

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 ℓ , where each link can point either to the left or right. The total length L of the rubber band is therefore

$$(0.1) \quad L = (N_R - N_L) \ell = (2N_R - N) \ell$$

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

$$(0.2) \quad \Omega = \binom{N}{N_R} = \frac{N!}{N_R!(N - N_R)!}$$

Using Stirling's approximation, the entropy is

$$(0.3) \quad S = k [N \ln N - N_R \ln N_R - (N - N_R) \ln (N - N_R)]$$

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

$$(0.4) \quad dU = T dS + F dL$$

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

$$(0.5) \quad F = -T \left(\frac{\partial S}{\partial L} \right)_U$$

From 0.1

$$(0.6) \quad dL = 2\ell dN_R$$

so from 0.3

$$(0.7) \quad \frac{\partial S}{\partial L} = \frac{1}{2\ell} \frac{\partial S}{\partial N_R}$$

$$(0.8) \quad = \frac{k}{2\ell} [-\ln N_R - 1 + \ln(N - N_R) + 1]$$

$$(0.9) \quad = \frac{k}{2\ell} \ln \frac{N - N_R}{N_R}$$

From 0.1

$$(0.10) \quad N_R = \frac{1}{2} \left(\frac{L}{\ell} + N \right)$$

so

$$(0.11) \quad \frac{\partial S}{\partial L} = \frac{k}{2\ell} \ln \frac{\frac{N}{2} - \frac{L}{2\ell}}{\frac{N}{2} + \frac{L}{2\ell}} = \frac{k}{2\ell} \ln \frac{N\ell - L}{N\ell + L}$$

$$(0.12) \quad F = -\frac{kT}{2\ell} \ln \frac{N\ell - L}{N\ell + L}$$

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:

$$(0.13) \quad F = -\frac{kT}{2\ell} \ln \frac{1 - L/N\ell}{1 + L/N\ell}$$

$$(0.14) \quad \approx -\frac{kT}{2\ell} \ln \left[(1 - L/N\ell)^2 \right]$$

$$(0.15) \quad = -\frac{kT}{\ell} \ln [1 - L/N\ell]$$

$$(0.16) \quad \approx \frac{kT}{N\ell^2} L$$

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

The formula 0.12 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.