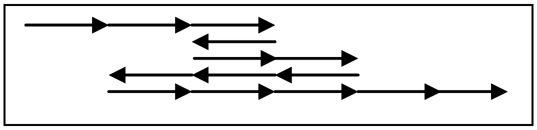
The Humble Rubber Band

We pretend that a rubber band, which is actually composed of long flexible chains of carbon atoms (with a sprinkle of other types), consists of N links that point either to the right or to the left, as shown below.



The overall length is

$$L = l(N_R - N_L),$$

but since

$$N = N_R + N_L,$$
$$L = l(2N_R - N)$$

where *l* is the length of one link. We assume that the links don't get in each other's way and are independent. Obviously, there are many ways to arrange the links to arrive at a given length and the macrostate is determined by N_R. There is only one way to get L=N*l* but many ways to get L=0 (negative L is possible but ignored).

The multiplicity of the macrostate is just the same as for the number of heads in a toss of N coins or up spins among N magnetic spins:

$$\Omega(N, N_R) = \frac{N!}{N_R!(N-N_R)!} \approx \frac{N^N}{N_R{}^N (N-N_R)^{(N-N_R)}}$$

$\Omega(N,N_R)$ counts the number of different ways to arrange a chain that has N_R links pointing to the right. Ω is maximal when N_R=N_L.

The entropy can be written as $S(N,U,N_R)$, where U is a vibrational term, independent of L. Because N_R is a function of L, i.e.

$$N_R = \frac{1}{2}(\frac{L}{l} + N)$$

We can also write the entropy as S(N,U,L).

The *thermodynamic identity* allows us to say some things about how the entropy changes as its variables change, without knowing many of the details.

$$dS = (\frac{\partial S}{\partial U})_{N,L} dU + (\frac{\partial S}{\partial L})_{U,N} dL + (\frac{\partial S}{\partial N})_{U,L} dN$$

N is assumed not to change and writing $\frac{\partial S}{\partial U} = \frac{1}{T}$ we get the identity

$$dS = \frac{1}{T} dU + (\frac{\partial S}{\partial L}) dL \; .$$

In analogy with the ideal gas, we might expect the term $(\frac{\partial S}{\partial L}) dL$ to be the one-dimensional equivalent of $(\frac{\partial S}{\partial V}) dV = \frac{P}{T}$.

Indeed, $\frac{\partial S}{\partial L}$ is the reaction of the rubber band to the force F that stretches it. Since entropy decreases as the rubber band is stretched, $\frac{\partial S}{\partial L} < 0$, so if the force is to be a positive number, we write:

$$(\frac{\partial S}{\partial L})_{U,N} = -\frac{F}{T} \; .$$

Thus we have the completely general relation:

$$TdS = dU - FdL$$

Here is the first cool result: If the vibrational component to the energy U actually does not depend on whether the rubber band is stretched, then at constant temperature we can assume dU=0. Thus we have

$$\begin{aligned} &TdS = -FdL \\ &or \;\; (formally) \\ &F = -T(\frac{\partial S}{\partial L}) \end{aligned}$$

This result predicts that the force should be approximately proportional to temperature at constant L, which is true, as you can easily verify. In class, a rubber band engine powered by a light bulb was demonstrated. You can also verify that the rubber band heats up as it is stretched, and cools when released. Why?

The second cool result comes from the actual functional form of the force, as derived from the entropy. You can show that a rubber band, if it obeys this simple model, exerts a force that is proportional to its extension (Hooke's Law), that is

$$F = -sL \, ,$$

where ***s*** is the spring constant. To derive the force F from the entropy:

$$F = -T\left(\frac{\partial S}{\partial L}\right) = -T\left(\frac{\partial S}{\partial N_R}\right)\left(\frac{\partial N_R}{\partial L}\right)$$

$$S/k = N\ln N - N_R \ln N_R - (N - N_R)\ln(N - N_R)$$

$$\frac{\partial S}{\partial N_R} = k\ln\left(\frac{N - N_R}{N_R}\right)$$

$$\frac{\partial N_R}{\partial L} = \frac{1}{2l}$$

Putting this together

$$F = -kT\ln\left(\frac{N - N_R}{N_R}\right)\frac{1}{2l}$$

Substituting for N_R and after a little algebra

$$F = \frac{kT}{2l}\ln\left(\frac{1 + \frac{L}{Nl}}{1 - \frac{L}{Nl}}\right)$$

When L << N*l* this equation is of the form

$$F = \frac{kT}{2l}\ln\left(\frac{1+x}{1-x}\right)$$

And, if x<<1, $\ln\left(\frac{1+x}{1-x}\right) \approx \ln(1+2x) \approx 2x$.

The force becomes simply

$$F = \frac{kT}{2l}\left(\frac{2L}{Nl}\right)$$

$$F = \frac{kT}{Nl^2}L$$

The effective "spring constant" is kT/Nl^2. The spring constant has units of energy per unit length squared, as expected.

In polymer physics, long chain molecules are often modeled as having stiff links connected by a hinge of length *l*, which is called the "persistence length". So, we can estimate the persistence length of the molecules in our rubber band by measuring the force as a function of temperature! To get N, we would have to have some idea of the size of the molecules, but this was done by chemists many years ago. It is amazing what you can do with thermodynamics.