The Freely Jointed Chain as an Entropic Spring

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April 24, 2008

1 Goals

Our goals for the rest of the semester are to present biological applications of the physics tools we've learned so far. For this lecture, we will build a simple model of the properties of DNA. Next lecture, we will use this model to describe an experiment that uses these properties of DNA.

2 Bending Modulus and Persistence Length

Consider a thin rod of length L, subject to a bending force F, which displaces the end by a distance x. From elastic solid mechanics, we know that

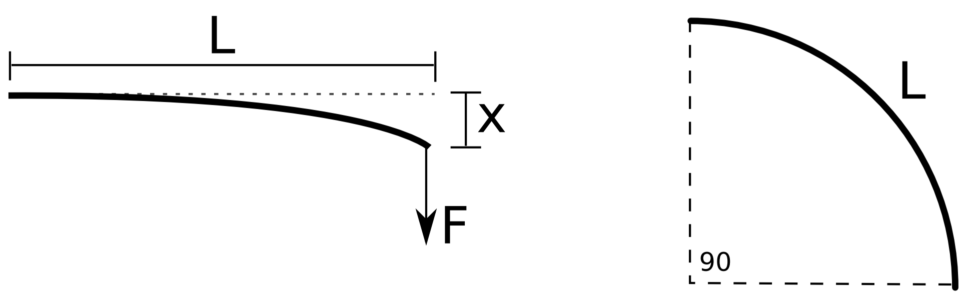

Figure 1:

$$x = \frac{FL^3}{\text{stiffness}} = \frac{FL^3}{3YI},$$

where $3YI$ is a measure of stiffness combining the Young's modulus and the bending moment.

How much energy does it take to bend the rod?

$$E = \int_0^x F dx = \int_0^x x \frac{3YI}{L^3} dx = \frac{3YI}{L^3} \frac{1}{2} x^2.$$

How much energy does it take to bend the rod by 90 degrees? We regard this as approximately equivalent to displacing the end point by a distance $x = L$.

$$E(L) = \frac{3YI}{2L}.$$

This is inverse with L, so as the rod gets longer, the amount of energy to bend it by 90 degrees decreases.

We now consider our flexible rod at thermal equilibrium at a temperature T, perhaps immersed in a fluid bath. We can now ask "How long a segment of a flexible rod will tend to be bent through 90 degrees at a temperature T?".

$$E(L) = \frac{1}{2} kT = \frac{3YI}{2L}.$$

$$L = \frac{3YI}{kT} \equiv \lambda.$$

We call λ the *persistence length* of the polymer. Segments of polymer shorter than λ will tend to be relatively straight, while segments of polymer longer than λ will tend to be bent back on themselves many times. Note that although the *magnitude* of the bending depends on the length of each segment, the *direction* of the bending is random.

3 Freely-Jointed Chain

Because segments shorter than λ are likely to be nearly straight, and segments much longer than λ are likely to be completely bent, it is sensible to model the continuous polymer as a chain of short straight segments that can rotate freely. It is customary to take the length of these chain segments to be 2λ, due to details involving the dimensionality of the system.

A freely jointed chain with N links of length 2λ is mathematically equivalent to a random walk with N steps of length 2λ. We already know, therefore, that

$$\langle d^2 \rangle = N(2\lambda)^2(n)$$

where n is a constant that may change depending on the number of dimensions.

To simplify the system so that we can understand it completely, we reduce the system to a one-dimensional random walk. This chain as an end-to-end distance of $k = 5$, a number of links $N = 11$, and therefore a number of right-steps $m = 8$. There are $\binom{11}{8}$ ways of

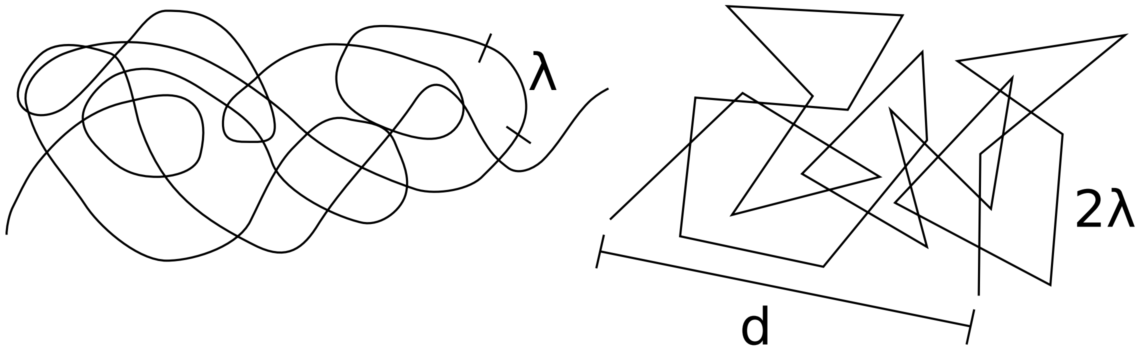

Figure 2:

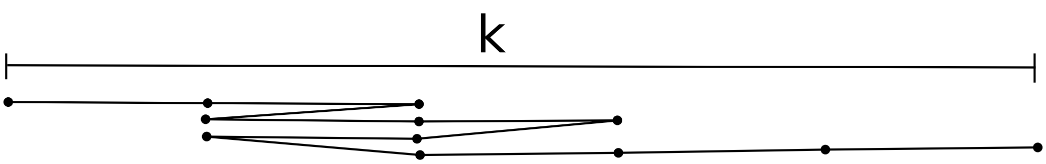

Figure 3:

having $m = 8$, which means there are $\frac{11!}{8!(11-8)!}$ different chain arrangements that result in an end-to-end distance of 5. We call this number $\Omega_m(8)$, or equivalently $\Omega_k(5)$. In general,

$$\Omega_m = \binom{N}{m} = \frac{N!}{m!(N-m)!} = \text{Binom}(m; N, \frac{1}{2}) \cdot 2^N.$$

We know that for $N \gg 1$ and $m - N/2 \ll N$, we may approximate this Binomial distribution as a Normal distribution. This limit corresponds to $k \ll N$, or a freely jointed chain whose ends have been moved apart only slightly.

$$\Omega_m \approx \sqrt{\frac{2}{\pi N}} e^{-\frac{(m-N/2)^2}{N/2}} 2^N.$$

Because k is more directly related to the total length of the chain, it is more convenient to rephrase $Omega$ in terms of k, given that $k = m - (N - m) = 2m - n$.

$$\Omega_k \approx \sqrt{\frac{2}{\pi N}} 2^N e^{-\frac{k^2}{2N}}.$$

4 Entropic Spring

If we hold the ends of a freely jointed chain apart, do we feel a force? Intuitively, the answer is yes. We may imagine holding a clothesline in an earthquake, and note that the random vibrations in the rope will tend to pull our hands together. However, as a physicist, one may be inclined to say that there should be no force, because the work-energy theorem tells us that

$$F = \frac{dE}{dx}.$$

In the case of a freely jointed chain, the internal energy E does not depend on its conformation at all, so $F = 0$. To resolve this, we need to make a physical model of the system and determine whether it exerts a force. This is not so easy, because our tools of statistical mechanics are phrased in terms of energy, not force. In order to measure force, we introduce a "scale", much like one you might use to weigh your groceries at a supermarket. A scale is nothing more than stiff linear spring, and we read out the force on it by observing its extension. We therefore model our system as a freely jointed chain, extended to a distance d,

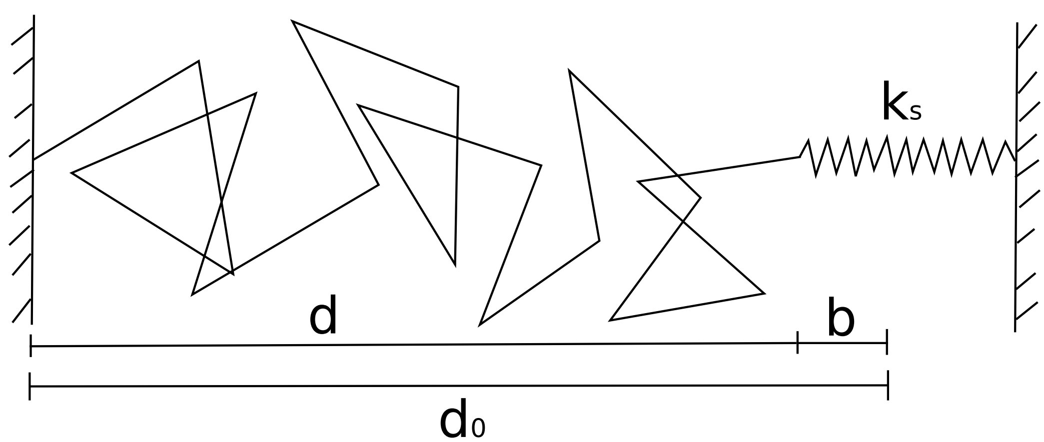

Figure 4:

and attached to a spring with constant k_s that may have been stretched from its equilibrium position by some distance b. We then define d_0 as the distance between the far end of the chain and the equilibrium position of the spring, which is also the value that d will take if the tension force is 0.

The instantaneous internal energy of this system is given by

$$E = \frac{1}{2}k_s b^2.$$

We might therefore be tempted to write, from the Boltzmann distribution, that the probability distribution of b is given by

$$P_b(b) = e^{-\frac{\frac{1}{2}k_s b^2}{k_B T}}$$

but *this is not correct.* The reason it is not correct is subtle, but critical. The Boltzmann distribution tells us the relative probability of being in distinct microstates:

$$\frac{P(s_1)}{P(s_2)} = e^{\frac{E_2 - E_1}{k_B T}}.$$

If there are a very large number of microstates that result in a given macroscopic state, then that macroscopic state will be more likely, even if that state does not have minimum energy. Each position b corresponds to a large number of different microstates counted by Ω. Therefore, the probability of each position is actually given by

$$P_b(b) = \frac{1}{Z}\Omega_b(b) e^{-\frac{E(b)}{k_B T}}$$

where Z is just a normalization constant. Adding in the details of our system, we get

$$P_b(b) = \frac{1}{Z}\Omega_k\left(\frac{d_0 - b}{2\lambda}\right) e^{-\frac{\frac{1}{2}k_s b^2}{k_B T}} = \frac{\sqrt{\frac{2}{\pi N}}2^N}{Z} e^{-\frac{(b-d_0)^2}{8\lambda^2 N}} e^{-\frac{b^2}{2k_B T/k_s}} = \frac{\sqrt{\frac{2}{\pi N}}2^N}{Z'} e^{-\frac{(b-\mu_b)^2}{2\sigma_b^2}}$$

for some mean μ_b and variance σ_b^2. We are most interested in μ_b, which represents the mean displacement of the spring, and therefore the mean force on the spring. If $\mu_b = 0$, then there is no force on the spring, on average. Instead, we may calculate that

$$\mu_b = d_0 \cdot \frac{1}{1 + \frac{4\lambda^2 N k_s}{k_B T}}$$

$$\langle F \rangle = k_s \mu_b = d_0 \cdot \frac{1}{\frac{1}{k_s} + \frac{4\lambda^2 N}{k_B T}}.$$

If we take the limit as our spring approaches infinite stiffness, we get

$$\langle F \rangle = \frac{k_B T}{4\lambda^2 N} d_0 = k_{\text{eff}} d_0.$$

Thus, we have learned not only that the freely jointed chain applies a force when extended, but that this force is directly proportional to distance, with some effective spring constant k_{eff}. The formula for k_{eff} is also very informative, as it tells us that the difficulty of extending the spring will go up as temperature increases or persistence length decreases.

Note that this model only applies when $d_0 \ll 2\lambda N$, because that is the range in which our approximation of the binomial as a Gaussian is valid. If this model is taken out of its range of validity, it makes nonsensical predictions. For example, it predicts that with a sufficiently large force, one may stretch the chain longer than $2\lambda N$, which is its intrinsic length when perfectly straight.

5 Free Energy

The preceding calculation was quite tedious, and required a great deal of work to tabulate Ω and then determine its effect. We were also left with a problem that, although there is a non-zero mean force exerted, there is no change in the internal energy. To address this problem, we might alter our bookkeeping for the Boltzmann equation:

$$\begin{aligned} P(x) &= \frac{\Omega}{Z} e^{-\frac{E}{k_B T}} \\ &= \frac{1}{Z} e^{\log(\Omega)} e^{-\frac{E}{k_B T}} \\ &= \frac{1}{Z} e^{-\frac{E - k_B T \log(\Omega)}{k_B T}}. \end{aligned}$$

At this point, we may, for convenience, define $S \equiv k_B \log(\Omega)$, so that

$$P(x) = \frac{1}{Z} e^{-\frac{E - TS}{k_B T}}.$$

We now recognize the numerator as the Free Energy, for example the Gibbs Free Energy for problems that involve pressure and volume. This Free Energy is then nothing more than a bookkeeping trick, designed to provide us with a new "effective energy" with the convenient property that

$$F = \frac{dG}{dx}.$$

This trick also allows us to avoid the computation of Ω, since for most problems, Ω is well-known, and so we may instead look up the equivalent value for S in a table.

6 Continuous Systems

The notion of Ω, the number of microstates consistent with some macroscopic state variable, is very important here, but it is hard to see how it applies to a continuous system (for example, a freely jointed chain in three dimensions). The number of configurations of a two- or three-dimensional chain with any fixed length is always infinite, and so $\Omega = \infty$. This is not helpful when trying to compare probabilities; it also renders the distribution non-normalizable (because it is ∞ everywhere). In order to resolve this problem, classical statistical mechanics is instead done in terms of "state space volume" and "density of states". These techniques are very effective, but quite difficult. Luckily, in quantum mechanics, state spaces are always composed of discrete microstates, so quantum statistical mechanics makes Ω very natural to use.