

## RUBBER BANDS AND ENTROPY

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Reference: Daniel V. Schroeder, *An Introduction to Thermal Physics*, (Addison-Wesley, 2000) - Problem 3.34.

We can model a rubber band as a one-dimensional chain of  $N$  polymer links each of length  $\ell$ , where each link can point either to the left or right. The total length  $L$  of the rubber band is therefore

$$L = (N_R - N_L) \ell = (2N_R - N) \ell \quad (1)$$

where  $N_{R,L}$  is the number of links pointing to the right or left, so that  $N = N_R + N_L$ . We'll assume that  $N_R > N_L$ , although the converse is just the mirror image and gives the same behaviour.

The entropy can be found by noting that the system is equivalent to a coin-flipping experiment, so for a given  $N_R$ , the multiplicity is

$$\Omega = \binom{N}{N_R} = \frac{N!}{N_R!(N - N_R)!} \quad (2)$$

Using Stirling's approximation, the entropy is

$$S = k [N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R)] \quad (3)$$

Since this is a one-dimensional system, the role of the pressure in a 3-d system is taken here by the tension force  $F$  generated by stretching the rubber band. If  $F > 0$  when the band is pulling inward, then work  $F \cdot dL$  is done *on* the band when it is stretched through a distance  $dL > 0$ .

The thermodynamic identity for this system is therefore

$$dU = TdS + FdL \quad (4)$$

If the band is stretched in such a way that its energy remains constant (e.g. by losing heat), then  $dU = 0$  and the force is given by

$$F = -T \left( \frac{\partial S}{\partial L} \right)_U \quad (5)$$

From 1

$$dL = 2\ell dN_R \quad (6)$$

so from 3

$$\frac{\partial S}{\partial L} = \frac{1}{2\ell} \frac{\partial S}{\partial N_R} \quad (7)$$

$$= \frac{k}{2\ell} [-\ln N_R - 1 + \ln(N - N_R) + 1] \quad (8)$$

$$= \frac{k}{2\ell} \ln \frac{N - N_R}{N_R} \quad (9)$$

From 1

$$N_R = \frac{1}{2} \left( \frac{L}{\ell} + N \right) \quad (10)$$

so

$$\frac{\partial S}{\partial L} = \frac{k}{2\ell} \ln \frac{\frac{N}{2} - \frac{L}{2\ell}}{\frac{N}{2} + \frac{L}{2\ell}} = \frac{k}{2\ell} \ln \frac{N\ell - L}{N\ell + L} \quad (11)$$

$$F = -\frac{kT}{2\ell} \ln \frac{N\ell - L}{N\ell + L} \quad (12)$$

If  $L \ll N\ell$ , the band is almost fully contracted since its length is much less than the maximum length. In this case we can get an estimate of the force:

$$F = -\frac{kT}{2\ell} \ln \frac{1 - L/N\ell}{1 + L/N\ell} \quad (13)$$

$$\approx -\frac{kT}{2\ell} \ln \left[ (1 - L/N\ell)^2 \right] \quad (14)$$

$$= -\frac{kT}{\ell} \ln [1 - L/N\ell] \quad (15)$$

$$\approx \frac{kT}{N\ell^2} L \quad (16)$$

That is,  $F \propto L$  which is Hooke's law for a spring, with spring constant  $kT/N\ell^2$ .

The formula 12 for  $F$  says that  $F$  should increase as the temperature is increased, that is, a rubber band should contract when heated (up to a point, obviously; after a while it will just melt). Although this relation was derived in the special case of constant energy  $U$ , it does seem to make sense. A higher temperature would increase the entropy, meaning that  $N_R$  gets closer to its maximum entropy value of  $\frac{N}{2}$ , which means that  $L$  gets smaller. By the same token, we'd expect a rubber band to get warmer if it is suddenly

stretched. I did try the experiment suggested, although I couldn't find a heavy rubber band, and it did seem to warm up a bit when it was stretched.