Lecture 3:
Ideal polymer chains

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1   Suggested reading

- *Polymer Physics* – Rubinstein and Colby: Chapter 2

- *Principles of Polymer Chemistry* – Flory: Chapter 10

- *Introduction to Polymer Physics* – Doi: Chapter 1

2   Conformations of ideal polymer chains

As we have discussed already, polymers are large, high molar mass molecules composed of a large number of monomers covalently bonded together to form a chain. We can imagine a polymer as a flexible chain, like a long piece of string, where the flexibility of the polymer is provided by the structure of the monomer and the bonds connecting the monomers together. In this and the coming lectures, we will present methods for theoretically describing the conformation of a polymer chain using several physical models. Here, we will discuss **ideal polymers**, which are the polymeric equivalent of an ideal gas. This means that the key assumption is that there is **no intramolecular steric interaction along the polymer chain**. That is the polymer is free to intersect itself without penalty. This is clearly not physical, but as we will see this simple model is surprisingly useful.

A key property that we are interested in when discussing a polymer chain is the **size** of the polymer. The size of a polymer is rarely equivalent to the sum of the lengths of all of its monomers since the flexibility of the polymer backbone (and entropy!) causes them to coil up. We will take linear polymers as the model for our discussion as it simplifies the math. A single polymer chain can adopt many possible conformations (or microstates) and we thus need to take a probabilistic approach to describing the size of even a single chain.

In general, we will describe polymer size as the **root-mean-square end-to-end distance** $\langle r^2 \rangle^{\frac{1}{2}}$. Here, r is the distance from one end of the polymer chain to the other in three-dimensional space. $\langle r^2 \rangle^{\frac{1}{2}}$ is the square root of the average of this distance squared. We square the distance to eliminate any negative values so that $\langle r^2 \rangle^{\frac{1}{2}} \geq 0$. Averaging can be thought of as averaging over a single chain over time as it explores conformational space or averaging over many such chains at an instant in time. In this manner, the average allows us to account for the fluctuations observed for polymer chains with a single parameter. We take the square root to ensure that the units of the measure are length.

As a simple exercise to see one extreme of $\langle r^2 \rangle^{\frac{1}{2}}$, we can imagine a linear polymer that is completely rigid or stretched out along its backbone in 1D. That is, a **rod-like polymer**. The end-to-end distance is then the length of each monomer ℓ multiplied by the number of monomers N. This results in a root-mean-square end-to-end distance:

$$\langle r^2 \rangle^{\frac{1}{2}} = N\ell = L. \tag{1}$$

Here, L is the **contour length** of the polymer and is the upper limit of $\langle r^2 \rangle^{\frac{1}{2}}$. As we will see, entropy often keeps us far from this limit and the true size of a polymer chain can be quite different from the contour length.

3   Freely Jointed Chain (Gaussian) model

In general, a polymer molecule has many internal spatial degrees of freedom. For example, the rotational freedom about each C–C bond in a polyethylene molecule. Thus, it is rarely seen in the fully extended case and possesses the flexibility to adopt many different configurations. On account of this high degree of flexibility, we can model a polymer chain as a long piece of string. The conformational degrees of freedom result in a more compact polymer form: $\langle r^2 \rangle^{\frac{1}{2}} << L$. There are many different models to calculate $\langle r^2 \rangle^{\frac{1}{2}}$ and one of the simplest, and surprisingly powerful, models is the **Freely Jointed Chain** (FJC) model.

In the FJC model, we define a monomer size ℓ and a number of monomers N, as above. We assume that each monomer is perfectly rigid for the length ℓ and free to rotate in any direction with respect to adjacent monomers, *i.e.*, we ignore restrictions on bond rotation that arise from real bonding and sterics. This is where

the term 'freely jointed' comes from. It is clear that the freely jointed assumption is non-physical – many polymers have C–C bonds along the backbone, which are often sp^3 hybridized with bond angles of $\sim 109.5°$.

With these assumptions, we can then model the polymer chain as a **random walk** on a lattice with spacing of length ℓ. In this approach, we can imaging 'walking' along the polymer backbone and placing each subsequent monomer in space at a fixed distance ℓ from the previous monomer with no restriction on the orientation. The orientation is perfectly random and allows for steps back directly along the polymer backbone. Mathematically, this means that the vector for monomer i and the vector for monomer $i + 1$ are uncorrelated $\langle \vec{r_i} \cdot \vec{r_j} \rangle_{i \neq j} = 0$. We will use the FJC model to approximate the mean-square end-to-end distance for a polymer chain.

First, consider a random walk on a one-dimensional (1D) lattice with the chain starting at the origin. We can use this model to calculate the probability of finding the end of a chain at a distance x from the origin after N steps (or monomers). On a 1D lattice, we can only move in the positive or negative direction, so we know that:

$$x = (n_+ - n_-)\ell \tag{2}$$

where n_+ is the number of steps in the positive direction, n_- is the number of steps in the negative direction, and $N = n_+ + n_-$. The probability of stopping at distance x after N steps can be computed by the binomial distribution introduced in Lecture 2 Notes. Based on the assumption of the freely jointed chain model: $p_+ = p_- = \frac{1}{2}$ and x is independent of the order in which the steps are taken. Therefore:

$$\Omega(n_+, N) = \frac{N!}{n_+!(N - n_+)!} \tag{3}$$

Here, Ω is equivalent to W, the multiplicity from last lecture. And thus the probability

$$P_{1D}(n_+, N) = \frac{N!}{2^N n_+!(N - n_+)!} \tag{4}$$

The probability distribution of n_+ given N monomers can then be used to calculate the end-to-end distance $x = (n_+ - n_-)\ell$. We know that $n_+ + n_- = N$, which we use to solve for n_-. Plugging this into $x = (n_+ - n_-)\ell$, it follows that $n_+ = \frac{N}{2} + \frac{x}{2\ell}$. Therefore, Eq. 4 can be rewritten as:

$$P_{1D}(x, N) = \frac{N!}{\left(\frac{N}{2} + \frac{x}{2\ell}\right)! \left(\frac{N}{2} - \frac{x}{2\ell}\right)!} \left(\frac{1}{2}\right)^N . \tag{5}$$

As before, Lecture 2 Notes, we can convert this into a Gaussian by taking the logarithm of $P_{1D}(x, N)$ then using Stirling's approximation (this time we use: $\ln n! \approx n \ln n - n + \frac{1}{2} \ln 2\pi n$) and a Taylor's series expansion and finally taking the exponential to get a simplified form of $P_{1D}(x, N)$.

$$\ln P_{1D}(x, N) = N \ln N - N + \frac{1}{2} \ln 2\pi N$$
$$- \left[\left(\frac{N}{2} + \frac{x}{2\ell}\right) \ln \left(\frac{N}{2} + \frac{x}{2\ell}\right) - \left(\frac{N}{2} + \frac{x}{2\ell}\right) + \frac{1}{2} \ln 2\pi \left(\frac{N}{2} + \frac{x}{2\ell}\right) \right]$$
$$- \left[\left(\frac{N}{2} - \frac{x}{2\ell}\right) \ln \left(\frac{N}{2} - \frac{x}{2\ell}\right) - \left(\frac{N}{2} - \frac{x}{2\ell}\right) + \frac{1}{2} \ln 2\pi \left(\frac{N}{2} - \frac{x}{2\ell}\right) \right] - N \ln 2. \tag{6}$$

We can rewrite the logarithms

$$\ln \left(\frac{N}{2} \pm \frac{x}{2\ell}\right) = \ln \left[\frac{N}{2}\left(1 \pm \frac{x}{N\ell}\right)\right] = \ln \frac{N}{2} + \ln \left(1 \pm \frac{x}{N\ell}\right), \tag{7}$$

and make use of the Taylor's series expansion

$$\ln \left(1 \pm \frac{x}{N\ell}\right) \approx \pm \frac{x}{N\ell} - \frac{1}{2} \left(\pm \frac{x}{N\ell}\right)^2 . \tag{8}$$

Combining Eqs. 6, 7, and 8, we arrive at

$$\ln P_{1D}(x, N) = \ln 2 - \frac{1}{2} \ln 2\pi N - \frac{x^2}{2N\ell^2} \tag{9}$$

If we now exponentiate both sides of the equation, we arrive at the Gaussian distribution

$$P_{1D}(x, N) = \frac{2}{\sqrt{2\pi N}} \, e^{-\frac{x^2}{2N\ell^2}}. \tag{10}$$

The original assumptions of the derivation came from a discrete probability distribution with values of x in multiples of 2ℓ. To turn this into a continuous probability distribution we need to divide by the density of integer x values per unit length, which is $\frac{1}{2\ell}$ arriving at our final expression for the 1D random walk:

$$P_{1D}(x, N) = \frac{1}{\sqrt{2\pi N\ell^2}} \, e^{-\frac{x^2}{2N\ell^2}}. \tag{11}$$

Going back to our polymer chain, in real space it can explore all three dimensions and we can generalize our 1D random walk to 3D. Here, we assume that the N is evenly distributed over the three dimensions x, y, and z as there is no bias in our walk so $N_x = N_y = N_z = \frac{N}{3}$. In addition, as the three dimension are completely uncorrelated or independent

$$P_{3D}(x, y, z, N) = P_{1D}(x, N_x)P_{1D}(y, N_y)P_{1D}(z, N_z) = \left(\frac{3}{2\pi N\ell^2}\right)^{\frac{3}{2}} e^{-\frac{3(x^2+y^2+z^2)}{2N\ell^2}}. \tag{12}$$

Taking $r^2 = x^2 + y^2 + z^2$ gives

$$P_{3D}(r, N) = \left(\frac{3}{2\pi N\ell^2}\right)^{\frac{3}{2}} e^{-\frac{3r^2}{2N\ell^2}}. \tag{13}$$

We should note at this point that while the Gaussian distribution is a good fit for values of $r < L$ there is a clear deviation at the tails. The Gaussian distribution allows for non-zero probability of values of r from $-\infty$ to $+\infty$ and this cannot be true as the polymer cannot be stretched (much more) than the contour length, L. Conveniently the Gaussian distribution allows us to read out $\langle r \rangle$ and $\langle r^2 \rangle$ trivially. For this distribution, $\langle r \rangle = 0$, which is necessitated by symmetry, and $\langle r^2 \rangle = N\ell^2$. Therefore,

$$\boxed{\langle r^2 \rangle^{\frac{1}{2}} = N^{\frac{1}{2}}\ell}. \tag{14}$$

That is the size of an **ideal polymer chain** scales with the square root of the degree of polymerization. This is first very important result of today's lecture that we will explore in more detail next lecture and use throughout the course. For now, all we need to know is that this simple model is a very good approximation for the size of an individual polymer chain.

4 Entropic elasticity of a single polymer chain

From our review of statistical mechanics, we recall that the entropy S can be defined as

$$S = k_B \ln \Omega. \tag{15}$$

We can also write $S(r, N)$ for a chain using the notation above:

$$S(r, N) = k_B \ln \Omega(r, N). \tag{16}$$

The probability distribution in Eq. 13 is equivalent to

$$P_{3D}(r, N) = \frac{\Omega(r, N)}{\int \Omega(r, N)dr}. \tag{17}$$

Combining Eqs. 16 and 17 we find that

$$S(r, N) = k_B \ln P_{3D}(r, N) + k_B \ln \int \Omega(r, N)dr. \tag{18}$$

Therefore

$$S(r, N) = -\frac{3}{2}k_B \frac{r^2}{N\ell^2} + \frac{3}{2}k_B \ln \frac{3}{2\pi N\ell^2} + k_B \ln \int \Omega(r, N)dr. \tag{19}$$

The last two terms have no dependence on r and can be lumped into a constant denoted as $S(0, N)$:

$$S(r, N) = -\frac{3}{2}k_B \frac{r^2}{N\ell^2} + S(0, N). \tag{20}$$

The **Helmholtz free energy** of the chain F can be defined as:

$$F(r, N) = U(r, N) - TS(r, N). \tag{21}$$

Because the monomers of the ideal polymer chain have no interaction energy, $U(r, N)$ is independent of the end-to-end distance r. Thus, the free energy can be written as:

$$F(r, N) = \frac{3}{2}k_B T \frac{r^2}{N\ell^2} + F(0, N), \tag{22}$$

where F(0,N) is the free energy of the chain with both ends at the origin. From the probability distribution, we know that the maximum number of conformations correspond to $r = 0$ and the polymer entropy decreases as r increases, leading to an increase in the free energy. Eq. 22 shows that the free energy increases quadratically with r and implies that the **entropic elasticity** of the chain satisfies Hooke's law. Thus, a single ideal polymer chain can be modeled as a simple elastic spring with an **entropic spring constant**:

$$\boxed{\vec{f} = \frac{\partial F(\vec{r}, N)}{\partial \vec{r}} = \frac{3k_B T}{N\ell^2}\vec{r}}. \tag{23}$$

This remarkable result will be foundational to many of the things we study this semester! As opposed to most traditional materials, the elasticity of a polymer is driven by entropy. This leads to many interesting properties that we will explore throughout the course and especially when we begin to 'construct' materials out of many individual polymer chains.