

Lecture 6: Real polymer chains – Flory theory

Prof. Mark W. Tibbitt – ETH Zürich – 10 March 2022

1 Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 3

2 Real Polymer Chains

So far, we have only considered the conformations of model polymer chains that ignore intramolecular steric or energetic interactions between monomers – so called, ideal polymer chains. This, of course, is non-physical and we must account for the fact that monomers occupy real volume and have the potential to interact with other monomers along the chain or surrounding solvent molecules. Here, we will investigate the effects of non-ideal interactions on polymer conformations. Polymer chains for which we consider intramolecular and solvent interactions will be referred to as **real polymer chains**. We will explore concepts related to the **excluded volume** of a monomer, the **Flory theory** of real polymer chain conformations, as well as scaling behavior in good, θ , and poor solvents.

3 Intrachain interactions and excluded volume

To understand the importance of intrachain interactions, we should first approximate the number of monomer-monomer interactions within a given polymer chain. That can be calculated knowing the probability that a given monomer interacts with another monomer along the backbone of the chain that is many bonds away. We can approximate this using a **mean-field** estimate for the general case of an ideal chain in d -dimensional space by substituting an ‘ideal gas’ of N monomers in the pervaded volume of the polymer chain $\sim r^3$. In this model the probability of a monomer interacting with another monomer within this volume is given by the critical volume fraction ϕ^* , which was discussed in Lecture 1 as the product of the monomer volume b^d and the number density of monomers in the pervaded volume N/r^d :

$$\phi^* \approx b^d \frac{N}{r^d}. \quad (1)$$

Moving forward, we will often talk about N Kuhn monomers and drop the subscript K with monomer length b . As the chain is assumed ideal for the time being, we have shown that it should obey Gaussian behavior and $r \propto bN^{1/2}$, giving a critical volume fraction:

$$\phi^* \approx b^d \frac{N}{(bN^{1/2})^d} \propto N^{1-d/2}. \quad (2)$$

This means that for an ideal polymer chain in three-dimensional space ($d = 3$) the probability of a given monomer interacting with a monomer of the same chain is $\phi^* \propto N^{-1/2} \ll 1$. However, this also implies that the number of monomer-monomer interactions along the whole polymer chain is the product of the number of monomers and the probability of a pairwise interaction:

$$N\phi^* \propto N^{1/2} \gg 1 \quad \text{for } d = 3 \text{ and } N \gg 1. \quad (3)$$

Therefore, it is important to account for these many interactions along the polymer chain and to understand how the energy arising from these numerous interactions affects the conformation of a real polymer chain. The effect of the interaction between pairs of monomers depends on the favorability of the direct interaction between monomer-monomer or between the monomer and other surrounding solvent molecules. In the case of highly favorable interactions between monomer and solvent, monomers will avoid being near each other and the chain will swell (**good solvent**). In the case of highly unfavorable interactions between monomer and solvent, monomers will prefer to be near each other and the chain will collapse (**poor solvent**). If the interaction between monomer and solvent is ‘just right’, the polymer will adopt ideal chain conformations. This occurs when there is no effective energetic difference between monomer-monomer and monomer-solvent interactions (θ **solvent**).

Therefore, we need a set of tools to quantify the monomer–monomer interactions within a polymer chain. For this we employ the concepts of the **Mayer f -function** and **excluded volume**. As we have discussed in Lecture 1, we can consider the energy $U(r)$ of bringing two monomers from $r = \infty$ to a distance r from one another in solvent. We have a hard-core repulsion barrier at a small enough r with an attractive well in the potential (monomers often ‘like’ each other more than a solvent) and the energy goes to 0 at $r = \infty$. The probability of finding a monomer pair with distance of separation r at temperature T is proportional to the Boltzmann factor $\exp[-U(r)/k_B T]$; the **relative probability** goes to zero at short distances due to the hard-core repulsion and to one at infinite distance. The Mayer f -function is defined as the difference between the Boltzmann factor and the case of no interaction or infinite distance:

$$f(r) = \exp[-U(r)/k_B T] - 1. \quad (4)$$

We can then define the excluded volume v as the negative of the integral of the Mayer f -function over all space:

$$v = - \int f(r) dr = \int 1 - \exp[-U(r)/k_B T] dr. \quad (5)$$

This single parameter v accounts for the net two-body interactions between monomers wherein the hard-core repulsion makes a negative contribution and the attraction between monomers makes a positive contribution to the excluded volume. Thus, we can have $v < 0$ for a net attraction (poor solvent), $v = 0$ for no interaction (θ solvent), and $v > 0$ for a net repulsion (good solvent).

4 Flory theory of a polymer chain

The problem of the conformations of real polymer chains was addressed quite successfully by Paul J. Flory (Nobel Prize in Chemistry, 1974) and is commonly known as the **Flory theory** of polymer chains. We will first consider the case of a polymer chain in a good solvent. Here the polymer chain experiences an effective repulsion between monomers that tend to swell the polymer chain, which is balanced by the entropy loss caused by such deformation. The simple model of Flory produces rough estimates for both the energetic contribution and entropic contribution in a clever way and avoids the need to count every possible chain conformation and pairwise energetic contribution (ϵ_{ij}). The genius of the Flory theory lies in the assumption that we can consider a real polymer chain as composed of two components: an ideal chain (entropic contribution) and a dilute ‘gas’ of monomers (energetic contribution).

The Flory approximation of the entropic contribution to the free energy of a real chain is the energy required to stretch an ideal chain to end-to-end distance r , which we have explored in depth in the previous lectures:

$$F_{\text{ent}} \approx k_B T \frac{r^2}{N b^2}. \quad (6)$$

To approximate the energetic contribution to the free energy of a real chain, we consider the sum of the energies associated with all pairwise monomer–monomer interactions in the chain. Each pairwise interaction carries an energetic cost of being excluded from this volume, which is $k_B T$ per exclusion. The number of interactions in the mean-field estimate is the product of N , the excluded volume v , and the number density of monomers in the pervaded volume N/r^3 . Therefore, for all N monomers in the chain the energetic contribution to the free energy of the chain is:

$$F_{\text{int}} \approx k_B T v \frac{N^2}{r^3}. \quad (7)$$

Thus, the total free energy for the real polymer chain in the Flory theory is the sum of the entropic and energetic contributions:

$$F = F_{\text{ent}} + F_{\text{int}} \approx k_B T \left(\frac{r^2}{N b^2} + v \frac{N^2}{r^3} \right). \quad (8)$$

The optimum end-to-end distance of the real chain in the Flory theory r_{Fl} can be determined from the minimum free energy of the chain with respect to r (set $\partial F/\partial r = 0$):

$$\frac{\partial F}{\partial r} = 0 = k_B T \left(-3v \frac{N^2}{r^4} + 2 \frac{r}{N b^2} \right) \quad (9)$$

$$r_{Fl}^5 \approx v b^2 N^3 \quad (10)$$

$$r_{Fl} \approx v^{1/5} b^{2/5} N^{3/5}. \quad (11)$$

This states that the end-to-end distance of a real polymer chain in a good solvent scales as:

$$\boxed{r \propto N^{3/5}}. \quad (12)$$

It should be noted that this simple model is surprisingly accurate. Our current best estimates based on more complicated theories and experiments set the scaling exponent $\nu \cong 0.588$! The success of the Flory theory is a fortunate cancelation of errors. On one hand, the Flory theory overestimates the repulsion energy because it does not account for correlations between monomers along the backbone. On the other hand, the Flory theory also overestimates the entropic elasticity because an ideal chain is assumed, which is de facto not the case. Modifications to the Flory theory that attempt to take these overestimations into account often fail and become much more difficult to work with and the Flory theory is still one of the most reliable models for real chain behavior. We will employ the general Flory construction in other sections of the course where we consider a mean-field estimate of the energetic part of a free energy combined with statistical descriptions of the entropy contributions.

We can generalize the Flory theory described above to account not only for good solvents but all solvent cases. The same logic is followed but we take the entropic contribution from stretching as well as compression (in the case of poor solvents) as well as a virial expansion of the ‘gas’ of monomers that accounts for two- and three-body interactions. First we consider the virial expansion of the dilute ‘gas’ of monomers:

$$\frac{F_{\text{int}}}{Vk_B T} = F_0 + \frac{1}{2}vc^2 + \frac{1}{6}wc^3 + \dots \quad (13)$$

where $c \approx N/r^3$ is the concentration of monomers in the pervaded volume of the chain and F_0 is the interaction energy of the ideal chain. Here, we also consider the entropic contribution of compression as we are considering also poor solvents that cause collapse of a polymer chain, which we will not derive here but takes the form $k_B T \frac{Nb^2}{r^2}$. With this additional term the entropic elasticity can be written as:

$$\frac{F_{\text{ent}}}{k_B T} = \frac{r^2}{Nb^2} + \frac{Nb^2}{r^2}. \quad (14)$$

Therefore, the full free energy expression for the real polymer chain can be written as (note the 1/2 and 1/6 have been combined with the prefactors v and w):

$$\frac{F}{k_B T} = \frac{r^2}{Nb^2} + \frac{Nb^2}{r^2} + vc^2 r^3 + wc^3 r^3. \quad (15)$$

Taking $c = N/r^3$ we have:

$$\boxed{\frac{F}{k_B T} = \frac{r^2}{Nb^2} + \frac{Nb^2}{r^2} + \frac{vN^2}{r^3} + \frac{wN^3}{r^6}}. \quad (16)$$

We can also define an expansion parameter α :

$$\alpha^2 \equiv \frac{\langle r^2 \rangle}{\langle r^2 \rangle_0} = \frac{r^2}{Nb^2}, \quad (17)$$

and rewrite the free energy as a function of α :

$$\frac{F}{k_B T} = \alpha^2 + \alpha^{-2} + \frac{vN^{1/2}}{b^3} \alpha^{-3} + \frac{w}{b^6} \alpha^{-6}. \quad (18)$$

Again, we can find the optimum end-to-end distance by setting the derivative of the free energy with respect to r equal to zero and consider the good solvent case ($\alpha \gg 1$) and the poor solvent case ($\alpha \ll 1$). The full derivation will be left for the next Exercise, but we arrive at the result that for a good solvent $\alpha \gg 1$ (as before):

$$\boxed{r \propto N^{3/5}}, \quad (19)$$

and for a poor solvent $\alpha \ll 1$:

$$\boxed{r \propto N^{1/3}}. \quad (20)$$