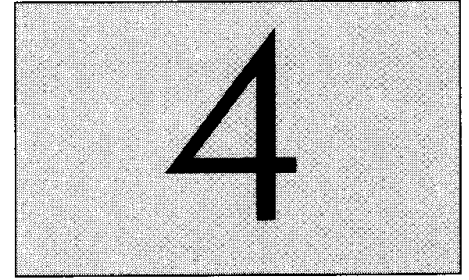


Thermodynamics of mixing



Mixtures are systems consisting of two or more different chemical species. **Binary mixtures** consist of only two different species. An example of a binary mixture is a blend of polystyrene and polybutadiene. Mixtures with three components are called **ternary**. An example of a ternary mixture is a solution of polystyrene and polybutadiene in toluene. If the mixture is uniform and all components of the mixture are intermixed on a molecular scale, the mixture is called **homogeneous**. An example of a homogeneous mixture is a polymer solution in a good solvent. If the mixture consists of several different phases (regions with different compositions), it is called **heterogeneous**. An example of a heterogeneous mixture is that of oil and water. Whether an equilibrium state of a given mixture is homogeneous or heterogeneous is determined by the composition dependence of the entropy and energy changes on mixing. Entropy always favours mixing, but energetic interactions between species can either promote or inhibit mixing.

4.1 Entropy of binary mixing

Consider the mixing of two species A and B. For the moment, assume that the two mix together to form a single-phase homogeneous liquid (criteria for such mixing will be determined later in this chapter). For purposes of illustration, the mixing is shown on a two-dimensional square lattice in Fig. 4.1. More generally, it is assumed that there is no volume change on mixing: volume V_A of species A is mixed with volume V_B of species B to make a mixture of volume $V_A + V_B$. The mixture is macroscopically uniform and the two components are randomly mixed to fill the entire lattice. The volume fractions of the two components in the binary mixture are ϕ_A and ϕ_B :

$$\phi_A = \frac{V_A}{V_A + V_B} \quad \text{and} \quad \phi_B = \frac{V_B}{V_A + V_B} = 1 - \phi_A. \quad (4.1)$$

While Fig. 4.1 shows the mixing of two small molecules of equal molecular volumes, similar mixing is possible if one or both of the species are polymers. In the more general case, the lattice site volume v_0 is defined by the smallest units (solvent molecules or monomers), and larger molecules

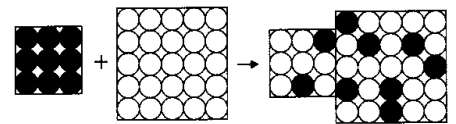


Fig. 4.1
Mixing two species with no volume change.

Thermodynamics of mixing

occupy multiple connected lattice sites. A molecule of species A has molecular volume

$$v_A = N_A v_0 \quad (4.2)$$

and a molecule of species B has molecular volume

$$v_B = N_B v_0, \quad (4.3)$$

where N_A and N_B are the numbers of lattice sites occupied by each respective molecule.¹ There are three cases of interest that are summarized in Table 4.1.

Table 4.1 The number of lattice sites occupied per molecule

	N_A	N_B
Regular solutions	1	1
Polymer solutions	N	1
Polymer blends	N_A	N_B

Regular solutions are mixtures of low molar mass species with $N_A = N_B = 1$. **Polymer solutions** are mixtures of macromolecules ($N_A = N \gg 1$) with the low molar mass solvent defining the lattice ($N_B = 1$). **Polymer blends** are mixtures of macromolecules of different chemical species ($N_A \gg 1$ and $N_B \gg 1$).

The combined system of volume $V_A + V_B$ occupies

$$n = \frac{V_A + V_B}{v_0} \quad (4.4)$$

lattice sites, while all molecules of species A occupy $V_A/v_0 = n\phi_A$ sites.

The entropy S is determined as the product of the Boltzmann constant k and the natural logarithm of the number of ways Ω to arrange molecules on the lattice (the number of states).

$$S = k \ln \Omega. \quad (4.5)$$

The number of translational states of a given single molecule is simply the number of independent positions that a molecule can have on the lattice, which is equal to the number of lattice sites. In a homogeneous mixture of A and B, each molecule has

$$\Omega_{AB} = n \quad (4.6)$$

possible states, where n is the total number of lattice sites of the combined system [Eq. (4.4)]. The number of states Ω_A of each molecule of species A before mixing (in a pure A state) is equal to the number of lattice sites occupied by species A.

$$\Omega_A = n\phi_A. \quad (4.7)$$

For a single molecule of species A, the entropy change on mixing is

$$\begin{aligned} \Delta S_A &= k \ln \Omega_{AB} - k \ln \Omega_A = k \ln \left(\frac{\Omega_{AB}}{\Omega_A} \right) \\ &= k \ln \left(\frac{1}{\phi_A} \right) = -k \ln \phi_A. \end{aligned} \quad (4.8)$$

¹ The lattice sites are of the order of monomer sizes, but do not necessarily correspond precisely to either the chemical monomer or the Kuhn monomer.

Since the volume fraction is less than unity ($\phi_A < 1$), the entropy change upon mixing is always positive $\Delta S_A = -k \ln \phi_A > 0$. Equation (4.8) holds for the entropy contribution of each molecule of species A, with a similar relation for species B. To calculate the total entropy of mixing, the entropy contributions from each molecule in the system are summed:

$$\Delta S_{\text{mix}} = n_A \Delta S_A + n_B \Delta S_B = -k(n_A \ln \phi_A + n_B \ln \phi_B). \quad (4.9)$$

There are $n_A = n\phi_A/N_A$ molecules of species A and $n_B = n\phi_B/N_B$ molecules of species B. The **entropy of mixing** per lattice site $\Delta \bar{S}_{\text{mix}} = \Delta S_{\text{mix}}/n$ is an intrinsic thermodynamic quantity:

$$\Delta \bar{S}_{\text{mix}} = -k \left[\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right]. \quad (4.10)$$

The entropy of mixing per unit volume is $\Delta \bar{S}_{\text{mix}}/v_0$, where v_0 is the volume per lattice site.

A regular solution has $N_A = N_B = 1$ and a large entropy of mixing:

$$\Delta \bar{S}_{\text{mix}} = -k [\phi_A \ln \phi_A + \phi_B \ln \phi_B] \quad \text{for regular solutions.} \quad (4.11)$$

A polymer solution has $N_A = N$ and $N_B = 1$:

$$\Delta \bar{S}_{\text{mix}} = -k \left[\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right] \quad \text{for polymer solutions.} \quad (4.12)$$

Equations (4.10)–(4.12) predict enormous differences between the entropies of mixing for regular solutions, polymer solutions, and polymer blends. Consider the 10×10 square lattice of Fig. 4.2 with three different mixtures that each have $\phi_A = \phi_B = 0.5$. A regular solution of small molecules is shown in Fig. 4.2(a), using 50 black balls and 50 white balls. A polymer solution with five 10-ball black chains and 50 white balls is shown in Fig. 4.2(b) and a polymer blend with ten 10-ball chains (five black and five white) is shown in Fig. 4.2(c). The entropies of mixing per site for these mixtures are summarized in Table 4.2.

Typically N is large, making the first term in Eq. (4.12) negligible compared to the second term. For solutions with $\phi_A = \phi_B = 0.5$, as in Fig. 4.2 and Table 4.2, the entropy of mixing for the polymer solution is roughly half of that for the regular solution. For polymer blends, both N_A and N_B

Table 4.2 The mixing entropy per site for the three situations depicted in Fig. 4.2

Mixture	$\Delta \bar{S}_{\text{mix}}/k$
50 black balls and 50 white balls	0.69
Five 10-ball black chains and 50 white balls	0.38
Five 10-ball black chains and five 10-ball white chains	0.069

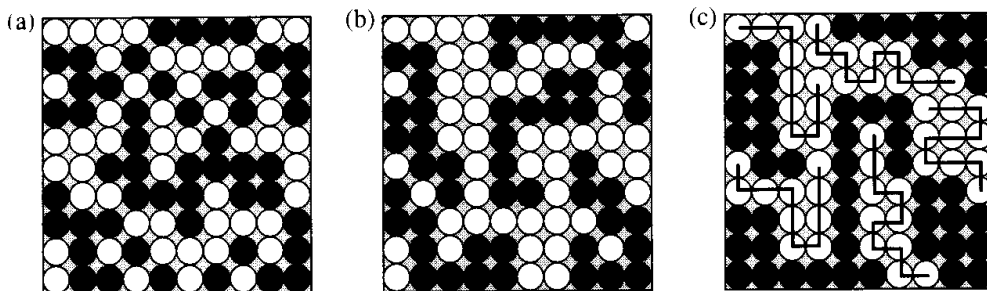
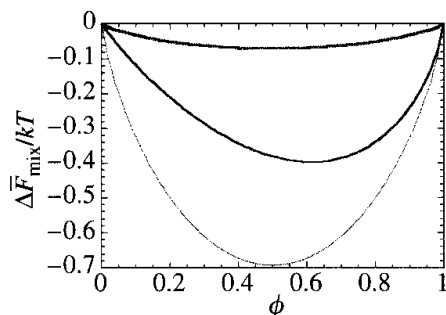


Fig. 4.2 Binary mixtures of (a) a regular solution of 50 white balls and 50 black balls, (b) a polymer solution of five black 10-ball chains, and (c) a polymer blend of five white 10-ball chains and five black 10-ball chains.

**Fig. 4.3**

The mixing free energy of an ideal mixture is always favourable and all compositions are stable. The bottom curve is a regular solution with $N_A = N_B = 1$. The middle curve is a polymer solution with $N_A = 10$ and $N_B = 1$. The top curve is a polymer blend with $N_A = N_B = 10$.

are typically large, making the entropy of mixing [Eq. (4.10)] very small. For this reason, polymers have *stymied entropy*. Connecting monomers into chains drastically reduces the number of possible states of the system. To illustrate this point, simply try to recreate Fig. 4.2(c) with molecules in a different state.

Despite the fact that the mixing entropy is small for polymer blends, it is always positive and hence promotes mixing. Mixtures with no difference in interaction energy between components are called **ideal mixtures**. Let us denote the volume fraction of component A by $\phi_A = \phi$ and the corresponding volume fraction of component B becomes $\phi_B = 1 - \phi$. The free energy of mixing per site for ideal mixtures is purely entropic:

$$\Delta\bar{F}_{\text{mix}} = -T\Delta\bar{S}_{\text{mix}} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) \right]. \quad (4.13)$$

Ideal mixtures are always homogeneous as a result of the mixing entropy always being positive. Figure 4.3 shows the mixing free energy of an ideal regular solution, an ideal polymer solution, and an ideal polymer blend.

The mixing entropy calculated above includes only the translational entropy that results from the many possible locations for the centre of mass of each component. The calculation assumes that the conformational entropy of a polymer is identical in the mixed and pure states. This assumption is very good for polymer blends, where each chain is nearly ideal in the mixed and pure states. However, many polymer solutions have excluded volume that changes the conformation of the polymer in solution, as discussed in Chapter 3. Another important assumption in the entropy of mixing calculation is no volume change on mixing. Real polymer blends and solutions have very small, but measurable, volume changes when mixed.

4.2 Energy of binary mixing

Interactions between species can be either attractive or repulsive. In most experimental situations, mixing occurs at constant pressure and the enthalpic interactions between species must be analysed to find a minimum of the Gibbs free energy of mixing. In the simplified lattice model (**Flory-Huggins theory**) discussed in the present chapter, components are mixed at constant volume and therefore we will be studying the energy of interactions between components and the change in the Helmholtz free energy of mixing.

The energy of mixing can be either negative (promoting mixing) or positive (opposing mixing). Regular solution theory allows for both possibilities, using the lattice model. To estimate the energy of mixing this theory places species into lattice sites randomly, ignoring any correlations. Thus, for all mixtures, favourable or unfavourable interactions between monomers are assumed to be small enough that they do not affect the random placement. Worse still, the regular solution approach effectively cuts the polymer chain into pieces that are the size of the solvent molecules

Energy of binary mixing

(the lattice size) and distributes these pieces randomly. Such a mean-field approach ignores the correlations between monomers along the chain (the chain connectivity). Here, for simplicity, it is assumed that in polymer blends the monomer volumes of species A and B are identical.

Regular solution theory writes the energy of mixing in terms of three pairwise interaction energies (u_{AA} , u_{AB} , and u_{BB}) between adjacent lattice sites occupied by the two species. A mean field is used to determine the average pairwise interaction U_A of a monomer of species A occupying one lattice site with a neighbouring monomer on one of the adjacent sites. The probability of this neighbour being a monomer of species A is assumed to be the volume fraction ϕ_A of these molecules (ignoring the effect of interactions on this probability). The probability of this neighbour being a monomer of species B is $\phi_B = 1 - \phi_A$. The average pairwise interaction of an A-monomer with one of its neighbouring monomers is a volume fraction weighted sum of interaction energies:

$$U_A = u_{AA}\phi_A + u_{AB}\phi_B. \quad (4.14)$$

The corresponding energy of a B-monomer with one of its neighbours is similar to Eq. (4.14):

$$U_B = u_{AB}\phi_A + u_{BB}\phi_B. \quad (4.15)$$

Each lattice site of a regular lattice has z nearest neighbours, where z is the **coordination number** of the lattice. For example, $z=4$ for a square lattice and $z=6$ for a cubic lattice. Therefore, the average interaction energy of an A monomer with all of its z neighbours is zU_A . The average energy per monomer is half of this energy ($zU_A/2$) due to the fact that every pairwise interaction is counted twice (once for the monomer in question and once for its neighbour). The corresponding energy per site occupied by species B is $zU_B/2$. The number of sites occupied by species A (the number of monomers of species A) is $n\phi_A$, where n is the total number of sites in the combined system. The number of sites occupied by monomers of species B is $n\phi_B$. Summing all the interactions gives the total interaction energy of the mixture:

$$U = \frac{zn}{2} [U_A\phi_A + U_B\phi_B]. \quad (4.16)$$

Denoting the volume fraction of species A by $\phi = \phi_A = 1 - \phi_B$, Eqs (4.14)–(4.16) are combined to get the total interaction energy of a binary mixture with n lattice sites:

$$\begin{aligned} U &= \frac{zn}{2} \{ [u_{AA}\phi + u_{AB}(1 - \phi)]\phi + [u_{AB}\phi + u_{BB}(1 - \phi)](1 - \phi) \} \\ &= \frac{zn}{2} [u_{AA}\phi^2 + 2u_{AB}\phi(1 - \phi) + u_{BB}(1 - \phi)^2]. \end{aligned} \quad (4.17)$$

The interaction energy per site in a pure A component before mixing is $zu_{AA}/2$, because each monomer of species A before mixing is only

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surrounded by species A. We ignore the boundary effects because of the very small surface-to-volume ratio for most macroscopic systems. The total number of monomers of species A is $n\phi$ and therefore the total energy of species A before mixing is

$$\frac{zn}{2}u_{AA}\phi$$

and the total energy of species B before mixing is

$$\frac{zn}{2}u_{BB}(1 - \phi).$$

The total energy of both species before mixing is the sum of the energies of the two pure components:

$$U_0 = \frac{zn}{2}[u_{AA}\phi + u_{BB}(1 - \phi)]. \quad (4.18)$$

The energy change on mixing is

$$\begin{aligned} U - U_0 &= \frac{zn}{2}[u_{AA}\phi^2 + 2u_{AB}\phi(1 - \phi) + u_{BB}(1 - \phi)^2 - u_{AA}\phi - u_{BB}(1 - \phi)] \\ &= \frac{zn}{2}[u_{AA}(\phi^2 - \phi) + 2u_{AB}\phi(1 - \phi) + u_{BB}(1 - 2\phi + \phi^2 - 1 + \phi)] \\ &= \frac{zn}{2}[u_{AA}\phi(\phi - 1) + 2u_{AB}\phi(1 - \phi) + u_{BB}\phi(\phi - 1)] \\ &= \frac{zn}{2}\phi(1 - \phi)(2u_{AB} - u_{AA} - u_{BB}) \end{aligned} \quad (4.19)$$

It is convenient to study the intensive property, which is the energy change on mixing per site:

$$\Delta\bar{U}_{\text{mix}} = \frac{U - U_0}{n} = \frac{z}{2}\phi(1 - \phi)(2u_{AB} - u_{AA} - u_{BB}). \quad (4.20)$$

The **Flory interaction parameter** χ is defined to characterize the difference of interaction energies in the mixture:

$$\chi \equiv \frac{z(2u_{AB} - u_{AA} - u_{BB})}{2kT}. \quad (4.21)$$

Defined in this fashion, χ is a dimensionless measure of the differences in the strength of pairwise interaction energies between species in a mixture (compared with the same species in their pure component states). Using this definition, we write the **energy of mixing** per lattice site as

$$\Delta\bar{U}_{\text{mix}} = \chi\phi(1 - \phi)kT. \quad (4.22)$$

This energy equation is a mean-field description of all binary regular mixtures: regular solutions, polymer solutions, and polymer blends.

Combining with Eq. (4.10) for the entropy of mixing, we arrive at the **Helmholtz free energy of mixing** per lattice site:

$$\begin{aligned}\Delta\bar{F}_{\text{mix}} &= \Delta\bar{U}_{\text{mix}} - T\Delta\bar{S}_{\text{mix}} \\ &= kT\left[\frac{\phi}{N_A}\ln\phi + \frac{1-\phi}{N_B}\ln(1-\phi) + \chi\phi(1-\phi)\right].\end{aligned}\quad (4.23)$$

The free energy of mixing per unit volume is $\Delta\bar{F}_{\text{mix}}/v_0$. Equation (4.23) was first calculated by Huggins and later independently derived by Flory, and is commonly referred to as the **Flory–Huggins equation**.

For non-polymeric mixtures with $N_A = N_B = 1$, this equation was developed earlier by Hildebrand and is called **regular solution theory**:

$$\Delta\bar{F}_{\text{mix}} = kT[\phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)].\quad (4.24)$$

For polymer solutions, $N_A = N$ and $N_B = 1$, reducing Eq. (4.23) to the **Flory–Huggins equation for polymer solutions**:

$$\Delta\bar{F}_{\text{mix}} = kT\left[\frac{\phi}{N}\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right].\quad (4.25)$$

The first two terms in the free energy of mixing [Eq. (4.23)] have entropic origin and always act to promote mixing, although with blends of long-chain polymers these terms are quite small. The last term has energetic origin, and can be positive (opposing mixing), zero [ideal mixtures—Eq. (4.13)], or negative (promoting mixing) depending on the sign of the interaction parameter χ .

If there is a net attraction between species (i.e. they like each other better than they like themselves), $\chi < 0$ and a single-phase mixture is favourable for all compositions. More often there is a net repulsion between species (they like themselves more than each other) and the Flory interaction parameter is positive $\chi > 0$. In Section 4.4, we will show that in this case the equilibrium state of the mixture depends not on the sign of the free energy of mixing $\Delta\bar{F}_{\text{mix}}$ at the particular composition of interest, but on the functional dependence of this free energy on the composition ϕ for the whole range of compositions. This functional dependence $\Delta\bar{F}_{\text{mix}}(\phi)$ depends on the value of the Flory interaction parameter χ as well as on the degrees of polymerization of both molecules N_A and N_B .

It is very important to know the value of the Flory interaction parameter χ for a given mixture. Methods of measuring this parameter are discussed in Section 4.6 and tables of χ parameters are listed in many reference books (see the 1996 review by Balsara).

For non-polar mixtures with species interacting mainly by dispersion forces, the interaction parameter χ can be estimated by the method developed by Hildebrand and Scott. It is based on the **solubility parameter** δ related to the energy of vapourization ΔE of a molecule. For example, for a molecule of species *A* the solubility parameter is defined as

$$\delta_A \equiv \sqrt{\frac{\Delta E_A}{v_A}},\quad (4.26)$$

Thermodynamics of mixing

where v_A is the volume of molecule A [Eq. (4.2)]. The energy of vapourization ΔE_A of a molecule A is the energy of all the interactions between the molecule and its neighbours that have to be disrupted to remove the molecule from the pure A state. The ratio $\Delta E_A/v_A$ is called the cohesive energy density and is the interaction energy per unit volume between the molecules in the pure A state. The interaction energy per site in the pure A state $zu_{AA}/2$ [see the paragraph below Eq. (4.17)] is therefore related to the solubility parameter δ_A .

$$-\frac{zu_{AA}}{2} = v_0 \frac{\Delta E_A}{v_A} = v_0 \delta_A^2, \quad (4.27)$$

where v_0 is the volume per site. Note that the minus sign is due to the fact that the interaction energy is negative $u_{AA} < 0$, while the energy of vapourization is defined to be positive. Similarly, the interaction energy per site in the pure B state is

$$-\frac{zu_{BB}}{2} = v_0 \frac{\Delta E_B}{v_B} = v_0 \delta_B^2, \quad (4.28)$$

where v_B is the volume of molecule B [Eq. (4.3)]. The cohesive energy density of interaction between molecules A and B is estimated from the geometric mean approximation

$$-\frac{zu_{AB}}{2} = v_0 \delta_A \delta_B. \quad (4.29)$$

Substituting Eqs (4.27)–(4.29) into the definition of the Flory interaction parameter [Eq. (4.21)] allows it to be written in terms of solubility parameter difference.²

$$\chi \approx v_0 \frac{[\delta_A^2 + \delta_B^2 - 2\delta_A \delta_B]}{kT} = \frac{v_0}{kT} (\delta_A - \delta_B)^2. \quad (4.30)$$

Since χ is related to the *square* of the difference in solubility parameters it is clear why the Flory interaction parameter is usually positive $\chi > 0$. The above approach works reasonably well for non-polar interactions, which only have van der Waals forces between species, and does not work in mixtures with strong polar or specific interactions, such as hydrogen bonds.

One of the major assumptions of the Flory–Huggins theory is that there is no volume change on mixing and that monomers of both species can fit on the sites of the same lattice. In most real polymer blends, the volume per monomer changes upon mixing. Some monomers may pack together better with certain other monomers. The volume change on mixing and local packing effects lead to a temperature-independent additive constant in the expression of the Flory interaction parameter. In practice, these

² Note that since the Flory χ parameter is defined in terms of energies *per site*, it is proportional to the site volume v_0 . The site volume, therefore, must be specified whenever χ is discussed.

effects are not fully understood and all deviations from the lattice model are lumped into the interaction parameter χ , which can display non-trivial dependences on composition, chain length, and temperature. Empirically, the temperature dependence of the Flory interaction parameter is often written as the sum of two terms:

$$\chi(T) \cong A + \frac{B}{T} \quad (4.31)$$

The temperature-independent term A is referred to as the ‘entropic part’ of χ , while B/T is called the ‘enthalpic part’. The parameters A and B have been tabulated for many polymer blends and we list representative examples in Table 4.3. Isotopic blends typically have small positive χ parameters (deuterated polystyrene blended with ordinary polystyrene dPS/PS is an example) making them only phase separate at very high molar masses. $PS/PMMA$ has four entries in Table 4.3, which reflect the differences encountered by labelling various species with deuterium. $PS/PMMA$ is typical of many polymer pairs, for which the χ parameter is positive and of order 0.01, making only low molar mass polymers form miscible blends. $PVME/PS$, PS/PPO , and $PS/TMPC$ have a strongly negative χ parameter over a wide range of temperatures (of order -0.01) but since $A > 0$ and $B < 0$, these blends phase separate on heating. $PEO/PMMA$, $PP/hhPP$ and $PIB/hhPP$, all represent blends with very weak interactions between components ($\chi \cong 0$).

Additionally, the parameters A and B are often found to depend weakly on chain lengths and composition. Shortcomings of the Flory–Huggins theory are usually lumped into the interaction parameter χ . The Flory–Huggins equation (with all the corrections combined in χ) contains all of the thermodynamic information needed to decide the equilibrium

Table 4.3 Temperature dependence of the Flory interaction parameters of polymer blends [Eq. (4.31)] with $v_0 = 100 \text{ \AA}^3$

Polymer blend	A	B (K)	T range ($^{\circ}\text{C}$)
dPS/PS	-0.00017	0.117	150–220
$dPS/PMMA$	0.0174	2.39	120–180
$PS/dPMMA$	0.0180	1.96	170–210
$PS/PMMA$	0.0129	1.96	100–200
$dPS/dPMMA$	0.0154	1.96	130–210
$PVME/PS$	0.103	-43.0	60–150
dPS/PPO	0.059	-32.5	180–330
$dPS/TMPC$	0.157	-81.3	190–250
$PEO/dPMMA$	-0.0021	-	80–160
$PP/hhPP$	-0.00364	1.84	30–130
$PIB/dhhPP$	0.0180	-7.74	30–170

dPS —deuterated polystyrene; PS —polystyrene; $PMMA$ —poly(methyl methacrylate); $dPMMA$ —deuterated poly(methyl methacrylate); $PVME$ —poly(vinyl methyl ether); PPO —poly(2,6-dimethyl 1,4-phenylene oxide); $TMPC$ —tetramethylpolycarbonate; PEO —poly(ethylene oxide); PP —polypropylene; $hhPP$ —head-to-head polypropylene; PIB —polyisobutylene; $dhhPP$ —deuterium labelled head-to-head polypropylene (after N. P. Balsara, *Physical Properties of Polymers Handbook*, AIP Press, 1996, Chapter 19).

state of a mixture and whether any metastable states are possible, as discussed next.

4.3 Equilibrium and stability

The definition of thermodynamic equilibrium is the state of the system with minimum free energy. Consider the states of a brick, shown in Fig. 4.4. The angle that the long side of the brick makes with the ground is θ , as defined in state A. The stable equilibrium state, or ground state of the brick, is shown as state B in Fig. 4.4, with the brick lying on the ground. This state is stable because any perturbations in the angle that the brick makes with the ground lead to its centre-of-mass being higher above the ground than the ground state, thereby increasing its potential energy. If the brick is balanced on its edge (state A in Fig. 4.4), any small fluctuations would lead to its fall and state A is called unstable. When standing on one end (state C), the brick has its centre-of-mass at half of the height of the brick. Any small change in θ from state C will increase the potential energy by raising the centre-of-mass of the brick. Thus, state C is **metastable**: small perturbations do not allow the brick to move from state C to state B, even though state B has lower energy and thus is the equilibrium state of the brick. Indeed, the brick in state C would stand until an earthquake causes it to move to state B. Hence, a long time duration of a given state is insufficient information to conclude that the state is the equilibrium state. The graph in Fig. 4.4 summarizes the free energy of the brick as a function of angle θ .

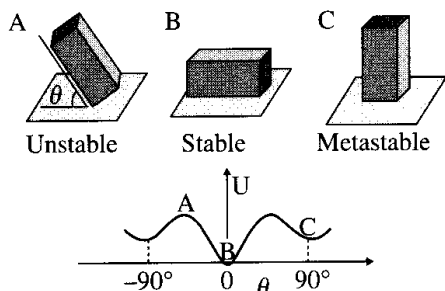


Fig. 4.4
The states of a brick.

Consider the local stability of a homogeneous mixture of composition ϕ_0 with free energy $F_{\text{mix}}(\phi_0)$ that is either locally concave or convex, shown in Fig. 4.5. Stability is determined by whether the free energy of the mixed state $F_{\text{mix}}(\phi_0)$ is higher or lower than that of a phase separated state, $F_{\alpha\beta}(\phi_0)$. If the system with overall composition ϕ_0 is in a state with two phases, with volume fraction of A species in the α phase ϕ_α and the fraction of A component in the β phase ϕ_β (see Fig. 4.5), the relative amounts of each phase are determined from the **lever rule**. With the fraction f_α of the volume of the material having composition ϕ_α (and fraction $f_\beta = 1 - f_\alpha$ having composition ϕ_β), the total volume fraction of A component in the system is the sum of contributions from the two phases:

$$\phi_0 = f_\alpha \phi_\alpha + f_\beta \phi_\beta. \quad (4.32)$$

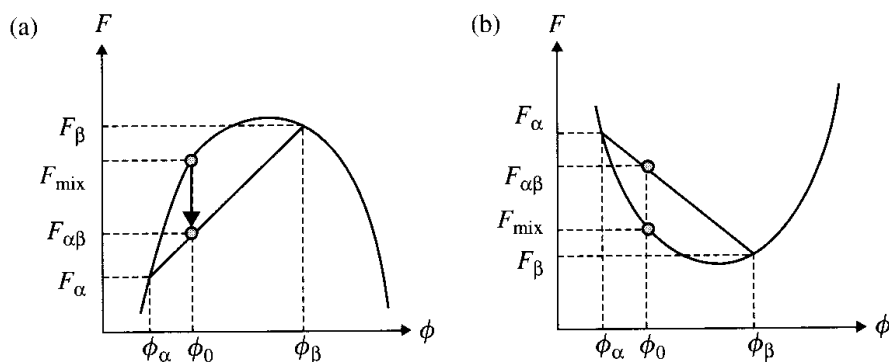


Fig. 4.5
Composition dependence of free energy, with examples of systems that are (a) unstable and (b) locally stable. Local stability is determined by the sign of the second derivative of free energy with respect to composition.

This equation can be solved for the fractions of the material that will have each composition (since $f_\beta = 1 - f_\alpha$):

$$f_\alpha = \frac{\phi_\beta - \phi_0}{\phi_\beta - \phi_\alpha} \quad \text{and} \quad f_\beta = 1 - f_\alpha = \frac{\phi_0 - \phi_\alpha}{\phi_\beta - \phi_\alpha}. \quad (4.33)$$

The free energy of the demixed state is the weighted average of the free energies of the material in each of the two states (F_α and F_β), neglecting the interfacial energy (surface tension) between the two phases:

$$F_{\alpha\beta}(\phi_0) = f_\alpha F_\alpha + f_\beta F_\beta = \frac{(\phi_\beta - \phi_0)F_\alpha + (\phi_0 - \phi_\alpha)F_\beta}{\phi_\beta - \phi_\alpha}. \quad (4.34)$$

This linear composition dependence of the free energy of the demixed state $F_{\alpha\beta}(\phi_0)$ results in the straight lines in Fig. 4.5 that connect the free energies F_α and F_β of the two compositions ϕ_α and ϕ_β . The local curvature of the free energy determines local stability, as demonstrated in Fig. 4.5. If the composition dependence of the free energy is concave [Fig. 4.5(a)], the system can spontaneously lower its free energy by phase separating into two phases, since $F_{\alpha\beta}(\phi_0) < F_{\text{mix}}(\phi_0)$.

On the other hand, when the composition dependence of the free energy is convex, as shown in Fig. 4.5(b), any mixed state has lower free energy than any state the blend could phase separate into $F_{\text{mix}}(\phi_0) < F_{\alpha\beta}(\phi_0)$, making the mixed state locally stable. The criterion for local stability is written in terms of the second derivative of the free energy:

$$\frac{\partial^2 F_{\text{mix}}}{\partial \phi^2} < 0 \quad \text{unstable}, \quad (4.35)$$

$$\frac{\partial^2 F_{\text{mix}}}{\partial \phi^2} > 0 \quad \text{locally stable}. \quad (4.36)$$

Ideal mixtures with $\Delta \bar{U}_{\text{mix}} = 0$ have their free energy of mixing [Eq. (4.13)] convex over the entire composition range, as can be seen in Fig. 4.3. To understand why it is convex, we differentiate Eq. (4.13) with respect to composition

$$\frac{\partial \Delta \bar{F}_{\text{mix}}}{\partial \phi} = -T \frac{\partial \Delta \bar{S}_{\text{mix}}}{\partial \phi} = kT \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1 - \phi)}{N_B} - \frac{1}{N_B} \right]. \quad (4.37)$$

Notice that this purely entropic contribution diverges at both extremes of composition ($\partial \Delta \bar{F}_{\text{mix}} / \partial \phi \rightarrow -\infty$ as $\phi \rightarrow 0$ and $\partial \Delta \bar{F}_{\text{mix}} / \partial \phi \rightarrow \infty$ as $\phi \rightarrow 1$). This divergence means that a small amount of either species will *always* dissolve even if there are strong unfavourable energetic interactions. Differentiating the free energy of mixing a second time determines the stability of the mixed state for ideal mixtures

$$\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} = -T \frac{\partial^2 \Delta \bar{S}_{\text{mix}}}{\partial \phi^2} = kT \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} \right] > 0. \quad (4.38)$$

Homogeneous ideal mixtures are stable for all compositions because *entropy always acts to promote mixing*, and the ideal mixture does not have any energetic contribution to its free energy.

The opposite case where the energy dominates is found at $T=0$ K, because the entropic contribution vanishes. The free energy only has an energetic part given, for example, by Eq. (4.22) for regular mixtures. Differentiating Eq. (4.22) twice with respect to composition determines whether the blend is locally stable at 0 K

$$\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} = \frac{\partial^2 \Delta \bar{U}_{\text{mix}}}{\partial \phi^2} = -2\chi kT \quad (4.39)$$

The stability criterion at $T=0$ K can be determined from either Eq. (4.21) or Eq. (4.31)

$$\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} = -z(2u_{AB} - u_{AA} - u_{BB}) = -2kB \quad (4.40)$$

The parameter B describes the temperature dependence of χ in Eq. (4.31). If the components of the mixture like themselves more than each other

$$u_{AB} > \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B > 0$$

the free energy of mixing is concave (Fig. 4.6, top curve) and homogeneous mixtures are unstable for all compositions at $T=0$ K because the second derivative of the free energy of mixing is negative [Eq. (4.35)]. Any mixture phase separates into the two pure components at $T=0$ K since entropy makes no contribution at this special temperature. This case corresponds to positive Flory interaction parameter $\chi > 0$.

If the components like each other better than themselves

$$u_{AB} < \frac{u_{AA} + u_{BB}}{2} \quad \text{or} \quad B < 0$$

the free energy of mixing is convex (Fig. 4.6, bottom curve) and homogeneous mixtures of any composition are stable at $T=0$ K. This case corresponds to negative Flory interaction parameter $\chi < 0$.

Real mixtures have both energetic and entropic contributions to their free energy of mixing. The local stability of the mixture is determined by the sign of the second derivative of the free energy with respect to composition:

$$\begin{aligned} \frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} &= \frac{\partial^2 \Delta \bar{U}_{\text{mix}}}{\partial \phi^2} - T \frac{\partial^2 \Delta \bar{S}_{\text{mix}}}{\partial \phi^2} \\ &= kT \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} \right] - 2\chi kT. \end{aligned} \quad (4.41)$$

At finite temperatures, $\Delta \bar{F}_{\text{mix}}$ is convex at both ends of the composition range because its second derivative is positive due to the diverging slope of the entropy of mixing $\Delta \bar{S}_{\text{mix}}$.

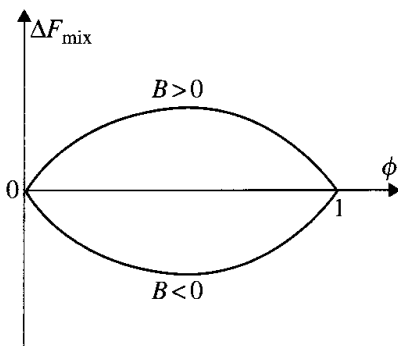


Fig. 4.6

At $T=0$ K, the mixing free energy is determined by the energy of mixing. If $B > 0$, mixing is unfavourable and all blend compositions are unstable. If $B < 0$, mixing is favourable and all blend compositions are stable.

For example, consider a polymer blend with $N_A = 200$ and $N_B = 100$, for which $\chi T = 5$ K. At high temperatures the entropic term of the mixing free energy dominates, and all blend compositions are stable, as shown in Fig. 4.7 at 350 K.

As temperature is lowered the entropic term diminishes, allowing the repulsive energetic term to start to be important at intermediate compositions. Entropy always dominates the extremes of composition (due to the divergent first derivative) making those extremes stable. Below some critical temperature T_c (defined in detail in Section 4.4), a composition range with concave free energy appears, which makes intermediate compositions unstable. Below T_c there is a range of compositions for which there are phase separated states with lower free energy than the homogeneous state. Many demixed states have lower free energy than the homogeneous state, but the lowest free energy state defines the equilibrium state. Straight lines connecting the two phase compositions determine the free energy of the phase separated state. In order to minimize the free energy, the system chooses the compositions that have the lowest possible straight line, which is a common tangent. The phases present are thus determined by the **common tangent rule**. This common tangent minimization of the free energy of mixing effectively requires that the chemical potential of each species in both phases are balanced at equilibrium. The two equilibrium compositions ϕ' and ϕ'' at 250 K correspond to a common tangent line in Fig. 4.7. For any overall composition in the **miscibility gap** between ϕ' and ϕ'' , the system can minimize its free energy by phase separating into two phases of composition ϕ' and ϕ'' . The amounts of each phase are determined by the lever rule outlined above [Eq. (4.33)]. The composition ranges $0 < \phi < \phi'$ or $\phi'' < \phi < 1$ are outside the miscibility gap and the homogeneously mixed state is the stable equilibrium state for these blend compositions.

Within the miscibility gap there are unstable and metastable regions, separated by inflection points at which the second derivative of the free energy is zero ($\partial^2 \Delta \bar{F}_{\text{mix}} / \partial \phi^2 = 0$). Between the inflection points, the second derivative of the free energy is negative and the homogeneously mixed state is unstable. Even the smallest fluctuations in composition lower the free energy, leading to spontaneous phase separation (called **spinodal decomposition**). Between the inflection points and the equilibrium phase separated compositions, there are two regions that have positive second derivative of the free energy of mixing. Even though the free energy of the homogeneous state is larger than that of the phase-separated state (on the common tangent line) the mixed state is locally stable to small composition fluctuations. Such states are metastable because large fluctuations are required for the system to reach thermodynamic equilibrium. Phase separation in this metastable regime occurs by **nucleation and growth**. The nuclei of the more stable phase must be larger than some critical size in order to grow in the metastable region because of the surface tension between phases (see Problem 4.15). The new phase can grow only when a sufficiently large fluctuation creates a domain larger than the critical size.

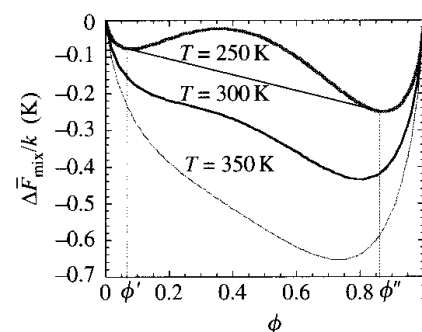


Fig. 4.7

Composition dependence of the free energy of mixing at three temperatures for a hypothetical blend with $N_A = 200$ and $N_B = 100$, for which $\chi = (5 \text{ K})/T$.

4.4 Phase diagrams

By considering the temperature dependence of the free energy of mixing, a phase diagram can be constructed to summarize the phase behaviour of the mixture, showing regions of stability, instability, and metastability. Recall the free energy of mixing for a polymer blend

$$\Delta\bar{F}_{\text{mix}} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln(1-\phi) + \chi\phi(1-\phi) \right]. \quad (4.42)$$

The phase boundary is determined by the common tangent of the free energy at the compositions ϕ' and ϕ'' corresponding to the two equilibrium phases

$$\left(\frac{\partial \Delta\bar{F}_{\text{mix}}}{\partial \phi} \right)_{\phi=\phi'} = \left(\frac{\partial \Delta\bar{F}_{\text{mix}}}{\partial \phi} \right)_{\phi=\phi''}. \quad (4.43)$$

This derivative of the free energy of mixing per site with respect to volume fraction of component A is

$$\frac{\partial \Delta\bar{F}_{\text{mix}}}{\partial \phi} = kT \left[\frac{\ln \phi}{N_A} + \frac{1}{N_A} - \frac{\ln(1-\phi)}{N_B} - \frac{1}{N_B} + \chi(1-2\phi) \right]. \quad (4.44)$$

For the simple example of a symmetric polymer blend with $N_A = N_B = N$, the common tangent line is horizontal.

$$\begin{aligned} \left(\frac{\partial \Delta\bar{F}_{\text{mix}}}{\partial \phi} \right)_{\phi=\phi'} &= \left(\frac{\partial \Delta\bar{F}_{\text{mix}}}{\partial \phi} \right)_{\phi=\phi''} \\ &= kT \left[\frac{\ln \phi}{N} - \frac{\ln(1-\phi)}{N} + \chi(1-2\phi) \right] = 0. \end{aligned} \quad (4.45)$$

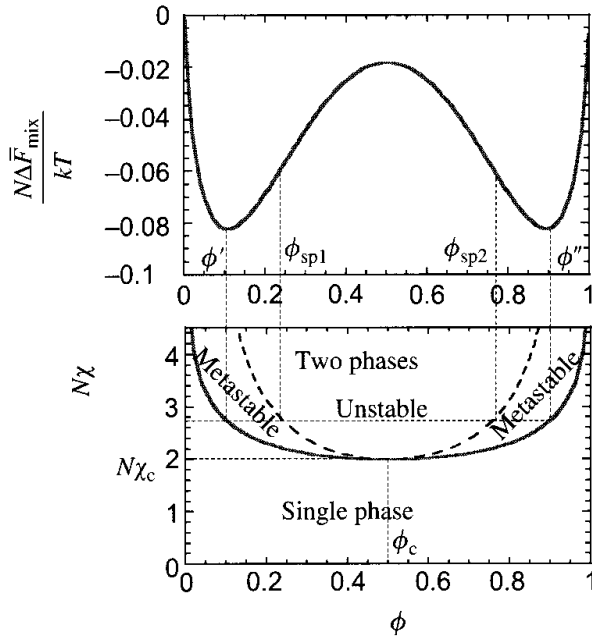
The above equation can be solved for the interaction parameter corresponding to the phase boundary—the **binodal** (solid line in the bottom part of Fig. 4.8) of a symmetric blend:

$$\chi_b = \frac{1}{2\phi-1} \left[\frac{\ln \phi}{N} - \frac{\ln(1-\phi)}{N} \right] = \frac{\ln(\phi/(1-\phi))}{(2\phi-1)N}. \quad (4.46)$$

Using the phenomenological temperature dependence of the interaction parameter [Eq. (4.31)], this relation can be transformed to the binodal of the phase diagram in the space of temperature and composition:

$$T_b = \frac{B}{\ln[\phi/(1-\phi)]/[(2\phi-1)N] - A}. \quad (4.47)$$

The binodal for binary mixtures coincides with the **coexistence curve**, since for a given temperature (or $N\chi$) with overall composition in the two-phase region, the two compositions that coexist at equilibrium can be read off the binodal. Any overall composition at temperature T within the miscibility gap defined by the binodal has its minimum free energy in a

**Fig. 4.8**

Composition dependence of the free energy of mixing for a symmetric polymer blend with the product $\chi N = 2.7$ (top figure) and the corresponding phase diagram (bottom figure). Binodal (solid curve) and spinodal (dashed curve) are shown on the phase diagram.

phase-separated state with the compositions given by the two coexistence curve compositions ϕ' and ϕ'' .

Returning to the general case of an asymmetric blend, the inflection points in $\Delta\bar{F}_{\text{mix}}(\phi)$ can be found by equating the second derivative of the free energy [Eq. (4.41)] to zero:

$$\frac{\partial^2 \Delta\bar{F}_{\text{mix}}}{\partial \phi^2} = kT \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} - 2\chi \right] = 0. \quad (4.48)$$

The curve corresponding to the inflection point is the boundary between unstable and metastable regions and is called the **spinodal** (the dashed line in the bottom part of Fig. 4.8):

$$\chi_s = \frac{1}{2} \left[\frac{1}{N_A \phi} + \frac{1}{N_B (1 - \phi)} \right]. \quad (4.49)$$

This spinodal can also be transformed to a phase diagram in the temperature–composition plane by using the experimentally determined $\chi(T)$ via Eq. (4.31):

$$T_s = \frac{B}{\frac{1}{2} [1/(N_A \phi) + 1/(N_B (1 - \phi))] - A}. \quad (4.50)$$

In a binary blend the lowest point on the spinodal curve corresponds to the **critical point**:

$$\frac{\partial \chi_s}{\partial \phi} = \frac{1}{2} \left[-\frac{1}{N_A \phi^2} + \frac{1}{N_B (1 - \phi)^2} \right] = 0. \quad (4.51)$$

Thermodynamics of mixing

The solution of this equation gives the **critical composition**:

$$\phi_c = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}}. \quad (4.52)$$

Substituting this critical composition back into the equation of the spinodal [Eq. (4.49)] determines the critical interaction parameter:

$$\chi_c = \frac{1}{2} \frac{(\sqrt{N_A} + \sqrt{N_B})^2}{N_A N_B} = \frac{1}{2} \left(\frac{1}{\sqrt{N_A}} + \frac{1}{\sqrt{N_B}} \right)^2. \quad (4.53)$$

Equation (4.31) can again be utilized to determine the **critical temperature** from χ_c :

$$T_c = \frac{B}{\chi_c - A} = \frac{B}{\frac{1}{2}(1/\sqrt{N_A} + 1/\sqrt{N_B})^2 - A}. \quad (4.54)$$

For a symmetric polymer blend ($N_A = N_B = N$), the whole phase diagram is symmetric (see Fig. 4.8) with the critical composition

$$\phi_c = \frac{1}{2} \quad (4.55)$$

and very small critical interaction parameter

$$\chi_c = \frac{2}{N}. \quad (4.56)$$

Since this critical interaction parameter is very small for blends of long chains, most polymer blends have $\chi > \chi_c$ and thus are phase separated over some composition range (within the miscibility gap). Only blends with either very weak repulsion ($0 < \chi < \chi_c$), or a net attraction between components of the mixture ($\chi < 0$) form homogeneous (single-phase) blends over the whole composition range.

In polymer solutions ($N_A = N$ and $N_B = 1$), the phase diagram is strongly asymmetric with low critical composition

$$\phi_c = \frac{1}{\sqrt{N} + 1} \cong \frac{1}{\sqrt{N}} \quad (4.57)$$

and critical interaction parameter close to 1/2

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \frac{1}{2N} \cong \frac{1}{2} + \frac{1}{\sqrt{N}}. \quad (4.58)$$

Note that the spinodal and binodal for any binary mixture meet at the critical point (Fig. 4.8). For interaction parameters χ below the critical one (for $\chi < \chi_c$) the homogeneous mixture is stable at any composition $0 \leq \phi \leq 1$. For higher values of the interaction parameter (for $\chi > \chi_c$) there is a miscibility gap between the two branches of the binodal in Fig. 4.8. For any composition in a miscibility gap, the equilibrium state corresponds to two phases with compositions ϕ' and ϕ'' located on the two branches of the coexistence curve at the same value of χ .

Experimentally, the interaction parameter is most conveniently changed by varying temperature T [see Eq. (4.31)]. Phase diagrams are typically plotted in the temperature – composition plane. Examples of phase diagrams for a polymer blend and a polymer solution are shown in Fig. 4.9. The binodal line separates the phase diagrams into a single-phase region and a two-phase region.

If $B > 0$ in Eq. (4.31), then χ decreases as temperature is raised. This situation is depicted in Fig. 4.10. The highest temperature of the two-phase region is the **upper critical solution temperature (UCST)** T_c . For all $T > T_c$, the homogeneous mixtures are stable. On the other hand, if $B < 0$ in Eq. (4.31), then χ decreases as temperature is lowered. The lowest temperature of the two-phase region is the **lower critical solution temperature (LCST)**, and this case is shown in Fig. 4.11. While the case of $B > 0$ is more

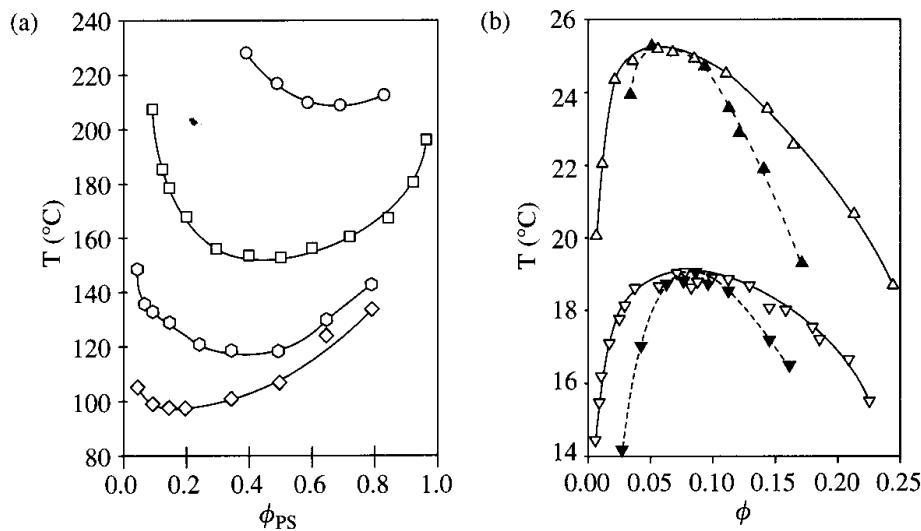


Fig. 4.9

Phase diagrams of polymer blends and solutions (open symbols are binodals and filled symbols are spinodals). (a) Polymer blends of poly(vinyl methyl ether) ($M = 51\,500\text{ g mol}^{-1}$) and various molar masses of polystyrene (circles have $M = 10\,000\text{ g mol}^{-1}$, squares have $M = 20\,400\text{ g mol}^{-1}$, hexagons have $M = 51\,000\text{ g mol}^{-1}$, diamonds have $M = 200\,000\text{ g mol}^{-1}$), data from T. K. Kwei and T. T. Wang, in: *Polymer Blends*, Vol. 1 (D. R. Paul and S. Newman, editors), Academic Press, 1978. (b) Polyisoprene solutions in dioxane (upside-down triangles have $M = 53\,300\text{ g mol}^{-1}$, triangles have $M = 133\,000\text{ g mol}^{-1}$), data from N. Takano *et al.*, *Polym. J.* **17**, 1123 (1985).

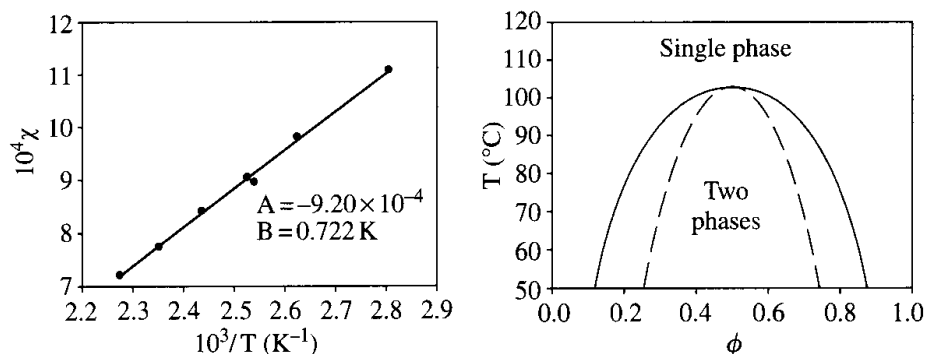
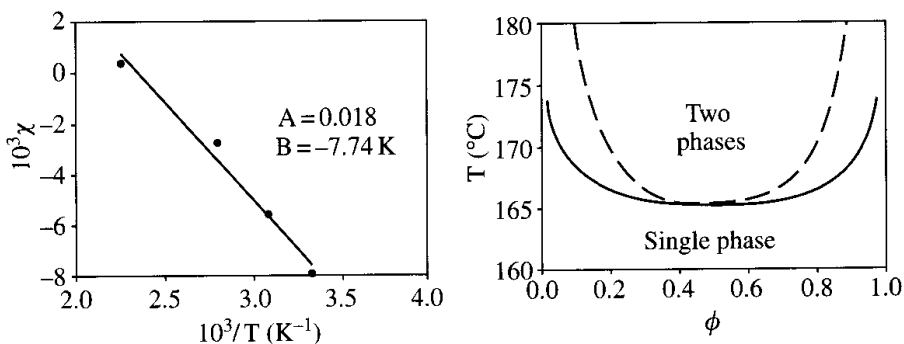


Fig. 4.10

Temperature dependence of χ for mixtures of hydrogenated polybutadiene (88% vinyl) and deuterated polybutadiene (78% vinyl) and the calculated phase diagram from Flory–Huggins theory with $N_A = N_B = 2000$ and $v_0 = 100\text{ \AA}^3$. The binodal is the solid curve and the spinodal is dashed. Adapted from N. P. Balsara, *Physical Properties of Polymers Handbook* (J. E. Mark, editor), AIP Press, 1996, Chapter 19.

Fig. 4.11

Temperature dependence of χ for mixtures of polyisobutylene and deuterated head-to-head polypropylene and the calculated phase diagram from Flory–Huggins theory with $N_A = N_B = 6000$ and $v_0 = 100 \text{ \AA}^3$. The binodal is the solid curve and the spinodal is dashed. Adapted from N. P. Balsara, *Physical Properties of Polymers Handbook* (J. E. Mark, editor), AIP Press, 1996, Chapter 19.



common and better understood, there are many examples of polymer blends that phase separate when temperature is raised, such as polystyrene/poly(vinyl methyl ether). There are also examples where B varies with temperature, changing sign as temperature is changed and resulting in both UCST and LCST, as seen for the polymer solution polystyrene/cyclopentane.

Consider a sudden temperature jump that brings a homogeneous mixture at the critical composition ϕ_c into the two-phase region. The system will spontaneously phase separate into two phases with compositions given by the values on the coexistence curve at that new temperature. This spontaneous phase separation, called spinodal decomposition, occurs because the mixture is locally unstable. Any small composition fluctuation is sufficient to initiate the phase separation process. At any point inside the spinodal curve, the mixture is locally unstable and spontaneously phase separates by the spinodal decomposition process.

The points of the phase diagram between the spinodal and binodal curves correspond to metastable mixtures. The metastable homogeneous state is stable against small composition fluctuations and requires a larger nucleation event to initiate phase separation into the equilibrium phases given by the coexistence curve. This phase separation process is called nucleation and growth.

4.5 Mixtures at low compositions

Consider adding a small amount of A molecules to a liquid of B molecules ($\phi \ll 1$). The free energy of mixing per site

$$\Delta \bar{F}_{\text{mix}} = kT \left[\frac{\phi}{N_A} \ln \phi + \frac{1-\phi}{N_B} \ln (1-\phi) + \chi \phi (1-\phi) \right] \quad (4.59)$$

can be expanded into a power series in composition ϕ of the A-molecules. For small values of composition $\phi \ll 1$, the expansion of the logarithm is $\ln(1-\phi) \cong -\phi - \phi^2/2 - \phi^3/3 - \dots$. The second term in the free energy of mixing [Eq. (4.59)] becomes a power series for small ϕ (written here up to the third order in ϕ):

$$\frac{(1-\phi)}{N_B} \ln(1-\phi) = \frac{1}{N_B} \left(-\phi + \frac{\phi^2}{2} + \frac{\phi^3}{6} + \dots \right). \quad (4.60)$$

The free energy of mixing per site can then be rewritten for small ϕ :

$$\Delta\bar{F}_{\text{mix}} = kT \left[\frac{\phi}{N_A} \ln \phi + \phi \left(\chi - \frac{1}{N_B} \right) + \frac{\phi^2}{2} \left(\frac{1}{N_B} - 2\chi \right) + \frac{\phi^3}{6N_B} + \dots \right]. \quad (4.61)$$

4.5.1 Osmotic pressure

Imagine a semipermeable membrane that prevents passage of A molecules, but allows passage of B molecules. The difference of pressure across this membrane is called the osmotic pressure of A molecules (see Section 1.7.1). The osmotic pressure is defined as the rate of change of the total free energy of the system $\Delta F_{\text{mix}} = n\Delta\bar{F}_{\text{mix}}$ with respect to volume at constant number of A molecules:

$$\Pi \equiv - \left. \frac{\partial \Delta F_{\text{mix}}}{\partial V} \right|_{n_A} \quad (4.62)$$

The volume fraction ϕ of n_A molecules each with N_A monomers is the ratio of their volume to the volume V of the system:

$$\phi = \frac{b^3 n_A N_A}{V}. \quad (4.63)$$

The derivative with respect to volume V can be expressed in terms of the derivative with respect to composition ϕ at constant number of A-molecules n_A :

$$\partial V = (b^3 n_A N_A) \partial \left(\frac{1}{\phi} \right) = - \frac{b^3 n_A N_A}{\phi^2} \partial \phi. \quad (4.64)$$

Note that the number of lattice sites n can be expressed in terms of the number of A molecules n_A as $n = n_A N_A / \phi$. The osmotic pressure is then calculated from the derivative of $\Delta\bar{F}_{\text{mix}}/\phi$ with respect to composition:

$$\begin{aligned} \Pi &= - \left. \frac{\partial (n\Delta\bar{F}_{\text{mix}})}{\partial V} \right|_{n_A} = \frac{\phi^2}{b^3 n_A N_A} \left. \frac{\partial (n_A N_A \Delta\bar{F}_{\text{mix}}/\phi)}{\partial \phi} \right|_{n_A} \\ &= \frac{\phi^2}{b^3} \left. \frac{\partial (\Delta\bar{F}_{\text{mix}}/\phi)}{\partial \phi} \right|_{n_A}. \end{aligned} \quad (4.65)$$

Differentiating the ratio of free energy of mixing $\Delta\bar{F}_{\text{mix}}$ and composition ϕ with respect to composition gives the mean-field expression for osmotic pressure, valid for small ϕ :

$$\Pi = \frac{kT}{b^3} \left[\frac{\phi}{N_A} + \frac{\phi^2}{2} \left(\frac{1}{N_B} - 2\chi \right) + \frac{\phi^3}{3N_B} + \dots \right]. \quad (4.66)$$

Thermodynamics of mixing

This expression of osmotic pressure can be written in the form of the virial expansion in terms of number density of A monomers $c_n = \phi/b^3$ [see Eq. (3.8)]

$$\begin{aligned}\Pi &= kT \left[\frac{c_n}{N_A} + \left(\frac{1}{N_B} - 2\chi \right) b^3 \frac{c_n^2}{2} + \frac{b^6}{3N_B} c_n^3 + \dots \right] \\ &= kT \left[\frac{c_n}{N_A} + \frac{v}{2} c_n^2 + w c_n^3 + \dots \right],\end{aligned}\quad (4.67)$$

where

$$v = \left(\frac{1}{N_B} - 2\chi \right) b^3 \quad (4.68)$$

is the measure of two-body interactions called excluded volume [see Eq. (3.8)] and

$$w = \frac{b^6}{3N_B} \quad (4.69)$$

is the three-body interaction coefficient (see Section 3.3.2.2).

The first term of this virial expansion [Eq. (4.67)] is linear in composition and is called the van't Hoff Law [Eq. (1.72)], which is valid for very dilute solutions:

$$\Pi = \frac{kT}{b^3} \frac{\phi}{N_A} = kT \frac{c_n}{N_A} = kT\nu. \quad (4.70)$$

The concentration $c_n = \phi/b^3$ is the number density of A monomers and $\nu = c_n/N_A$ is the number density of A molecules. The last relation of the above equation is a general statement of the van't Hoff Law, as each solute molecule contributes kT to the osmotic pressure in very dilute solutions. The membrane allows the B molecules to pass freely, but restricts all A molecules to stay on one side. This restriction leads to a pressure which is analogous to the ideal gas law (the osmotic pressure is kT per restricted molecule $\Pi = kT\nu$). This pressure is due to the translational entropy loss caused by the confinement of the A molecules.

In polymer solutions $N_A = N$ and $N_B = 1$, so the osmotic pressure [Eq. (4.66)] at low polymer concentrations has the virial expansion form

$$\Pi = \frac{kT}{b^3} \left[\frac{\phi}{N} + (1 - 2\chi) \frac{\phi^2}{2} + \frac{\phi^3}{3} + \dots \right]. \quad (4.71)$$

At the θ -temperature, the interaction parameter $\chi = 1/2$ and *the energetic part of two-body interactions exactly cancels the entropic part, making the net two-body interaction zero* ($v = (1 - 2\chi) b^3 = 0$). For $\chi < 1/2$, the two-body interactions increase the osmotic pressure of dilute polymer solutions. Hence, measurement of the osmotic pressure in dilute solutions provides a direct way of determining the Flory interaction parameter χ .

Near the θ -temperature, the second virial coefficient A_2 is related to χ and v by comparing Eqs (1.74) and (4.71), remembering that mass concentration $c = M_0\phi/(b^3\mathcal{N}_{Av})$ and molar mass $M = M_0N$:

$$\frac{v}{b^3} = \frac{2M_0^2}{b^3\mathcal{N}_{Av}} A_2 \approx 1 - 2\chi \approx \frac{T - \theta}{T}. \quad (4.72)$$

As χ is lowered, the polymer likes the solvent more, increasing the osmotic pressure. However, the mean-field theory that is the basis of Eq. (4.71) is only valid close to the θ -temperature, where chains interpenetrate each other freely [Eq. (3.102)]. Far above the θ -temperature (in good solvent), the second virial coefficient A_2 is related to chain volume [Eq. (3.104)] rather than monomer excluded volume v . Recall that the second virial coefficient can also be determined from the concentration dependence of scattering intensity [Eq. (1.91)].

4.5.2 Polymer melts

Consider a binary blend of chemically identical chains with a small concentration of chains with N_A monomers in a melt of chains with N_B monomers. For such a blend there is no energetic contribution to mixing ($\chi = 0$) and the excluded volume contains only a small entropic part:

$$v = \frac{b^3}{N_B}. \quad (4.73)$$

This parameter describes the excluded volume interactions of an A molecule with itself, mediated by the melt of B molecules. This excluded volume is small for polymer melts because each chain has difficulty distinguishing contacts with itself from contacts with surrounding chains. This very important result was first pointed out by Flory: *melts of long polymers have $v \approx 0$ and adopt nearly ideal chain conformations.*

The effect of this interaction on the conformations of an A chain can be analysed using the scaling approach described in detail in Chapter 3. On small length scales (smaller than the thermal blob size ξ_T), the excluded volume interactions barely affect the Gaussian statistics of the chain $\xi_T \approx bg_T^{1/2}$, where g_T is the number of monomers in a thermal blob. The thermal blob is defined as the section of the chain with excluded volume interactions of order of the thermal energy:

$$kTv \frac{g_T^2}{\xi_T^3} \approx kT \frac{v}{b^3} \frac{g_T^2}{g_T^{3/2}} \approx kT. \quad (4.74)$$

The number of monomers in a thermal blob is very large when the excluded volume is small:

$$g_T \approx \frac{b^6}{v^2} \approx N_B^2. \quad (4.75)$$

The thermal blob has random walk statistics:

$$\xi_T \approx bg_T^{1/2} \approx bN_B. \quad (4.76)$$

If an A chain is smaller than the thermal blob ($N_A < N_B^2$), its conformation is almost ideal. In a monodisperse melt with $N_A = N_B$, or in a weakly polydisperse melt, all chains have ideal statistics. On the other hand, strongly asymmetric binary blends of dilute long chains in a melt of short chains with $N_A > N_B^2$ have swollen long chains. The size of these swollen long chains can be estimated as a self-avoiding walk of thermal blobs (as described in Chapter 3):

$$\begin{aligned} R_A &\approx \xi_T \left(\frac{N_A}{g_T} \right)^\nu \approx bN_B \left(\frac{N_A}{N_B^2} \right)^\nu \\ &= \frac{b}{N_B^{2\nu-1}} N_A^\nu = bN_A^{1/2} \left(\frac{N_A}{N_B^2} \right)^{\nu-1/2}. \end{aligned} \quad (4.77)$$

The swelling coefficient $(N_A/N_B^2)^{0.088} \approx (N_A/g_T)^{0.088}$ for $\nu \cong 0.588$ increases as the number of monomers in the long chains N_A increases beyond that in a thermal blob $g_T \approx N_B^2$. The size of the A chain R_A is plotted as a function of N_A in Fig. 4.12(a) and as a function of N_B in Fig. 4.12(b). When $N_B = 1$, the thermal blob is one monomer and the athermal solvent chain size is recovered [Eq. (3.130)]. Figure 4.12(b) shows how the long chain deswells and eventually crosses over to the ideal chain size at $N_B \approx \sqrt{N_A}$ as the length of the short chains increases.

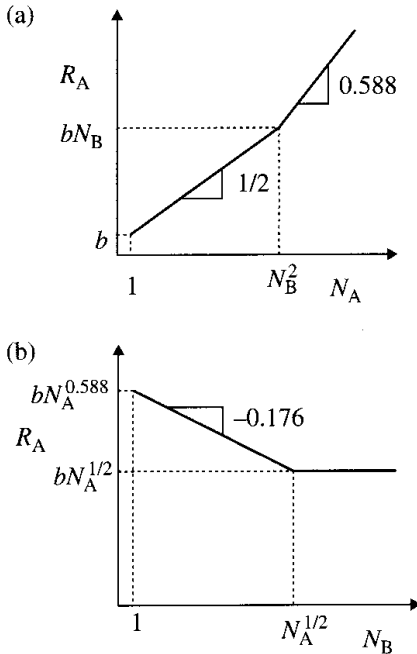


Fig. 4.12

The size of the long A chain as functions of (a) the number of monomers in the A chain and (b) the number of monomers in the B chain, on logarithmic scales.

Three-dimensional polymer melts are strongly interpenetrating. To demonstrate this point, consider a monodisperse melt with $N_A = N_B = N$. The average number of other chains that are inside the pervaded volume of a given polymer (the overlap parameter P , defined in Chapter 1) is the product of this volume $R^3 = N^{3/2}b^3$ and polymer number density $1/Nb^3$ and is equal to $P = \sqrt{N}$. Since N is large, chains are strongly interpenetrated in three-dimensional polymer melts. The presence of so many other chains means that each chain has difficulty distinguishing the intramolecular contacts, that give rise to the excluded volume interaction, from intermolecular contacts. The surrounding chains in the melt have effectively screened the excluded volume interaction, with $\nu = b^3/N \cong 0$. For this reason, Flory's insightful conjecture that chains in the melt are nearly ideal is correct.

Two-dimensional melts are quite different. The thermal blob for a dilute A polymer in a two-dimensional melt of chemically identical B polymers with excluded area $a = b^2/N_B$ can be estimated in a similar way. The excluded area interactions of a thermal blob with g_T monomers and size $\xi_T \approx bg_T^{1/2}$ is written by analogy with Eq. (3.74):

$$kTa \frac{g_T^2}{\xi_T^2} \approx kTa \frac{g_T^2}{b^2 g_T} \approx kT \quad \text{for two-dimensional melts.} \quad (4.78)$$

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The number of monomers in a two-dimensional thermal blob is smaller than in the three-dimensional thermal blob.

$$g_T \approx \frac{b^2}{a} \approx N_B \quad \text{for two-dimensional melts.} \quad (4.79)$$

The chains in a monodisperse two-dimensional melt are roughly the size of a thermal blob and are therefore barely ideal. The number of the other chains in a pervaded area of a given chain is the product of this area $R^2 \approx Nb^2$ and the two-dimensional number density of chains $1/Nb^2$ and is of the order of unity ($P \approx 1$). Thus, chains do not significantly interpenetrate each other in two dimensions. This is the expected result whenever the fractal dimension of the object and the dimension of space are the same.

4.6 Experimental investigations of binary mixtures

The Flory interaction parameter χ can be determined in homogeneous single-phase blends by measuring composition fluctuations using scattering. Consider a homogeneous blend at equilibrium with average composition of A monomers $\bar{\phi}$. In a small volume containing n total monomers with $n_A = \bar{\phi}n$ A monomers, a small fluctuation in composition $\delta\phi$ can occur spontaneously at equilibrium:

$$\delta\phi \equiv \phi - \bar{\phi}. \quad (4.80)$$

This fluctuation corresponds to a transfer of δn_A A monomers from the rest of the blend into the small volume with a concurrent transfer of the same number of B monomers out of the small volume (an effective exchange of A and B monomers):

$$\delta n_A = n\delta\phi. \quad (4.81)$$

The free energy of mixing in this small volume ΔF_{mix} can be expanded in powers of this fluctuation $\delta\phi$:

$$\Delta F_{\text{mix}}(\phi) = \Delta F_{\text{mix}}(\bar{\phi}) + \frac{\partial \Delta F_{\text{mix}}}{\partial \phi} \delta\phi + \frac{1}{2} \frac{\partial^2 \Delta F_{\text{mix}}}{\partial \phi^2} (\delta\phi)^2 + \dots \quad (4.82)$$

The term linear in $\delta\phi$ can be rewritten in terms of the number of monomers exchanged:

$$\frac{\partial \Delta F_{\text{mix}}}{\partial \phi} \delta\phi = \frac{\partial \Delta F_{\text{mix}}}{\partial (n\phi)} n\delta\phi = \frac{\partial \Delta F_{\text{mix}}}{\partial n_A} \delta n_A. \quad (4.83)$$

The derivative of the free energy of mixing with respect to the number of A monomers is the **exchange chemical potential**, the change in free energy of mixing arising from the exchange of one A monomer for one B monomer. The exchange changes the free energy in the rest of the blend by the exchange chemical potential multiplied by the change in number of

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A monomers ($-\delta n_A$) in the rest of the blend:

$$\frac{\partial \Delta F_{\text{mix}}}{\partial n_A} (-\delta n_A).$$

The free energy change in the system δF arising from this fluctuation is the sum of the free energy change in the small volume containing n monomers and the free energy change in the rest of the blend:

$$\begin{aligned} \delta F &= \Delta F_{\text{mix}}(\phi) - \Delta F_{\text{mix}}(\bar{\phi}) - \frac{\partial \Delta F_{\text{mix}}}{\partial n_A} \delta n_A \\ &= \frac{1}{2} \frac{\partial^2 \Delta F_{\text{mix}}}{\partial \phi^2} (\delta \phi)^2 + \dots \end{aligned} \quad (4.84)$$

Note that the rest of the blend is considered very large and exchange of δn_A A monomers does not change its composition significantly. The typical free energy change is of the order of the thermal energy, $\delta F \approx kT$, giving a simple relation for the mean-square composition fluctuation:³

$$\langle (\delta \phi)^2 \rangle \approx kT \left(\frac{\partial^2 \Delta F_{\text{mix}}}{\partial \phi^2} \right)^{-1} = \frac{kT}{n} \left(\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} \right)^{-1}. \quad (4.85)$$

The final relation involves the free energy of mixing per site, $\Delta \bar{F}_{\text{mix}}$, an intensive quantity. Hence, Eq. (4.85) clearly shows that thermally-driven composition fluctuations diminish as the volume considered (reflected in the number of sites n) increases. Small volumes with only a few monomers (small n) can have large fluctuations, but any macroscopic volume (large n) has a composition that is indistinguishable from the mean blend composition. The mean-square fluctuation is related to the low wavevector limit of the scattering function [Eq. (3.126)]

$$S(q) = \frac{\langle (\delta n_A)^2 \rangle}{n} = n \langle (\delta \phi)^2 \rangle, \quad (4.86)$$

where the number of monomers in the small volume is $n = (qb)^{-3}$. Since $\langle (\delta \phi)^2 \rangle \sim 1/n$, $S(q)$ saturates at small values of the wavevector. The scattering function at zero wavevector $S(0)$ is thus related to the second derivative of the free energy of mixing:

$$S(0) = n \langle (\delta \phi)^2 \rangle = kT \left(\frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} \right)^{-1}. \quad (4.87)$$

This is an example of a much more general thermodynamic relationship between $S(0)$ and osmotic compressibility [see Eq. (1.91)].

³ The real derivation of the mean-square fluctuation is obtained from an average over all magnitudes of the composition fluctuation with the corresponding Boltzmann factor $\exp(-\delta F/kT)$:

$$\langle (\delta \phi)^2 \rangle = \frac{\int_{-\infty}^{\infty} (\delta \phi)^2 \exp(-\delta F/kT) d(\delta \phi)}{\int_{-\infty}^{\infty} \exp(-\delta F/kT) d(\delta \phi)} = kT \left(\frac{\partial^2 \Delta F_{\text{mix}}}{\partial \phi^2} \right)^{-1}.$$

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Using Eq. (4.48), the Flory–Huggins theory predicts

$$\frac{1}{S(0)} = \frac{1}{kT} \frac{\partial^2 \Delta \bar{F}_{\text{mix}}}{\partial \phi^2} = \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi. \quad (4.88)$$

This means that the Flory interaction parameter χ can be determined from the low wavevector limit of the scattering function of a single-phase blend of A chains (with N_A monomers) and B chains (with N_B monomers), where ϕ is the volume fraction of A chains. In practice, the concentration fluctuations in the blend provide sufficient scattering contrast for neutron scattering, as long as one of the components is at least partially labelled with deuterium.

The standard assumption, called the **random-phase approximation**, extends Eq. (4.88) to non-zero wavevectors q using the form factor of an ideal chain $P(q, N)$:

$$\frac{1}{S(q)} = \frac{1}{N_A \phi P(q, N_A)} + \frac{1}{N_B(1-\phi)P(q, N_B)} - 2\chi. \quad (4.89)$$

Recall from Section 2.8.4 that the form factor for an ideal chain is the Debye function [Eq. (2.160)]. The high q limit of the Debye function is

$$P(q, N) \cong \frac{2}{q^2 \langle R_g^2 \rangle} = \frac{12}{q^2 N b^2} \quad \text{for } q \gg 1/R_g, \quad (4.90)$$

where we used the standard radius of gyration for an ideal chain $\langle R_g^2 \rangle = N b^2 / 6$ [Eq. (2.54)]. The low q limit of any form factor is $P(q, N) = 1$, and a simple crossover expression emerges for the reciprocal of the Debye function:⁴

$$\frac{1}{P(q, N)} = 1 + \frac{q^2 N b^2}{12}. \quad (4.91)$$

Substituting this result into Eq. (4.89) (twice) gives a simple result for the reciprocal scattering function:

$$\begin{aligned} \frac{1}{S(q)} &= \frac{1}{N_A \phi} + \frac{q^2 b^2}{12 \phi} + \frac{1}{N_B(1-\phi)} + \frac{q^2 b^2}{12(1-\phi)} - 2\chi \\ &= \frac{1}{N_A \phi} + \frac{1}{N_B(1-\phi)} - 2\chi + \frac{q^2 b^2}{12} \left(\frac{1}{\phi} + \frac{1}{1-\phi} \right) \\ &= \frac{1}{S(0)} + \frac{q^2 b^2}{12 \phi(1-\phi)}. \end{aligned} \quad (4.92)$$

The final result made use of Eq. (4.88).

This form for scattering is actually far more general, valid for many systems with scattering arising from random fluctuations. Small angle

⁴ This crossover expression is never more than 15% different from the Debye function over all q . For small qR_g a better expression is Eq. (2.146) or (2.161).

neutron scattering data on miscible polymer blends are customarily fit to the Ornstein–Zernike scattering function:

$$S(q) = \frac{S(0)}{1 + (q\xi)^2} \quad (4.93)$$

Comparing Eqs (4.92) and (4.93) reveals the correlation length for the mean-field theory of binary mixtures:

$$\xi = \sqrt{\frac{b^2 S(0)}{12\phi(1-\phi)}} \quad (4.94)$$

The correlation length effectively divides the form of the scattering into two regions. For $q \ll 1/\xi$, the scattering function approaches its zero wavevector limit $S(0)$. For $q \gg 1/\xi$, the scattering function decreases as a power law $S(q) \sim q^{-2}$. Ideally, experiments would extend to sufficiently low q at which the zero wavevector limit would be nearly realized. However, in practice this is often not the case, with q of order $1/\xi$ for most small-angle neutron scattering (SANS) data on single-phase blends. SANS data at three temperatures for a blend of a polyisobutylene with a deuterium-labelled ethylene–butene random copolymer are shown in Fig. 4.13. This blend phase separates on heating at $95 \pm 5^\circ\text{C}$. The scattering intensity increases as temperature is raised, which means that concentration fluctuations are getting stronger. The data at all three temperatures are reasonably fit by the Ornstein–Zernike equation [curves are fits to Eq. (4.93)]. The scattering intensity is independent of temperature at high $q \gg 1/\xi$ because

$$S(q) = \frac{S(0)}{(q\xi)^2} = \frac{12\phi(1-\phi)}{(qb)^2} \quad \text{for } q \gg 1/\xi \quad (4.95)$$

in this limit.

Like $S(0)$, the correlation length ξ has important physical significance and is related to concentration fluctuations. On length scales smaller than the correlation length, correlated chain sections of $(qb)^{-2}$ monomers fluctuate in and out of the volume q^{-3} . Mean-square fluctuations in the number of A and B chain sections is proportional to $(qb)^{-1}$, the number of these sections in the volume q^{-3} . Mean-square fluctuations in the number of A and B monomers in this small volume is the product of the mean-square fluctuations in the number of chain sections and the square of the number of monomers in each chain section $\langle(\delta n_A)^2\rangle \sim (qb)^{-5}$. From Eq. (4.86) we find that coherent fluctuations of chain sections on length scales smaller than the correlation length ($q^{-1} < \xi$) lead to $S(q) \sim \langle(\delta n_A)^2\rangle/n \sim (qb)^{-2}$ [Eq. (4.95)] independent of ξ or χ . This makes the scattered intensity at high q in Fig. 4.13 independent of temperature [Eq. (4.95)]. Concentration fluctuations in different correlation volumes are incoherent, so on length scales larger than the correlation length, mean-square fluctuations in the number of A and B monomers in the large volume q^{-3} is proportional to the product of the mean-square fluctuations within a correlation volume $(\xi/b)^5$ and $(\xi q)^{-3}$, the number of correlation volumes

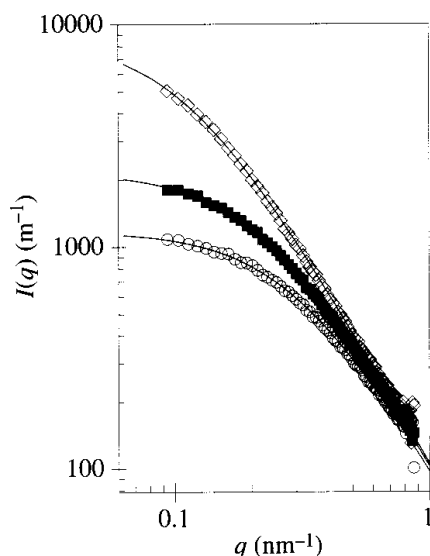


Fig. 4.13

SANS intensity for a $\phi = 0.5$ miscible blend of polyisobutylene ($M_w = 160\,000\text{ g mol}^{-1}$) and a random copolymer of ethylene and butene (66 wt% butene, $M_w = 114\,000\text{ g mol}^{-1}$) at three temperatures with fits to Eq. (4.93) (curves). Open circles are at 27°C , where $I(0) = 1180\text{ m}^{-1}$ and $\xi = 3.3\text{ nm}$. Filled squares are at 51°C , where $I(0) = 2180\text{ m}^{-1}$ and $\xi = 4.5\text{ nm}$. Open diamonds are at 83°C , where $I(0) = 8850\text{ m}^{-1}$ and $\xi = 9.1\text{ nm}$. Data from R. Krishnamoorti *et al.*, *Macromolecules* **28**, 1252 (1995).

in the volume q^{-3} . From Eq. (4.86), it follows that the structure factor saturates at low $q < \xi^{-1}$ with $S(0) \sim (\xi/b)^2$ [Eq. (4.94)]. Both $S(0)$ and ξ^2 contain the same information about the Flory interaction parameter χ and it is important to realize that this information is only obtained at low q . Since SANS has a limited q -range, in practice $S(0)$ and ξ are determined by fitting data to Eq. (4.93), as shown in Fig. 4.13.

The astute reader will recognize that the scattering function for polymer blends [Eq. (4.86)] is defined in a subtly different manner than for polymer solutions [Eq. (3.126)]. In both cases, the scattering function is normalized by the number of monomers in the system. In Section 3.5, monomers occupy volume fraction ϕ of the total volume, while in the blend the combined volume fraction of monomers of type A and B is unity. The scattering function of Section 3.5 is related to that of the present section as $S(q)/\phi$. To facilitate comparison, we rewrite Eq. (4.88):

$$\frac{\phi}{S(0)} = \frac{1}{N_A} + \frac{\phi}{N_B(1-\phi)} - 2\chi\phi. \quad (4.96)$$

For a polymer solution $N_B = 1$ and $\phi \ll 1$

$$\frac{\phi}{S(0)} \cong \frac{1}{N_A} + (1 - 2\chi)\phi, \quad (4.97)$$

which is the usual virial expansion in dilute solutions [Eq. (1.91)].

The equilibrium concentrations of two-phase blends are calculated from the phase diagram—a coexistence curve in the temperature–composition plane. The phase diagram can be conveniently determined by monitoring light scattering as a function of temperature for various overall compositions, as long as sufficient time is allowed to reach equilibrium at each temperature. Starting at a temperature in the single-phase state, the blend is transparent and the scattering is low. When the temperature reaches the binodal curve, the scattering increases, as phase separation creates domains with different refractive indices.⁵ Simple thermodynamic considerations link the phase boundary to the interaction parameter, as described in this chapter.

4.7 Summary of thermodynamics

In this chapter, the thermodynamics of binary mixtures was discussed in the framework of a lattice model. For simplicity, polymers were divided into ‘monomers’ that fit onto this lattice and the free energy of mixing was written *per lattice site* ($\Delta\bar{F}_{\text{mix}}$). Rescaling the monomers to more conventional definitions (such as either the chemical monomer of Chapter 1 or the Kuhn monomer of Chapter 2) is trivial because the volume of an A chain $v_A = N_A v_0$ and the volume of a B chain $v_B = N_B v_0$ must be independent of the choice of lattice site volume v_0 . In practice, fitting the monomers onto the lattice is inconvenient and in this summary results are given for the more usual case of mixing two polymers with

⁵ For this reason, the binodal is often referred to as the cloud point.

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different monomer volumes, in terms of the free energy *per unit volume* (called the free energy density $\Delta\bar{F}_{\text{mix}}/v_0$).

The free energy of mixing has two parts: entropic and energetic. The entropic part per unit volume,

$$-\frac{T\Delta S_{\text{mix}}}{V} = -\frac{T\Delta\bar{S}_{\text{mix}}}{v_0} = kT \left[\frac{\phi}{v_A} \ln \phi + \frac{1-\phi}{v_B} \ln(1-\phi) \right], \quad (4.98)$$

simply counts translational entropy of the mixed state compared with the pure component states. Entropy always promotes mixing. Mixtures of two small molecules have large entropy of mixing, solutions of polymers in small molecule solvents have less entropy of mixing, and blends of two polymers have very little mixing entropy.

The energetic part of the free energy density

$$\frac{\Delta U_{\text{mix}}}{V} = \frac{\Delta\bar{U}_{\text{mix}}}{v_0} = kT \frac{\chi}{v_0} \phi(1-\phi) = \frac{k}{v_0} (AT + B) \phi(1-\phi) \quad (4.99)$$

is the difference of intermolecular interaction energies in the mixed and pure states, and is reflected in the Flory interaction parameter χ . Equation (4.99) clearly points out the importance of specifying the reference volume v_0 when stating the value of the Flory χ parameter.⁶ The energy of mixing can be either positive (meaning that the different species prefer to be next to themselves) favouring segregation, or negative (meaning that the different species prefer each other) promoting mixing. Interactions between components are often of the van der Waals type, meaning that they are weak and repulsive. Despite this repulsion, many simple liquid pairs form regular solutions that have entropically driven mixing. It is somewhat less likely for a polymer to dissolve in a solvent simply because of lower entropy of mixing for larger molecules. However, most polymers will dissolve in a number of common solvents. On the other hand, miscible polymer blends are very unlikely because the entropy of mixing two long-chain polymers is extremely small. The rule of thumb is that polymers never mix, but there are many exceptions to this rule because interactions between components are not always repulsive.

The shape of the free energy density of mixing as a function of composition

$$\begin{aligned} \frac{\Delta F_{\text{mix}}}{V} &= \frac{\Delta\bar{F}_{\text{mix}}}{v_0} = \frac{\Delta\bar{U}_{\text{mix}}}{v_0} - \frac{T\Delta\bar{S}_{\text{mix}}}{v_0} \\ &= kT \left[\frac{\phi}{v_A} \ln \phi + \frac{1-\phi}{v_B} \ln(1-\phi) + \frac{\chi}{v_0} \phi(1-\phi) \right] \\ &= kT \left[\frac{\phi}{v_A} \ln \phi + \frac{1-\phi}{v_B} \ln(1-\phi) + \frac{A}{v_0} \phi(1-\phi) \right] \\ &\quad + \frac{kB}{v_0} \phi(1-\phi). \end{aligned} \quad (4.100)$$

⁶ All numbers for the Flory χ parameter in this book use a reference volume of $v_0 = 100 \text{ \AA}^3$.

determines the stability of a homogeneously mixed state. This function is always convex near the boundaries of the composition range (for small ϕ and for ϕ near unity) because the entropic part always dominates there at any practical (non-zero) temperature. If the composition dependence of the free energy of mixing is convex over the whole composition range, the mixture is homogeneous at all compositions. If the free energy is concave in some part of the composition range, the line of common tangent to the free energy curve determines the range of the miscibility gap (see Fig. 4.7).

The mean-field lattice model of Flory and Huggins predicts that $A \equiv 0$ but in practice this is not observed. If $A < 0$ and $B < 0$, then all four terms in Eq. (4.100) are negative and miscible mixtures are stable at all temperatures. If $A > 0$ and $B < 0$, the blend has a LCST and phase separates at high temperatures. If $B > 0$, the blend has an UCST and phase separation occurs as temperature is lowered.

The Flory interaction parameter in miscible polymer blends is measured using small-angle neutron scattering, usually involving deuterium labeling of one blend component. The χ parameter is determined from the zero wavevector limit of the scattering function $S(0)$:

$$\chi = \frac{v_0}{2} \left[\frac{1}{v_A \phi} + \frac{1}{v_B (1 - \phi)} \right] - \frac{1}{2S(0)}. \quad (4.101)$$

The binodal separates the homogeneous (single phase) and heterogeneous (two phase) regions in the phase diagram (see Figs 4.10 and 4.11). For binary mixtures, the binodal line is also the coexistence curve, defined by the common tangent line to the composition dependence of the free energy of mixing curve, and gives the equilibrium compositions of the two phases obtained when the overall composition is inside the miscibility gap. The spinodal curve, determined by the inflection points of the composition dependence of the free energy of mixing curve, separates unstable and metastable regions within the miscibility gap.

Melts of long chains have nearly ideal conformations because the excluded volume is screened by the presence of other chains ($v \approx 0$). The excluded volume in a melt is $v \approx b^3/N$. Excluded volume therefore gradually increases as the short chains in a polymer blend are shortened. The short B chains make the A chains swell when $N_A > N_B^2$. Hence, miscible blends of high molar mass polymers with $N_A < N_B^2$ have nearly ideal conformations.

Problems

Section 4.1

- 4.1 (i) Calculate the number of ways to arrange 10 identical solute molecules on a lattice of 100 sites. Each molecule occupies one lattice site.
- (ii) Calculate the number of ways of arranging an oligomer consisting of 10 repeat units on a cubic lattice of 100 sites. Each repeat unit occupies one lattice site. Ignore long-range (along the chain) excluded volume interactions. Assume that each site has coordination number $z = 6$ (ignore the boundary effects).

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- 4.2 Calculate the entropy of mixing per site $\Delta\bar{S}_{\text{mix}}$ on a three-dimensional cubic lattice of:
- 100 black 50-ball chains with 100 white 50-ball chains on a lattice with 10 000 sites (one ball per site).
 - 100 black 50-ball chains with 100 identical black 50-ball chains on a lattice with 10 000 sites (one ball per site).
- Explain the difference between cases (i) and (ii).

Section 4.2

- 4.3 Estimate the Flory interaction parameter χ between polystyrene and polybutadiene at room temperature if the solubility parameter of polystyrene is $\delta_{\text{PS}} = 1.87 \times 10^4 \text{ (J m}^{-3}\text{)}^{1/2}$ and the solubility parameter of polybutadiene is $\delta_{\text{PB}} = 1.62 \times 10^4 \text{ (J m}^{-3}\text{)}^{1/2}$. For simplicity assume $v_0 \cong 100 \text{ \AA}^3$.
- 4.4 What is the free energy of mixing 1 mol of polystyrene of molar mass $M = 2 \times 10^5 \text{ g mol}^{-1}$, with $1 \times 10^4 \text{ L}$ of toluene, at $25 \text{ }^\circ\text{C}$ (Flory interaction parameter $\chi = 0.37$). The density of polystyrene is 1.06 g cm^{-3} , the density of toluene is 0.87 g cm^{-3} . Assume no volume change upon mixing.
- 4.5 Compare the magnitudes of the two terms in Eq. (4.31) for χ using the data for the 11 polymer blends in Table 4.3 at the lowest temperature studied (corresponding to the largest value of B/T). Is the Flory–Huggins assumption that $|B/T| \gg |A|$ correct?
- 4.6 (i) Derive the relation between A and B in Eq. (4.31) and the Hildebrand–Scott solubility parameter difference.
(ii) What values of A and B are possible in the solubility parameter approach?

Section 4.3

- 4.7 At $T = 0 \text{ K}$, the entropic contributions to the free energy of mixing disappear, and only the energetic contributions remain. Substitute Eq. (4.31) into the Flory–Huggins equation to write the free energy of mixing in terms of the parameters A and B . Sketch the composition dependence of the free energy for cases where $B < 0$, $B = 0$, and $B > 0$, and discuss whether any of those situations lead to a stable mixture at $T = 0 \text{ K}$. Does your answer depend on whether regular solutions, polymer solutions, or polymer blends are considered?
- 4.8 Plot on a single graph, the composition dependence of the free energy of mixing per site (normalized by the thermal energy) $\Delta\bar{F}_{\text{mix}}/kT$ of a symmetric polymer blend with $N_{\text{A}} = N_{\text{B}} = 100$ using five different choices for the parameter $\chi = 0, 0.01, 0.02, 0.03, 0.04$. Which choices of χ make the blends miscible in all proportions (i.e. over the whole composition range $0 \leq \phi \leq 1$) and why?

Section 4.4

- 4.9 The free energy of mixing (per mole of lattice sites) for the regular solution theory can be written as

$$\mathcal{R}T[\phi \ln \phi + (1 - \phi) \ln (1 - \phi) + \chi\phi(1 - \phi)],$$

where \mathcal{R} is the gas constant and the interaction parameter is $\chi = B/T$, where $B = 600 \text{ K}$. Construct the binodal and spinodal curves in the temperature–composition phase diagram.

- 4.10** The free energy of mixing (per mole of lattice sites) of a polymer solution (according to the Flory–Huggins model) is

$$\mathcal{R}T \left[\frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right],$$

where \mathcal{R} is the gas constant and the interaction parameter is $\chi = B/T$ where $B = 300$ K. Plot the critical parameters (ϕ_c , χ_c , and T_c) for the solution as a function of the degree of polymerization N .

- 4.11** Calculate the free energy density $\Delta F_{\text{mix}}/V$ of mixing polystyrene of molar mass $20\,000$ g mol⁻¹ with cyclohexane at 34 °C, to make up a 5% by volume solution? Assume no volume change upon mixing.

Note that 34 °C is the θ -temperature for a polystyrene solution in cyclohexane (Flory interaction parameter $\chi = 1/2$):

the density of polystyrene is 1.06 g cm⁻³;

the density of cyclohexane is 0.78 g cm⁻³;

the molar mass of cyclohexane (C₆H₁₂) is 84 g mol⁻¹.

- 4.12** (i) What is the free energy of mixing 1 g of polystyrene of molar mass $M = 10^5$ g mol⁻¹, with 1 mol of cyclohexane at 34 °C? Note that 34 °C is the θ -temperature for a polystyrene solution in cyclohexane (Flory interaction parameter $\chi = 1/2$). The molar volume of polystyrene is $v_{\text{ps}} = 9.5 \times 10^4$ cm³ mol⁻¹, the molar volume of cyclohexane is $v_{\text{cyc}} = 108$ cm³ mol⁻¹. Assume no volume change upon mixing and assume that the volume of one solvent molecule is the lattice site volume v_0 .
- (ii) What does the sign of the free energy of mixing imply about the stability of a homogeneous solution?
- (iii) Under what conditions does the homogeneous solution spontaneously phase separate by spinodal decomposition?
- (iv) When is the homogeneous solution metastable?
- 4.13** Since the mean-field Flory–Huggins theory puts everything that is not understood about thermodynamics into the χ parameter, this parameter is experimentally found to vary with composition and temperature. For solutions of linear polystyrene in cyclohexane, the interaction parameter

$$\chi = 0.2035 + \frac{90.65 \text{ K}}{T} + 0.3092\phi + 0.1554\phi^2 \quad (4.102)$$

was determined by R. Koningsveld *et al.*, *J. Polym. Sci. A-2* **8**, 1261 (1970).

- (i) What is the critical temperature for a very high molar mass polystyrene in cyclohexane with polymer volume fraction $\phi = 0.01$?
- (ii) Does the polystyrene/cyclohexane system have a UCST or an LCST?
- (iii) Determine the θ -temperature at a volume fraction $\phi = 0.1$.
- 4.14** (i) Derive a general expression for the critical temperature of a mixture in terms of the solubility parameter difference $\delta_A - \delta_B$ and the number of monomers in each component N_A and N_B .
- (ii) What is the criterion for miscibility in this approach?
- (iii) What is the largest solubility parameter difference that allows small molecule mixtures (with $N_A = N_B = 1$) to be miscible?

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- (iv) What is the largest solubility parameter difference that allows polymer solutions (with $N_A = 10^4$ and $N_B = 1$) to be miscible?
- (v) What is the largest solubility parameter difference that allows polymer blends (with $N_A = N_B = 10^4$) to be miscible?

4.15 Consider a nucleation process from a uniform metastable state of a polymer solution. Denote by $\Delta\mu = \mu_1 - \mu_2$ the chemical potential difference between N -mers in a uniform solution μ_1 and in a phase separated solution μ_2 . If $\Delta\mu$ is positive, the phase separated solution is the equilibrium state. However, a small drop of a phase with higher concentration of molecules c/N formed in the homogeneous phase could be unstable due its positive surface energy with surface tension γ . Calculate the Gibbs free energy of a spherical drop of concentrated phase of radius R and determine the critical radius R_c for nucleation in terms of γ , $\Delta\mu$ and the number density of chains. Nuclei smaller than R_c shrink and disappear, while larger ones grow into domains of the dense phase.

- 4.16** (i) What is the critical value of χ required for high molar mass polymers to dissolve in a solvent in all proportions?
- (ii) In Chapter 5, we will learn that polymer solutions are not described well by the mean-field theory because the connectivity of the chains keeps monomers from being uniformly distributed in solution (particularly at low polymer concentrations). An empirical form that better relates χ to the Hildebrand solubility parameters in polymer solutions is widely used with an entropic part of χ of 0.34:

$$\chi = 0.34 + \frac{v_0}{kT}(\delta_A - \delta_B)^2. \quad (4.103)$$

Use the following table to decide which solvents will dissolve poly (dimethyl siloxane) ($\delta_{\text{PDMS}} = 14.9 \text{ (MPa)}^{1/2}$) and which will dissolve polystyrene ($\delta_{\text{PS}} = 18.7 \text{ (MPa)}^{1/2}$) at room temperature.

Solvent	<i>n</i> -Heptane	Cyclohexane	Benzene	Chloroform	Acetone
Molar volume ($\text{cm}^3 \text{ mol}^{-1}$)	195.9	108.5	29.4	80.7	74.0
Solubility parameter $\delta \text{ (MPa)}^{1/2}$	15.1	16.8	18.6	19.0	20.3

- (iii) Which solvent is closest to the athermal limit for each polymer?

Section 4.5

4.17 Consider a melt of B chains with degree of polymerization $N_B = 100$ and Kuhn length $b = 3 \text{ \AA}$. What is the root-mean-square end-to-end distance of isolated chemically identical A -chains in this melt with degree of polymerization:

- (i) $N_A = 10^2$? (ii) $N_A = 10^4$? (iii) $N_A = 10^6$?

4.18 Consider a monodisperse melt of randomly branched polymers with N Kuhn monomers of length b . Randomly branched polymers in an ideal state (in the absence of excluded volume interactions) have fractal dimension $D = 4$. Do these randomly branched polymers overlap in a three-dimensional monodisperse melt?

Hint: What would be the N -dependence of density if monodisperse randomly branched polymers overlapped in the melt?

- 4.19* Demonstrate that the excluded volume in a polydisperse melt is $v = b^3/N_w$, where N_w is the weight-average molar mass of the melt.

Section 4.6

4.20 Ginzburg criterion for polymer blends

Estimate the size of the critical region near the critical point in a symmetric polymer blend by comparing the mean-square composition fluctuations $\langle(\delta\phi_A)^2\rangle$ with the square of the difference in volume fractions of the two phases $(\phi'' - \phi')^2$ in the miscibility gap. Such considerations determine the point where mean-field theory (which assumes fluctuations are small) fails, known as the Ginzburg criterion.

- (i) Expand the equation for the binodal (Eq. 4.47 with $A = 0$) near the critical composition $\phi_c = 1/2$ to derive the dependence of the order parameter $\phi'' - \phi'$ on the relative temperature difference from the critical temperature $(T - T_c)/T_c$.

$$\phi'' - \phi' \approx \sqrt{\frac{T_c - T}{T_c}} \quad \text{for } T < T_c$$

- (ii) Demonstrate that the mean-square composition fluctuations on the scale of the correlation length are of order

$$\langle(\delta\phi)^2\rangle \approx \sqrt{\frac{1}{N} \frac{T_c - T}{T_c}} \quad \text{for } T < T_c$$

- (iii) Estimate the size of the critical region (Ginzburg criterion) by comparing the square of the order parameter $(\phi'' - \phi')^2$ with the mean-square composition fluctuations on the scale of correlation length $\langle(\delta\phi)^2\rangle$.

$$\frac{T_c - T}{T_c} \approx \frac{1}{N} \quad \text{for } T < T_c$$

For blends of long chain polymers (large N) the critical region is very small and the mean-field theory applies at nearly all temperatures.

- 4.21 Use the data in Table 4.3 to calculate the zero wavevector limit of the scattering function $S(0)$ and the mean-square concentration fluctuation $\langle(\delta\phi)^2\rangle$ at a 50 Å scale (at $q = 2\pi/50 \text{ Å}^{-1} = 0.126 \text{ Å}^{-1}$) assuming the Ornstein-Zernike form for $S(q)$, for the blends listed below (with $N_A = N_B = 100$ in each case). For each blend, plot $S(0)$ and $\langle(\delta\phi)^2\rangle$ as functions of temperature over the temperature range of Table 4.3.

- (i) 50% by volume poly(vinyl methyl ether) mixed with polystyrene;
- (ii) 50% by volume polyisobutylene mixed with deuterated head-to-head polypropylene;
- (iii) 30% by volume poly(ethylene oxide) mixed with deuterated polymethyl (methacrylate).

Identify the blends that phase separate and state whether they have an LCST or a UCST.

- 4.22 (i) Use the fitting results in the caption of Fig. 4.13 for the three different temperatures to plot $S(0)$ against ξ^2 to demonstrate their proportionality. What is the physical significance of $S(0) \sim \xi^2$?

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- (ii) The correlation length diverges at the critical temperature T_c as a power law:

$$\xi \sim \left(\frac{T_c - T}{T_c} \right)^{-1/2}. \quad (4.105)$$

Use the fitting results in the caption of Fig. 4.13 for the three different temperatures to estimate the critical temperature T_c . How does this critical temperature compare with the observed cloud point for this blend of 95 ± 5 °C?

- (iii) Determine χ at each of the three temperatures in Fig. 4.13 and fit those determinations to Eq. (4.31).

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