

7.1: Thermodynamics of Mixing

The formalism introduced in Chapter is suitable for small molecules in the gas phase, but does not easily extend to condensed phases or to larger molecules with several rotameric states, let alone to macromolecules, such as synthetic polymers, proteins, nucleic acids, and carbohydrates. Nevertheless, statistical thermodynamics is an important theory for understanding such systems. In this Chapter we introduce some of the concepts of statistical thermodynamics that do not depend on explicit computation of the partition function. We start with the entropy of mixing and, for simplicity, restrain the discussion to binary mixtures.

Entropy of Binary Mixing

We consider mixing of two species A with volume V_A and B with volume V_B and neglect volume change, so that the total volume is $V_A + V_B$. The volume fractions of the two components in the mixture are thus given by

$$\phi_A = \frac{V_A}{V_A + V_B} \quad (7.1.1)$$

$$\phi_B = \frac{V_B}{V_A + V_B} = 1 - \phi_A. \quad (7.1.2)$$

To consider the statistics of the problem we use a lattice model.

Concept 7.1.1: Lattice model

A *lattice model* is a discrete representation of a system as opposed to a continuum representation. A three-dimensional lattice model is a regular arrangement of sites in Cartesian space, such as a crystal lattice is a regular arrangement of atoms in Cartesian space. The state of the model is defined by the distribution of units of matter, for instance molecules or the repeat units of a polymer (short: monomers), on the lattice sites. In statistical thermodynamics, one particular arrangement of the units on the lattice is a microstate. Energy of the microstate depends on interactions of units between lattice sites, in the simplest case only between direct neighbor sites. By considering the statistical distribution of microstates, thermodynamic state functions of the macrostate of the system can be obtained.

In our example we assign the lattice site a volume v_0 , which cannot be larger than the volume required for one molecule of the smaller component in the mixture. The other component may then also occupy a single site (similarly sized components) or several lattice sites. A macromolecule with a large degree of polymerization consists of a large number of monomers and will thus occupy a large number of lattice sites. The molecular volumes of the species are

$$v_A = N_A v_0 \quad (7.1.3)$$

$$v_B = N_B v_0, \quad (7.1.4)$$

where N_A and N_B are the number of sites occupied by one molecule of species A and B, respectively. We consider the three simple cases listed in Table 7.1.1. *Regular solutions* are mixtures of two low molecular weight species with $N_A = N_B = 1$. *Polymer solutions* are mixtures of one type of macromolecules ($N_A = N \gg 1$) with a solvent, whose molecular volume defines the lattice site volume v_0 ($N_B = 1$). *Polymer blends* correspond to the general case $1 \neq N_A \neq N_B \neq 1$. They are mixtures of two different species of macromolecules, so that $N_A, N_B \gg 1$.

Table 7.1.1: Number of lattice sites occupied per molecule in different types of mixtures.

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

The mixture occupies

$$n = \frac{V_A + V_B}{v_0} \quad (7.1.5)$$

lattice sites, whereas component A occupies $V_A/v_0 = n\phi_A$ of these sites. We consider a microcanonical ensemble and can thus express entropy as

$$s = k_B \ln \Omega, \quad (7.1.6)$$

where Ω is the number of ways in which the molecules can be arranged on the lattice (number of microstates). In a homogeneous mixture, a molecule or monomer of component A can occupy any of the n lattice sites. Before mixing, it can occupy only one of the lattice sites in volume V_A . Hence, the entropy change for one molecule of species A is

$$\Delta S_A = k_B \ln n - k_B \ln \phi_A n \quad (7.1.7)$$

$$= k_B \ln \frac{n}{\phi_A n} \quad (7.1.8)$$

$$= -k_B \ln \phi_A. \quad (7.1.9)$$

The total mixing entropy for both species is

$$\Delta s_{\text{mix}} = -k_B (n_A \ln \phi_A + n_B \ln \phi_B). \quad (7.1.10)$$

We note the analogy with the expression that we had obtained in phenomenological thermodynamics for an ideal mixture of ideal gases, were we had used the molar fraction x_i instead of the volume fraction ϕ_i . For ideal gases, $V_i \propto n_i$ and thus $\phi_i = x_i$. Equation 7.1.10 generalizes the result to any ideal mixture in condensed phase. The mixture is ideal because we did not yet consider energy of mixing and thus could get away with using a microcanonical ensemble.

For discussion it is useful to convert the extensive quantity Δs_{mix} to the intensive entropy of mixing per lattice site,

$$\Delta \bar{S}_{\text{mix}} = -k_B \left(\frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B \right), \quad (7.1.11)$$

where we have used the number of molecules per species $n_i = n\phi_i/N_i$ and normalized by the total number n of lattice sites.

For a regular solution with $N_A = N_B = 1$ we obtain the largest entropy of mixing at given volume fractions of the components,

$$\Delta \bar{S}_{\text{mix}} = -k_B (\phi_A \ln \phi_A + \phi_B \ln \phi_B) \quad (\text{regular solutions}). \quad (7.1.12)$$

For a polymer solution with $N_A = N \gg 1$ and $N_B = 1$ we have

$$\Delta \bar{S}_{\text{mix}} = -k_B \left(\frac{\phi_A}{N} \ln \phi_A + \phi_B \ln \phi_B \right) \quad (7.1.13)$$

$$\approx -k_B \phi_B \ln \phi_B, \quad (7.1.14)$$

where the approximation by Equation 7.1.14 holds for $\phi_B \gg 1/N$, i.e. for solving a polymer and even for any appreciable swelling of a high-molecular weight polymer by a solvent. For polymer blends, Equation 7.1.11 holds with $N_A, N_B \gg 1$. Compared to formation of a regular solution or a polymer solution, mixing entropy for a polymer blend is negligibly small, which qualitatively explains the difficulty of producing such polymer blends. Nevertheless, the entropy of mixing is always positive, and thus the Helmholtz free energy $\Delta \bar{F}_{\text{mix}} = -T \Delta \bar{S}_{\text{mix}}$ always negative, so that an *ideal* mixture of two polymers should form spontaneously. To see what happens in real mixtures, we have to consider the energetics of mixing.

Before doing so, we note the limitations of the simple lattice model. We have neglected conformational entropy of the polymer, which will be discussed in Section [subsection:conf_entropy]. This amounts to the assumption that conformational entropy does not change on mixing. For blends of polymers, this is a very good assumption, whereas in polymers solutions there is often an excluded volume that reduces conformational space. We have also neglected the small volume change that occurs on mixing, most notably for regular solutions. For polymer solutions and blends this volume change is very small.

Energy of Binary Mixing

To discuss the internal energy contribution to the free energy of mixing, we continue using the simplified lattice model. In particular, we consider mixing at constant volume and we assume that attractive or repulsive interactions between lattice sites are sufficiently small to not perturb random distributions of solvent molecules and monomers on lattice sites. We also ignore that the polymer chain is connected, as this would exclude random distribution of the monomers to the lattice sites. Regular solution theory, as we consider it here, is a mean-field approach where the interaction at a given lattice site is approximated by a mean interaction with the other lattice sites. This neglects correlations. Although the model may appear crude (as many models in polymer physics),

it provides substantial insight and an expression that fits experimental data surprisingly well (as is the case for many crude models in polymer physics).

We start by defining three pairwise interaction energies u_{AA} , u_{AB} , and u_{BB} between adjacent sites of the lattice. For random distribution, the probability that a molecule or monomer A has a neighbor A is ϕ_A and the probability that it has a neighbor B is $1 - \phi_A$. We neglect boundary effects, as the ratio between the number of surface sites and inner sites is very small for a macroscopic system. The mean-field interaction energy per lattice site occupied by an A unit is thus

$$U_A = \phi_A u_{AA} + (1 - \phi_A) u_{AB} \quad (7.1.15)$$

and the corresponding expression for a lattice site occupied by a B unit is

$$U_B = \phi_A u_{AB} + (1 - \phi_A) u_{BB} . \quad (7.1.16)$$

To continue, we need to specify the lattice, as the number of sites a adjacent to the site under consideration depends on that. For a cubic lattice we would have $a = 6$. We keep a as a parameter in the hope that we can eliminate it again at a later stage. If we compute a weighted sum of the expressions (Equation 7.1.15) and (Equation 7.1.16) we double count each pairwise interaction, as we will encounter it twice. Hence, total interaction energy of the mixture is

$$u = \frac{an}{2} [\phi_A U_A + (1 - \phi_A) U_B] , \quad (7.1.17)$$

where we have used the probability ϕ_A of encountering a site occupied by a unit A and $(1 - \phi_A)$ of encountering a site occupied by a unit B. By inserting Eqs. 7.1.15 and 7.1.16 into Equation 7.1.17 and abbreviating $\phi_A = \phi$, we obtain

$$u = \frac{an}{2} \{ \phi [\phi u_{AA} + (1 - \phi) u_{AB}] + (1 - \phi) [\phi u_{AB} + (1 - \phi) u_{BB}] \} \quad (7.1.18)$$

$$= \frac{an}{2} [\phi^2 u_{AA} + 2\phi(1 - \phi) u_{AB} + (1 - \phi)^2 u_{BB}] . \quad (7.1.19)$$

Before mixing the interaction energy per site in pure A is $au_{AA}/2$ and in B $au_{BB}/2$. Hence, the total interaction energy before mixing is

$$u_0 = \frac{an}{2} [\phi u_{AA} + (1 - \phi) u_{BB}] , \quad (7.1.20)$$

so that we obtain for the energy change $\Delta u = u - u_0$ on mixing

$$\Delta u = \frac{an}{2} [\phi^2 u_{AA} + 2\phi(1 - \phi) u_{AB} + (1 - \phi)^2 u_{BB} - \phi u_{AA} - (1 - \phi) u_{BB}] \quad (7.1.21)$$

$$= \frac{an}{2} [(\phi^2 - \phi) u_{AA} + 2\phi(1 - \phi) u_{AB} + (1 - 2\phi + \phi^2 - 1 + \phi) u_{BB}] \quad (7.1.22)$$

$$= \frac{an}{2} [\phi(\phi - 1) u_{AA} + 2\phi(1 - \phi) u_{AB} + \phi(\phi - 1) u_{BB}] \quad (7.1.23)$$

$$= \frac{an}{2} \phi(1 - \phi) (2u_{AB} - u_{AA} - u_{BB}) . \quad (7.1.24)$$

We again normalize by the number n of lattice sites to arrive at the energy change per site on mixing:

$$\Delta \bar{U}_{\text{mix}} = \frac{a}{2} \phi(1 - \phi) (2u_{AB} - u_{AA} - u_{BB}) . \quad (7.1.25)$$

For discussion we need an expression that characterizes the mixing energy per lattice site as a function of composition ϕ and that can be easily combined with the mixing entropy to free energy. The *Flory interaction parameter*,

$$\chi = \frac{a}{2} \cdot \frac{2u_{AB} - u_{AA} - u_{BB}}{k_B T} , \quad (7.1.26)$$

elegantly eliminates the number of adjacent lattice sites and provides just such an expression:

$$\Delta \bar{U}_{\text{mix}} = \chi \phi(1 - \phi) k_B T . \quad (7.1.27)$$

Introducing such a parameter is an often-used trick when working with crude models. If the parameter is determined experimentally, the expression may fit data quite well, because part of the deviations of reality from the model can be absorbed by the parameter and its dependence on state variables. We finally obtain the **Flory-Huggins equation** for the Helmholtz free energy of mixing, $\Delta \bar{F}_{\text{mix}} = \Delta \bar{U}_{\text{mix}} - T \Delta \bar{S}_{\text{mix}}$,

$$\Delta \bar{F}_{\text{mix}} = k_{\text{B}} T \left[\frac{\phi}{N_{\text{A}}} \ln \phi + \frac{1-\phi}{N_{\text{B}}} \ln(1-\phi) + \chi \phi(1-\phi) \right]. \quad (7.1.28)$$

As the entropy contribution (first two terms in the brackets on the right-hand side of Equation 7.1.28) to $\Delta \bar{F}_{\text{mix}}$ is always negative, entropy always favors mixing. The sign of $\Delta \bar{F}_{\text{mix}}$ depends on the sign of the Flory parameter χ and the ratio between the energy and entropy. The Flory parameter is negative and thus favors mixing, if $2u_{\text{AB}} < u_{\text{AA}} + u_{\text{BB}}$, i.e., if the interaction in AB pairs is more attractive than the mean interaction in AA and BB pairs. Such cases occur, but are rare. In most cases, the Flory parameter is positive. Since the entropy terms are very small for polymer blends, such blends tend to phase separate. In fact, high molecular weight poly(styrene) with natural isotope abundance phase separates from deuterated poly(styrene).

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