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5.0 Thermodynamics of Polymer Solutions

In this section, we investigate the solubility of polymers in small molecule solvents. Solubility, whether a chain goes “into solution”, *i.e.* is dissolved in solvent, is an important property. Full solubility is advantageous in processing of polymers; but it is also important for polymers to be fully insoluble - think of plastic shoe soles on a rainy day! So far, we have briefly touched upon thermodynamic solubility of a single chain- a “good” solvent swells a chain, or mixes with the monomers, while a “poor” solvent “de-mixes” the chain, causing it to collapse upon itself.

Whether two components mix to form a homogeneous solution or not is determined by minimisation of a free energy. Here we will express free energy in terms of canonical variables $\{T, P, N\}$, *i.e.*, temperature, pressure, and number (of moles) of molecules. The free energy expressed in these variables is the Gibbs free energy

$$G \equiv G(T, P, N). \quad (1)$$

In previous sections, we referred to the Helmholtz free energy, F , the free energy in terms of the variables $\{T, V, N\}$. Let ΔG^m denote the free energy change upon homogeneous mixing. For a 2-component system, *i.e.* a solute-solvent system, this is simply the difference in the free energies of the solute-solvent mixture and pure quantities of solute and solvent: $\Delta G^m \equiv G(T, P, N_1, N_2) - (G^0(T, P, N_1) + G^0(T, P, N_2))$, where the superscript ⁰ denotes the pure component. If the Gibbs free energy of mixing is negative, $\Delta G^m < 0$, the solute will go into solution; if the Gibbs free energy is positive, $\Delta G^m > 0$, then the solute and solvent will not mix and remain as two pure “phases”. ΔG^m is the sum of enthalpic and entropic terms, and consequently, a sensitive balance between the entropy of mixing, ΔS^m , and the enthalpy of mixing, ΔH^m , determines the solubility:

$$\Delta G^m = \Delta H^m - T\Delta S^m.$$

As the entropy change upon mixing is always positive, $-T\Delta S^m$ is always negative: entropy *always* favours dissolution or mixing. In cases where $\Delta H^m < 0$, *i.e.*, where the interactions between solute and solvent favour mixing, then ΔG^m will be negative for all temperatures T and the solute and solvent will mix favourable at all temperatures and compositions. However, where the interactions disfavour mixing, $\Delta H^m > 0$, then whether the solute and solvent mix depends upon the balance of the favourable entropy gain of mixing and the disfavourable enthalpic penalty of mixing, moderated by temperature, T . At lower temperatures, the enthalpic term dominates and no mixing occurs. In contrast, at high temperatures, the entropic term dominates and mixing of solute and solvent occurs, either partially (at moderate temperatures) or homogeneously (at higher temperatures). “Partial mixing” or “phase separation” occurs when the mixing proceeds through the formation of 2 phases, each phase containing a homogeneous mixture of solute and solvent, but with the compositions differing in each of the phases.

In this section, we are going to explore the thermodynamics of phase separation of binary mixtures made of two components, solute and solvent. First, we need to understand thermodynamic-based constraints/rules that apply to all solute/solvent systems, including simple liquid mixtures, polymer-solvent solutions, or even metallic mixtures. There exists a basic framework that applies generally to all of these systems. This framework starts with a given expression for ΔG^m in terms of the number of moles of solvent, N_1 , and solute, N_2 , and temperature, T , and prescribes how mixing, partial mixing, and no-mixing is predicted from the expression for ΔG^m . This is the topic of section 5.1. Two solution models will be presented in sections 5.2 and 5.3: the Regular Solution model for equi-sized solvent and solute molecules, and the Flory-Huggins Solution (FH) model, an extension of the Regular Solution model to polymeric solutes. Both of these models are simplistic, but capture the essential physics of the dissolution process. Finally in section 5.4, we focus upon the solubility of polymers in solution, providing some solubility features that are not predicted by simplistic FH model.

5.1 Thermodynamic framework for understanding partial-mixing

Assume an expression for ΔG^m is known as a function of the total number of moles, N , comprised of the number of moles of solvent, N_1 , and the number of moles of solute, N_2 :

$$N \equiv N_1 + N_2.$$

Furthermore, let x_1 and x_2 represent the total mole fractions of solvent and solute, respectively:

$$1 \equiv x_1 + x_2.$$

That is, if you mix N_1 moles of solvent with N_2 moles of solute, your total mole fraction, irrespective of the formation of phases, is $x_1 = N_1/N$ and $x_2 = N_2/N$.

5.1.1 $\Delta G^m/N$ at high temperatures where homogeneous mixing occurs

Figure 1 shows a representative $\Delta G^m/N$ versus x_1 at a fixed temperature T , for a completely homogeneously mixed system. There are a few things to note from this figure:

- $\Delta G^m < 0$ for all x_1 , indicating that solvent and solute can be mixed in any proportion to create a mixed solution of arbitrary concentration.
- The curvature of ΔG^m versus x_1 (or the second derivative of ΔG^m with respect to x_1) is positive for all x_1 : $d^2(\Delta G^m/N)/dx_1^2 > 0$, or the “curve holds water”. This indicates that the mixing is homogeneous over the entire composition range.
- $\Delta G^m = 0$ for $x_1 = 0$ and $x_1 = 1$, indicating that there is no change in the free energy of mixing for a solution comprised of a pure component.

There is more information available from Figure 1 when considering two general thermodynamic relations.

The first of these relations is effectively a definition: the change in the free energy of mixing for a homogeneous mixture at composition x_1 and $x_2 = 1 - x_1$ at constant T and P is

$$\Delta G^m/N = x_1(\mu_1 - \mu_1^\circ) + x_2(\mu_2 - \mu_2^\circ). \quad (2)$$

Here μ_1 is the chemical potential of species 1 in the homogeneous mixture and μ_1° is the chemical potential of species 1 in its pure, undiluted state. You will recall that the chemical potential is defined as

$$\mu_1 = \left(\frac{\partial G}{\partial N_1} \right)_{T,P,N_2}, \quad (3)$$

i.e., it is the change in the free energy brought about by infinitesimally increasing the amount of species 1 while keeping T , P , and N_2 constant. It is a partial molar (intensive) property:

$$\begin{aligned} G_1^\circ &= \mu_1^\circ N_1 \\ G_2^\circ &= \mu_2^\circ N_2 \\ G &= \mu_1 N_1 + \mu_2 N_2. \end{aligned}$$

such that $\Delta G^m = G - (G_1^\circ - G_2^\circ)$ yields equation 3.

The second relation is the Gibbs-Duhem equation, which states that in a closed system, at constant T , P , and total number of moles N ,

$$x_1 d\mu_1 + x_2 d\mu_2 = 0. \quad (4)$$

Physically this says that any change on the partial molar Gibbs free energy of species 1 must be balanced by a restoring change in the partial molar Gibbs free energy or chemical potential of species 2, and that this balance is determined by the molar amounts of species 1 and 2.

Eqns 2 and 4 are thermodynamic constraints that MUST adhere to binary systems at constant T and P . Taken together, these equations can be re-written with a little algebra as

$$\mu_1 - \mu_1^\circ = \Delta G^m/N + x_2 \frac{d(\Delta G^m/N)}{dx_1} \quad (5)$$

and

$$\mu_2 - \mu_2^\circ = \Delta G^m/N + x_1 \frac{d(\Delta G^m/N)}{dx_2}. \quad (6)$$

You can simply derive eqn 5 by taking the derivative of both sides of eqn 2:

$$\begin{aligned} \frac{d\Delta G^m/N}{dx_1} &= \frac{d}{dx_1} \left(x_1(\mu_1 - \mu_1^\circ) \right) + \frac{d}{dx_1} \left(x_2(\mu_2 - \mu_2^\circ) \right) \\ &= (\mu_1 - \mu_1^\circ) + x_1 \frac{d\mu_1}{dx_1} + \frac{dx_2}{dx_1} (\mu_2 - \mu_2^\circ) + x_2 \frac{d\mu_2}{dx_1}. \end{aligned}$$

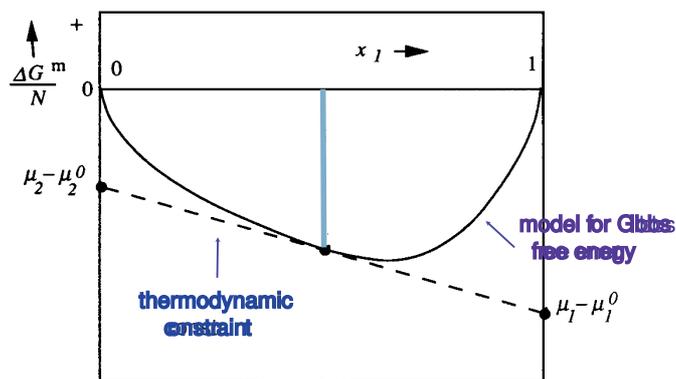


Figure 1: $\Delta G^m/N$ versus mole fraction of species 1, x_1 , for a binary system.

By Gibbs-Duhem, eqn 4, the second and fourth terms on the RHS of the last expression sum to 0 so that

$$\begin{aligned}\frac{d\Delta G^m/N}{dx_1} &= (\mu + 1_1 - \mu_1^\circ) + \frac{dx_2}{dx_1}(\mu_2 - \mu_2^\circ) \\ &= (\mu_1 - \mu_1^\circ) - (\mu_2 - \mu_2^\circ).\end{aligned}$$

Now, we can rewrite the last expression as

$$(\mu_2 - \mu_2^\circ) = (\mu_1 - \mu_1^\circ) - \frac{d\Delta G^m/N}{dx_1}$$

and substitute this into eqn 2 to yield

$$\Delta G^m/N = x_1(\mu_1 - \mu_1^\circ) + x_2\left((\mu_1 - \mu_1^\circ) - \frac{d\Delta G^m/N}{dx_1}\right),$$

and

$$\Delta G^m/N = (\mu_1 - \mu_1^\circ) - x_2 \frac{d\Delta G^m/N}{dx_1} \quad (7)$$

You will recognise this last equation as eqn 5, simply rearranged. You can similarly derive eqn 6.

Eqns 5 and 6 are thermodynamic relations that tell you how the chemical potential of each species changes as it goes from the initial pure system to the homogeneous mixture. You will also see that eqns 5 and 6, rearranged as in eqn 7, correspond to the tangents of the $\Delta G^m/N$ versus x_1 curve. That is, eqn 7 is a line of the form

$$y = mx + b$$

where m is the slope and b is the intercept (or the value of y at $x = 0$). The slope is simply the tangent to the curve, $\Delta G^m/N$, or $d(\Delta G^m/N)/dx_1$, and the intercept is simply $\mu_1 - \mu_1^\circ$. Recognising that $x_2 = 1 - x_1$ and that $d(\Delta G^m/N)/dx_1 = -d(\Delta G^m/N)/dx_2$, you can additionally show that eqn 6 is the identical line given by eqn 5 but additionally provides the intercept at $x_1 = 1$ of $\mu_2 - \mu_2^\circ$.

This is valuable. This construction tells you the chemical potential of the species in homogeneous mixtures at ANY composition.

5.1.2 $\Delta G^m/N$ at temperatures where partial mixing occurs.

Figure 2 shows a representative $\Delta G^m/N$ versus x_1 curve at a fixed temperature, T , for a partially mixed system where two phases of different composition co-exist. There are a few things to note from this figure:

- $\Delta G^m < 0$ for all x_1 , indicating that solvent and solute can be mixed in any proportion to create a mixed solution.
- $\Delta G^m = 0$ for $x_1 = 1$ or $x_1 = 0$, indicating that there is no change in the Gibbs free energy of mixing for a pure component.

- The curvature of ΔG^m versus x_1 (or the second derivative of ΔG^m with respect to x_1) is negative, $d^2(\Delta G^m/N)/dx_1^2 < 0$ over an intermediate concentration range, or the “curve spills water”. This indicates that the mixing is not homogeneous over this particular range for composition ranges. Homogeneous solutions can be made only for those compositions where $d^2(\Delta G^m/N)/dx_1^2 > 0$

The thermodynamic “mantra” that systems evolve to lower their free energy applies here. Consider that you are trying to make a homogeneous mixture of composition x_1 , where the curvature of $\Delta G^m/N$ is negative. From Figure 2, you can see that the system can lower its free energy by separating into two phases. However, the composition of these phases is NOT given by the minima of $\Delta G^m/N$. This is because the system has to minimise its free energy with an additional thermodynamic constraint: the chemical potential of each species in different phases MUST BE IDENTICAL. That is, the compositions are given by a single tangent to the $\Delta G^m/N$ curve so that $\mu_1 - \mu_1^0$ is the change in the chemical potential of species 1 irrespective of which phase a molecule of species 1 partitions to. Likewise, $\mu_2 - \mu_2^0$ is the chemical potential change of species 2. The compositions at which the tangent “kisses” the $\Delta G^m/N$ curve are referred to as the *binodals* and are the compositions of the two co-existing phases.

So now we can describe the mixing or partial mixing that results at this temperature over the entire compositions range. First, let x_1^{b1} be the binodal composition of the phase lean in species 1, and x_1^{b2} be the binodal composition of the phase rich in species 1. If we try to make a homogeneous mixture with mole fractions in the ranges $0 < x_1 < x_1^{b1}$ or $x_1^{b2} < x_1 < 1$, we will be successful. The change in chemical potential of the species is found by constructing the line that is tangent to $\Delta G^m/N$ at x_1 as described in Section 5.1.1. However, if we try to construct a homogeneous solution with composition in the unstable composition range $x_1^{b1} < x_1 < x_1^{b2}$, we will fail and instead achieve two separated or unmixed phases with compositions x_1^{b1} and x_1^{b2} . The relative amount or volume of these two phases will depend upon the total amounts of species 1 and 2 added. For mole fractions a little larger than x_1^{b1} , there will be one majority phase of composition x_1^{b1} and a small or minority phase of compositions x_1^{b2} . As more species 2 is added, the concentrations of the two phases remains constant at x_1^{b1} and x_1^{b2} , but the volume of the minority phase will grow. At total mole fractions a little smaller than x_1^{b2} , the minority

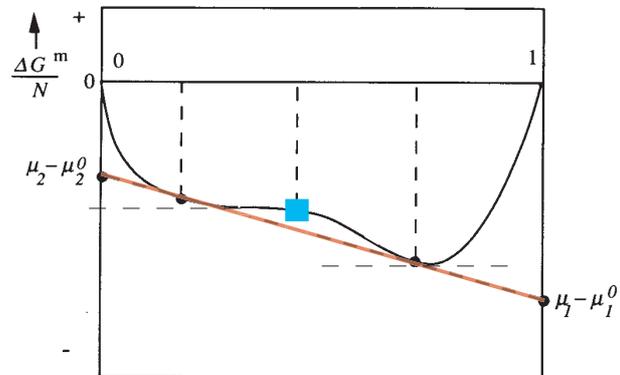


Figure 2: $\Delta G^m/N$ versus mole fraction of species 1, x_1 for a binary system at a temperature where partial mixing occurs. At a composition noted by the blue box on the $\Delta G^m/N$ curve, the solution can lower its energy by separating into two mixed phases. On first “guess-timate”, you might expect that the composition of the phases is given by the local minima of the $\Delta G^m/N$ curve, *i.e.*, where $\Delta G^m/N = 0$. However the tangents to these minima (grey dashed lines) suggest that the chemical species differs in the phases. This cannot happen: the compositions of the co-existing phases must be such that the chemical potential of each species is identical. That is, there must be one tangent that “kisses” the $\Delta G^m/N$ curve at two compositions. These binodal compositions are *not* the composition at the local minima.

phase will be of composition $x_1^{b_1}$ and the majority phase will be of composition $x_1^{b_2}$. The relative amounts of the binodal phases is determined by a mole balance.

If partial mixing or phase separation occurs at any given temperature, then there exist inflection points in the $\Delta G^m/N$ versus x_1 curve. An inflection point occurs at a value of x_1 where the curvature changes sign, or $d^2(\Delta G^m/N)/dx_1^2 = 0$. If partial mixing occurs at a given temperature, then there will be exactly two inflection points, referred to as *spinodals*, Figure 3. The spinodal compositions, *i.e.*, the mole fractions at which $d^2(\Delta G^m/N)/dx_1^2 = 0$, lie inside the unstable composition range, $x_1^{b_1} < x_1 < x_1^{b_2}$. That is, if $x_1^{spinodal_1}$ represents the spinodal composition that is lean in species 1, then

$$x_1^{b_1} < x_1^{spinodal_1} < x_1 < x_1^{spinodal_2} < x_1^{b_2}.$$

For a total concentration that lies between the spinodals, $d^2(\Delta G^m/N)/dx_1^2 < 0$. Suppose you could create a “homogeneous” solution of concentration, x_1 , $x_1^{spinodal_1} < x_1 < x_1^{spinodal_2}$; this solution would be unstable to small fluctuations in the local concentration. Any local fluctuation in concentration would lower the energy of the solution, see figure 4(a), and consequently the homogeneous solution would “spontaneously decompose” and phase separate. The kinetics of this process is referred to as *spinodal decomposition* and it can be studied, not in simple solutions where the decomposition is very fast, but in metallic systems where the kinetics are limited by the small diffusion coefficients.

For total concentrations that lie between the binodal-spinodal, *i.e.* $x_1^{b_1} < x_1 < x_1^{spinodal_1}$ and $x_1^{spinodal_2} < x_1 < x_1^{b_2}$, the curvature is positive. Thus a homogeneous solution in these concentration ranges will phase separate, but will do so more slowly. This is because phase separation *will* lower the free energy; however, the homogeneous solution is stable to small fluctuations in the local concentration, see Figure 4(b). We say that the solution is *metastable*. Only large local fluctuations will lower the energy and consequently, as large fluctuations are not as frequent as smaller fluctuations in the concentration, the process of phase separation is slow in comparison to spinodal decomposition. The process by which these metastable solutions phase separate is referred to as *nucleation and growth*.

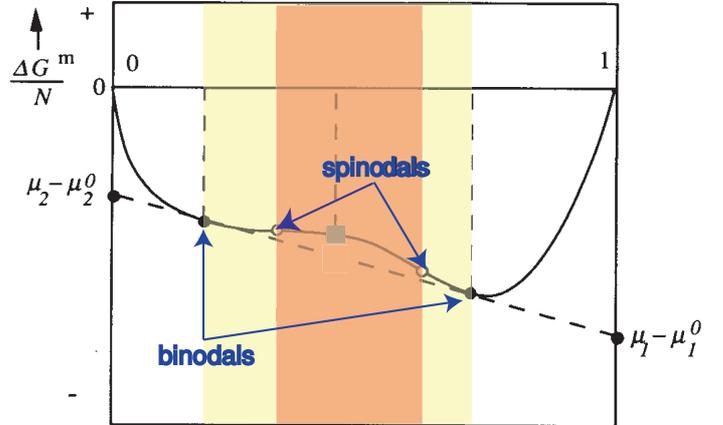


Figure 3: $\Delta G^m/N$ versus mole fraction of species 1, x_1 for a binary system at a temperature where particle mixing occurs. The compositions over which homogeneous mixtures are unstable are shown in the shaded region, bounded by the compositions at the binodals. The spinodals or inflection points in the $\Delta G^m/N$ curve, bound the region of instability (center orange). Between the spinodal and binodal compositions lies a region of metastability, where a homogeneous mixed solution is stable to only small fluctuations in local concentration.

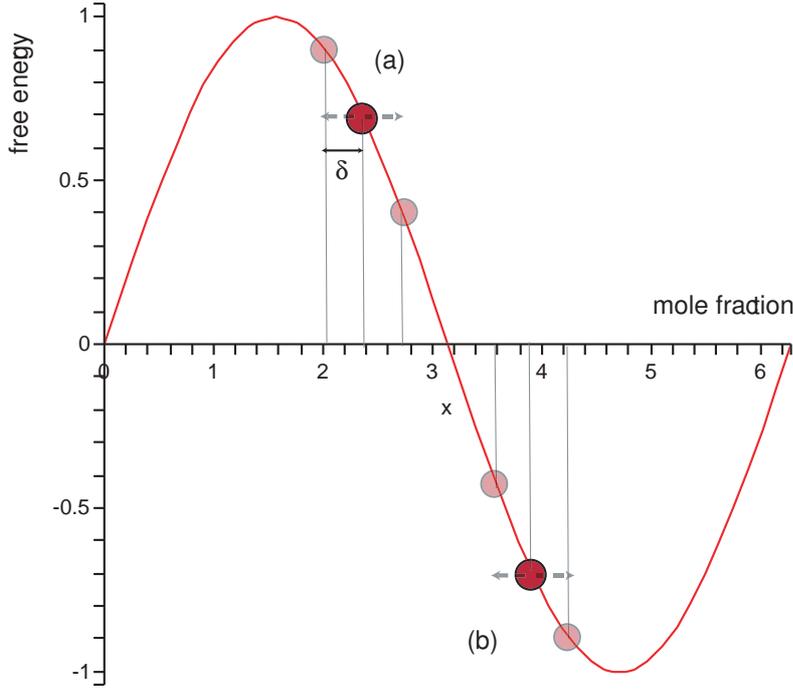


Figure 4: A graphical explanation why negative curvature leads to instantaneous de-mixing while positive curvature in $\Delta G^m/N$ is indicative of metastable mixtures. Shown is a model $\Delta G^m/N$ curve that has both (a) negative and (b) positive curvature. Let the dark circles represent hypothetical, homogeneous mixtures which are unstable and have free energy g^0 . Consider a local concentration fluctuation of magnitude $\pm\delta$, leading to local partial de-mixing to transient phases (lighter circles) with free energies of $g(\delta)$ and $g(-\delta)$. (a) Under negative curvature, the solution is unstable to the small local fluctuations, *i.e.*, $g(\delta) + g(-\delta) < 2g^0$. You can see from a simple Taylor expansion ($g(\delta) = g^0 + \delta g' + \delta^2 g'' + \dots$) that in order for the energy of the new phases to be lower, or $g(\delta) + g(-\delta) < 2g^0$, that the curvature has to be negative, or $g'' < 0$. (b) Under positive curvature, the solution is stable to small local concentration fluctuations *i.e.* $g(\delta) + g(-\delta) > 2g^0$. Again, inspection of the Taylor expansion shows that the free energy under small fluctuations is greater than the homogeneous mixture if $g'' > 0$.

Figure 5 shows several $\Delta G^m/N$ -composition curves at different temperatures. As the temperature increases, the unstable concentration range shrinks as the inflection points, or spinodals approach one another. At a critical temperature, T_c , the spinodals coalesce and the unstable region disappears, T_c is found as that temperature at which

$$\frac{d}{dx_1} \frac{d^2 \Delta G^m/N}{dx_1^2} = 0 \quad (8)$$

A solution that is more prone to de-mixing is one that has a higher T_c . The higher T_c , the more difficult it is to get the solute into solution.

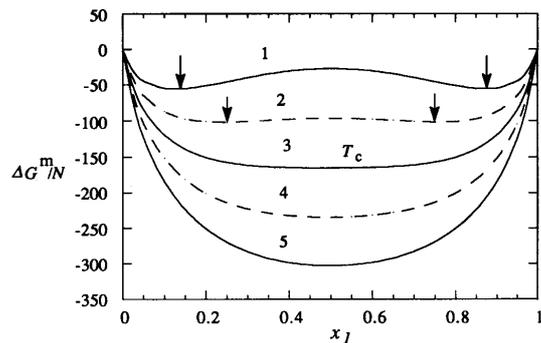


Figure 5: $\Delta G^m/N$ versus x_1 for a range of temperatures, $T_1 < T_2 < T_3, T_4, T_5$. Arrows indicate the binodals found at the two temperatures T_1 and T_2 . T_3 corresponds to a critical temperature at which the spinodals merge and mixing occurs. For this collection of curves, you can construct a phase diagram showing the composition of phases as a function of temperature.

5.2 The Regular Solution Model for $\Delta G^m/N$

The Regular Solution Model (RSM) provides a fundamental model for the mixing of equi-size solutes and solvents. The RSM is based upon simple expressions for the enthalpic and entropic contributions to the free energy,

$$G = H - TS,$$

constructed using a lattice whose sites are filled with solute and solvent molecules. The entropy change of mixing solute and solvent molecules is found by counting the number of different ways of randomly placing N_1 solvent molecules and N_2 solvent molecules on a lattice of $N = N_1 + N_2$ sites:

$$\Delta S^m = k_B \ln \left[\frac{N!}{N_1!N_2!} \right] - k_B \ln \left[\frac{N_1!}{N_1!} \right] - k_B \ln \left[\frac{N_2!}{N_2!} \right] \quad (9)$$

where the last two terms are the number of ways of filling a lattice entirely with indistinguishable solvent or solute molecules, respectively. Approximating the logarithmic terms of the factorials with $\ln N! \sim N \ln N - N$ and converting to fractions of molecules yields

$$\frac{\Delta S^m}{k_B} = -N(x_1 \ln x_1 + x_2 \ln x_2). \quad (10)$$

To construct the enthalpic contribution, we assume that we are given the enthalpic energies of solvent-solvent, solvent-solute, and solute-solute molecule pairs: ϵ_{11} , ϵ_{12} , and ϵ_{22} . The enthalpy is then

$$H = N_{11}\epsilon_{11} + N_{12}\epsilon_{12} + N_{22}\epsilon_{22}$$

where N_{11} is the number of nearest-neighbor solvent-solvent pairs on the lattice, N_{12} is the number of nearest-neighbor solvent-solute pairs, and N_{22} is the number of nearest-neighbor solute-solute pairs on the lattice. You can approximate these numbers as the molecules are placed randomly on the lattice. N_{11} is the number of solvent molecules times the probability of finding a solvent molecule on one of the z nearest-neighbor lattice sites, zx_1 , divided by 2 to correct for double-counting:

$$N_{11} = N_1 \times \frac{zx_1}{2}.$$

Likewise, the number of nearest-neighbor pairs of solvent-solute and solute-solute on the lattice are

$$\begin{aligned} N_{22} &= N_2 \times \frac{zx_2}{2}, \\ N_{12} &= N_1 \times zx_2. \end{aligned}$$

Thus the change in enthalpy upon mixing will be

$$\Delta H^m = (N_{11} - N_{11}^0)\epsilon_{11} + (N_{12} - N_{12}^0)\epsilon_{12} + (N_{22} - N_{22}^0)\epsilon_{22},$$

where the superscript \circ denotes the number of pairs in a pure solution of solvent or solute, or

$$\Delta H^m = Nx_1x_2 \times z\left(\epsilon_{12} - \frac{\epsilon_{11}}{2} - \frac{\epsilon_{12}}{2}\right).$$

The last factor in the above expression is often cast as \mathcal{B}/N_A where N_A is Avogadro's number. Combining the enthalpic and entropic terms gives the RSM model

$$\Delta G^m/N = \frac{\mathcal{B}}{N_A}x_1x_2 + k_B T(x_1 \ln x_1 + x_2 \ln x_2),$$

or if N is taken to be the number of moles and x_i the mole fraction, the RSM yields

$$\Delta G^m/N = \mathcal{B}x_1x_2 + RT(x_1 \ln x_1 + x_2 \ln x_2). \quad (11)$$

Equation 12 is a model that is symmetric about $x_1 = 0.50$. This is a result of the assumption of equi-sized solutes and solvents. It is possible to include different sizes of solutes and solvents in a similar analysis and achieve a model $\Delta G^m/N$ that is asymmetrical in composition. This is referred to as the Hildebrand-Scott Solution Theory for solute-solvent molecules that differ in size, but not by much. Clearly, for polymer solution theory, the solute (polymer) molecule is *much* larger than the size of a solvent molecule.

5.3 The Flory Huggins Model for $\Delta G^m/N$

The Flory-Huggins Model (FH) for polymer solutions is effectively a modification of the RSM to account for the large size of the solute or polymer molecule, relative to the solvent molecule. FH is a lattice-based model. The sites of the lattice are not filled with solvent/solute randomly, but rather with solvent and monomer units. The monomer units cannot be placed randomly, as they must be linked linearly to form chains of \mathcal{N} units. Thus the FH is a lattice-based model where the sites of the lattice are filled with N_1 solvent molecules and $\mathcal{N}N_2$ monomer units where N_2 is the number of polymer molecules.

5.3.1 ΔS^m for Flory-Huggins

To determine ΔS^m , we need to count the number of ways of placing N_2 polymers, each of \mathcal{N} monomers, on a lattice. We do this by considering the number of ways of placing the first chain, the second chain, *etc.*

Consider placement of the first chain in an empty lattice of N sites. There are N possible sites to place the first monomer. The second monomer must be in one of the z nearest-neighbor sites that are empty. The probability that any site is empty is $(N - 1)/N$ so that the number of ways of placing the first two monomers of the first chain is

$$N \times z \frac{N - 1}{N}.$$

The number of ways of placing the third monomer is $z - 1$ (the chain cannot lie on top of itself, thus there is one less vertex available for occupation) times the probability that these sites are empty, which is taken as the probability that any site is empty, $(N - 1)/N$. The approximation that the probability that a site is empty is equivalent to the average or random occupancy of the entire lattice is the mean-field approximation. It is an oversimplification, but it allows us to count the configurations.

The number of ways of putting all \mathcal{N} monomers of the first chain, Ω_1 is

$$\Omega_1 = N \times z \left(\frac{N-1}{N} \right) \times (z-1) \left(\frac{N-2}{N} \right) \times (z-1) \left(\frac{N-3}{N} \right) \times \dots \times (z-1) \left(\frac{N-\mathcal{N}-1}{N} \right).$$

For the second chain, it is

$$\begin{aligned} \Omega_2 = & (N-\mathcal{N}) \times z \left(\frac{N-\mathcal{N}-1}{N} \right) \times (z-1) \left(\frac{N-\mathcal{N}-2}{N} \right) \times (z-1) \left(\frac{N-\mathcal{N}-3}{N} \right) \times \\ & \dots \times (z-1) \left(\frac{N-2\mathcal{N}-1}{N} \right). \end{aligned}$$

For the third chain, it is

$$\begin{aligned} \Omega_3 = & (N-2\mathcal{N}) \times z \left(\frac{N-2\mathcal{N}-1}{N} \right) \times (z-1) \left(\frac{N-2\mathcal{N}-2}{N} \right) \times (z-1) \left(\frac{N-2\mathcal{N}-3}{N} \right) \\ & \times \dots \times (z-1) \left(\frac{N-3\mathcal{N}-1}{N} \right), \end{aligned}$$

and for the last chain it is

$$\begin{aligned} \Omega_{N_2} = & (N-(N_2-1)\mathcal{N}) \times z \left(\frac{N-(N_2-1)\mathcal{N}-1}{N} \right) \times (z-1) \left(\frac{N-(N_2-1)\mathcal{N}-2}{N} \right) \times \\ & (z-1) \left(\frac{N-(N_2-1)\mathcal{N}-3}{N} \right) \times \dots \times (z-1) \left(\frac{N-N_2\mathcal{N}-1}{N} \right). \end{aligned}$$

The total number of configurations, Ω^m is

$$\begin{aligned} \Omega^m &= \Omega_1 \times \Omega_2 \times \dots \times \Omega_{N_2} \\ &= \left(\frac{z}{z-1} \right)^{N_2} \left(\frac{z-1}{N} \right)^{(\mathcal{N}-1)N_2} N!. \end{aligned}$$

We further divide by N_1 and N_2 as the molecules are indistinguishable:

$$\Omega^m = \left(\frac{z}{z-1} \right)^{N_2} \left(\frac{z-1}{N} \right)^{(\mathcal{N}-1)N_2} \frac{N!}{N_1!N_2!}. \quad (12)$$

We also need to find the number of configurations of the initial pure solvent and initial pure polymer. For the pure solvent, it is simply the number of ways we can put N_1 indistinguishable solvent molecules only N_1 sites: one way. For the pure polymer, the number of ways of putting N_2 chains onto $\mathcal{N}N_2$ sites is found from Ω^m where the total number of sites is set to $\mathcal{N}N_2$ and $N_1 = 0$, resulting in

$$\Omega^0 = \left(\frac{z}{z-1} \right)^{N_2} \left(\frac{z-1}{N} \right)^{(\mathcal{N}-1)N_2} \frac{(\mathcal{N}N_2)!}{N_2!}. \quad (13)$$

The change in entropy upon mixing is found from

$$\Delta S^m = k_B \ln \left[\frac{\Omega^m}{\Omega^0} \right],$$

equations (12) and (13), and Stirling's approximation ($\ln x! \sim x \ln x - x$):

$$\Delta S^m = -R(N_1 \ln \left(\frac{N_1}{N} \right) + N_2 \ln \left(\frac{\mathcal{N}N_2}{N} \right)), \quad (14)$$

where we use the gas constant R instead of k_B as we let N_1 and N_2 represent the number of moles (rather than number of molecules). Because mole fractions of polymers can be exceptionally

small, it is more convenient to express concentrations of polymer solutions in terms of volume fractions:

$$\begin{aligned}\phi_1 &= \frac{N_1}{N_1 + \mathcal{N}N_2}, \\ \phi_2 &= \frac{\mathcal{N}N_2}{N_1 + \mathcal{N}N_2},\end{aligned}$$

resulting in

$$\Delta S^m = -R(N_1 + \mathcal{N}N_2)\left(\phi_1 \ln \phi_1 + \frac{\phi_2}{\mathcal{N}} \ln \phi_2\right). \quad (15)$$

5.3.2 ΔH^m for Flory-Huggins

In counting the number of ways of putting a polymer molecules, each of \mathcal{N} monomers, onto a lattice, we assumed that the local concentration of monomer was equivalent to the global or average lattice concentration. This was the mean field approximation. This approximation is exactly the same approximation used to find ΔH^m for the Regular Solution Model. Hence, FH and RSM use the same enthalpic term:

$$\Delta H^m = (N_1 + \mathcal{N}N_2)\mathcal{B}\phi_1\phi_2. \quad (16)$$

5.3.3. The Flory Huggins model for $\Delta G^m/N$

Combining the FH entropy of mixing and the standard RS enthalpy of mixing yields the FH solution theory for polymers:

$$\frac{\Delta G^m}{N} = \mathcal{B}\phi_1\phi_2 + RT\left(\phi_1 \ln \phi_1 + \frac{\phi_2}{\mathcal{N}} \ln \phi_2\right).$$

As written above, this equation is comparable to the free energy of mixing from the Regular Solution Model. Notice that the expressions differ in two ways: first, FH is cast in volume fractions rather than mole fractions, and second, FH is no longer symmetric in concentration due to the $1/\mathcal{N}$ factor in the entropy term. We need to do one more thing before completing this derivation of FH: insert the Flory-Huggins parameter, χ , which is defined as

$$\chi = \frac{\mathcal{B}}{RT}, \quad (17)$$

so that the Flory-Huggins free energy of mixing is:

$$\frac{\Delta G^m}{NRT} = \chi\phi_1\phi_2 + \phi_1 \ln \phi_1 + \frac{\phi_2}{\mathcal{N}} \ln \phi_2. \quad (18)$$

Now, the mechanics of determining phase behaviour from eqn 18 remains unchanged and are listed below:

1. To determine if partial de-mixing or phase separation occurs at any given temperature T , check to see if there are inflection points in $\Delta G^m/(NRT)$. A simple way of doing this is to plot $\partial^2(\Delta G^m/(NRT))/\partial\phi_1^2$ versus ϕ_1 or equivalently $\partial^2(\Delta G^m/(NRT))/\partial\phi_2^2$ versus ϕ_2 . If there is phase separation then:

- (a) The spinodal compositions are given by the intersection of $\partial^2(\Delta G^m/(NRT))/\partial\phi_1^2$ versus ϕ_1 with the composition coordinate.
- (b) The binodal compositions are given by the double intersection of $\Delta G^m/(NRT)$ with the thermodynamic constraints.¹

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \Delta G^m/(NRT) + \phi_2 \left(\frac{\partial(\Delta G^m/(NRT))}{\partial\phi_1} \right)$$

and

$$\frac{\mu_2 - \mu_2^\circ}{RT} = \Delta G^m/(NRT) + \phi_1 \left(\frac{\partial(\Delta G^m/(NRT))}{\partial\phi_2} \right).$$

- (c) The critical temperature, T_c , is found at the temperature at which the spinodals merge into one compositions, Φ_2^c . These are found from

$$\frac{\partial}{\partial\phi_1} \left(\frac{\partial^2(\Delta G^m/(NRT))}{\partial\phi_1^2} \right) = 0.$$

2. If there is no phase separation, then the solution is completely stable as a homogeneous mixture.

We expect that the longer the chains are, *i.e.* the larger the number of monomers per chain, \mathcal{N} , the more difficult it is to completely solubilise them in a homogeneous mixture. Longer chains are more difficult to keep in solution. This is because their entropy of mixing is not as large as the entropy of mixing for smaller chains. You can see this from the FH model by inspecting how T_c varies with \mathcal{N} . T_c is found as that temperature at which the spinodals merge,

$$\frac{\partial}{\partial\phi_1} \left(\frac{\partial^2(\Delta G^m/(NRT))}{\partial\phi_1^2} \right) \equiv \frac{\partial}{\partial\phi_1} \left(\frac{\partial\mu_1}{\partial\phi_1} \right) \equiv \frac{\partial}{\partial\phi_2} \left(\frac{\partial\mu_1}{\partial\phi_2} \right) = 0.$$

Using the combined FH - thermodynamic constraint,

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \ln\phi_1 + \left(1 - \frac{1}{\mathcal{N}}\right)\phi_2 + \chi\phi_2^2 \quad (19)$$

$$\frac{\partial}{\partial\phi_2} \left(\frac{\mu_1 - \mu_1^\circ}{RT} \right) \equiv \frac{\partial\mu_1}{\partial\phi_2} = -\frac{1}{\phi_1} + \left(1 - \frac{1}{\mathcal{N}}\right) + 2\chi\phi_2 \quad (20)$$

$$\frac{\partial^2\mu_1}{\partial\phi_2^2} = -\frac{1}{\phi_1^2} + 2\chi \quad (21)$$

The existence of the spinodal, given by eqn 20 set to 0, and the merging of the spinodals at the critical temperatures, given by eqn 21, yields expressions for ϕ_2^c and χ_c :

$$\phi_2^c = \frac{1}{1 + \mathcal{N}} \quad (22)$$

$$\chi_c \equiv \frac{B}{RT_c} = \frac{1}{2} + \frac{1}{2\mathcal{N}} + \frac{1}{\sqrt{\mathcal{N}}}. \quad (23)$$

¹Often these thermodynamic constraints are reported with the model free energy inserted. Thus sometimes, you will see the FH model reported as

$$\frac{\mu_1 - \mu_1^\circ}{RT} = \ln\phi_1 + \left(1 - \frac{1}{\mathcal{N}}\right)\phi_2 + \chi\phi_2^2$$

and

$$\frac{\mu_2 - \mu_2^\circ}{RT} = \ln\phi_2 + \left(1 - \frac{1}{\mathcal{N}}\right)\phi_1 + \chi\phi_1^2.$$

These are simply eqn 18 inserted into the thermodynamic constraints that follow.

The FH predictions given in eqns 22 and 23 are qualitatively found in experimental phase diagrams of polymer solutions:

- Larger polymers are more difficult to solubilise. This is reflected in eqn 23, which details how larger \mathcal{N} leads to larger T_c . You only have to lower the temperature a little to precipitate out large polymer chains in solution; you have to lower the temperature further to precipitate out smaller chains.
- When chains first de-mix from solution at T_c , the volume fraction of monomer is very low. This is evidenced in eqn 22 where $\phi_2^c \sim \mathcal{N}^{-1}$.
- For a given monomer-solvent pair where B is a constant, χ_c decreases with increasing number of monomers. In the limit of $\mathcal{N} \rightarrow \infty$, $\chi_c = 0.5$.

Figure 6 shows the experimentally found phase diagram ($T-\phi_2$) for solutions of poly-isobutylene at three different molecular weights. The FH solution theory does not quantitatively predict correctly the binodals, however FH *does* capture the qualitative features of the phase separation: (a) larger chains have larger T_c s and are more difficult to keep in solution, and (b) ϕ_2^c is small and becomes smaller as the molecular weight or \mathcal{N} increases.

T_c is also referred to as the “theta” temperature or θ -temperature. At $T > T_c$, the chains are homogeneously mixed in solution, indicative of a “good” solvent where monomer-solvent interactions are favourable. At $T < T_c$, the monomer-solvent interactions are no longer favourable and the polymer solution de-mixes into phases of compositions at which these unfavourable interactions balance mixing entropy. At T_c , the monomer-solvent interactions are neither favourable or unfavourable and the chain is unperturbed by interactions. As explained earlier, these interactions, as described by the second virial coefficient, change sign in going from good solvent to poor solvent, so that T_c or the “theta” temperature can be identified with vanishing second virial coefficient. Thus, in the limit of $\mathcal{N} \rightarrow \infty$, these chains behave as ideal chains, exhibiting random walk or Gaussian statistics.

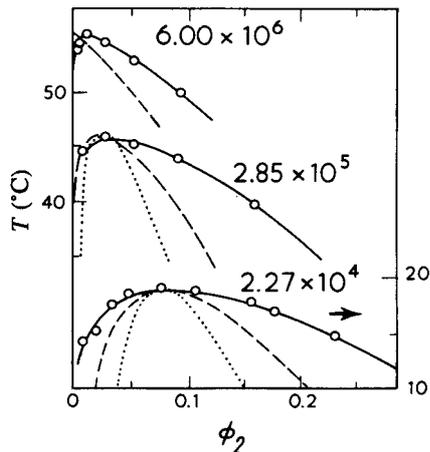


Figure 6: Experimental and calculated phase diagrams, T versus ϕ_2 , for three polyisobutylene polymer solutions with different molecular weights. The dashed curves are the binodals calculated from FH and the dotted curves are the spinodals. Open circles and their connecting lines are experimental results. Reproduced from Boyd & Phillips.

Finally, most homogeneous polymer solutions will phase separate again when the temperature is increased. This high temperature de-mixing is not described by FH theory and is the result of enthalpic changes at high temperatures. Thus, there is an additional critical temperature that is larger than the T_c discussed above. This second critical temperature is referred

to as the Lower Critical Solution Temperature or LCST - temperatures higher than the LCST will result in demixing. So while the take-home-message from FH is that polymers are difficult to solubilise in solutions, it is actually even more difficult than FH suggests: there is only a temperature *window* over which a polymer will solubilise at all compositions.