

Physics 202: Class Notes

Lecture 8: Polymers

The tools we have already allow us to study some interesting classical systems. One of these is the statistical mechanics of polymers—long molecules. Although this has been studied for decades, it has become particularly exciting recently because biopolymers, such as DNA, allow the investigation of individual polymers. In turn, the statistical mechanics of such polymers is important in the biological function. In this lecture I will introduce some very simple issues and discuss some related experiments on single strands of DNA.

Polymers and random walks

The simplest model of a polymer is a chain of like monomers, of length a , where each link is completely free to rotate in any direction. A polymer of N such links is equivalent to a random walk of N steps of length a .

One dimensional random walk In one dimension the probability distribution of arriving at X after N steps starting from the origin is given by the binomial distribution

$$P(X, N) = P_{bin}(m, N) \quad (1)$$

with $X = (2m - N)a$ (m forward steps minus $N - m$ backwards steps). Using the properties of the binomial distribution (see lecture and homework 1) we have $\langle X \rangle = 0$, $\langle X^2 \rangle = Na^2$. We also showed that for large N the probability distribution approaches a Gaussian. In this limit we are usually interested in $X \gg a$, and so can also replace the discrete possible X by a continuum. The probability density $p(X)$ (such that $p(X)dX$ gives the probability of ending between X and $X+dX$) is

$$p(X) = \frac{1}{\sqrt{2\pi\sigma_1^2}} \exp\left(-\frac{X^2}{2\sigma_1^2}\right) \quad (2)$$

with $\sigma_1^2 = Na^2$. The large N results also follow from the central limit theorem. Since $X = \sum_{i=1}^N x_i$ is the sum of N independent random variables, for large N the distribution is Gaussian, with variance Na^2 .

Three-dimensional random walk

For a three dimensional polymer the large N result is similarly Gaussian. Now $\vec{R} = (X, Y, Z) = \sum \vec{x}_i$, so that the probability of ending up at x -coordinate X is

$$p(X) = \frac{1}{\sqrt{2\pi\sigma_x^2}} \exp\left(-\frac{X^2}{2\sigma_x^2}\right), \quad \sigma_x^2 = N\langle x_i^2 \rangle = Na^2/3 \quad (3)$$

with similar results for $p(Y)$, $p(Z)$. Then the probability density for ending up at \vec{R} is

$$p(\vec{R}) = p(X)p(Y)p(Z) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{R^2}{2\sigma^2}\right) \quad (4)$$

with $\sigma^2 = Na^2/3$. Thus a long polymer will form a ball of radius of order $\sqrt{Na^2}$, much smaller than the stretched length $L = Na$. The ball is often characterized by the radius of gyration $R_G = \sqrt{\langle (\vec{x}_i - \vec{x}_j)^2 \rangle}$ (with the average over all links i, j and over fluctuations). R_G is also of order $\sqrt{Na^2}$. We can obtain an exact expression for $p(R)$, albeit one that must be evaluated numerically. Probability distribution function that the end-to-end vector of a chain of N -link is \vec{R} is given by (see Reif Sec. 1.10)

$$p(\vec{R}) = \frac{\int \cdots \int d^2 x_1 d^2 x_2 \cdots d^2 x_N \delta\left(\sum_i x_i - \vec{R}\right)}{\int \cdots \int d^2 x_1 d^2 x_2 \cdots d^2 x_N} \quad (5)$$

where $\int d^2 x$ denotes the integral over the surface of the sphere of radius a . This expression is hard to evaluate due to the constraint $\delta\left(\sum_i x_i - \vec{R}\right)$. However, following representation of the delta function makes life easier.

$$\delta(r) = \frac{1}{(2\pi)^3} \int dk e^{i\vec{k} \cdot \vec{r}} \quad (6)$$

Also we have $\int d^2 x_1 \cdots \int d^2 x_N = (4\pi a^2)^N$. Using these two relations we can write equ. 5 as

$$\begin{aligned} p(\vec{R}) &= \frac{1}{(2\pi)^3 (4\pi a^2)^N} \int dk \int d^2 x_1 \cdots \int d^2 x_N e^{i\vec{k} \cdot \left(\sum_i \vec{x}_i - \vec{R}\right)} \\ &= \frac{1}{(2\pi)^3 (4\pi a^2)^N} \int dk e^{-i\vec{k} \cdot \vec{R}} \left[\int d^2 x e^{i\vec{k} \cdot \vec{x}} \right]^N \\ &= \frac{1}{(2\pi)^3 (4\pi a^2)^N} \int dk e^{-i\vec{k} \cdot \vec{R}} \left[4\pi a^2 \frac{\sin ka}{ka} \right]^N \\ &= \frac{1}{(2\pi)^3} \prod_{\varepsilon=x,y,z} \int_{-\infty}^{\infty} dk_{\alpha} e^{-ik_{\alpha} R_{\alpha}} \left[\frac{\sin ka}{ka} \right]^N \end{aligned} \quad (7)$$

In general the above integral is hard to evaluate. So we need to do some approximation. For N large, $\frac{\sin ka}{ka}$ is very small unless ka is small. For $ka \ll 1$, we can expand the last term in the integral as follows:

$$\left[\frac{\sin ka}{ka} \right]^N = \left(1 - \frac{k^2 a^2}{6} \right)^N = \exp\left(-\frac{Nk^2 a^2}{6}\right) \quad (8)$$

With this equ. 7 becomes

$$p(\vec{R}) = \frac{1}{(2\pi)^3} \prod_{\varepsilon=x,y,z} \int_{-\infty}^{\infty} dk_{\alpha} e^{(-ik_{\alpha} R_{\alpha} - \frac{Nk^2 a^2}{6})} \quad (9)$$

The integral is standard Gaussian integral of the following type

$$\int_{-\infty}^{\infty} dx \exp(-ax^2 + bx) = \sqrt{\frac{\pi}{a}} \exp\left[\frac{b^2}{4a}\right] \quad (10)$$

Using equation 10, we have from equ. 9,

$$p(\vec{R}) = \left(\frac{3}{2\pi N a^2} \right)^{3/2} \exp\left[-\frac{3R^2}{2Na^2}\right] \quad (11)$$

Also from equ. 7 we have the exact expression for the end-to-end distance probability distribution

$$\begin{aligned}
p(\vec{R}) &= \frac{1}{(2\pi)^3} \int dk e^{-i\vec{k} \cdot \vec{R}} \left[\frac{\sin ka}{ka} \right]^N \\
&= \frac{1}{2\pi^2} \int_0^\infty \frac{\sin kR}{kR} \left[\frac{\sin ka}{ka} \right]^N dk \\
&= \frac{1}{2\pi^2 a^3} \int \frac{\sin(NQR/L)}{NQR/L} \left[\frac{\sin Q}{Q} \right]^N dQ, \quad \text{where we have } Q = qa \text{ and } L = Na
\end{aligned} \tag{12}$$

Note that result depends on the fractional extension R/L , and from equation 12 we find that $p(R)=0$ for $R/L=1$ (the fully stretched case). In figure 1 we have plotted equ. 11 and 12. Remarkably the Gaussian approximation is quite accurate even for N as small as 5.

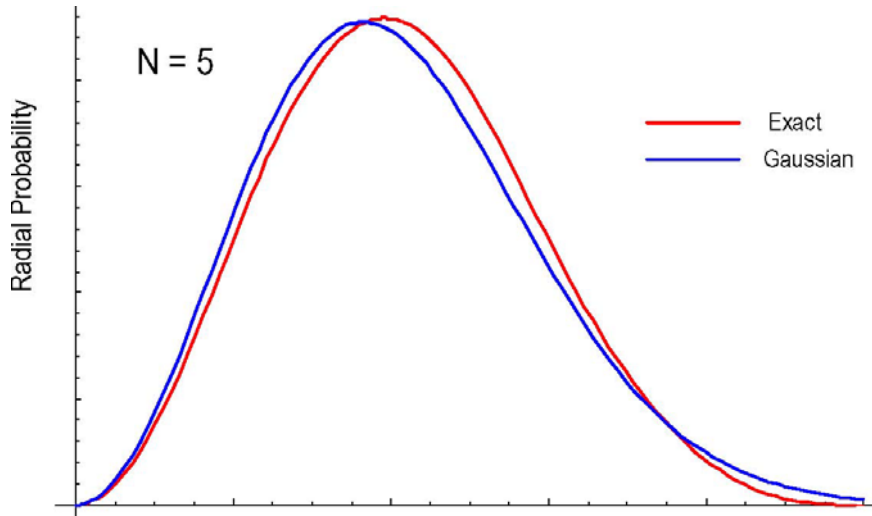


Figure 1: Comparison of exact and Gaussian expressions for the radial probability distribution $4\pi R^2 p(\vec{R})$ for a 3-D random walk or ideal polymer.

Entropy method (microcanonical ensemble) Consider a polymer tethered to two points on the x -axis, one at $x=0$ and the other at $x=X$. Left to itself, the most probable configuration would be $X=0$ —to stretch the polymer to endpoint separation X therefore decreases the entropy. The force can be calculated as

$$\frac{F}{T} = - \frac{\partial S}{\partial X} \tag{13}$$

with $S(X) = k \ln \Omega(X)$, and $\Omega(X)$ the number of microstates consistent with the fixed endpoints. We could show this for example by tethering the polymer to a piston that changes the volume of a gas, and then by

maximizing the total entropy show that this expression gives the right force to balance the force on the piston from the gas.

(Elasticity of ideal Gas)

Consider a Ideal gas in a vessel with a piston. Remember the ideal gas law relating P,V and T

$$PV=NKT$$

The force acting on the piston will be

$$F=PA = NKT A/V, \text{ where } A \text{ is the surface area of the piston.}$$

Suppose we have pushed the piston down by Δx and slightly compressed the gas. The volume of the gas is decreased by $\Delta V=A \Delta x$.

If Δx is very small we can neglect the variation of force and pressure while the piston is moving. So the work done will be given by

$$F\Delta x= PA\Delta x = P\Delta V = NKT\Delta V/V$$

Use the following fact:

$$\Delta(\ln V)=\frac{\partial(\ln V)}{\partial V}\Delta V \approx \frac{\Delta V}{V}$$

$$\text{So } N\frac{\Delta V}{V} = N\Delta(\ln V)=\Delta(\ln V^N)$$

$$F\Delta x=kT\Delta(\ln V^N)$$

$$\text{So } \Rightarrow F=-\frac{U_{eff}}{\Delta x} \text{ where } U_{eff}=-kT\Delta(\ln V^N)$$

The number of states $\Omega(X)$ is simply proportional to the probability of the polymer *with a free end* arriving at X (microcanonical ensemble \rightarrow probability \propto number of states)

$$\Omega(X) \propto \exp\left(-\frac{3X^2}{2Na^2}\right)$$

$$\text{So } S(X)=-\frac{3k}{2Na^2}X^2 \quad (14)$$

Which gives the following Force-extension equ.

$$F(X)=\frac{3kT}{a} \frac{X}{L} \quad (15)$$

(introducing the stretched out length $L=Na$ again). We have used the Gaussian expression for $p(X)$ which is only good for X not too large (i.e. not approaching L), and so the force expression is good for small X only. Notice that we get *Hookes Law* with a spring constant proportional to kT . The force arises completely from entropic effects. Similar arguments can be used to calculate the elasticity of ideal rubber (crosslinked polymers) where again the elasticity is entropy dominated.

Energy method (Gibbs-like ensemble) We can also do the calculation by fixing the force F (rather than the endpoint X) and the temperature T . For an applied force F the energy of a configuration with endpoint separation X is $E=-FX$. The partition function is then

$$Q = \sum_{state} e^{\beta F \sum_i x_i} = \sum_{state} e^{\beta Fa \sum_i \cos \theta_i} \quad (16)$$

with θ_i the angle of the i th link to the x -axis. We have calculated this before! It is just the partition function of classical moments $\mu=a$ in a magnetic field $B=F$ (or do the integrals directly)

$$Q = \left(\frac{4\pi \sinh \beta F a}{\beta F a} \right)^N \quad (17)$$

The extension $X = \sum_i x_i$ is analogous to the magnetic moment

$$X = Na [\coth(\beta F a) - 1/(\beta F a)] \quad (18)$$

(and the function in the [] is the Langevin function).

For $Fa \ll kT$ we use the small argument expansion of the Langevin function, and get

$$X \approx \frac{Na^2}{3kT} F \quad (\text{the same result as before}).$$

For the strong stretching limit $Fa \gg kT$ we have

$$X \approx Na \left(1 - \frac{kT}{Fa} \right) \quad (19)$$

so that the force to stretch out the polymer diverges as $X \rightarrow L$

$$Fa/kT = \frac{1}{1 - X/L} \quad (20)$$

More realistic models

The freely jointed chain is an oversimplified model for a polymer. Two effects we might want to include are the stiffness against bond bending and the hard-core repulsion of the atomic cores.

Stiff polymers To model the stiffness of a polymer chain we restrict the free rotation of each bond by assuming there is an energy cost for a nonzero angle between successive bonds. The simplest model is to assume the energy depends on the angle between the bonds, but not on the orientation of the plane formed by the bonds. The *Kratky-Porod* model supposes the energy for each bond pair is proportional to $\vec{t}_j \cdot \vec{t}_{j+1}$, with \vec{t}_j the direction of the j th link (a unit vector). The Hamiltonian of this model is (for a polymer of $N+1$ monomers)

$$H = -K \sum_{j=1}^N \vec{t}_j \cdot \vec{t}_{j+1} = -K \sum_{j=1}^N \cos \theta_j \quad (21)$$

where in the latter expression θ_j is the angle between the j th and the $j+1$ th link. To calculate the elasticity we would add the extension energy to give

$$H = - \sum \vec{t}_j \cdot \vec{t}_{j+1} - a\vec{F} \cdot \sum \vec{t}_j \quad (22)$$

Again this has an exact magnetic analogy: to a $1d$ Heisenberg spin model of classical spins \vec{s}_j taken to be unit magnitude, with associated moment $\mu = a$ in a field $B = F$ and with a nearest neighbor interaction proportional to $\vec{s}_j \cdot \vec{s}_{j+1}$.

First consider the $F=0$ case. This model can be solved exactly—for the magnetic calculation see the paper by Michael Fisher [1]. The partition function is

$$Q_N = \prod_{j=1}^N \int d\Omega_j e^{\beta K \sum_{j=1}^N \cos \theta_j} = (Q_1)^N$$

with

$$Q_1 = 2\pi \int_{-1}^1 d(\cos \theta) e^{\beta K \cos \theta} = 4\pi \frac{\sinh \beta K}{\beta K} \quad (23)$$

The thermodynamic quantities can be calculated in the usual way.

To calculate $\langle \bar{R}^2 \rangle$ we need

$$\langle \bar{R}^2 \rangle = a^2 \left\langle \left(\sum_{ij} \vec{t}_i \cdot \vec{t}_j \right)^2 \right\rangle = a^2 \sum_{ij} \langle \vec{t}_i \cdot \vec{t}_j \rangle \quad (24)$$

i.e. the correlation between the directions of any two bonds. The nearest neighbor correlation is easy

$$\langle \vec{t}_j \cdot \vec{t}_{j+1} \rangle = \langle \cos \theta \rangle = \frac{\int d\Omega \cos \theta e^{\beta K \cos \theta}}{\int d\Omega e^{\beta K \cos \theta}} = \frac{d \ln Q_1}{d(\beta K)} = c(\beta K) = \coth(\beta K) - 1/\beta K \quad (25)$$

Here c is the Langevin Function. The correlation involving nth link (see the paper by Fisher) is given by

$$\langle \vec{t}_j \cdot \vec{t}_{j+n} \rangle = c^n = e^{-n \ln(1/c)} \quad (26)$$

In terms of correlation length or the persistence length ξ_p

$$\langle \vec{t}_j \cdot \vec{t}_{j+n} \rangle = e^{-na/\xi_p}$$

$$\text{with } \xi_p = \frac{a}{\ln(1/c)} \quad (27)$$

For stiff polymer $K/kT \gg 1$ and we have

$$c \approx 1 - kT/K \Rightarrow \ln(1/c) \approx kT/K \Rightarrow \xi_p = a \frac{K}{kT} \quad (28)$$

Using equ. 26 equation 24 can be written as

$$\frac{\langle \bar{R}^2 \rangle}{a^2} = \sum_{i=1}^N \left[\sum_{j=1}^{i-1} c^{i-j} + \sum_{j=i+1}^N c^{j-i} \right]$$

For a long chain, for most i the two sums in the braces can be replaced by

$$\sum_{k=1}^{\infty} c^k = \frac{c}{1-c}$$

and then

$$\langle \bar{R}^2 \rangle \approx Na^2 \left(1 + \frac{2c}{1-c} \right) = Na^2 \frac{1+c}{1-c}$$

The factor $(1+c/(1-c)) > 1$ multiplying the ideal result Na^2 is known as the Flory Factor C_F .

We define the Kuhn length

$$b = \frac{1+c}{1-c} a$$

In terms of Kuhn length and fully stretch length $L=Na$

$$\langle \bar{R}^2 \rangle = Lb$$

The Kuhn length gives the effective link length of the polymer needed to regain the ideal polymer results.

For the stiff polymer $K \gg kT$ expanding b to the first order in kT/K using equation 28, we have

$$b = 2\xi_p \quad (30)$$

so that the Kuhn length and persistence length are quite comparable.

Nonlinear elasticity: the worm-like chain Model (WLC)

The Kratky-Porod model including the stretching force Eq. 22 cannot be solved exactly. To make progress we go to continuum version known as the worm-like chain model – think of the polymer as an unstretchable worm, with an energy cost for wriggling.

The Hamiltonian in such model is given by (see Marko and Siggia paper)

$$H = kT\xi_p \int \left[\frac{1}{2} \left(\frac{d\vec{r}}{ds} \right)^2 - Ft_x \right] ds \quad (31)$$

Marko and Siggia suggested the following interpolation formula (equation 7 in the paper)

$$F \approx \frac{kT}{\xi_p} \left[\frac{X}{L} + \frac{1}{4} \frac{1}{(1 - X/L)^2} - \frac{1}{4} \right] \quad (32)$$

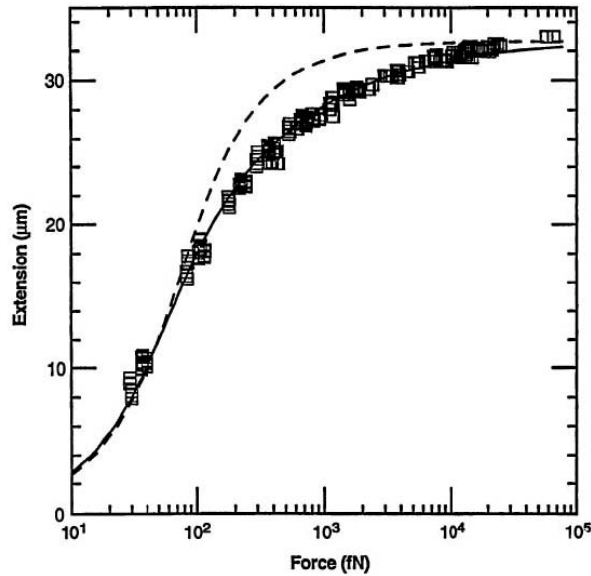


Figure 2: Fit to worm-like chain model with $L = 32.8\mu$ and $\beta p = 53.4\text{nm}$ (from Bustamante et al. [3])

Polymer with repulsive interactions

We can include some of the effect of the repulsive interaction by supposing each monomer is surrounded by an excluded volume v , fixed by supposing that the interaction strength is of order kT for monomers separated

by $v^{1/3}$. This will tend to swell the polymer from the size $R \approx \sqrt{Na^2}$

In terms of random walks we might suppose that the walk is “self avoiding” rather than free. This is most easily formulated on a lattice, where each link is a bond on the lattice. For a self avoiding random walk we demand that the walk cannot visit a site that has previously been visited. This is a hard statistical mechanical problem, since the constraints although local in space are nonlocal along the chain. Numerical simulations give the *scaling result*

$$R \sim N^\nu \quad (33)$$

with the exponent $\nu \approx 0.588$ in $3d$.

Flory suggested a very simple approximation for calculating the effect of the excluded volume. He wrote the free energy as the sum of the repulsive energy and the extra entropy for stretching the polymer. The repulsive energy per monomer for a polymer of N monomers occupying volume R^3 is estimated as kT times the number of monomers within the volume v , giving $E \sim NkT \times Nv/R^3$. The stretch entropy is given by Eq. 14 with $X \rightarrow R$. Thus the total free energy is

$$F \sim kT \left(\frac{N^2 v}{R^3} + \frac{R^2}{Na^2} \right)$$

Minimizing with respect to R gives Eq. (33) with $\lambda = 3/5$. Note that this result is very close to the value found from the self avoiding random walk on the lattice.

Polymers are usually in solution. The effective interaction of the monomers is given by the balance of the self repulsion and the interaction with the solvent molecules. For a good solvent, the self repulsion dominates, and the result $R \sim N^{0.6}$ just calculated holds. For a poor solvent, the repulsive interaction with the solvent dominates, and the effective interaction is negative. In this case the polymer collapses to a small globule of size $R \sim N^{1/3}$. By tuning a parameter (often the temperature) between these cases, a value can be found for which the effective interaction is zero, and the polymer behaves as if ideal, $R \sim N^{1/2}$. This is known as a *theta solvent* or the *theta point*.

Other References

A standard reference on polymers is *The Theory of Polymer Dynamics* by M. Doi and S. F. Edwards. Chapter 2 covers the equilibrium properties, at a more sophisticated level than I used.

One of the first papers to describe the measurement of the elastic properties of a single DNA molecule is Smith et al. [4]. A review of the theoretical ideas and experimental methods is by Strick et al. [5], and Bouchiat et al. [6] give a critical analysis of the worm-like chain model. There are also nice experiments done in Quake’s lab at Caltech [7].

References

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