

# The lattice model of polymer solutions

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## 1 The lattice model of polymer solutions

In the last note, we looked at the lattice model of small-molecule solutions. We now turn to polymers, using the same machinery. The lattice theory of polymer solutions is known as **Flory-Huggins** theory. In many ways, you will find this theory similar to the small-solute case, except that the statistics are a little more complicated given that a polymer is a connected entity.

Figure 1 shows a lattice model of a polymer. Each filled circle represents a **chain segment**, a piece of the polymer that is about the same size as a solvent molecule. A chain segment is not necessarily a monomer. In fact, for many polymeric materials, a chain segment will be smaller than a monomer. A polymer is taken to be made up of  $\nu_s$  chain segments (on average). The value of  $\nu_s$  can be estimated as the ratio of the molar volumes of the polymer and solvent.

As in the small-molecule case, the solvent is assumed to have a coordination number  $z$ . Recall again that the flat illustration of figure 1 is only an aid to visualization and that, in general, the lattice will be three-dimensional, and may have a non-cubic geometry (e.g. it could be a hexagonal close-packed lattice). Neglecting the ends of a chain, which, for long polymers, represent a tiny minority of segments, a linear polymer segment makes  $z - 2$  contacts with lattice sites to which the segment is not bonded.

Another key assumption in the present note is that all the monomers are the same. There is therefore no energetic difference between placing one monomer or another in contact with the solvent. That being the case, there are only two significant possibilities to consider: Either the polymer is well solvated, i.e. it assumes a more-or-less random conformation in the solvent, or it doesn't dissolve at all. In the next lecture, we will talk about a class of polymers for which this is not true, namely proteins.

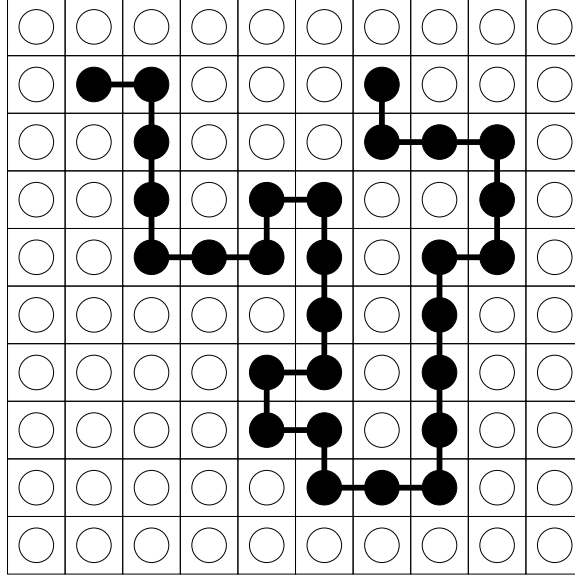


Figure 1: Lattice model of a polymer. The open circles represent solvent molecules. The filled circles connected by bonds represent the polymer. Each filled circle is a chain segment, a piece of the polymer (not necessarily a monomer) whose size is about the same as that of a solvent molecule.

## 2 Enthalpy of solution

The derivation of the enthalpy of solution for a polymer is extremely similar to that for a small-molecule solution. There is an energy difference of

$$\Delta\epsilon = \epsilon_{12} - \frac{1}{2}(\epsilon_{11} + \epsilon_{22})$$

per solute-solvent (i.e. polymer-solvent) contact made. The derivation of this equation is about the same as before, except that we have to consider one polymer segment and its neighbors rather than a small solute molecule.

We now ask how many solute-solvent contacts there are in the solution on average. A given segment has  $z - 2$  neighbors that could be occupied either by solvent or by a non-bonded polymer segment. If we have  $N_2$  polymer molecules, each with an average of  $\nu_s$  segments, and  $N_1$  solvent molecules, then the probability that a given lattice point that does not contain a segment bonded to the segment of interest, is occupied by a solvent molecule is  $N_1/(N_1 + \nu_s N_2 - 3) \approx N_1/(N_1 + \nu_s N_2)$ . The  $-3$  in the first part of this equation accounts for the fact that the segment of interest and its two directly bonded segments are excluded. Of course, for macroscopic systems, this term is negligible. Since there are  $z - 2$  non-bonded sites adjacent to any segment (neglecting the ends of the polymer) and there are  $\nu_s N_2$  segments in total, the total number of solute-solvent contacts should be  $(z - 2)\nu_s N_2 N_1 / (N_1 + \nu_s N_2) = (z - 2)N_1 \nu_s N_2 / (N_1 + \nu_s N_2) = (z - 2)N_1 \phi_2$ , where  $\phi_2$  is the

**volume fraction** of the polymer:

$$\phi_2 = \frac{V_2}{V_1 + V_2} = \frac{\nu_s N_2}{N_1 + \nu_s N_2}$$

in the lattice model since each polymer segment or solvent molecule occupies the same volume (one lattice site).

The enthalpy of solution is then simply the number of solute-solvent contacts times the enthalpy change per contact, or

$$\Delta_{\text{sol}}H = (z - 2)N_1\phi_2\Delta\epsilon.$$

This is essentially identical (give or take the factor of  $z - 2$  instead of  $z$ ) to the van Laar equation. The same factors which affect the enthalpy of solution for small molecules are thus important to the enthalpy of solution of polymers. One qualitative difference is the size of  $\phi_2$ : It takes a lot of small solute molecules to make the solute volume fraction significant, but relatively few polymer molecules due to the large sizes of polymer molecules. If we compare two solutes with similar positive values of  $\Delta\epsilon$ , one of which is a small molecule and one a polymer, the polymer may be only sparingly soluble while the small molecule has moderate solubility due to this difference.

### 3 Entropy of solution

The entropy of solution can have several components. One component, perhaps the obvious one and the one we will focus on here, is the **conformational entropy**, i.e. the entropy associated with the different possible arrangements of the polymer in solution. There can also be entropy associated with the movements of parts of the polymer other than the “backbone” if the polymer has significant side chains, and these entropy terms can be different between the pure and solvated polymer. If, for instance, the side chains are locked in position in the pure polymer and are free to move in solution, the theory presented here will underestimate the entropy of solution, and thus the solubility of a polymer. In many cases though, these effects are relatively small compared to the conformational entropy.

There is another issue of significance in polymer science which doesn't arise in the small-molecule theory. When we calculated the entropy of solution in the small-molecule case, because the lattice model only allows one microstate for the segregated state, we had  $\Delta_{\text{sol}}S = S_{\text{mixture}} - S_{\text{segregated}} = S_{\text{mixture}}$ . If the solid polymer is crystalline, this relationship can be approximately true for polymer solutions as well. Even crystalline polymers are generally not perfectly crystalline and will usually have amorphous regions (figure 2). In fact, we often characterize polymers in terms of their percent crystallinity, which is rarely more than 90% and can be substantially lower. Some solid polymers in fact exist in an essentially entirely **amorphous state**, which can be either a glass (hard) or a rubber (soft).<sup>1</sup> An amorphous polymer would have a significant entropy, which would then reduce the entropy of solution

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<sup>1</sup>Most amorphous polymers go through a phase transition between a glassy and a rubbery phase at some specific temperature, so these are not categories of polymers but categories of behavior.

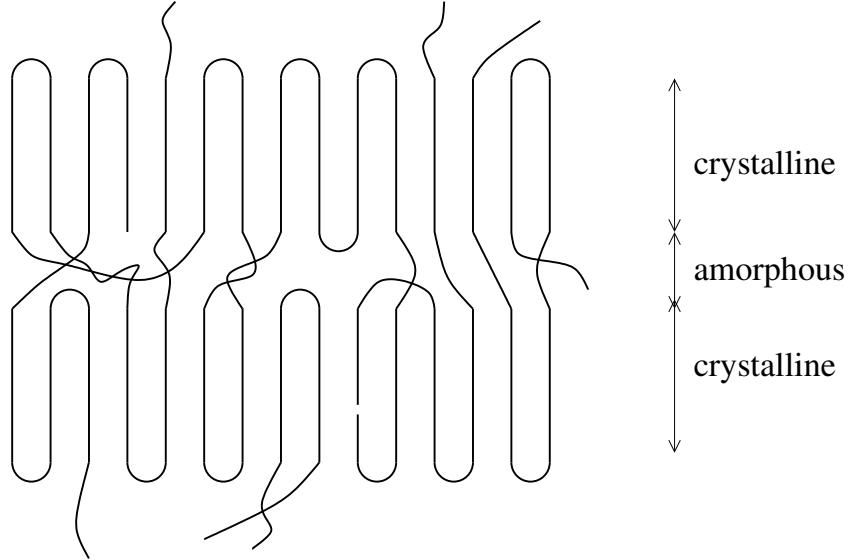


Figure 2: Schematic representation of a polymer with a high percent of crystallinity. The crystalline regions consist of orderly rows of polymer strands. These strands can be joined by turns or by amorphous strands.

and make these polymers *less* soluble than crystalline equivalents. The Flory-Huggins theory describes the solubility of an amorphous polymer. In a lattice model, there is no distinction between an amorphous solid polymer and a liquid polymer, so the theory also applies to solutions made from polymer melts.

We want to count the number of different ways we can put  $N_2$  polymer molecules, each of which has  $\nu_s$  chain segments, in a lattice with  $N_0 = N_1 + \nu_s N_2$  sites. The remaining sites will of course be filled with the solvent molecules. Suppose that we have already placed  $i$  polymer molecules in the lattice. Let  $\xi_{i+1}$  be the number of different ways we can place the  $(i + 1)$ st polymer molecule in the lattice. We calculate  $\xi_{i+1}$  by considering each segment in turn. Since the first  $i$  polymers occupy  $\nu_s i$  sites, there are  $N_0 - \nu_s i$  ways we can place the first segment. The probability that any given neighboring site to the first segment is unoccupied is  $p_0 = (N_0 - \nu_s i - 1)/N_0 \approx (N_0 - \nu_s i)/N_0$ . Since there are  $z$  neighboring sites, on average there are  $p_0 z$  different ways we can place the second segment. The second segment has  $z - 1$  neighbors, excluding the neighboring site occupied by the first segment. The probability that any given one of these  $z - 1$  neighboring sites is unoccupied is  $p_1 = (N_0 - \nu_s i - 2)/N_0 \approx p_0$ , so the number of different ways to place the third segment is approximately  $p_0(z - 1)$ . This same reasoning, with the same probability  $p_0$  that neighboring sites are empty, applies to any subsequent segment in our polymer, provided  $N_0 \gg \nu_s$ .<sup>2</sup> The number of different ways

<sup>2</sup>Quite apart from the approximation used explicitly above,  $p_0$  is an overestimate of the probability that an adjacent site is unoccupied since it takes no account of the fact that adjacent sites are more likely to be occupied by segments from the same polymer than by segments from other polymers because of the connectivity of the polymer molecules. This can be fixed, but it's a relatively small correction which doesn't improve the fit of the theory to experimental data.

we can place the  $\nu_s$  segments of the  $(i + 1)st$  polymer in the lattice is therefore

$$\begin{aligned}
\xi_{i+1} &\approx (N_0 - \nu_s i) p_0^{\nu_s - 1} z (z - 1)^{\nu_s - 2} \\
&\approx (N_0 - \nu_s i) p_0^{\nu_s - 1} (z - 1)^{\nu_s - 1} \\
&= (N_0 - \nu_s i) (z - 1)^{\nu_s - 1} \left( \frac{N_0 - \nu_s i}{N_0} \right)^{\nu_s - 1} \\
&= (N_0 - \nu_s i)^{\nu_s} \left( \frac{z - 1}{N_0} \right)^{\nu_s - 1}.
\end{aligned}$$

In the second step, we approximated  $z(z - 1)^{\nu_s - 2}$  by  $(z - 1)^{\nu_s - 1}$ , which is reasonable provided  $z$  is not too small and  $\nu_s$  is reasonably large. Now note that

$$\begin{aligned}
\frac{[N_0 - \nu_s i]!}{[N_0 - \nu_s(i + 1)]!} &= [N_0 - \nu_s i][N_0 - \nu_s i - 1] \dots [N_0 - \nu_s(i + 1) + 1] \\
&\approx (N_0 - \nu_s i)^{\nu_s}
\end{aligned}$$

to the same level of approximation as we used to replace  $p_1, p_2, \dots$  by  $p_0$ . Thus we have

$$\xi_{i+1} \approx \frac{[N_0 - \nu_s i]!}{[N_0 - \nu_s(i + 1)]!} \left( \frac{z - 1}{N_0} \right)^{\nu_s - 1},$$

or

$$\xi_i \approx \frac{[N_0 - \nu_s(i - 1)]!}{[N_0 - \nu_s i]!} \left( \frac{z - 1}{N_0} \right)^{\nu_s - 1}. \quad (1)$$

The number of ways of placing all  $N_2$  polymer molecules in the lattice is

$$W = \frac{1}{N_2!} \prod_{i=1}^{N_2} \xi_i.$$

The factor of  $1/N_2!$  arises because our expression for  $\xi_i$  assumes that we are placing the polymers into the lattice one after the other. Since the solution process is not ordered, we have to divide by the number of permutations of the  $N_2$  molecules. If we substitute equation 1 into  $W$ , we can separate the product into two terms:

$$\begin{aligned}
W &= \frac{1}{N_2!} \left( \prod_{i=1}^{N_2} \frac{[N_0 - \nu_s(i - 1)]!}{[N_0 - \nu_s i]!} \right) \left( \prod_{i=1}^{N_2} \left( \frac{z - 1}{N_0} \right)^{\nu_s - 1} \right) \\
&= \frac{1}{N_2!} \left( \frac{z - 1}{N_0} \right)^{N_2(\nu_s - 1)} \left( \prod_{i=1}^{N_2} \frac{[N_0 - \nu_s(i - 1)]!}{[N_0 - \nu_s i]!} \right).
\end{aligned}$$

The remaining product can be evaluated by expanding the factorials. In the equation that follows, the terms collected together in braces each represent one term in the product:

$$\begin{aligned}
\prod_{i=1}^{N_2} \frac{[N_0 - \nu_s(i - 1)]!}{[N_0 - \nu_s i]!} &= \{N_0(N_0 - 1) \dots (N_0 - \nu_s + 1)\} \\
&\quad \times \{(N_0 - \nu_s)(N_0 - \nu_s - 1) \dots (N_0 - 2\nu_s + 1)\} \\
&\quad \times \dots \{\dots (N_0 - N_2\nu_s + 1)\} \\
&= \frac{N_0!}{(N_0 - N_2\nu_s)!}.
\end{aligned}$$

$W$  is therefore

$$W = \frac{N_0!}{N_2!(N_0 - N_2\nu_s)!} \left( \frac{z-1}{N_0} \right)^{N_2(\nu_s-1)} = \frac{(N_1 + N_2\nu_s)!}{N_1!N_2!} \left( \frac{z-1}{N_1 + N_2\nu_s} \right)^{N_2(\nu_s-1)}.$$

The conformational entropy is  $S_c = k \ln W$ . Using our expression for  $W$  and simplifying, we get

$$S_c = k \left\{ N_1 \ln \left( \frac{N_1 + N_2\nu_s}{N_1} \right) + N_2 \ln \left( \frac{N_1 + N_2\nu_s}{N_2} \right) + N_2(\nu_s - 1) [\ln(z-1) - 1] \right\}. \quad (2)$$

The entropy of solution is given by

$$\Delta_{\text{sol}}S = S_c - S_p,$$

where  $S_p$  is the entropy of the pure polymer, since the entropy of the pure solvent is zero in the lattice model. We can easily get the entropy of an amorphous polymer (or of a molten polymer) from equation 2 by setting  $N_1 = 0$ :

$$S_p = kN_2 \{ \ln \nu_s + (\nu_s - 1) [\ln(z-1) - 1] \}.$$

The entropy of solution is therefore, after a small rearrangement,

$$\Delta_{\text{sol}}S = k \left\{ N_1 \ln \left( \frac{N_1 + N_2\nu_s}{N_1} \right) + N_2 \ln \left( \frac{N_1 + N_2\nu_s}{N_2\nu_s} \right) \right\}.$$

This equation can be rewritten in terms of the volume fractions of the solvent and polymer:

$$\Delta_{\text{sol}}S = -k (N_1 \ln \phi_1 + N_2 \ln \phi_2),$$

of, if you prefer to use moles,

$$\Delta_{\text{sol}}S = -R (n_1 \ln \phi_1 + n_2 \ln \phi_2).$$

Although this equation is identical in form to that derived for small molecules, there is an important difference. For small molecules,  $\phi_i \approx X_i$ . For polymers, this is of course not the case. This leads to large deviations from ideal behavior for polymer solutions, as observed for instance in vapor pressure measurements where we find large deviations from Raoult's law.

### Exercises

1. A classic demonstration involves dissolving packing peanuts, which are made from expanded polystyrene, into acetone. A huge amount of polystyrene will dissolve in acetone. Acetone has a density of  $0.79 \text{ g/cm}^3$  and a molar mass of  $58.08 \text{ g/mol}$ . Polystyrene has a density of  $1.05 \text{ g/cm}^3$ . A particular sample of polystyrene has an average molar mass of  $3.5 \text{ kg/mol}$ . Suppose that we dissolve  $100 \text{ g}$  of polystyrene in  $100 \text{ g}$  of acetone. What is the entropy of solution?
2. Suppose that we have a solvent for which  $z = 8$  and  $V_{1,m} = 200 \text{ mL/mol}$ , and a polymer with  $V_{2,m} = 5000 \text{ mL/mol}$  and an average molar mass of  $20 \text{ kg/mol}$ . The interaction energy per contact is  $\epsilon = 500 \text{ J/mol}$ . What is the solubility, in  $\text{g/L}$ , of the polymer in this solvent at  $25^\circ\text{C}$ ?