

# Physics 127a: 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

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

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  $N\langle x_i^2 \rangle = Na^2$ .

**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

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

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

$$p(\vec{R}) = p(X)p(Y)p(Z) = \frac{1}{(\sqrt{2\pi}\sigma)^3} \exp\left(-\frac{R^2}{2\sigma^2}\right), \quad (4)$$

with  $\sigma^2 = Na^2/3$ . Thus a long polymer will form a ball of radius of order  $\sqrt{Na}$ , 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  $\sqrt{Na}$ .

We can obtain an exact expression for  $p(\vec{R})$ , albeit one that must be evaluated numerically. We start with

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

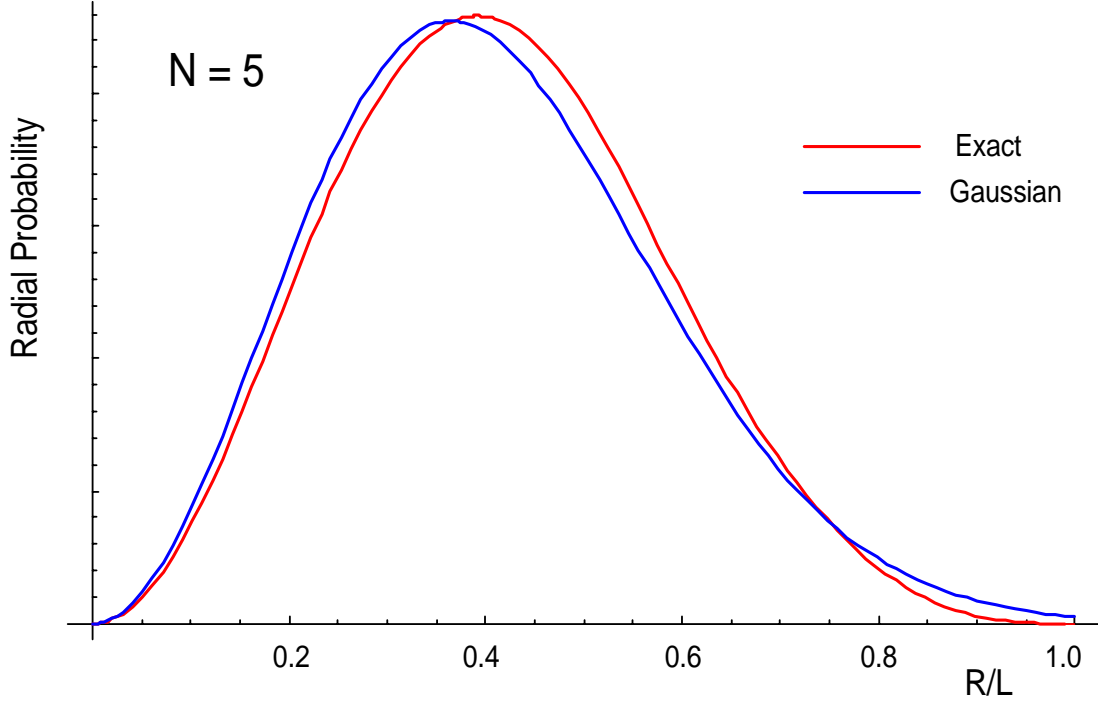


Figure 1: Comparison of exact and Gaussian expressions for the radial probability distribution  $4\pi R^2 p(\vec{R})$  for a 3d random walk or ideal polymer.

where here  $\int d^2x$  denotes the integral over the surface of a sphere of radius  $a$ . This expression is hard to evaluate because of the constraint  $\sum \vec{x}_i = \vec{R}$ . However if we take the Fourier transform

$$\tilde{p}(\vec{q}) = \int e^{i\vec{q}\cdot\vec{R}} p(\vec{R}) d^3R \quad (6)$$

the constraint gives  $\exp(i \sum_i \vec{q}\cdot\vec{x}_i)$ , and the integral factorizes

$$\tilde{p}(\vec{q}) = \left( \frac{\int d^2x e^{i\vec{q}\cdot\vec{x}}}{4\pi a^2} \right)^N. \quad (7)$$

This trick of using a Fourier transform to simplify the manipulation of a delta-function constraint is often useful. The integral in the numerator of Eq. (7) is

$$2\pi a^2 \int_{-1}^1 d(\cos\theta) e^{iqa\cos\theta} = \frac{4\pi a^2 \sin(qa)}{qa}. \quad (8)$$

Inverting the Fourier transform gives

$$p(\vec{R}) = \frac{1}{(2\pi)^3} \int e^{-i\vec{q}\cdot\vec{R}} \left( \frac{\sin qa}{qa} \right)^N d^3q. \quad (9)$$

The integration over the angles of  $\vec{q}$  is easily done, to give

$$p(\vec{R}) = \frac{1}{2\pi^2} \int_0^\infty \frac{\sin qR}{qR} \left( \frac{\sin qa}{qa} \right)^N dq. \quad (10)$$

It is useful to introduce  $Q = qa$  and  $L = Na$ , when the expression reduces to

$$p(\vec{R}) = \frac{1}{2\pi^2 a^3} \int_0^\infty \frac{\sin(NQR/L)}{(NQR/L)} \left( \frac{\sin Q}{Q} \right)^N dQ. \quad (11)$$

This is now easy to evaluate and plot in Mathematica, for example. Note that result depends on the fractional extension  $R/L$ , and if you evaluate Eq. (11) for various  $N$  you will find that  $p(\vec{R}) = 0$  for  $R/L = 1$  (the fully stretched case). It is probably best to plot  $4\pi R^2 p(R)$  giving the probability of finding the endpoint at distance  $R$  from the origin. Remarkably, the Gaussian approximation is quite accurate even for  $N$  as small as 5, see Fig. (1).

## Elasticity of the 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

$$\frac{F}{T} = -\frac{\partial S}{\partial X}, \quad (12)$$

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.

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)

$$\Omega(X) \propto \exp\left(-\frac{X^2}{2Na^2/3}\right). \quad (13)$$

So

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

and the force is

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

(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 *Hooke's 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

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

with  $\theta_i$  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  $X = \sum x_i$  is analogous to the magnetic moment

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

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

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

$$X \simeq \frac{Na^2}{3kT} F, \quad (19)$$

the same result as before. For the strong stretching limit  $Fa \gg kT$  we have

$$X \simeq Na \left(1 - \frac{kT}{Fa}\right) \quad (20)$$

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

$$\frac{Fa}{kT} \rightarrow \frac{1}{1 - X/L}. \quad (21)$$

(Presumably this could also be calculated in the microcanonical ensemble, but I haven't tried this.)

### Confined Polymers

Confining a polymer to a small region also lowers the number of accessible states and so raises the entropy. This type of problem can be treated using the fact that the probability distribution for a random walk satisfies the *diffusion equation*. If we think of growing the ideal polymer link by link, the probability  $p(x, N)$  evolves as

$$\frac{\partial p}{\partial N} = D \nabla^2 p \quad (22)$$

with  $D = a^2/6$ , and we are treating  $N$  as a continuous variable. (Check that Eq. (4) satisfies this.)

First consider a one dimensional problem of an ideal polymer confined between rigid walls at  $x = 0, L$ . The probability  $w(x_1, x_2, N)$  that a polymer that starts at  $x_1$  will end at  $x_2$  is  $p(x_2, N)$  where  $p$  satisfies

$$\frac{\partial p}{\partial N} = D \frac{\partial^2 p}{\partial x^2}, \quad (23)$$

with the initial condition

$$p(x, N) = \delta(x - x_1), \quad (24)$$

and the boundary conditions

$$p(0, N) = p(L, N) = 0. \quad (25)$$

By expanding in the modes  $\sin n\pi x/L$  you can show that the solution for  $p(x_2, N)$  and so  $w(x_1, x_2, N)$  is

$$w(x_1, x_2, N) = \frac{2}{L} \sum_n \sin\left(\frac{n\pi x_1}{L}\right) \sin\left(\frac{n\pi x_2}{L}\right) \exp\left(-\frac{Dn^2\pi^2}{L^2} N\right). \quad (26)$$

The partition function

$$Q_{1d} = \int dx_1 \int dx_2 w(x_1, x_2, N) \quad (27)$$

$$= \frac{8L}{\pi^3} \sum_{n \text{ odd}} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2}{L^2} N\right). \quad (28)$$

For  $L \ll \sqrt{Na}$  only the  $n = 1$  mode contributes

$$Q_{1d} \simeq \frac{8L}{\pi^3} \exp\left(-\frac{D\pi^2}{L^2}N\right) \quad (29)$$

giving a free energy of confinement (using  $D = a^2/6$ )

$$A = N \frac{\pi^2 a^2}{6L^2} + O(\ln L). \quad (30)$$

The  $3d$  problem of confinement in a cube of side  $L$  is given by repeating this calculation in each of the three directions, giving

$$Q_{3d} = \left(\frac{8}{\pi^3}\right)^3 V \exp\left(-\frac{\pi^2 a^2}{2L^2}N\right) \quad (31)$$

and a free energy of confinement

$$A = N \frac{\pi^2 a^2}{2L^2} + O(\ln V). \quad (32)$$

### 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)

$$H = -K \sum_{j=1}^N \vec{t}_j \cdot \vec{t}_{j+1} = -K \sum_{j=1}^N \cos \theta_j \quad (33)$$

where in the latter expression  $\theta_j$  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

$$H = -K \sum_{j=1}^N \vec{t}_j \cdot \vec{t}_{j+1} - a \vec{F} \cdot \sum_j \vec{t}_j. \quad (34)$$

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  $\vec{B} = \vec{F}$ , 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

$$Q_N = \prod_{j=1}^N \int d\Omega_j e^{\beta K \sum_{j=1}^N \cos \theta_j} = (Q_1)^N \quad (35)$$

with (using  $\int d\Omega \rightarrow \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta$ )

$$Q_1 = 2\pi \int_{-1}^1 d(\cos \theta) e^{\beta K \cos \theta} = 4\pi \frac{\sinh \beta K}{\beta K}. \quad (36)$$

The thermodynamic quantities  $A$ ,  $U$  etc. can be calculated in the usual way.

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

$$\langle \vec{R}^2 \rangle = a^2 \left\langle \left( \sum \vec{t}_j \right)^2 \right\rangle = a^2 \sum_{ij} \langle \vec{t}_i \cdot \vec{t}_j \rangle, \quad (37)$$

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

$$\langle \vec{t}_j \cdot \vec{t}_{j+1} \rangle = \langle \cos \theta \rangle = \frac{\int d\Omega \cos \theta e^{\beta K \cos \theta}}{\int d\Omega e^{\beta K \cos \theta}} = \frac{d \ln Q_1}{d(\beta K)}. \quad (38)$$

This gives

$$\langle \vec{t}_j \cdot \vec{t}_{j+1} \rangle = c(\beta K) = \coth \beta K - \frac{1}{\beta K} \quad (39)$$

again involving the langevin function. The correlation with the  $n$ th link is

$$\langle \vec{t}_j \cdot \vec{t}_{j+n} \rangle = c^n = e^{-n \ln(1/c)}. \quad (40)$$

This can be seen geometrically—only the projection along the preceding link is transmitted to the next one— or more formally, as in the paper by Fisher. In terms of the separation measured along the chain, this can be written in terms of a correlation length or the *persistence length*  $\xi_p$

$$\langle \vec{t}_j \cdot \vec{t}_{j+n} \rangle = e^{-na/\xi_p} \quad (41)$$

with

$$\xi_p = \frac{a}{\ln(1/c)}. \quad (42)$$

For a stiff polymer  $K/kT \gg 1$

$$c \simeq 1 - \frac{kT}{K}, \quad (43)$$

$$\ln(1/c) \simeq \frac{kT}{K} \quad (44)$$

and then

$$\xi_p \simeq a \frac{K}{kT}. \quad (45)$$

Now we can work out  $\langle \vec{R}^2 \rangle$

$$\frac{\langle \vec{R}^2 \rangle}{a^2} = \sum_{i=1}^N \left[ \sum_{j=1}^{i-1} c^{i-j} + 1 + \sum_{j=i+1}^N c^{j-i} \right]. \quad (46)$$

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

$$\sum_{k=1}^{\infty} c^k = \frac{c}{1-c}, \quad (47)$$

and then

$$\langle \vec{R}^2 \rangle \simeq Na^2 \left( 1 + \frac{2c}{1-c} \right) = Na^2 \frac{1+c}{1-c}. \quad (48)$$

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

$$\langle \vec{R}^2 \rangle = Lb \quad (49)$$

with  $L = Na$  the fully stretched length, and then

$$b = \frac{1 + c}{1 - c} a \quad (50)$$

the *Kuhn length*. 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 first order in  $kT/K$  using Eq. (43) gives

$$b \simeq 2\xi_p, \quad (51)$$

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

**Elasticity of stiff polymers** The Hamiltonian including the stretching energy Eq. (34) cannot be solved exactly. We can however derive the extension in the small force limit. The method is quite general, and is analogous to the result  $\langle (E - \langle E \rangle)^2 \rangle = kT^2 C$  that we derived for energy fluctuations (here  $C = dU/dT$  is the thermal capacity).

We work with a general polymer Hamiltonian with a term for a force in the  $x$ -direction

$$H = H_0 - FX, \quad X = a \sum_{j=1}^{N+1} t_{jx}. \quad (52)$$

Then the average extension is

$$\langle X \rangle = \frac{\sum_{\text{states}} X e^{-\beta(H_0 - FX)}}{\sum_{\text{states}} e^{-\beta(H_0 - FX)}} = \frac{d \ln Q_N}{d(\beta F)}. \quad (53)$$

Differentiating this expression with respect to  $\beta F$  gives

$$\frac{d \langle X \rangle}{d\beta F} = \langle X^2 \rangle - \langle X \rangle^2 \quad (54)$$

and so

$$\left. \frac{d \langle X \rangle}{dF} \right|_{F \rightarrow 0} = \beta \langle X^2 \rangle_{F \rightarrow 0}. \quad (55)$$

Using  $\langle X^2 \rangle = \langle \vec{R}^2 \rangle / 3$  gives

$$F = \frac{3kT}{\langle \vec{R}^2 \rangle} X = \frac{3kT}{b} \frac{X}{L}. \quad (56)$$

For the stiff polymer this can be written

$$F = \frac{3kT}{2\xi_p} \frac{X}{L}. \quad (57)$$

**Nonlinear elasticity: the worm-like chain model** The Kratky-Porod model including the stretching force Eq. (34) cannot be solved exactly. To make progress we go to a continuum version known as the *worm-like chain* model—think of the polymer as an unstretchable worm, with an energy cost for wriggling. The WLC model is given by taking  $a \rightarrow 0$  maintaining  $Na = L$  constant, and expanding  $\vec{t}_j \cdot \vec{t}_{j+1} \simeq 1 - \theta_j^2/2$ . This gives (apart from an additional constant)

$$H = kT\xi_p \int \left[ \frac{1}{2} \left( \frac{d\vec{t}}{ds} \right)^2 - Ft_x \right] ds \quad (58)$$

using  $Ka \rightarrow kT\xi_p$ . The integral is over the polymer contour  $s$ , and the force is in the  $x$  direction. Marco and Siggia [2] discuss the full solution. We will only look at the small  $F$  limit (already done) and the large  $F$  limit—for intermediate values numerics are needed.

If the polymer is nearly fully extended, we can expand quadratically in  $\vec{t}_\perp$ , the component of  $\vec{t}$  perpendicular to the extent. Using  $ds \simeq dx$  and

$$t_x = \sqrt{1 - (\vec{t}_\perp)^2} \simeq 1 - \frac{1}{2}(\vec{t}_\perp)^2 \quad (59)$$

reduces the Hamiltonian to

$$H \simeq kT \int \left[ \frac{\xi_p}{2} \left( \frac{d\vec{t}_\perp}{dx} \right)^2 + \frac{f}{2}(\vec{t}_\perp)^2 \right] dx + \text{const}, \quad (60)$$

with  $f = F/kT$ . This *quadratic* Hamiltonian can be solved using equipartition.

Expand in normal modes (assuming  $\vec{t}_\perp = 0$  at  $x = 0, L$ )

$$\vec{t}_\perp = \sum_n \sin\left(\frac{n\pi x}{L}\right) \vec{t}_\perp^{(n)}. \quad (61)$$

Using the orthogonality of the functions on  $[0, L]$  gives

$$H \simeq \frac{1}{2}kTL \sum_n \left( \frac{\xi_p}{2} \frac{n^2\pi^2}{L^2} + \frac{f}{2} \right) (\vec{t}_\perp^{(n)})^2. \quad (62)$$

Equipartition gives

$$\langle (t_y^{(n)})^2 \rangle = \langle (t_z^{(n)})^2 \rangle = \frac{2}{L} \frac{1}{\xi_p \frac{n^2\pi^2}{L^2} + f}. \quad (63)$$

The average length is

$$X \simeq \int dx \left( 1 - \frac{1}{2} \langle \vec{t}_\perp^2 \rangle \right) \quad (64)$$

$$= L \left( 1 - \sum_n \frac{1}{\xi_p \frac{n^2\pi^2}{L^2} + f} \right). \quad (65)$$

For a long chain the sum can be approximated by an integral, using  $q = n\pi/L$  and  $dq = \pi/L$ , to give

$$\frac{X}{L} = 1 - \frac{1}{\pi} \int_0^\infty \frac{1}{\xi_p q^2 + f} dq = 1 - \frac{1}{2} \left( \frac{kT}{F\xi_p} \right)^{1/2}. \quad (66)$$

Writing in terms of the force  $F$  to give extension  $\langle X \rangle$

$$F = \frac{kT}{\xi_p} \frac{1}{4(1 - X/L)^2}. \quad (67)$$



Notice the divergence for  $X \rightarrow L$  is as  $(1 - X/L)^{-2}$  compared with the  $-1$  power found for the ideal polymer.

Marco and Siggia [2] suggest the interpolation formula

$$F \simeq \frac{kT}{\xi_p} \left[ \frac{X}{L} + \frac{1}{4} \frac{1}{(1 - X/L)^2} - \frac{1}{4} \right] \quad (68)$$

which agrees with the limiting results Eq. (57) and (67), and is close to their numerical results for intermediate values.

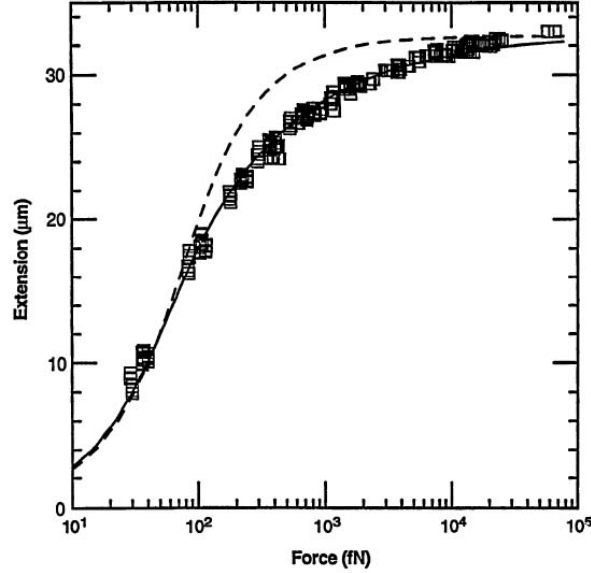


Figure 2: Fit to worm-like chain model with  $L = 32.8\mu$  and  $\xi_p = 53.4\text{nm}$  (from Bustamante et al. [3])

To get a feel for the numbers consider  $\lambda$ -phage DNA. This molecule is found to have  $\xi_p \simeq 50\text{nm}$ , which corresponds to 150 base pairs, i.e. the polymer is indeed stiff so that  $\xi_p$  is much longer than the monomer length. Experiments are often done on molecules with lengths of several tens of microns. Taking  $L = 30\mu$  gives  $\langle R^2 \rangle \sim 2\mu$ . The order of magnitude of the tensile forces to stretch the DNA is

$$\frac{kT}{\xi_p} \sim 0.1\text{pN} \quad (69)$$

so that for large extensions

$$F \sim 0.1\text{pN} \times \frac{1}{4(1 - X/L)^2}. \quad (70)$$

Such forces can be measured in single molecule experiments. The measured force-extension curves agree well with the expression Eq. (68), see Fig. (2).

**Polymers 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  $R \sim \sqrt{Na}$ .

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*

$$R \sim N^\nu \quad (71)$$

with the exponent  $\nu \simeq 0.588$  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

$$F \sim kT \left( \frac{N^2v}{R^3} + \frac{R^2}{Na^2} \right). \quad (72)$$

Minimizing with respect to  $R$  gives Eq. (71) with  $\nu = 3/5$ . 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  $R \sim N^{1/3}$ . (Note that the confinement entropy Eq. (32) is not large enough to stop this collapse.) 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. On the other hand *Molecular Driving Forces* by Ken A. Dill and Sarina Bromberg presents a discussion from the very beginning—chapters 32 and 33 are most relevant.

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]. You can find out what  $\lambda$ -*phage DNA* is at the Molecular Genetics Workshop website [8].

Another interesting application of statistical mechanics to DNA is the denaturing transition in which the pair of polymers bound in the helix splits apart. The review by Michael Peyraud (see in particular §VI) describes a simple model calculation.

## References

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