Statistical Molecular Thermodynamics

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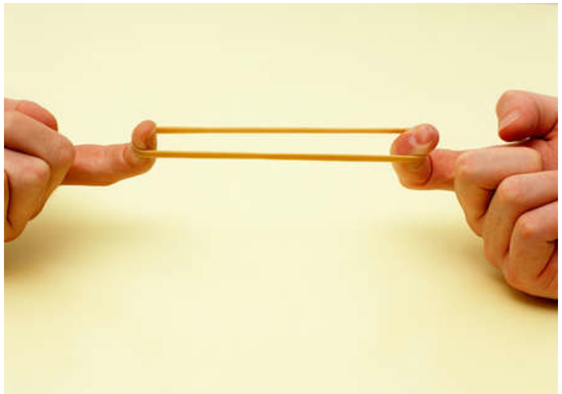
Video 8.5

Rubber Band Thermodynamics

Stretching a Rubber Band



A restoring force f is present when a rubber band is stretched to be longer than its equilibrium length—for modest displacements, *f* is a constant independent of length l

Work must be done on the rubber band to stretch it, and that work is given by:

$$\delta w = f dl - P dV$$

non-PV work PV work

Note that f is positive as work is done *on* the sytem to *increase* the rubber band length Δl

Isothermal Stretching

We can safely assume that the volume change of the rubber band is negligible for small stretches, in which case for an isothermal stretch, we will be working at constant T and V; this suggests that we should consider the Helmholtz free energy.

$$A = U - TS$$

If we take the the differential:

$$\begin{aligned} dA &= dU - TdS - SdT \\ &= \delta q_{rev} + \delta w_{rev} - TdS - SdT \\ &= TdS + fdl - PdV - TdS - SdT \\ &= fdl - PdV - SdT \\ &= fdl \end{aligned}$$

$dV = dT = 0$ at constant T and V

$$\Longrightarrow \quad f = \left(\frac{\partial A}{\partial l}\right)_T$$

Relating Force to Entropy

$$A = U - TS$$

$$f = \left(\frac{\partial A}{\partial l}\right)_T$$

Differentiate A wrt l :

$$\left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T$$

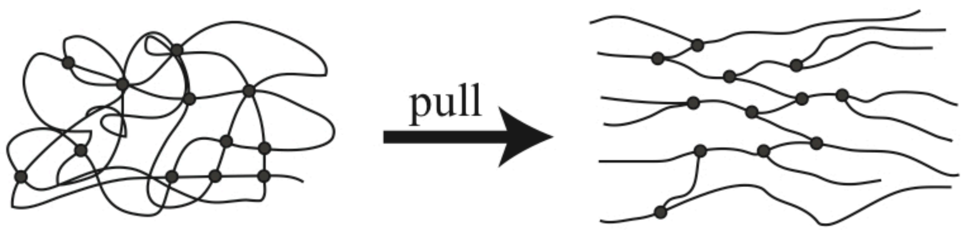
The internal energy U of a perfect elastomer depends only on temperature T and not on length l, much as U for an ideal gas depends only on T and not on volume V

$$\Longrightarrow \quad \left(\frac{\partial A}{\partial l}\right)_T = f = -T\left(\frac{\partial S}{\partial l}\right)_T$$

Relating Force to Entropy

This relationship suggests that with increasing T, the force will *decrease* if the entropy *increases* with stretching, but the force will *increase* if the entropy *decreases* with stretching. So, what does one intuitively expect?

$$f = -T\left(\frac{\partial S}{\partial l}\right)_T$$



A rubber band is composed of a collection of tangled, cross-linked polymers. Stretching forces those polymers to align themselves more closely to the axis of elongation, leading to greater ordering and *decreased* entropy

Thus, heating the rubber band should *increase* its restoring force

Adiabatic Stretching

If we stretch the ideal rubber band *suddenly*, so that there is no time for heat transfer from the environment, the stretching will be *adiabatic*, in which case

$$\begin{aligned} dU &= \delta q + \delta w \\ &= 0 + fdl \end{aligned}$$

Since for a perfect elastomer, U depends only on T, we may define a constant length heat capacity

$$C_l(T) = \left(\frac{dU}{dT}\right)_l \qquad \text{i.e.,} \qquad dU = C_l(T)dT$$

$$\Rightarrow \quad fdl = C_l(T)dT$$

Improvisational Lip Warming

$$f\Delta l = C_l(T)\Delta T$$

We know that f is positive, and the constant length heat capacity must also be positive (the energy increases with increasing temperature), which implies that a positive displacement Δl should lead to an increase in temperature in linear proportion to the increase in length

This experiment is easily tried at home: Take a rubber band, stretch it suddenly, and hold it to your (sensitive) upper lip thermometer — it should feel noticeably warmer after stretching than before. Thermodynamics in action!