T)] = v_s[P - \Pi(\phi, T)] + \mu_s^{(0)}(T) \tag{2.27}$$

Dilute solution: virial expansion



When the solute concentration is sufficiently low, the effect of interaction between solute molecules can be ignored, and the osmotic pressure is given by van't Hoff's law: the osmotic pressure is proportional to the number density $n = N_p/V = \phi/v_p$ of solute molecules:

$$\Pi = \frac{N_p k_B T}{V} = \frac{\phi k_B T}{v_p} \tag{2.29}$$

The interaction between solute molecules gives correction terms to van't Hoff's law. At low concentration, the correction terms are written as a power series in ϕ:

$$\Pi = \frac{\phi k_B T}{v_p} + A_2\phi^2 + A_3\phi^3 + \cdots \tag{2.30}$$

The coefficients A_2 and A_3 are called the second and third virial coefficients, respectively. The virial coefficients are expressed in terms of the effective interaction potential between solute molecules. If the interaction is repulsive, A_2 is positive, while if the interaction is attractive, A_2 can be negative.

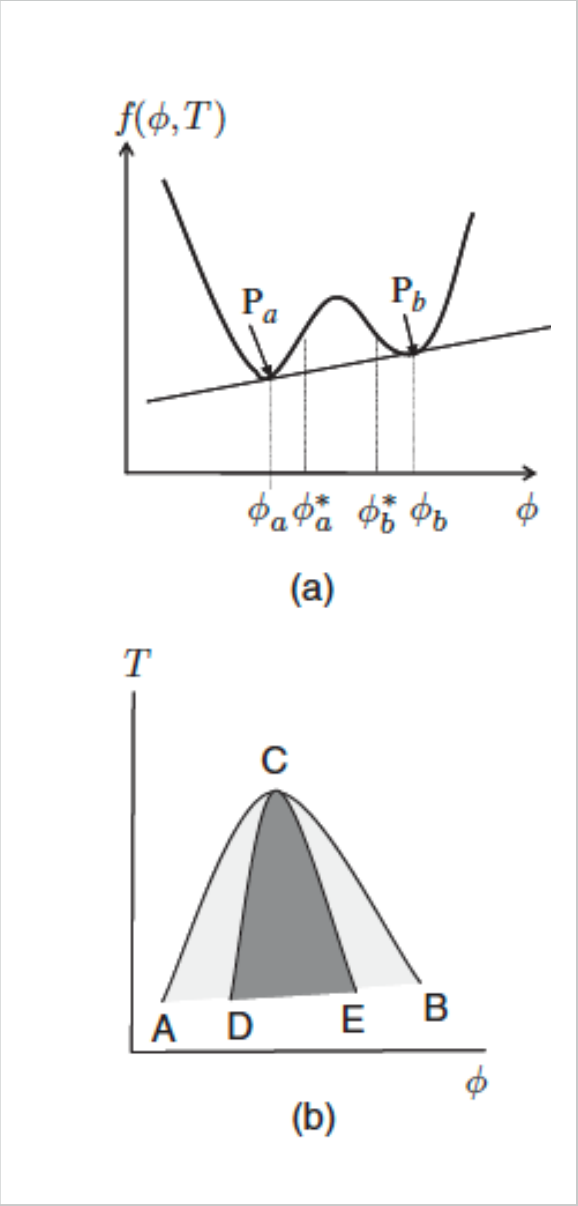
Free energy and chemical potentials of dilute solutions

$$f(\phi) = f_0 + k_0\phi + \frac{k_BT}{v_p}\phi\ln\phi + A_2\phi^2 + \frac{1}{2}A_3\phi^3 + \cdots$$

$$\mu_s(\phi) = \mu_s^0 + Pv_s - \frac{v_s}{v_p}k_BT\phi - v_s(A_2\phi^2 + A_3\phi^3 + \cdots)$$

$$\begin{aligned}\mu_p(\phi) = {} & \mu_p^0 + Pv_p + k_BT\ln\phi \\ & + v_p\left[\left(2A_2 - \frac{k_BT}{v_p}\right)\phi + \left(\frac{3}{2}A_3 - A_2\right)\phi^2 + \cdots\right]\end{aligned}$$

Phase separation: coexistence of two phases



Free energy and phase diagram of a solution.

(a) ϕa and ϕb are the concentrations at which the line connecting the points Pa and Pb on the curve is tangent to the free energy curve f(ϕ). ϕ*a and ϕ*b are the concentrations at which $\partial^2 f(\phi)/\partial\phi^2$ becomes equal to zero. A solution of concentrations ϕ (ϕa < ϕ < ϕb) can minimize its free energy by phase separating into two solutions of concentrations ϕa and ϕb. The solution is unstable if ϕ*a < ϕ < ϕ*b , and is locally stable if ϕa < ϕ < ϕ*a or ϕ*b < ϕ < ϕb.

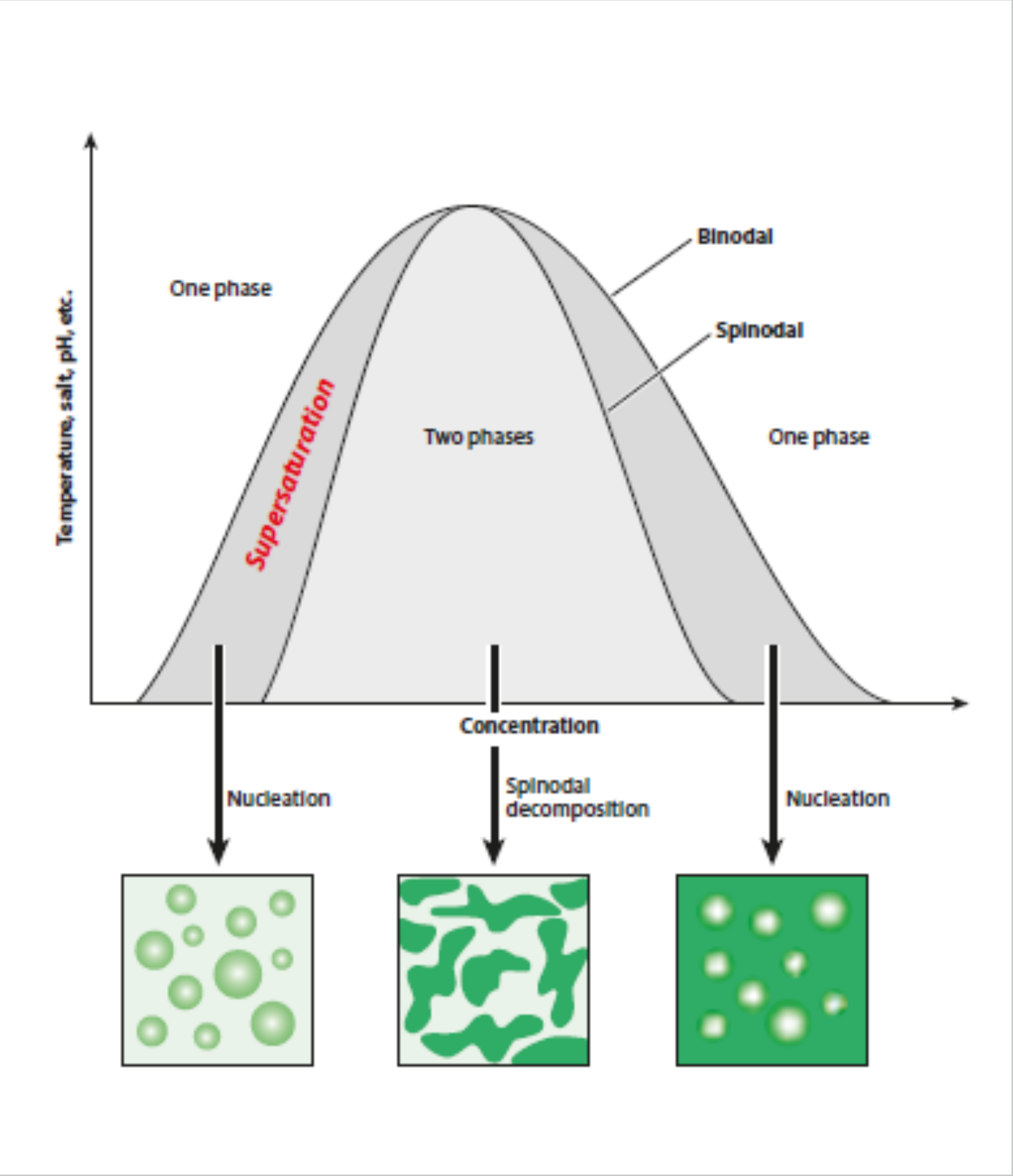
(b) Phase diagram obtained by plotting ϕa, ϕb, ϕ*a, ϕ*b as a function of temperature. Solutions in the dark grey region are unstable and solutions in the light grey region are metastable.

Phase separation

The phenomenon of phase separation in solution is analogous to the phenomenon of the gas–liquid transition in a one-component system.

For example, if a vapour of water is cooled, a certain part of the water condenses and forms a liquid phase (high-density phase), while the rest remains as a gas phase (low-density phase). Likewise, the phase separation of a solution results in the coexistence of a concentrated phase and a dilute phase: the density and the pressure in the gas–liquid transition correspond to the concentration and the osmotic pressure, respectively, in the phase separation of solutions.

Phase separation



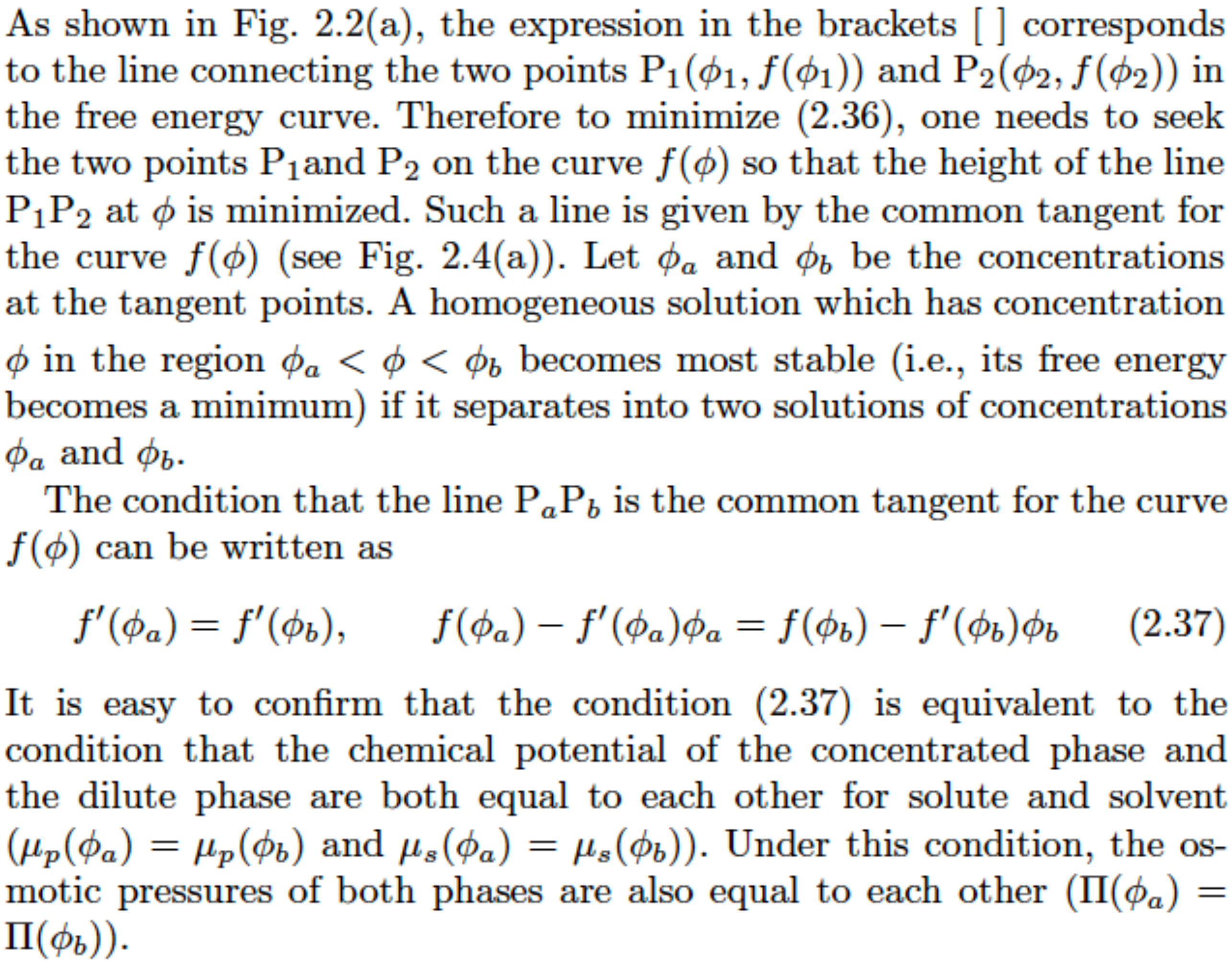
Phase separation

Thermodynamic criteria for the phase separation can be obtained in the same way as the criterion of mixing. Suppose that a homogeneous solution of volume V and concentration ϕ separates into two solutions, one having volume V1 and concentration ϕ1 and the other having volume V2 and concentration ϕ2. The volumes V1 and V2 are determined by the conservation of the solution volume, V = V1 + V2, and the conservation of the solute volume, ϕV = ϕ1V1 + ϕ2V2. This gives

$$V_1 = \frac{\phi_2 - \phi}{\phi_2 - \phi_1} V, \qquad V_2 = \frac{\phi - \phi_1}{\phi_2 - \phi_1} V$$

$$F = V_1 f(\phi_1) + V_2 f(\phi_2) = V \left[\frac{\phi_2 - \phi}{\phi_2 - \phi_1} f(\phi_1) + \frac{\phi - \phi_1}{\phi_2 - \phi_1} f(\phi_2) \right]$$

Binodal: Common tangent construction



As shown in Fig. 2.2(a), the expression in the brackets [ ] corresponds to the line connecting the two points $P_1(\phi_1, f(\phi_1))$ and $P_2(\phi_2, f(\phi_2))$ in the free energy curve. Therefore to minimize (2.36), one needs to seek the two points $P_1$and P_2 on the curve $f(\phi)$ so that the height of the line P_1P_2 at ϕ is minimized. Such a line is given by the common tangent for the curve $f(\phi)$ (see Fig. 2.4(a)). Let ϕ_a and ϕ_b be the concentrations at the tangent points. A homogeneous solution which has concentration ϕ in the region $\phi_a < \phi < \phi_b$ becomes most stable (i.e., its free energy becomes a minimum) if it separates into two solutions of concentrations ϕ_a and ϕ_b.

The condition that the line P_aP_b is the common tangent for the curve $f(\phi)$ can be written as

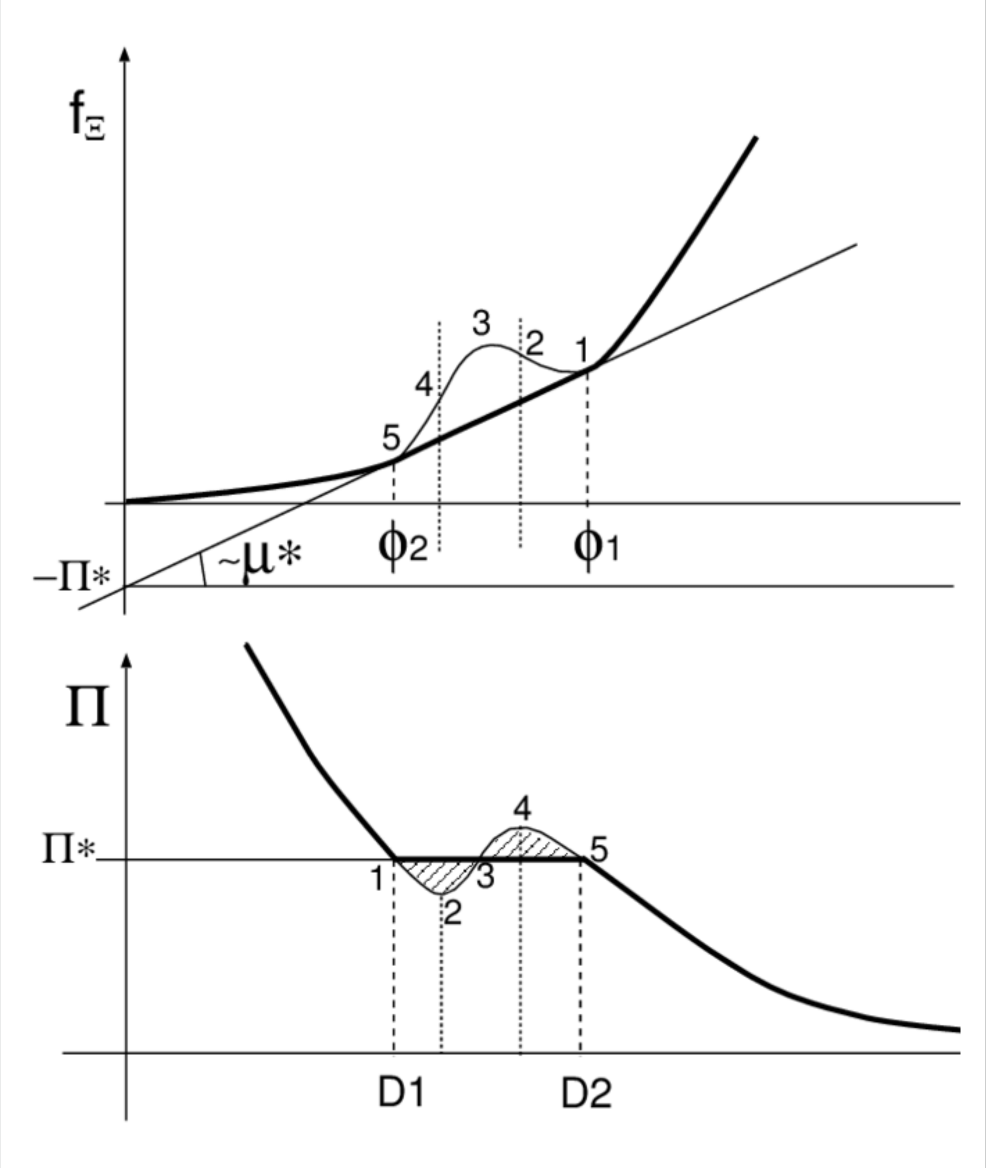
$$f'(\phi_a) = f'(\phi_b), \qquad f(\phi_a) - f'(\phi_a)\phi_a = f(\phi_b) - f'(\phi_b)\phi_b \tag{2.37}$$

It is easy to confirm that the condition (2.37) is equivalent to the condition that the chemical potential of the concentrated phase and the dilute phase are both equal to each other for solute and solvent ($\mu_p(\phi_a) = \mu_p(\phi_b)$ and $\mu_s(\phi_a) = \mu_s(\phi_b)$). Under this condition, the osmotic pressures of both phases are also equal to each other ($\Pi(\phi_a) = \Pi(\phi_b)$).

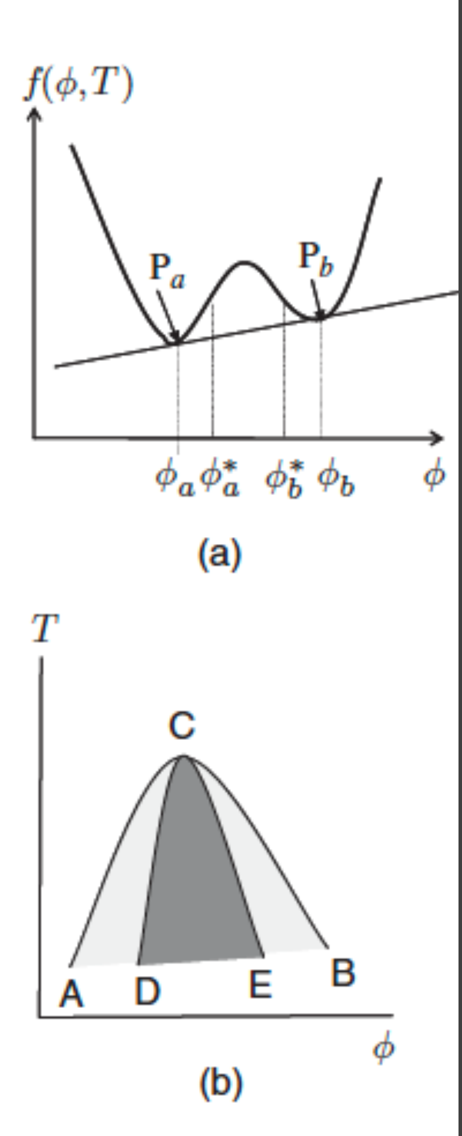
Common tangent

or

Maxwell equal areas

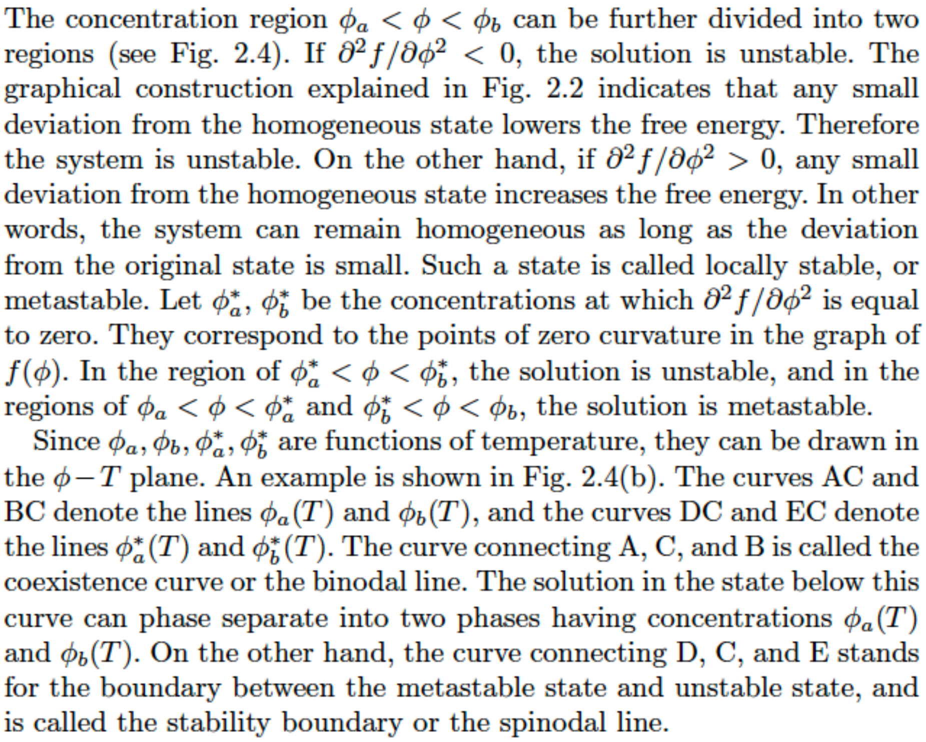


Stability & metastability



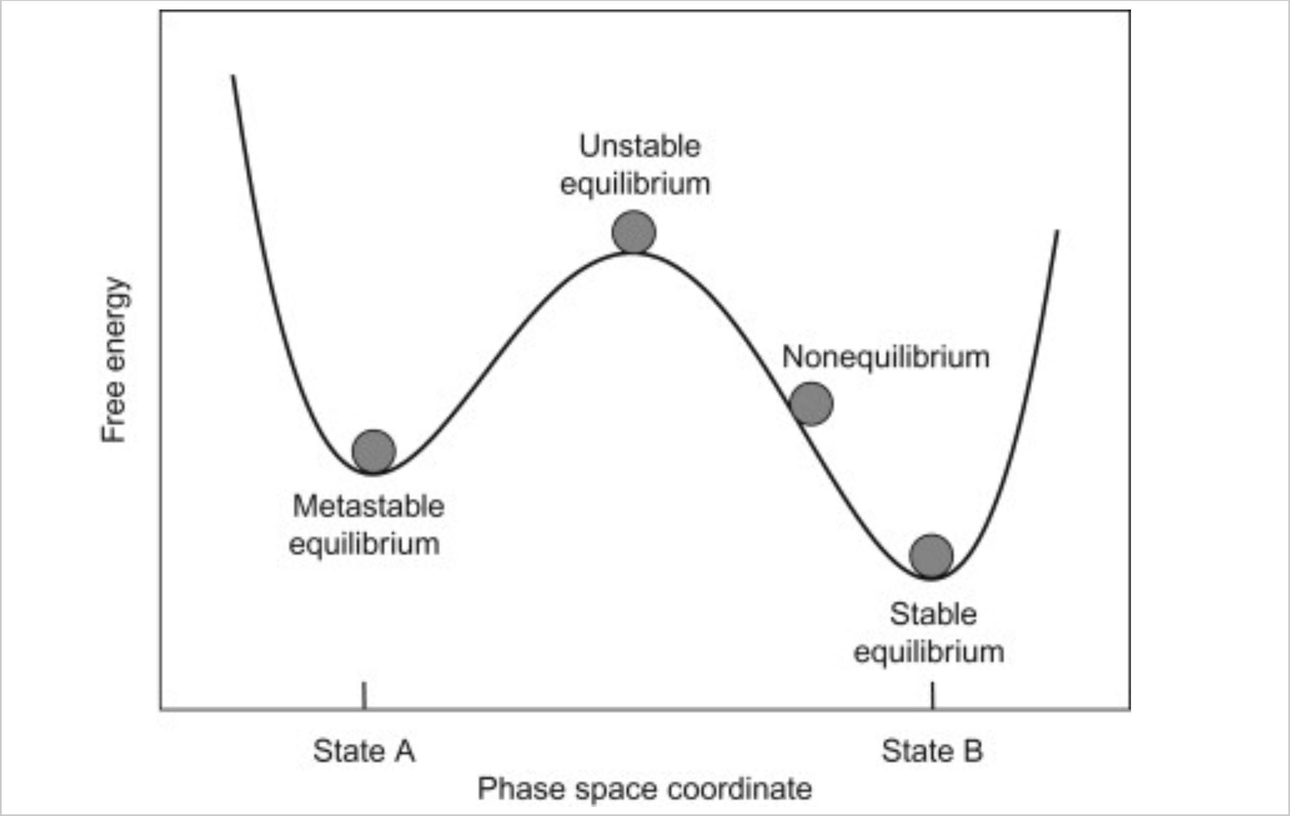
(a)

(b)

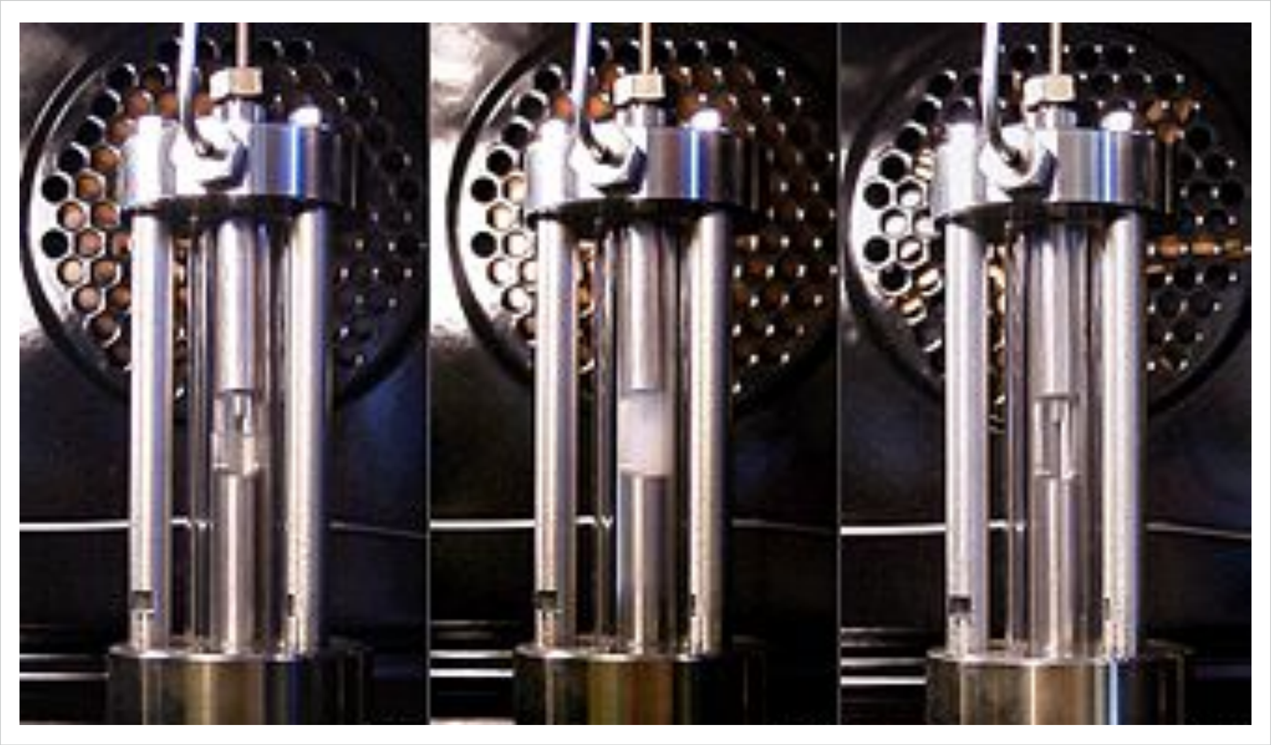


The concentration region $\phi_a < \phi < \phi_b$ can be further divided into two regions (see Fig. 2.4). If $\partial^2 f/\partial\phi^2 < 0$, the solution is unstable. The graphical construction explained in Fig. 2.2 indicates that any small deviation from the homogeneous state lowers the free energy. Therefore the system is unstable. On the other hand, if $\partial^2 f/\partial\phi^2 > 0$, any small deviation from the homogeneous state increases the free energy. In other words, the system can remain homogeneous as long as the deviation from the original state is small. Such a state is called locally stable, or metastable. Let ϕ_a^*, ϕ_b^* be the concentrations at which $\partial^2 f/\partial\phi^2$ is equal to zero. They correspond to the points of zero curvature in the graph of $f(\phi)$. In the region of $\phi_a^* < \phi < \phi_b^*$, the solution is unstable, and in the regions of $\phi_a < \phi < \phi_a^*$ and $\phi_b^* < \phi < \phi_b$, the solution is metastable.

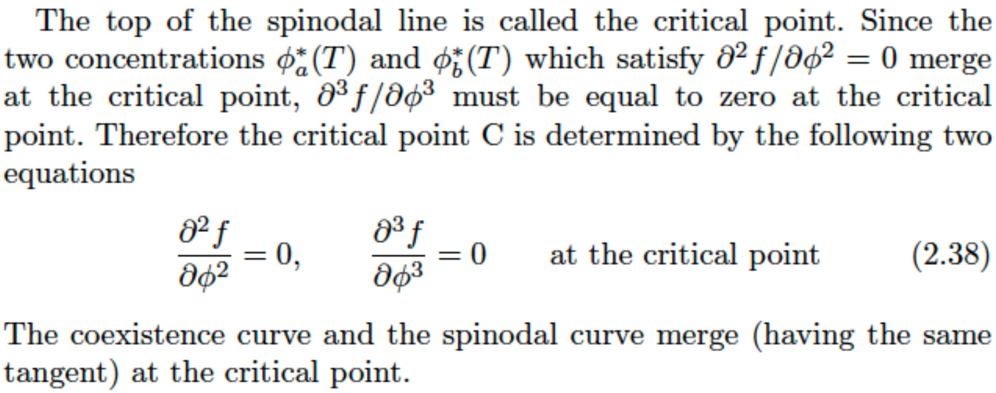
Since $\phi_a, \phi_b, \phi_a^*, \phi_b^*$ are functions of temperature, they can be drawn in the $\phi - T$ plane. An example is shown in Fig. 2.4(b). The curves AC and BC denote the lines $\phi_a(T)$ and $\phi_b(T)$, and the curves DC and EC denote the lines $\phi_a^*(T)$ and $\phi_b^*(T)$. The curve connecting A, C, and B is called the coexistence curve or the binodal line. The solution in the state below this curve can phase separate into two phases having concentrations $\phi_a(T)$ and $\phi_b(T)$. On the other hand, the curve connecting D, C, and E stands for the boundary between the metastable state and unstable state, and is called the stability boundary or the spinodal line.



Metastable state



Critical point



The top of the spinodal line is called the critical point. Since the two concentrations $\phi_a^*(T)$ and $\phi_b^*(T)$ which satisfy $\partial^2 f/\partial\phi^2 = 0$ merge at the critical point, $\partial^3 f/\partial\phi^3$ must be equal to zero at the critical point. Therefore the critical point C is determined by the following two equations

$$\frac{\partial^2 f}{\partial \phi^2} = 0, \qquad \frac{\partial^3 f}{\partial \phi^3} = 0 \qquad \text{at the critical point} \tag{2.38}$$

The coexistence curve and the spinodal curve merge (having the same tangent) at the critical point.

Liquid-vapour binodal

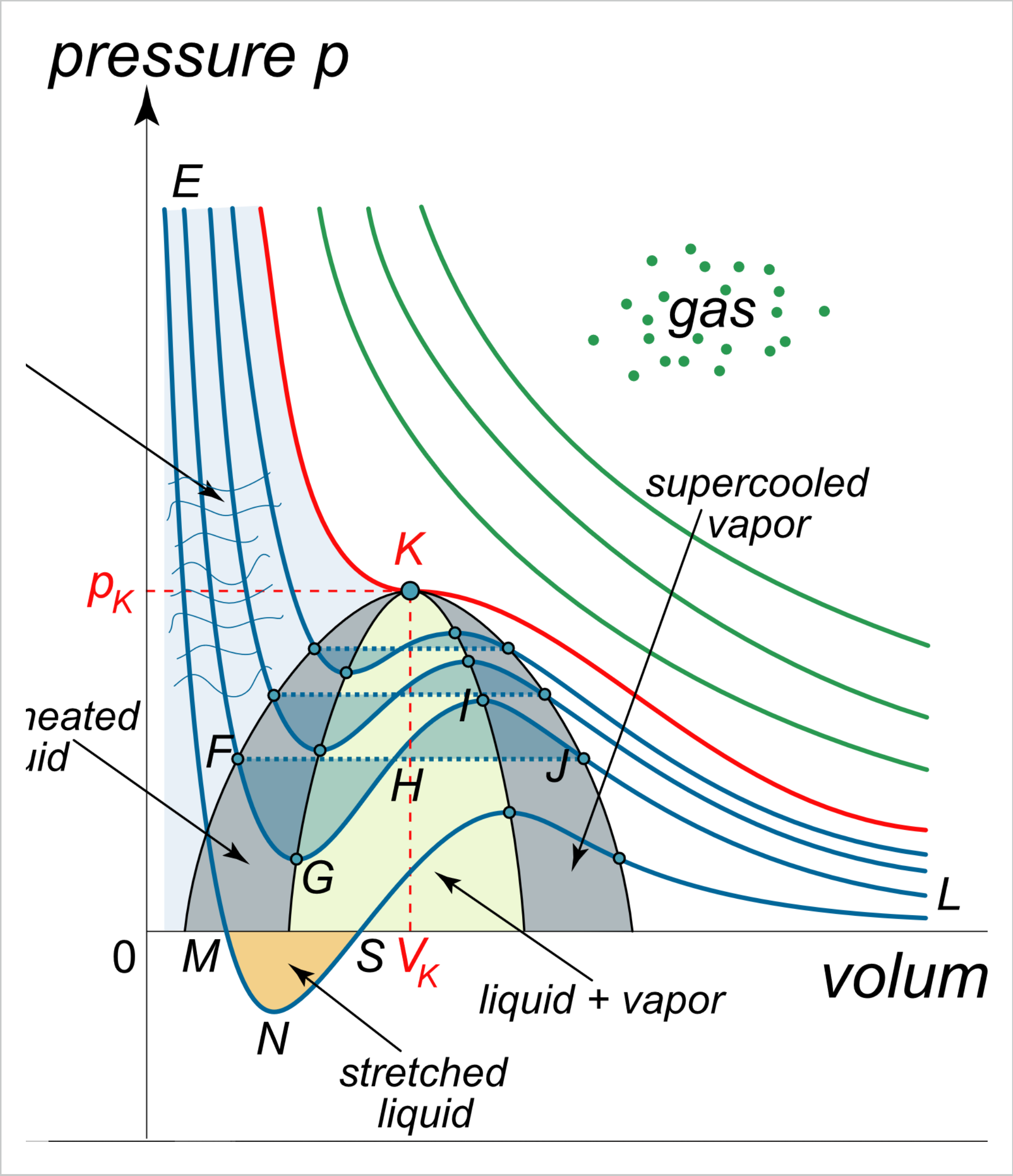
A single component system has a similar phase diagram, as we have considered the two-component mixture INCOMPRESSIBLE, reducing the number of degrees of freedom by 1.

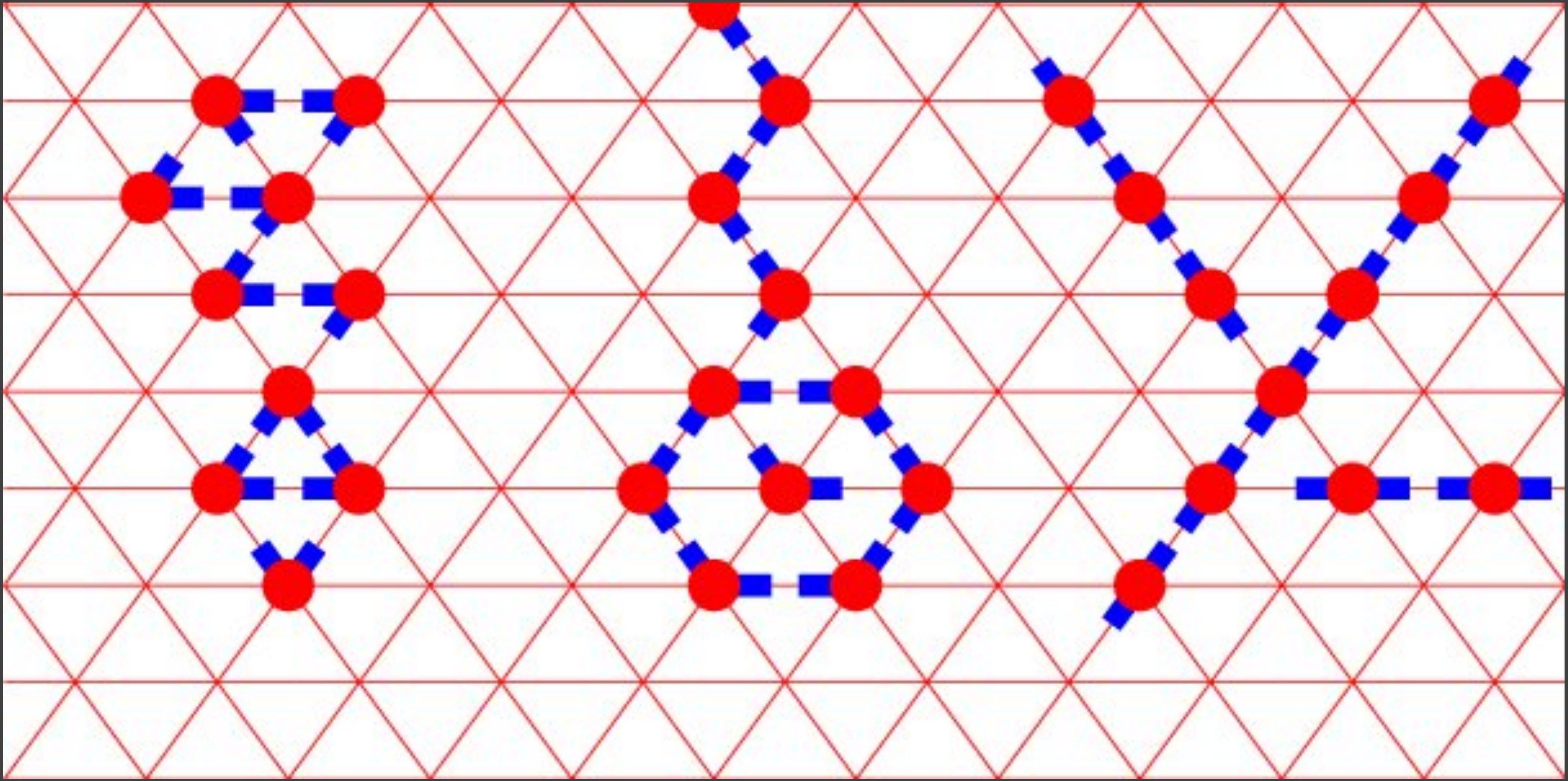
The correspondence is

$$P \rightarrow \Pi$$

and

$$\frac{N}{V} = \rho \rightarrow x$$





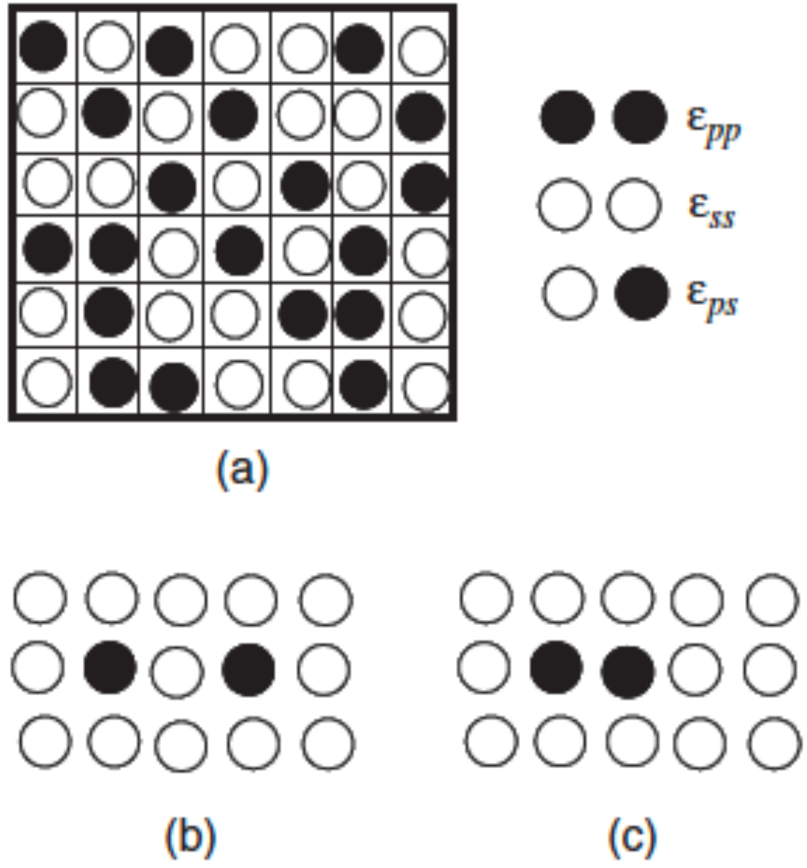
Lattice models

Lattice models originally occurred in the context of condensed matter physics, where the atoms of a crystal automatically form a lattice. Currently, lattice models are quite popular in theoretical physics, for many reasons. Some models are exactly solvable, and thus offer insight into physics beyond what can be learned from perturbation theory. Lattice models are also ideal for study by the methods of computational physics, as the discretization of any continuum model automatically turns it into a lattice model. Examples of lattice models in condensed matter physicsinclude the Ising model, the Potts model, the XY model, the Toda lattice.

Lattice model

Lattice model for symmetric solutions.

Solute and solvent molecules are represented by black and white circles, respectively.



Free energy

f(ϕ) can be calculated if the Hamiltonian of the system is known.

For simplicity, we assume that the solute molecule and the solvent molecule have the same volume v_c, and that each cell in a lattice is occupied by either a solute molecule or a solvent molecule (incompressibility). The solution volume V and the solute volume fraction ϕ are given by $V = v_c/N_{tot}$, $\phi = N_p/N_{tot}$

The energy E_i for a certain configuration i is calculated by

$$E_i = \epsilon_{pp} N_i^{(pp)} + \epsilon_{ss} N_i^{(ss)} + \epsilon_{ps} N_i^{(ps)}$$

$$Z = \sum_i \exp(-E_i/k_B T)$$

$$f(\phi, T) = -\frac{k_B T}{V} \ln Z$$

Partition function & free energy density

Mean-field approximation

As an approximation, we replace E_i in the summation by the mean value $\overline{E}$.

$$Z \simeq W \exp(-\overline{E}/k_B T)$$

where W is the number of terms in the summation. W is equal to the number of ways of placing N_p molecules on $N_{tot} = N_p + N_s$ cells, and is given by

$$W = \frac{(N_p + N_s)!}{N_p! N_s!}$$

Average energy

Each cell in the lattice has z neighbouring cells (z is called the coordination number). Among the z cells, zϕ cells are, on average, occupied by solute molecules, and the remaining z(1−ϕ) cells are occupied by solvent molecules. Then

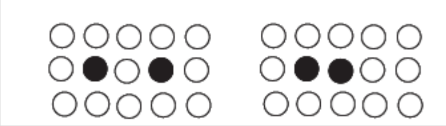
$$\overline{N_{pp}} = (1/2)z\phi N_p = zN_{tot}\phi^2/2$$

$$\overline{N_{ss}} = zN_{tot}(1-\phi)^2/2$$
$$\overline{N_{ps}} = zN_{tot}\phi(1-\phi)$$

$$\begin{aligned}\overline{E} &= \epsilon_{pp}\overline{N_{pp}} + \epsilon_{ps}\overline{N_{ps}} + \epsilon_{ss}\overline{N_{ss}} \\ &= \frac{1}{2}N_{tot}z\left[\epsilon_{pp}\phi^2 + 2\epsilon_{ps}\phi(1-\phi) + \epsilon_{ss}(1-\phi)^2\right] \\ &= \frac{1}{2}N_{tot}z\Delta\epsilon\phi^2 + C_0 + C_1\phi\end{aligned}$$

$$\Delta\epsilon = \epsilon_{pp} + \epsilon_{ss} - 2\epsilon_{ps}$$

The energy $\Delta\epsilon$ represents the effective interaction between the solute molecules in the solution. Notice that this energy depends on the interaction energy between all pairs. When the pair is brought into contact with each other

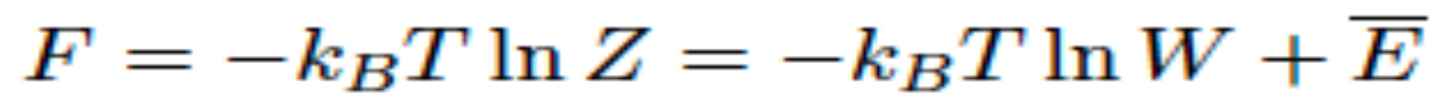


two pairs of solute–solvent molecules disappear, and two new pairs (a solute–solute pair and a solvent–solvent pair) appear. The energy change associated with this recombination is $\Delta\epsilon$.

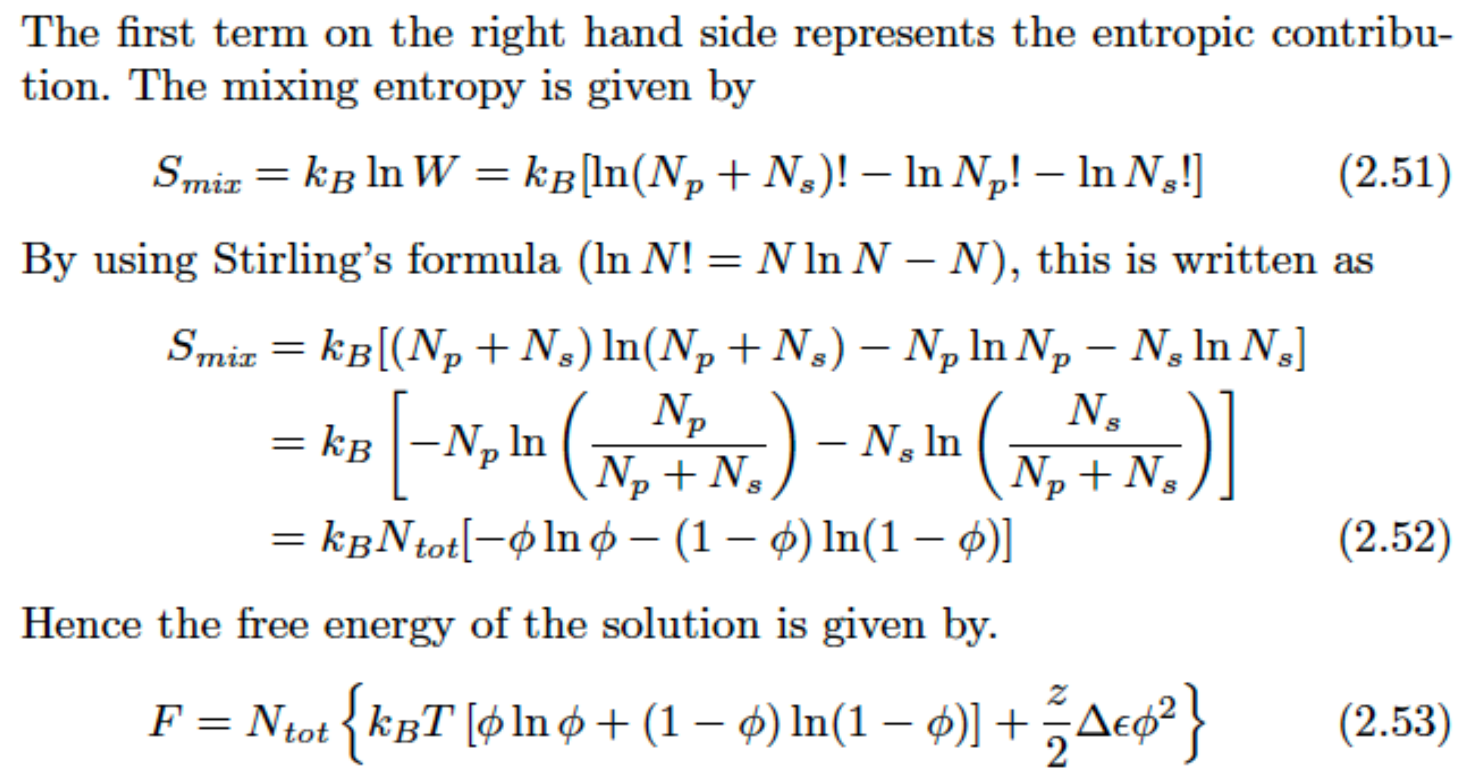
The above argument indicates that whether solute molecules like each other or not in solutions is not determined by ϵ_{pp} alone. It depends on the interaction energy of other pairs. For example, the pair of solute molecules which attract each other in vacuum (i.e., ϵ_{pp} is negative) may repel each other in solutions if the attractive interaction between solute and solvent molecules is stronger than the attractive interaction between solute molecules.

The effective interaction between solute molecules is determined by $\Delta\epsilon$. If $\Delta\epsilon$ is positive, solute molecules tend to stay away, and the solution is homogeneous. On the other hand, if $\Delta\epsilon$ is negative, solute molecules attract each other, and if their attraction is strong enough, phase separation takes place.

Mean-field free energy



$$F = -k_B T \ln Z = -k_B T \ln W + \overline{E}$$



The first term on the right hand side represents the entropic contribution. The mixing entropy is given by

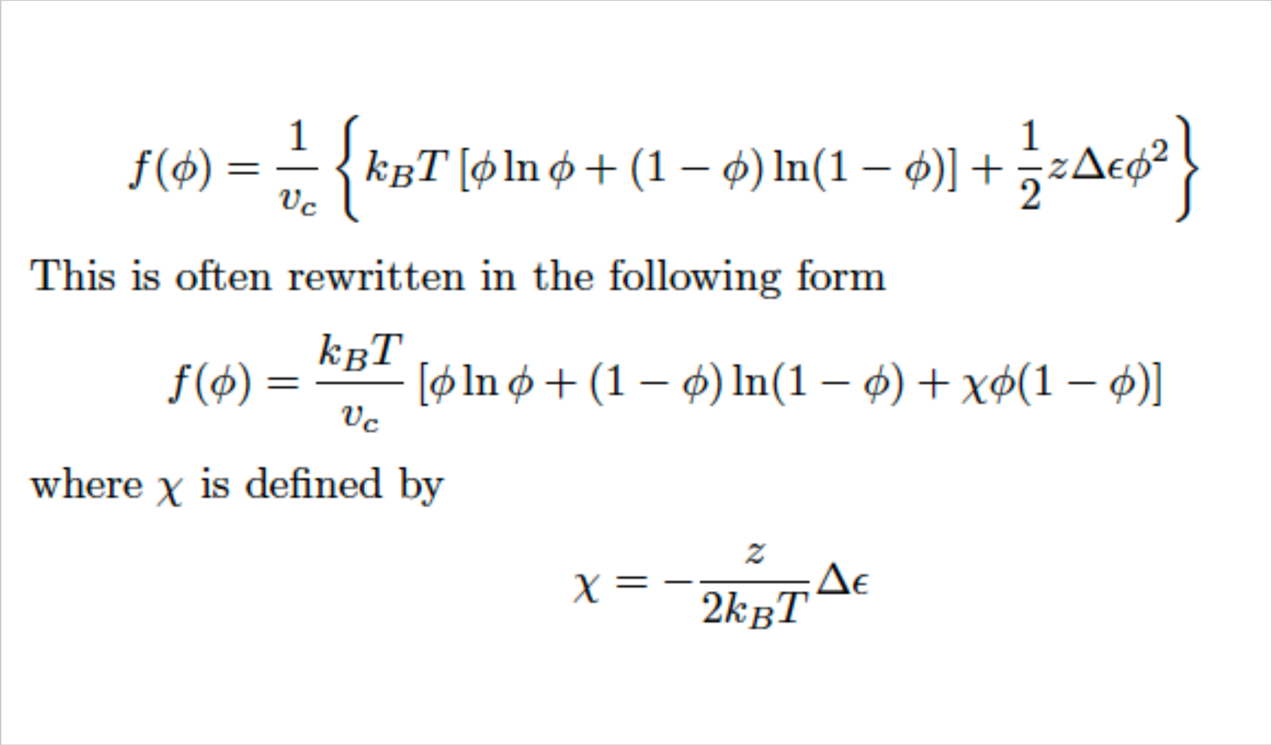
$$S_{mix} = k_B \ln W = k_B[\ln(N_p + N_s)! - \ln N_p! - \ln N_s!] \qquad (2.51)$$

By using Stirling's formula ($\ln N! = N \ln N - N$), this is written as

$$\begin{aligned} S_{mix} &= k_B[(N_p + N_s)\ln(N_p + N_s) - N_p \ln N_p - N_s \ln N_s] \\ &= k_B \left[-N_p \ln\left(\frac{N_p}{N_p + N_s}\right) - N_s \ln\left(\frac{N_s}{N_p + N_s}\right)\right] \\ &= k_B N_{tot}[-\phi \ln \phi - (1-\phi)\ln(1-\phi)] \qquad (2.52) \end{aligned}$$

Hence the free energy of the solution is given by.

$$F = N_{tot}\left\{k_B T\left[\phi \ln \phi + (1-\phi)\ln(1-\phi)\right] + \frac{z}{2}\Delta\epsilon\phi^2\right\} \qquad (2.53)$$



$$f(\phi) = \frac{1}{v_c}\left\{k_BT\left[\phi\ln\phi + (1-\phi)\ln(1-\phi)\right] + \frac{1}{2}z\Delta\epsilon\phi^2\right\}$$

This is often rewritten in the following form

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

where χ is defined by

$$\chi = -\frac{z}{2k_BT}\Delta\epsilon$$

Free energy density

Linear terms have been added/removed, for convenience, as they do not contribute to the phase diagram.

Osmotic pressure

The osmotic pressure of the solution is calculated by eq. (2.23)

$$\Pi = -f(\phi) + \phi f'(\phi) + f(0) = \frac{k_B T}{v_c}\left[-\ln(1-\phi) - \chi\phi^2\right]$$

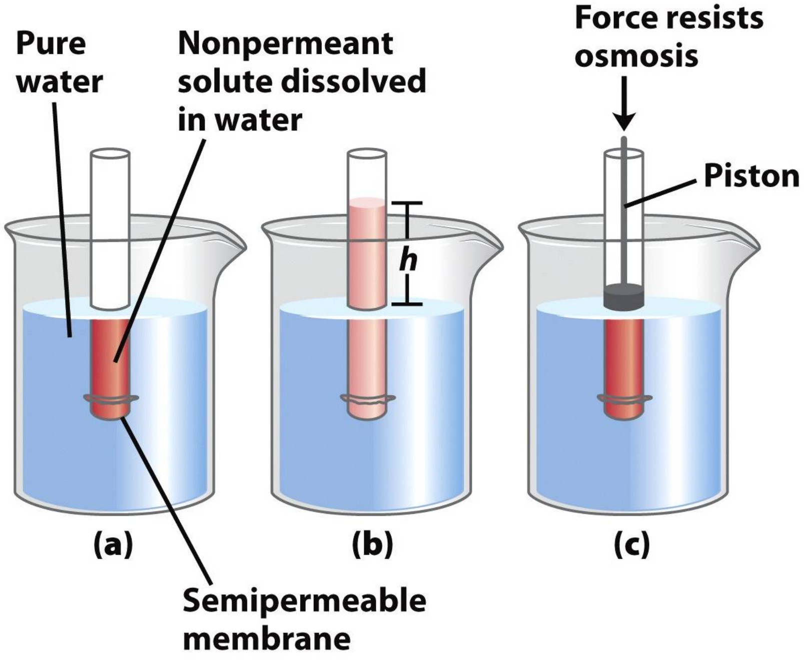


Figure 2-11
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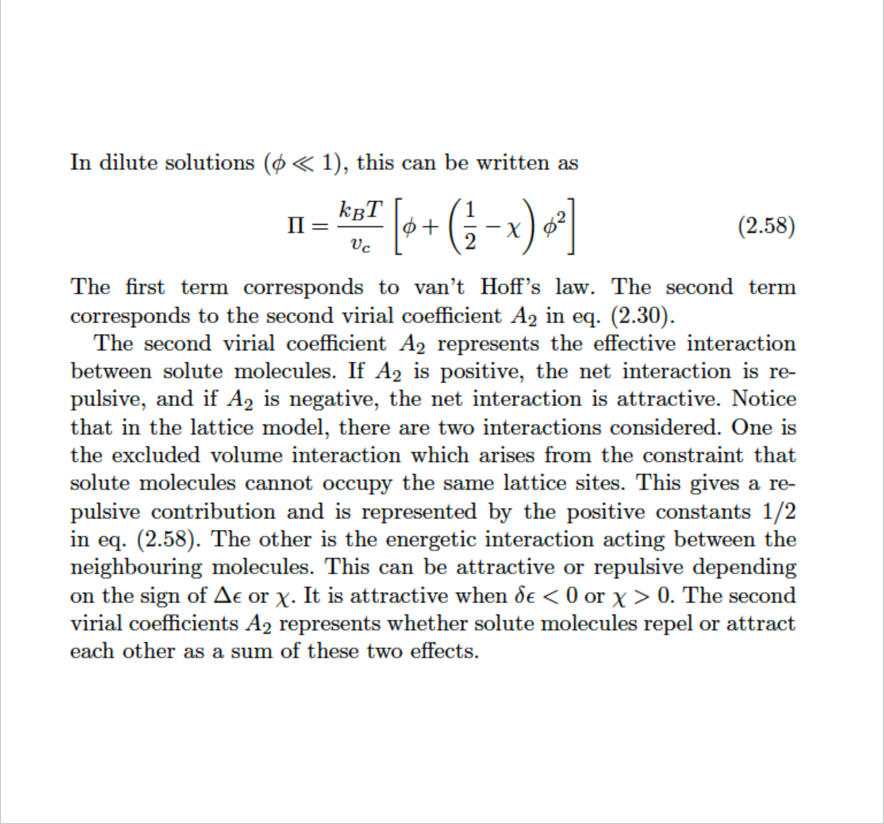


In dilute solutions ($\phi \ll 1$), this can be written as

$$\Pi = \frac{k_B T}{v_c}\left[\phi + \left(\frac{1}{2} - \chi\right)\phi^2\right] \qquad (2.58)$$

The first term corresponds to van't Hoff's law. The second term corresponds to the second virial coefficient A_2 in eq. (2.30).

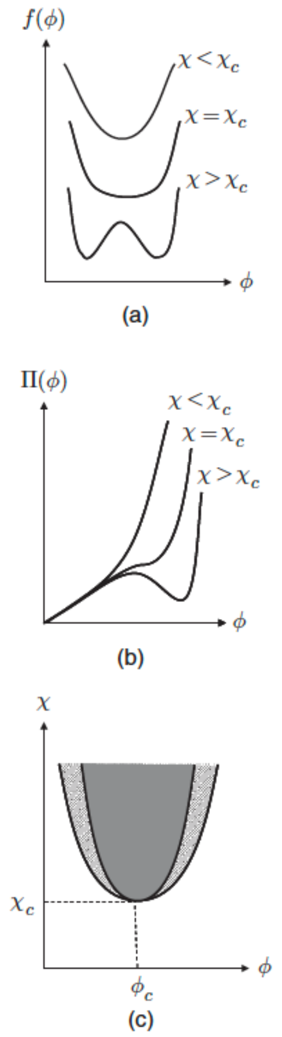
The second virial coefficient A_2 represents the effective interaction between solute molecules. If A_2 is positive, the net interaction is repulsive, and if A_2 is negative, the net interaction is attractive. Notice that in the lattice model, there are two interactions considered. One is the excluded volume interaction which arises from the constraint that solute molecules cannot occupy the same lattice sites. This gives a repulsive contribution and is represented by the positive constants 1/2 in eq. (2.58). The other is the energetic interaction acting between the neighbouring molecules. This can be attractive or repulsive depending on the sign of $\Delta\epsilon$ or χ. It is attractive when $\delta\epsilon < 0$ or $\chi > 0$. The second virial coefficients A_2 represents whether solute molecules repel or attract each other as a sum of these two effects.

Phase separation

(a) The free energy f(ϕ) for a symmetric solution is plotted against solute volume fraction ϕ for various values of χ.

(b) Osmotic pressure is plotted against ϕ.

(c) Phase diagram of the solution. The dark shaded region is the unstable region, and the light shaded region is the metastable region.



Critical point and spinodal

$f(\phi)$ has a mirror symmetry with respect to the line $\phi = 1/2$. If χ is less than a certain critical value χ_c, $f(\phi)$ has only one minimum at $\phi = 1/2$, while if χ is larger than χ_c, $f(\phi)$ has two local minima.

The value of χ_c is determined by the condition that the curvature at $\phi = 1/2$ changes sign; i.e., $\partial^2 f/\partial\phi^2 = 0$ at $\phi = 1/2$. This condition gives the critical point

$$\chi_c = 2, \qquad \phi_c = \frac{1}{2}$$

The spinodal line is determined by $\partial^2 f/\partial\phi^2 = 0$, and is given by

$$\chi = \frac{1}{2}\frac{1}{\phi(1-\phi)}$$

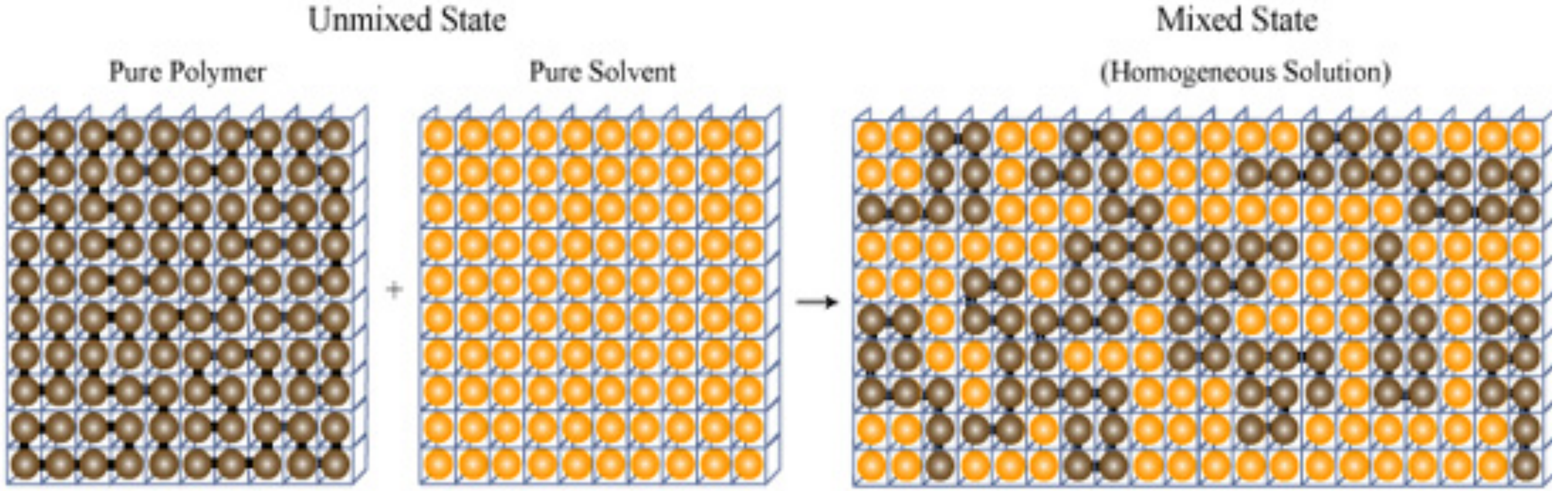
Phase diagram

The coexistence curve is obtained by the common tangent construction. Since the free energy f(ϕ) curve has a mirror symmetry with respect to the line at ϕ = 1/2, the common tangente line is given by the line connecting the two local minima of f(ϕ).

Thus the concentrations $\phi_a(T)$ and $\phi_b(T)$ in the coexistence region are given by the two solutions of the equation ∂f/∂ϕ = 0. This is given by

$$\chi = \frac{1}{1-2\phi} \ln\left(\frac{1-\phi}{\phi}\right)$$

Lattice model of a polymer solution

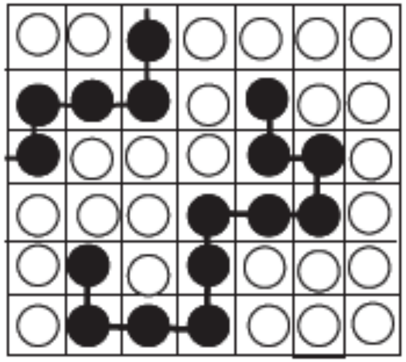


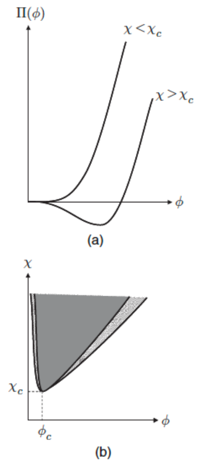
Polymer solutions

A polymer is represented by N dark circles connected in series. The building block of the polymer (i.e., the dark circle) is called the segment.

(a) Osmotic pressure of polymer solutions is plotted against ϕ.

(b) Phase diagram of polymer solutions. The dark shaded region is the unstable region, and the light shaded region is the metastable region.





Free energy

In solutions of soft matter, e.g., polymer solutions and colloidal solutions, solute molecules (or particles) are much larger than solvent molecules. Let us now consider how this asymmetry in size affects the solution properties.

A polymer is represented by N segments (represented by the black circles) connected by bonds. The segment corresponds to a monomer before the polymerization reaction. Here, for simplicity, it is assumed that the segment and solvent molecules have the same size. For such a model, the free energy density is now given by

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

Osmotic pressure

The difference is the factor 1/N in front of ϕ ln ϕ. This factor comes from the fact that the mixing entropy per segment of a polymer molecule is now given by ϕ ln ϕ/N since N segments are connected and cannot be placed independently.

The osmotic pressure is given by

$$\Pi = \frac{k_B T}{v_c}\left[\frac{\phi}{N} - \ln(1-\phi) - \phi - \chi\phi^2\right]$$

For ϕ << 1, this is written as

$$\Pi = \frac{k_B T}{v_c}\left[\frac{\phi}{N} + \left(\frac{1}{2} - \chi\right)\phi^2\right]$$

Spinodal

Due to the factor 1/N, the first term is usually negligibly small compared with the second term. Therefore the osmotic pressure of a polymer solution is usually written as

$$\Pi = A_2\phi^2$$

The polymer size effect also appears in the phase diagram, in the form of an asymmetric shape. The spinodal line is calculated by $\partial^2 f/\partial\phi^2 = 0$, and is given by

$$\chi = \frac{1}{2}\left[\frac{1}{1-\phi} + \frac{1}{N\phi}\right]$$

Critical point

$$\phi_c = \frac{1}{1+\sqrt{N}}, \qquad \chi_c = \frac{1}{2}\left(1+\frac{1}{\sqrt{N}}\right)^2$$

For large N, χ_c is equal to 1/2. This is the value of χ at which the second virial coefficient A_2 changes from positive to negative.

In the case of polymer solutions, the effect of entropy is small, and therefore phase separation takes place as soon as the second virial coefficient becomes negative.

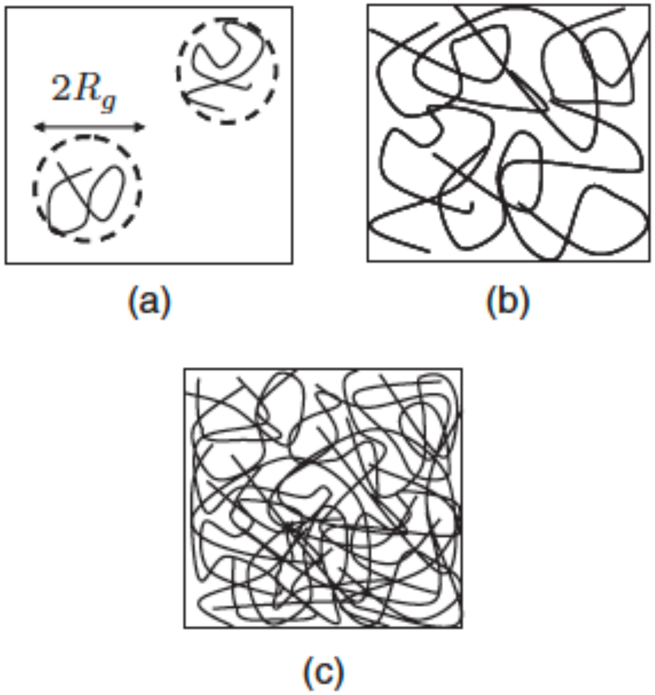
Polymer correlations

Polymer solutions at various concentrations.

In a very dilute solution, polymers are separated from each other and there is a strong correlation in the segment density.

As concentration increases, polymers starts to overlap, but the correlation effect is still there.

At high concentration, the correlation effect becomes weak, and the segment density is nearly homogeneous.



(a) (b)

(c)

Polymer correlations

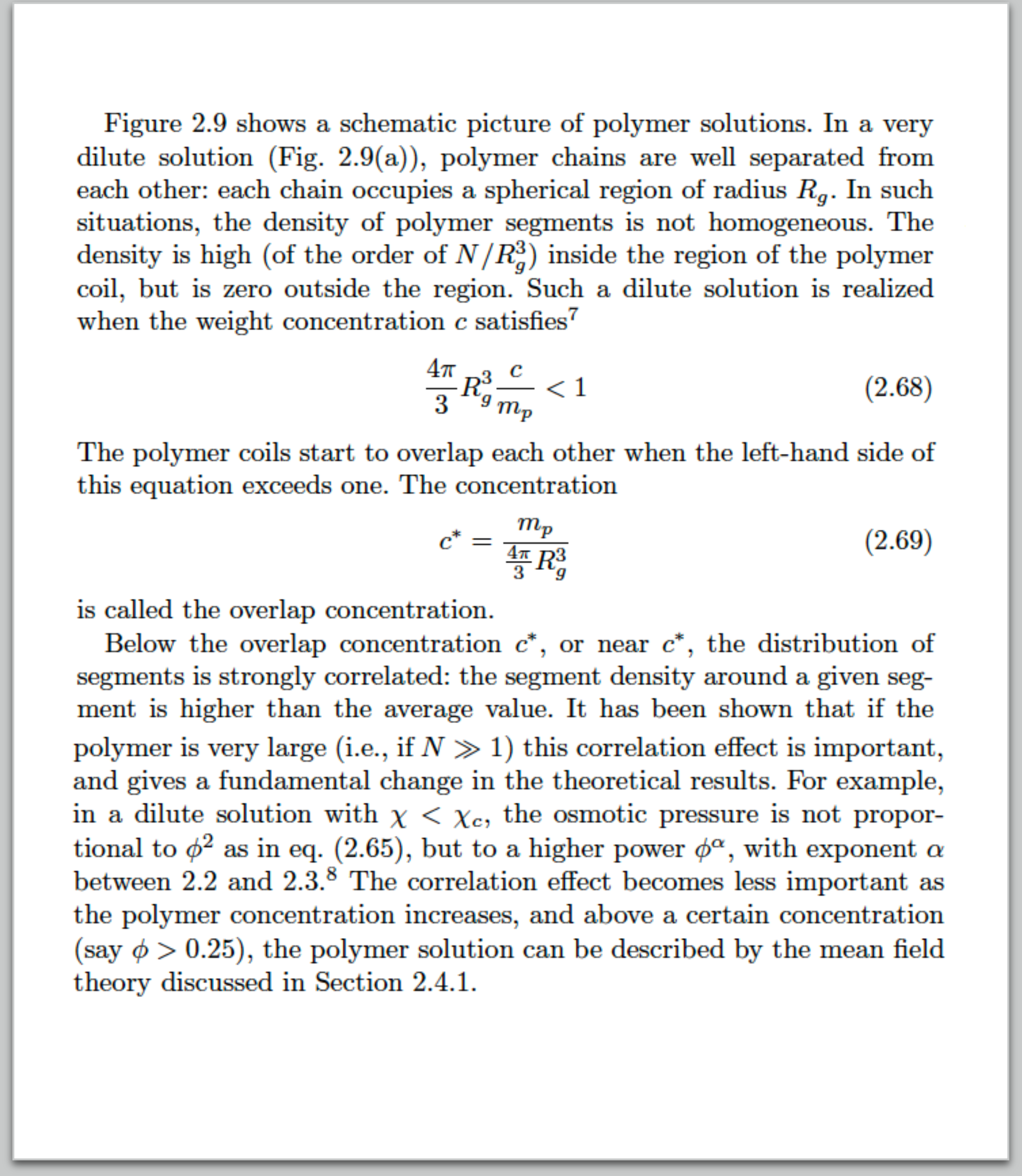


Figure 2.9 shows a schematic picture of polymer solutions. In a very dilute solution (Fig. 2.9(a)), polymer chains are well separated from each other: each chain occupies a spherical region of radius R_g. In such situations, the density of polymer segments is not homogeneous. The density is high (of the order of N/R_g^3) inside the region of the polymer coil, but is zero outside the region. Such a dilute solution is realized when the weight concentration c satisfies[7]

$$\frac{4\pi}{3}R_g^3\frac{c}{m_p} < 1 \tag{2.68}$$

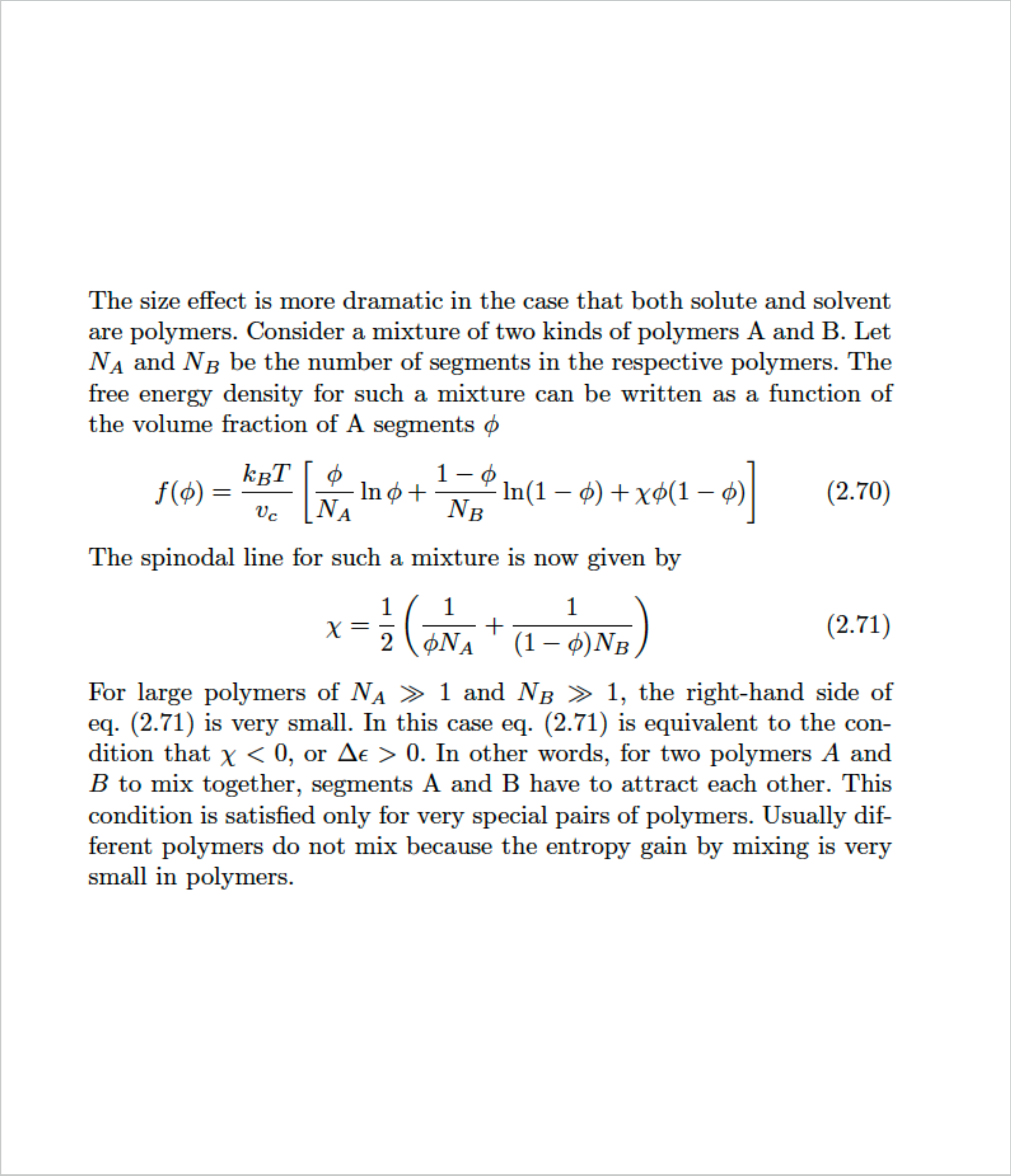
The polymer coils start to overlap each other when the left-hand side of this equation exceeds one. The concentration

$$c^* = \frac{m_p}{\frac{4\pi}{3}R_g^3} \tag{2.69}$$

is called the overlap concentration.

Below the overlap concentration c^*, or near c^*, the distribution of segments is strongly correlated: the segment density around a given segment is higher than the average value. It has been shown that if the polymer is very large (i.e., if $N \gg 1$) this correlation effect is important, and gives a fundamental change in the theoretical results. For example, in a dilute solution with $\chi < \chi_c$, the osmotic pressure is not proportional to ϕ^2 as in eq. (2.65), but to a higher power ϕ^α, with exponent α between 2.2 and 2.3.[8] The correlation effect becomes less important as the polymer concentration increases, and above a certain concentration (say $\phi > 0.25$), the polymer solution can be described by the mean field theory discussed in Section 2.4.1.

Polymer blends



The size effect is more dramatic in the case that both solute and solvent are polymers. Consider a mixture of two kinds of polymers A and B. Let N_A and N_B be the number of segments in the respective polymers. The free energy density for such a mixture can be written as a function of the volume fraction of A segments ϕ

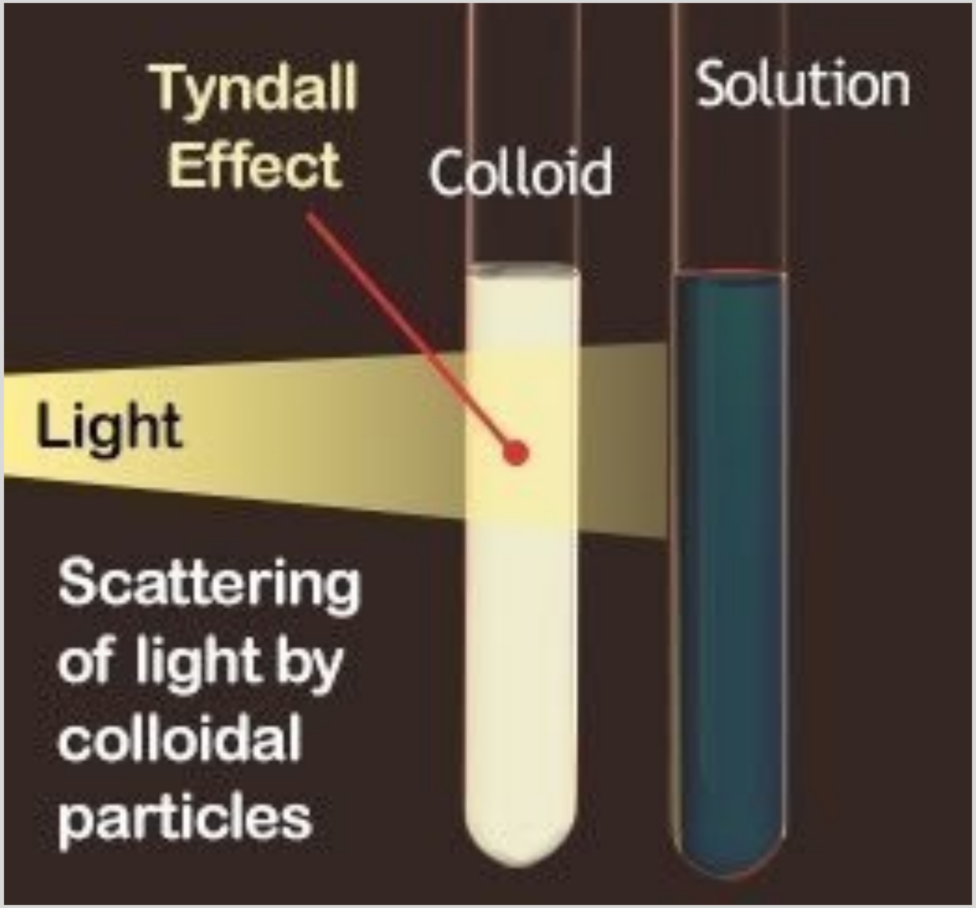
$$f(\phi) = \frac{k_B T}{v_c}\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)\right] \tag{2.70}$$

The spinodal line for such a mixture is now given by

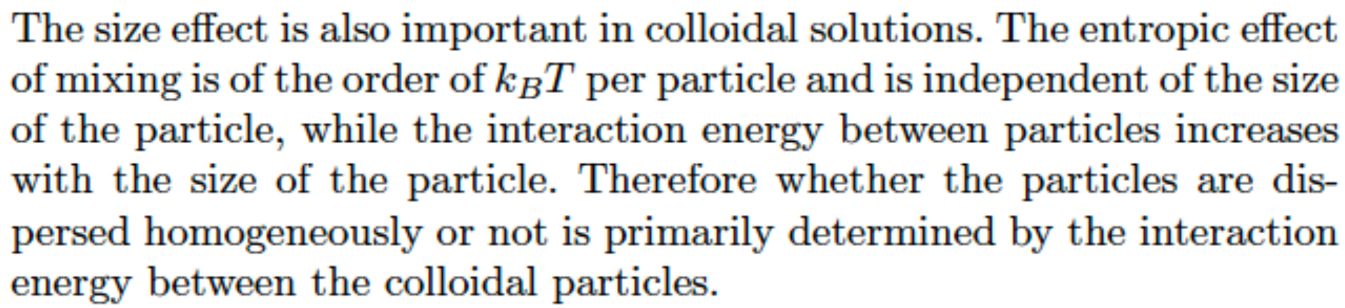
$$\chi = \frac{1}{2}\left(\frac{1}{\phi N_A} + \frac{1}{(1-\phi)N_B}\right) \tag{2.71}$$

For large polymers of $N_A \gg 1$ and $N_B \gg 1$, the right-hand side of eq. (2.71) is very small. In this case eq. (2.71) is equivalent to the condition that $\chi < 0$, or $\Delta\epsilon > 0$. In other words, for two polymers A and B to mix together, segments A and B have to attract each other. This condition is satisfied only for very special pairs of polymers. Usually different polymers do not mix because the entropy gain by mixing is very small in polymers.

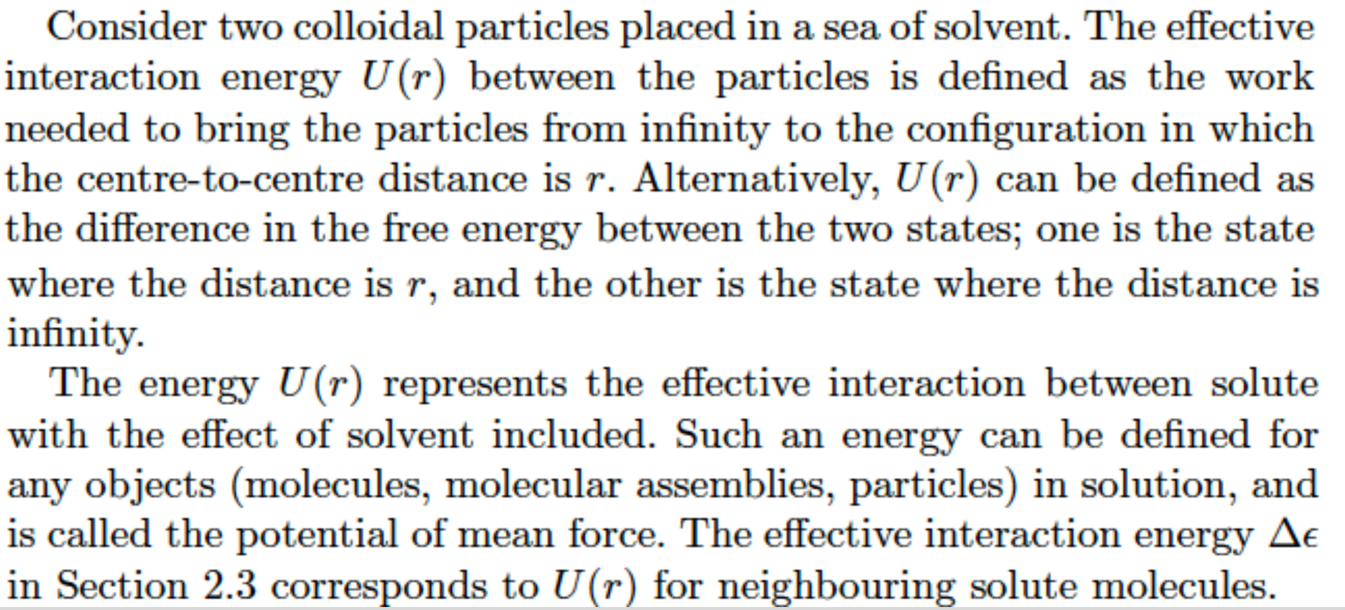
Colloids


Tyndall Effect
Colloid
Solution
Light
Scattering of light by colloidal particles

Colloidal solutions



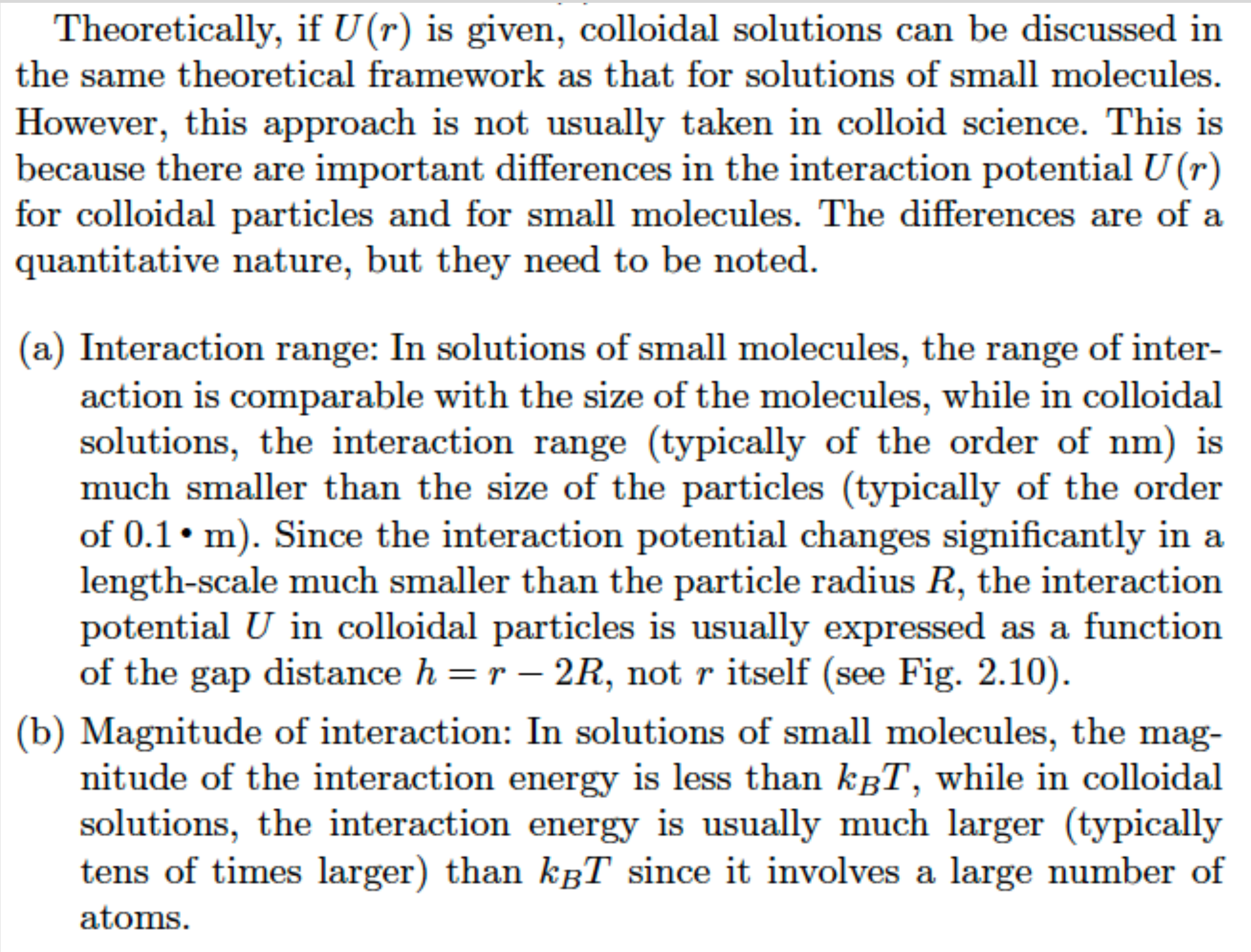
The size effect is also important in colloidal solutions. The entropic effect of mixing is of the order of $k_B T$ per particle and is independent of the size of the particle, while the interaction energy between particles increases with the size of the particle. Therefore whether the particles are dispersed homogeneously or not is primarily determined by the interaction energy between the colloidal particles.



Consider two colloidal particles placed in a sea of solvent. The effective interaction energy $U(r)$ between the particles is defined as the work needed to bring the particles from infinity to the configuration in which the centre-to-centre distance is r. Alternatively, $U(r)$ can be defined as the difference in the free energy between the two states; one is the state where the distance is r, and the other is the state where the distance is infinity.

The energy $U(r)$ represents the effective interaction between solute with the effect of solvent included. Such an energy can be defined for any objects (molecules, molecular assemblies, particles) in solution, and is called the potential of mean force. The effective interaction energy $\Delta\epsilon$ in Section 2.3 corresponds to $U(r)$ for neighbouring solute molecules.

Colloidal solutions



Theoretically, if $U(r)$ is given, colloidal solutions can be discussed in the same theoretical framework as that for solutions of small molecules. However, this approach is not usually taken in colloid science. This is because there are important differences in the interaction potential $U(r)$ for colloidal particles and for small molecules. The differences are of a quantitative nature, but they need to be noted.

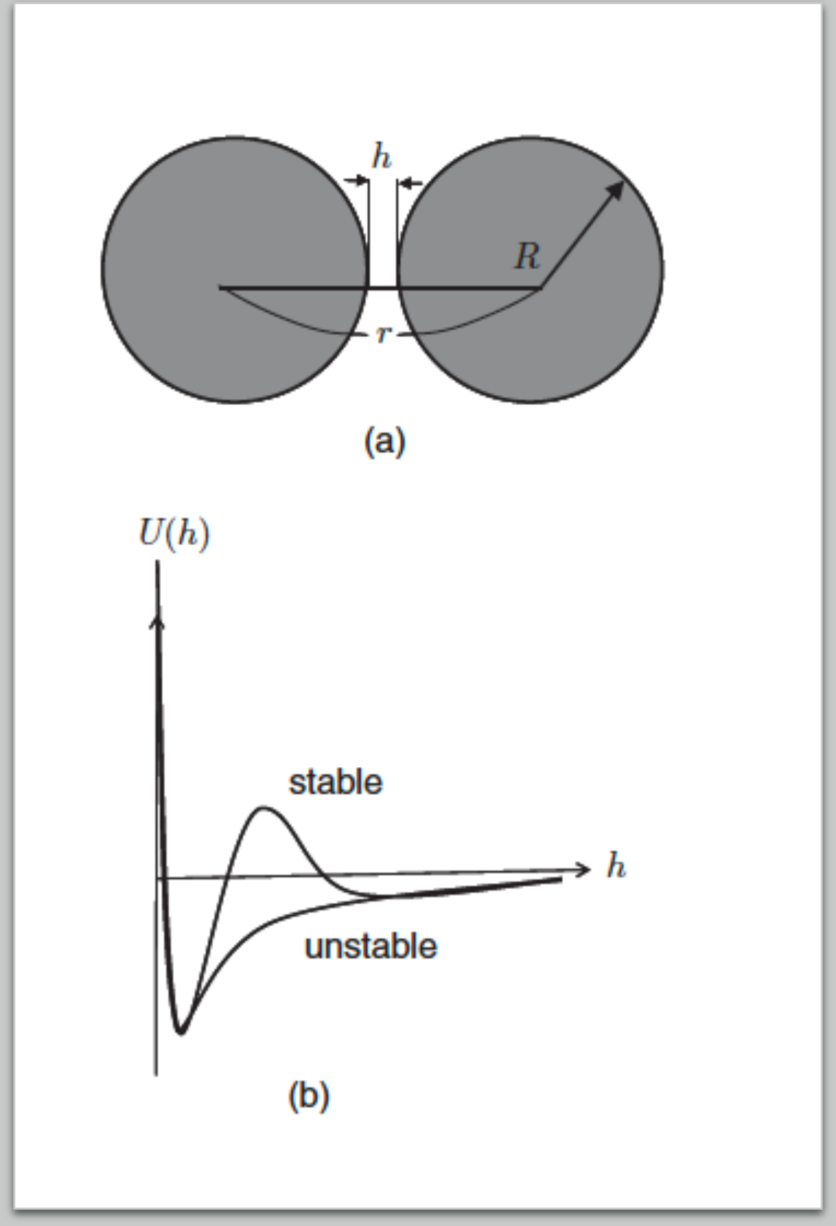
(a) Interaction range: In solutions of small molecules, the range of interaction is comparable with the size of the molecules, while in colloidal solutions, the interaction range (typically of the order of nm) is much smaller than the size of the particles (typically of the order of 0.1 • m). Since the interaction potential changes significantly in a length-scale much smaller than the particle radius R, the interaction potential U in colloidal particles is usually expressed as a function of the gap distance $h = r - 2R$, not r itself (see Fig. 2.10).

(b) Magnitude of interaction: In solutions of small molecules, the magnitude of the interaction energy is less than $k_B T$, while in colloidal solutions, the interaction energy is usually much larger (typically tens of times larger) than $k_B T$ since it involves a large number of atoms.

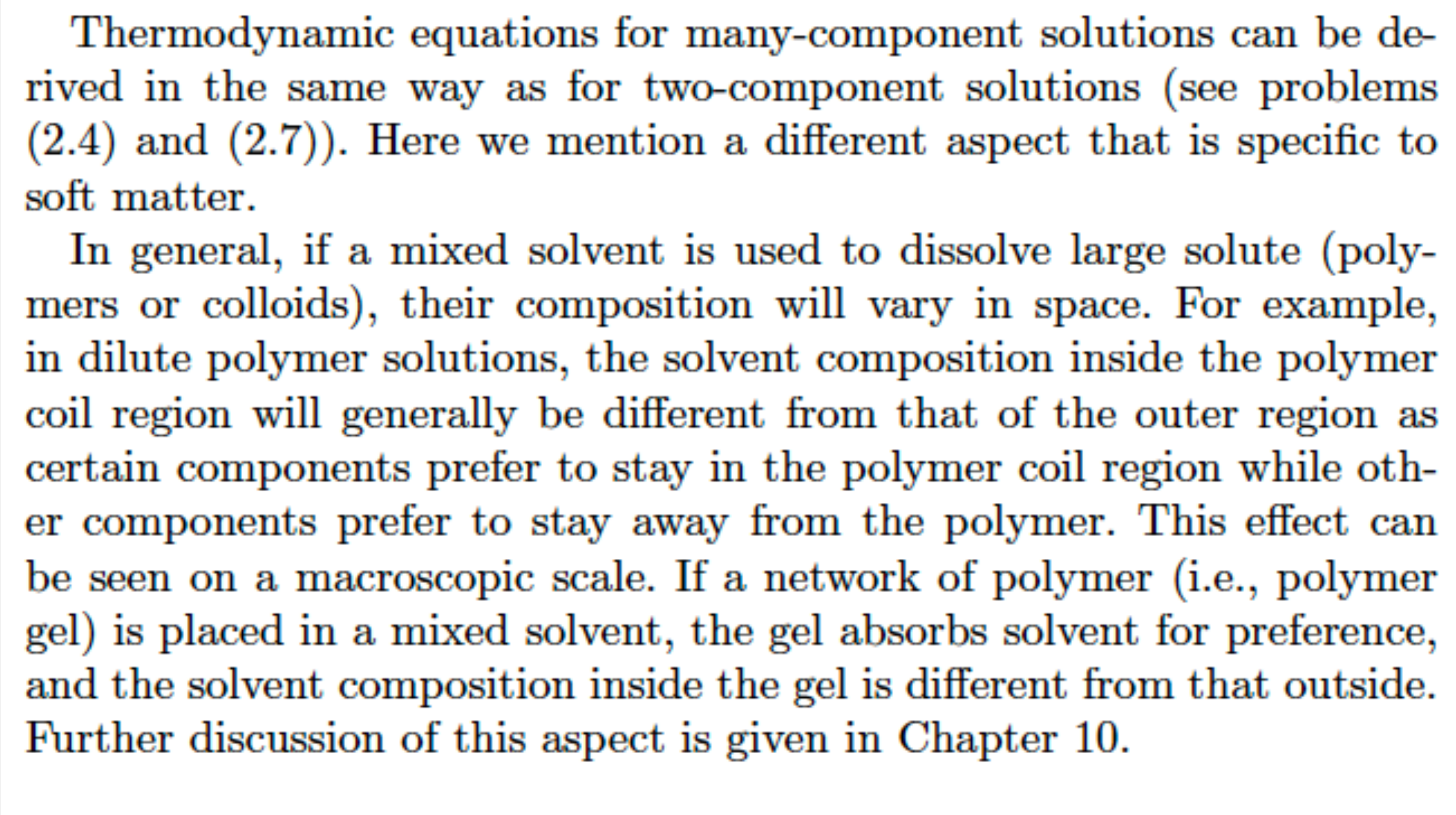
Colloidal interactions

(a) Interaction between two colloidal particles.

(b) An exemple of the effective interaction potential between colloidal particles. Here ‘unstable’ indicates the potential for the unstable dispersion in which particles aggregate quickly, while ‘stable’ indicates the potential for the stable dispersions in which aggregation takes place so slowly that the dispersion look stable.



Multicomponent solutions



Thermodynamic equations for many-component solutions can be derived in the same way as for two-component solutions (see problems (2.4) and (2.7)). Here we mention a different aspect that is specific to soft matter.

In general, if a mixed solvent is used to dissolve large solute (polymers or colloids), their composition will vary in space. For example, in dilute polymer solutions, the solvent composition inside the polymer coil region will generally be different from that of the outer region as certain components prefer to stay in the polymer coil region while other components prefer to stay away from the polymer. This effect can be seen on a macroscopic scale. If a network of polymer (i.e., polymer gel) is placed in a mixed solvent, the gel absorbs solvent for preference, and the solvent composition inside the gel is different from that outside. Further discussion of this aspect is given in Chapter 10.