Lecture 8: The Flory-Huggins Theory

Classification of solutions

We have already seen that single polymer molecules in an athermic solution (no interactions except for excluded volume ones) swell. Let us consider now a polymer solution. In our lattice model this will correspond to \( n \) polymer chains of \( N \) monomers each (we consider a monodisperse situation) present simultaneously on a lattice of \( N_0 \) sites. The overall number of monomers will be \( N_{\text{mon}} = nN \), and we will denote the number concentration of these monomers by \( \Phi = N_{\text{mon}} / N_0 \). The volume concentration of the monomers will be denoted by

\[
\phi = \frac{\Phi}{a^3} = \frac{N_{\text{mon}}}{N_0 a^3} = \frac{N_{\text{mon}}}{V}.
\]

The concentration of molecules is \( N \) times smaller, \( c = \frac{n}{V} = \frac{\phi}{N} \). Note that the distance between the two molecules is \( l = c^{-1/3} \) when measured in meters, or \( l = \Phi^{-1/3} / N \) when measured in the lattice spacing units, and that the size of each molecule is \( R_F \approx aN^{\nu} \) rsp. \( R_F \approx N^{\nu} \) when measured in the same units. Therefore for \( c \ll c^* = \frac{1}{R_F^3} = a^{-3}N^{-3\nu} \) (or \( \Phi \ll N^{1-3\nu} \)) the molecules do not overlap: this is a regime of a dilute solution. When \( c > c^* \) the molecules start to overlap and interact strongly. The solutions with \( c > c^* \) but \( \Phi \ll 1 \), i.e. ones with \( N^{1-3\nu} \ll \Phi \ll 1 \), are called semidilute solutions. The cases with \( \Phi \approx 1 \) correspond to concentrated solutions, and the limiting case \( \Phi = 1 \) corresponds to a polymer melt (if fluid) or to a solid. Our aim now is to learn as much as possible about polymer solutions and melts.

Binary alloy

Let us first consider an auxiliary problem. In one of our first homeworks we considered a lattice gas, a model in which \( n \) molecules can take one of \( N_0 \gg 1 \) possible positions on the lattice. The concentration of the molecules was \( \Phi = n / N_0 \). The entropy of the lattice gas is

\[
S = k_B \ln W
\]

with

\[
W = \frac{N_0!}{n!(N_0 - n)!}
\]

was approximately given by the following expression

\[
S = \text{const} - k_B N_0 [(1 - \Phi) \ln (1 - \Phi) + \Phi \ln \Phi]
\]

or

\[
S = S_0 - k_B [N_1 \ln (\Phi_1) + n \ln \Phi]
\]
where $N_i$ and $\Phi_i$ is the number and concentration of empty spaces. Of course, nothing will change if we consider not a lattice gas, but a binary alloy, i.e. assume that $n$ sites of our lattice are occupied by atoms of type A (say Cu), and the rest of $N_i = N_0 - n$ sites by atoms of type B (say Zn). The two terms in Eq.(1) are interpreted as translational entropies of the atoms of two types. The form of a translational entropy for each sort of atoms is $const - k_B n \ln \Phi$ with $n$ being the number of atoms of the given sort and $\Phi$ the corresponding concentration.

However, a lattice gas was an athermal model, and the atoms at neighboring places in a lattice can interact. This interaction in the simplest form (Bragg-Williams model) is given by the following consideration. Let the interaction energy of a pair of neighboring sites be $\varepsilon_{AA}$ if both of them are occupied by A-atoms, $\varepsilon_{AB}$ if one is occupied by A- and another one by B-atom, and $\varepsilon_{BB}$ if both atoms are B. If the numbers of the corresponding pairs is $N_{AA}$, $N_{AB}$ and $N_{BB}$ then the internal energy of the system can be represented as

$$U = \varepsilon_{AA}N_{AA} + \varepsilon_{AB}N_{AB} + \varepsilon_{BB}N_{BB}.$$ 

Fig.1: The binary alloy model on a square lattice with $N_0 = 64$ sites: Black circles (16 on total) represent the A atoms, and white (empty) ones the B atoms.

Now let $C$ be the coordination number of our lattice, $N_A = \Phi N_0$ be the number of A-atoms and $N_B = (1 - \Phi)N_0$ be the number of B atoms. Let us consider sites occupied by A, and all $CN_A$ bonds emanating from them. These bonds correspond either to AB or to AA pairs of nearest neighbors, so that

$$CN_A = 2N_{AA} + N_{AB}.$$ 

The prefactor 2 is connected to the fact that an AA-bond is counted twice in $CN_A$, starting with each of its ends. The similar equation for $CN_B$ reads
$CN_B = 2N_{bb} + N_{ab}.$

From this we get:

$$N_{aa} = \frac{C}{2}N_A - \frac{1}{2}N_{ab}$$

$$N_{bb} = \frac{C}{2}N_B - \frac{1}{2}N_{ab}$$

and therefore $U$ can be put into the form

$$U = \varepsilon_{aa}N_{aa} + \varepsilon_{ab}N_{ab} + \varepsilon_{bb}N_{bb}$$

$$= \left[ \frac{C}{2}\varepsilon_{aa}N_A + \frac{C}{2}\varepsilon_{bb}N_B \right] + \left( \varepsilon_{ab} - \frac{1}{2}\varepsilon_{aa} - \frac{1}{2}\varepsilon_{bb} \right)N_{ab}.$$

The term in square brackets in the second line is simply the sum of the internal energies of pure elements A and B, and the second term in the second line is the interaction energy:

$$U = U_0 + \left( \varepsilon_{ab} - \frac{1}{2}\varepsilon_{aa} - \frac{1}{2}\varepsilon_{bb} \right)N_{ab}.$$

The simplest assumption about $N_{ab}$ in our model of homogeneous, disordered solution (or alloy) is to take that for each bond its each end corresponds to A or B atom with probability $\Phi$ or $1-\Phi$ respectively. Since there are exactly $C$ bonds per site in our lattice (i.e. $NC$ bonds on total), we get $N_{ab} = NC\Phi(1-\Phi)$. The free energy of our homogeneous solution is thus

$$F = U - TS = F_0 + N_0C\left( \varepsilon_{ab} - \frac{1}{2}\varepsilon_{aa} - \frac{1}{2}\varepsilon_{bb} \right)\Phi(1-\Phi) + k_BTN_0[(1-\Phi)\ln(1-\Phi) + \Phi\ln\Phi]$$

with $F_0 = U_0 - TS_0$. Recalling the form of $U_0$ we see that $F_0 = \Phi F_A + (1-\Phi)F_B$ can be considered as the free energy of the system in which $N_A = \Phi N_0$ sites are filled by A and $N_B = (1-\Phi)N_0$ sites are filled by B compactly, while fully neglecting the interaction between them (i.e. neglecting the surface tension on the boundary). Thus, $F_0$ can be considered as a free energy of the pure elementary materials before mixing, and the additional term describes changes in the free energy due to mixing.

**Flory-Huggins theory of polymer solutions**

Considering the polymer solution, a change in our previous consideration is needed. This one concerns the contribution of the polymer molecules into the whole entropy of the system.
Fig.2: The polymer model on a square lattice with $N_0 = 64$ sites: Black circles represent two polymer molecules of 8 monomer each (16 monomers on total), and white (empty) ones the solvent molecules. Note that in Fig.1 it is impossible to connect the circles into molecules represented by connected neighboring sites: The number of configurations of such connected objects is much smaller than the ones for disconnected “atoms”. The entropy of the polymeric solution is thus (much) lower than of the one of disconnected monomers.

In a system of $N_0$ sites with $n$ polymers of $N$ monomers each (i.e. $n$ non-intersecting strings of $N$ neighboring sites) and $N_1 - nN$ solvent molecules (former “B-atoms”) we will get

$$W = \frac{N_0!}{N!W(n,N)}$$

where $W(n,N)$ is the number of ways to organize the monomers in the corresponding polymeric molecules and the molecules among themselves. If the position of the molecule is defined by position of its first monomer, than for a given such position the number of conformations of one molecule would be $W_n \propto C^N N_{N-1}$ if no other molecules were present, and since other molecules are there it is $W_n < C^N N_{N-1}$ due to geometric hindrance of polymers by each other (but still much larger than one). When passing to the entropy by taking the logarithm of the corresponding expression this will give us at the best the constant contribution. There is however still the possibility of permutation of different molecules, i.e. $n!$ different ways to number them. Therefore

$$W \approx \frac{N_0!}{N!nW(N)}$$

Now we can pass to the entropy and taking $\Phi$ to be the concentration of monomers (so that $n = \frac{N_0\Phi}{N}$ and $N_0 - nN = (1 - \Phi)N_0$), we get for the entropy
\[ S = \text{const} - k_B N_0 \left[ (1 - \Phi) \ln(1 - \Phi) + \frac{\Phi}{N} \ln \frac{\Phi}{N} \right]. \]

(the deviation of the logarithm of the number of conformation per molecule from a constant is neglected). This is our first approximation, which is essentially not a bad one. The problem arises when we consider the internal energy term. This one is taken in the same form as in a theory of simple solutions or alloys:

\[ U = U_0 + N_0 C \left( \epsilon_{AB} - \frac{1}{2} \epsilon_{AA} - \frac{1}{2} \epsilon_{BB} \right) \Phi(1 - \Phi) \]

i.e. fully disregards the fact that monomers are organized in chains and assumes them to be well-mixed with the solvent molecules. This approximation works well for dilute and for concentrated solutions but fails (to some extent, not fatally) in the intermediate case. The free energy of our polymeric solution is therefore

\[ F = F_0 + N_0 C \left( \epsilon_{AB} - \frac{1}{2} \epsilon_{AA} - \frac{1}{2} \epsilon_{BB} \right) \Phi(1 - \Phi) + k_B T N_0 \left[ (1 - \Phi) \ln(1 - \Phi) + \frac{\Phi}{N} \ln \frac{\Phi}{N} \right] \]

The interaction parameter measured in units of \( k_B T \) is called the Flory-Huggins parameter and is denoted by

\[ \chi = \frac{1}{k_B T} \frac{C}{2} \left( 2 \epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB} \right), \]

so that

\[ F - F_0 = N_0 k_B T \left[ \chi \Phi(1 - \Phi) + (1 - \Phi) \ln(1 - \Phi) + \frac{\Phi}{N} \ln \frac{\Phi}{N} \right]. \]

The athermal situation (no interactions within the pairs) corresponds to \( \chi = 0 \).

**Osmotic pressure in the Flory-Huggins model**

Let us for example calculate the osmotic pressure in the Flory-Huggins model, \( p = -\frac{\partial F}{\partial V} \).

First we note that the number of monomers \( N_{\text{mon}} = nN \) stays fixed when the volume \( V = a^3 N_0 \) changes. The overall number of sites \( N_0 \) thus reads \( N_0 = N_{\text{mon}}/\Phi \) and the changes of \( V \) can be translated into changes of \( \Phi \) via \( V = N_{\text{mon}} a^3 / \Phi \). Let us moreover note that

\[ F = F_0 + N_0 f(\Phi) \quad \text{with} \quad f(\Phi) = k_B T \left[ \chi \Phi(1 - \Phi) + (1 - \Phi) \ln(1 - \Phi) + \frac{\Phi}{N} \ln \frac{\Phi}{N} \right], \]

and that the constant contribution \( F_0 \) disappears after differentiation anyhow. Therefore

\[ -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V} (N_0 f(\Phi)) = -\frac{\partial}{\partial V} \left[ \frac{N_{\text{mon}}}{\Phi} f(\Phi) \right] = -\frac{d}{d\Phi} \left[ \frac{N_{\text{mon}}}{\Phi} f(\Phi) \right] \frac{d\Phi}{dV}. \]

Note that
\[
\frac{d\Phi}{dV} = \frac{1}{dV\frac{d\Phi}{d\Phi}} = \frac{1}{\Phi} - \frac{\Phi}{N_{\text{mon}} a^3} = -\Phi^2
\]

and therefore
\[
-\frac{\partial F}{\partial V} = \frac{d}{d\Phi} \left[ \frac{N_{\text{mon}} f(\Phi)}{\Phi} \right] \frac{\Phi^2}{N_{\text{mon}} a^3} = \frac{1}{a^3} \left[ -f(\Phi) + \Phi \frac{d}{d\Phi} f(\Phi) \right].
\]

Evaluating this expression we get:
\[
p = \frac{k_B T}{a^3} \left[ \frac{\Phi}{N} \ln(1-\Phi) - \Phi - \chi \Phi^2 \right]
\]

The first term here is the pressure of the ideal gas of polymer molecules, the rest are corrections due to interactions. For small concentrations \(\Phi\) we can expand the logarithm and get the virial expansion
\[
p = \frac{k_B T}{a^3} \left[ \frac{\Phi}{N} + \frac{\Phi^2}{2} + \frac{\Phi^3}{3} \ldots - \Phi - \chi \Phi^2 \right] = \frac{k_B T}{a^3} \left[ \frac{\Phi}{N} - \left( \frac{1}{2} \right) \Phi^2 + \ldots \right]
\]

i.e. the ideal gas behavior prevails for all small \(\Phi\) and even for quite moderate \(\Phi\) if \(\chi = 1/2\), the so-called \(\theta\)-solution.

For moderate concentrations \(\Phi/N < \Phi^2 << 1\) in the case \(\chi < 1/2\) the second term dominates:
\[
p \approx \frac{1}{2} \frac{k_B T}{a^3} (1 - 2\chi) \Phi^2,
\]

in which case there are some deviations from experimental (and scaling) results. Note that this situation \(1/N << \Phi << 1\) belongs to the domain of semidilute solutions.

\textbf{Note that for } \(\chi > 1/2\ \text{ the theory delivers a negative pressure, which makes no sense. As we proceed to show, this domain corresponds to the case of bad solvents, in which the solution phase separates and the assumption of well-mixedness does not work!}

For concentrations close to unity the logarithmic term plays the major role (and cannot be expanded) so that
\[
p = \frac{k_B T}{a^3} \ln \frac{1}{1-\Phi}
\]

which result is again quite good.