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

$$L = (N_R - N_L)\,\ell = (2N_R - N)\,\ell \tag{1}$$

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

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

Using Stirling's approximation, the entropy is

$$S = k\left[N\ln N - N_R\ln N_R - (N - N_R)\ln(N - N_R)\right] \tag{3}$$

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

$$dU = TdS + FdL \tag{4}$$

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

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

From 1

$$dL = 2\ell dN_R \tag{6}$$

so from 3

$$\begin{aligned}
\frac{\partial S}{\partial L} &= \frac{1}{2\ell}\frac{\partial S}{\partial N_R} && (7)\\
&= \frac{k}{2\ell}\left[-\ln N_R - 1 + \ln(N-N_R) + 1\right] && (8)\\
&= \frac{k}{2\ell}\ln\frac{N-N_R}{N_R} && (9)
\end{aligned}$$

From 1

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

so

$$\begin{aligned}
\frac{\partial S}{\partial L} &= \frac{k}{2\ell}\ln\frac{\frac{N}{2}-\frac{L}{2\ell}}{\frac{N}{2}+\frac{L}{2\ell}} = \frac{k}{2\ell}\ln\frac{N\ell-L}{N\ell+L} && (11)\\
F &= -\frac{kT}{2\ell}\ln\frac{N\ell-L}{N\ell+L} && (12)
\end{aligned}$$

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:

$$\begin{aligned}
F &= -\frac{kT}{2\ell}\ln\frac{1-L/N\ell}{1+L/N\ell} && (13)\\
&\approx -\frac{kT}{2\ell}\ln\left[(1-L/N\ell)^2\right] && (14)\\
&= -\frac{kT}{\ell}\ln\left[1-L/N\ell\right] && (15)\\
&\approx \frac{kT}{N\ell^2}L && (16)
\end{aligned}$$

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.