Polymer Theory: Freely Jointed Chain

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We'll talk today about the most simple model for a single polymer in solution. It's called the freely jointed chain model. Each monomer occupies a point in d dimensional space. We will denote these points by $\{\mathbf{r}_i\}$ for $i = 0, 1, \ldots N$. With these points, we can also define the bonds that connect together these monomers.

$$\mathbf{b}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \tag{1}$$

for $i = 1 \ldots N$. To construct a probabilistic model for the polymer, we say that $\mathbf{r}_i$ must be a distance b away from $\mathbf{r}_{i-1}$, and each direction in space has the same probability. To formulate this mathematically, we write down the following distribution for the bond vectors.

$$P(\mathbf{b}_i) = \frac{1}{4\pi b^2}\delta(|\mathbf{b}_i| - b) \tag{2}$$

The delta function says that the length of the bond must be b, and the fraction gives the correct normalization factor in three dimensional space. Each bond is statistically independent from every other bond, so

$$P(\mathbf{b}_i, \mathbf{b}_j) = P(\mathbf{b}_i)P(\mathbf{b}_j) \tag{3}$$

the joint probability distribution can be factored into single bond probability distributions. For an chain of N bonds, we have a joint probability distribution of

$$P(\{\mathbf{b}_j\}_{j=1}^{N}) = \prod_{j=1}^{N} P(\mathbf{b}_j) \tag{4}$$

for the set N bonds. Note that this is an unphysical model for a polymer, since we allow two monomers to be arbitrarily close to each other; there is no 'excluded volume' interaction between any two monomers. Still, it is a useful model to start with. Also note that constructing the polymer chain with N bonds is equivalent to a random walk of N steps.

We are interested in certain properties of this model. First, we want to know properties of the end-to-end distance of the polymer.

$$\mathbf{R} = \sum_{j=1}^{N} \mathbf{b}_j \tag{5}$$

We would like to know the moments of this quantity, or $\langle \mathbf{R} \rangle$ and $\langle \mathbf{R}^2 \rangle$, over the probability distribution $P(\{\mathbf{b}_j\}_{j=1}^N)$. Firstly, $\langle \mathbf{R} \rangle = \sum_{j=1}^N \langle \mathbf{b}_j \rangle = \mathbf{0}$ because of the property

$$\langle \mathbf{b}_j \rangle = \int \mathbf{b}_j P(\mathbf{b}_j) d\mathbf{b}_j = \mathbf{0} \tag{6}$$

where the integration over $d\mathbf{b}_j$ is over all points in $\mathbf{R}^3$. There is no prefered direction for any bond, so the average vector for each bond is the zero vector. For $\langle \mathbf{R}^2 \rangle$,

$$\begin{aligned}
&\left\langle \mathbf{R}^2 \right\rangle \\
&= \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \mathbf{b}_i \cdot \mathbf{b}_j \right\rangle = \sum_{i,j=1}^{N} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle \\
&= \sum_{i=1}^{N} \left\langle |\mathbf{b}_i|^2 \right\rangle + \sum_{i \neq j=1}^{N} \langle \mathbf{b}_i \cdot \mathbf{b}_j \rangle = N b^2
\end{aligned}$$

All of the cross terms vanish because the distribution of the individual bonds are statistically independent. There are N remaining terms that each give a factor of b^2. Also, note that this implies that $\sqrt{\langle \mathbf{R} \cdot \mathbf{R} \rangle} = \bar{R} = bN^{1/2}$, or the root mean square distance of a polymer grows as N to the $1/2$ power.

We are also interested in the distribution of the end-to-end vector. We can calculate this using the distribution of the bonds.

$$P(\mathbf{R}) = \int P(\{\mathbf{b}_j\}_{j=1}^N) \delta \left(\mathbf{R} - \sum_{i=1}^{N} \mathbf{b}_i \right) \prod_{j=1}^{N} d\mathbf{b}_j \tag{7}$$

The above expression says that we can obtain the probability of the end-to-end distance's being $\mathbf{R}$ by integrating over all possibilities for the bonds and keeping only those contributions such that the end-to-end distance is **R**. To do this calculation, we'll use the integral representation of the delta function.

$$\delta(\mathbf{R}) = \frac{1}{(2\pi)^3}\int e^{-i\mathbf{k}\cdot\mathbf{R}}d\mathbf{k} \tag{8}$$

This is not mathematically rigorous, but it is sometimes useful in doing calculations. So then we obtain

$$\begin{aligned} &P(\mathbf{R}) \\ &= \frac{1}{(2\pi)^3}\int P(\{\mathbf{b}_j\}_{j=1}^N)\int \exp\left(-i\mathbf{k}\cdot\left(\mathbf{R}-\sum_{i=1}^N \mathbf{b}_i\right)\right)d\mathbf{k}\prod_{j=1}^N d\mathbf{b}_j \\ &= \frac{1}{(2\pi)^3}\int e^{-i\mathbf{k}\cdot\mathbf{R}}\prod_{j=1}^N\left(\int\frac{1}{4\pi b^2}\delta(|\mathbf{b}_j|-b)e^{i\mathbf{k}\cdot\mathbf{b}_j}d\mathbf{b}_j\right)d\mathbf{k}\end{aligned}$$

It is possible to evaluate the integral within the parentheses for each j using polar coordinates with $\mathbf{k}$ pointed along the z direction.

$$\begin{aligned} &\int\frac{1}{4\pi b^2}\delta(|\mathbf{b}_j|-b)e^{i\mathbf{k}\cdot\mathbf{b}_j}d\mathbf{b}_j \\ &= \int_0^{2\pi}d\phi\int_0^{\pi}\sin\theta d\theta\int_0^\infty b_j^2 db_j\frac{1}{4\pi b^2}\delta(|b_j|-b)e^{ikb_j\cos\theta} \\ &= \int_0^{2\pi}d\phi\int_0^\infty\frac{1}{4\pi b^2}\delta(|b_j|-b)b_j^2 db_j\left(\int_0^\pi \sin\theta e^{ikb_j\cos\theta}d\theta\right)\end{aligned}$$

For the integral over θ,

$$\begin{aligned} &\int_0^\pi \sin\theta e^{ikb_j\cos\theta}d\theta \\ &= \left.\frac{-1}{ikb_j}e^{ikb_j\cos\theta}\right|_o^\pi = \frac{-1}{ikb_j}\left(e^{-ikb_j}-e^{ikb_j}\right) = \frac{2\sin kb_j}{kb_j}\end{aligned}$$

so then the previous integral becomes

$$\begin{aligned} &\int\frac{1}{4\pi b^2}\delta(|\mathbf{b}_j|-b)e^{i\mathbf{k}\cdot\mathbf{b}_j}d\mathbf{b}_j \\ &= 2\pi\int_0^\infty\frac{1}{4\pi b^2}\delta(b_j-b)b_j^2\frac{2\sin kb_j}{kb_j}db_j = \frac{\sin kb}{kb}\end{aligned}$$

With this calculation, the distribution can now be written as

$$P(\mathbf{R}) = \frac{1}{(2\pi)^3}\int e^{-i\mathbf{k}\cdot\mathbf{R}}\left(\frac{\sin kb}{kb}\right)^N d\mathbf{k}. \tag{9}$$

So far, the calculation is exact for all N. To proceed, we need to make certain approximations to evaluate the integral. Firstly, we're interested in large N, since we're interested in long polymer chains. One can check that $\lim_{N\to\infty}(\sin kb/kb)^N = 0$ for all $kb > 0$.[1] So the important part of the integral is for small values of kb. Then we can use the fact that

$$\frac{\sin kb}{kb} \approx 1 - \frac{(kb)^2}{3!} \approx \exp\left(-(kb)^2/6\right) \tag{10}$$

by expanding the power series for sin. The distribution now becomes

$$P(\mathbf{R}) = \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\cdot\mathbf{R}} e^{-k^2 b^2 N/6} d\mathbf{k} \tag{11}$$

To evaluate this, we need to do the integral

$$\int e^{-ikr} e^{-k^2 b^2 N/6} dk \tag{12}$$

for each spatial dimension. This leads us to the topic of Gaussian integrals.

From what I understand, the Gaussian integral is the basis for all analytic calculations in field theories. We'll start from the beginning with this integral.

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx \tag{13}$$

The trick to evaluating this integral is to consider its square

$$I^2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dx dy \tag{14}$$

and evaluate this quantity in $\mathbf{R}^2$ using polar coordinates.

$$I^2 = \int_0^{\infty} r dr \int_0^{2\pi} d\theta e^{-ar^2} = 2\pi \frac{-1}{2a} e^{-ar^2}\Big|_0^{\infty} = \frac{\pi}{a} \tag{15}$$

which gives us the result that

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \tag{16}$$

This is the basis for all the other results we will obtain.

[1]This is easy for $kb \geq 1$, since the numerator is bounded and the denominator blows up. For $0 < x \leq 1$, one can use the fact that $\sin kb < kb$.

Another interesting fact. Suppose we want to know the moments of the Gaussian distribution.

$$\langle x^n \rangle = \int_{-\infty}^{\infty} e^{-ax^2} dx \tag{17}$$

By symmetry, $\langle x^n \rangle = 0$ for all odd n. For the even powers, there is a trick. Consider the Gaussian integral a function of a

$$I(a) = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \tag{18}$$

and differentiate with respect to a. Switching a differential and an integral requires proof. Assume for now we can do it.

$$\int_{-\infty}^{\infty} -x^2 e^{-ax^2} dx = \sqrt{\pi} \frac{-1}{2a^{3/2}} \tag{19}$$

$$\int_{-\infty}^{\infty} -x^4 e^{-ax^2} dx = \sqrt{\pi} \frac{-3}{2^2 a^{5/2}} \tag{20}$$

We can get the general formula:

$$\left\langle x^{2n} \right\rangle = \int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = \sqrt{\pi} \frac{(2n-1)\cdot(2n-3)\cdots 3\cdot 1}{2^n a^{(2n+1)/2}} \tag{21}$$

This formula comes in handy. Also, this calculation can be done using integration by parts.

Now consider the integral:

$$H = \int_{-\infty}^{\infty} e^{-ax^2+bx} dx \tag{22}$$

The general trick to evaluating this integral is completing the square in the argument of the exponential. In other words, we want to find a constant D in terms of a and b such that

$$-ax^2 + bx = -ax^2 + bx - D + D = -(\sqrt{a}x - \sqrt{D})^2 + D \tag{23}$$

Then there is a square in the exponential that we can evaluate using our previous result. Straightforward algebra gives us that

$$-b = 2\sqrt{aD} \longrightarrow D = \frac{b^2}{4a} \tag{24}$$

so then we get

$$H = e^{b^2/(4a)} \int_{-\infty}^{\infty} e^{-(ax^2 - bx + D)} dx = e^{b^2/(4a)} \int_{-\infty}^{\infty} e^{-a(x-\sqrt{D/a})^2} dx \tag{25}$$

We use a simple change of variable $x' = x - \sqrt{D/a}$ to evaluate the integral with our previous result, which gives

$$H = \int_{-\infty}^{\infty} e^{-ax^2 + bx} dx = \sqrt{\frac{\pi}{a}} e^{b^2/(4a)} \tag{26}$$

There are also multi-dimensional generalizations of this result that can be derived.

We can apply the previous formula to evaluate the integral for $P(\mathbf{R})$.

$$\begin{aligned} P(\mathbf{R}) &= \frac{1}{(2\pi)^3} \int e^{-i\mathbf{k}\cdot\mathbf{R}} e^{-k^2 b^2 N/6} d\mathbf{k} \\ &= \frac{1}{(2\pi)^3} \left(\frac{6\pi}{b^2 N} \right)^{3/2} e^{-3|\mathbf{R}\cdot\mathbf{R}|^2/(2b^2 N)} \end{aligned}$$

We can write this in a more simple form if we note that the probability distribution for the vector $\mathbf{R}$ only depends on its length R.

$$P(R) = \left(\frac{3}{2\pi b^2 N} \right)^{3/2} e^{-3R^2/(2b^2 N)} \tag{27}$$

This is a Gaussian distribution in 3 dimensions.