11/18/05

Last time showed

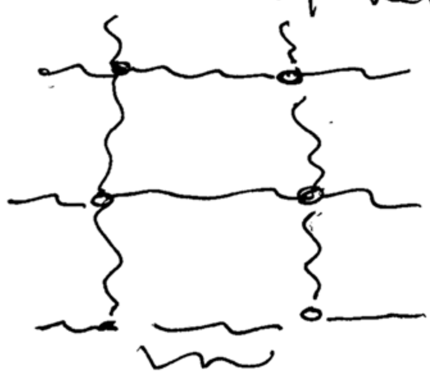
$$f_{elastic} = -\frac{3kTx}{Nb^2}$$

Consider PEO chain @ 300K $b = 0.34\,nm$

$$f_{el} = -37\frac{x/b}{N}\ pN$$

$N = 1000 \Rightarrow$ requires 3.7 pN to stretch 34 nm

Rubber elasticity - network of chains, crosslinked



m total chains in network
ideal, freely jointed
identical

distance between crosslinks

$$\langle r_0^2 \rangle = \langle x_0^2 \rangle + \langle y_0^2 \rangle + \langle z_0 \rangle^2 = Nb^2$$

(same as individual chain)

Now stretch chain λ_x factor

macro scopic object is also stretched λ_x

"affine" deformation

New end-end distance

$$r^2 = x^2 + y^2 + z^2 = (\lambda_x x_0)^2 + (\lambda_y y_0)^2 + (\lambda_z z_0)^2$$

(we presume V = constant thus $x_0 y_0 z_0 = \lambda_x x_0 \lambda_y y_0 \lambda_z z_0$)

Free energy change for <u>one</u> of the m chains
(Helmholtz)

$$\Delta A_{\text{single chain}} = A_{\text{deformed}} - A_{\text{relaxed}}$$

$$= kT \ln\left(\frac{P(x,y,z,N)}{P(x_0,y_0,z_0,N)}\right) = \frac{3kT}{2Nb^2}(r^2 - r_0^2)$$

For the entire network of m chains (all equivalent)

$$\Delta A = \frac{3kT}{2Nb^2}\sum_{i=1}^{m}(r_i^2 - r_0^2) = \frac{3kT}{2Nb^2} m\left(\langle r^2\rangle - \langle r_0^2\rangle\right)$$

Simplify: to give in terms of λs

$$\Delta A = \frac{3kT}{2Nb^2} m\left[(\lambda_x^2 - 1)\langle x_0\rangle^2 + (\lambda_z^2 - 1)\langle z_0\rangle^2 + (\lambda_y^2 - 1)\langle y_0\rangle^2\right]$$

For an isotropic rubber: $\langle x_o^2 \rangle = \langle y_o^2 \rangle = \langle z_o^2 \rangle = \frac{Nb^2}{3}$

This simplies to

$$\frac{\Delta F}{kT} = \frac{m}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right]$$

So now if we stretch a rubber band along x-axis

We presume if isotropic $\lambda_y = \lambda_z$

Since $V = x_o y_o z_o = \lambda_x x_o \lambda_y y_o \lambda_z z_o$

$$\lambda_y \lambda_z = \frac{1}{\lambda_x} \Rightarrow \lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda_x}}$$

Plug in to free energy change

$$\frac{\Delta F}{kT} = \frac{m}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right) = \frac{m}{2}\left(\lambda_x^2 + \frac{1}{\lambda_x} + \frac{1}{\lambda_x} - 3\right)$$

$$\frac{\Delta F}{kT} = \frac{m}{2}\left(\lambda_x^2 + \frac{2}{\lambda_x} - 3\right)$$

What force is required? $f_x = -\frac{\partial \Delta F}{\partial x} = -\frac{1}{x_o}\frac{\partial \Delta F}{\partial \lambda_x} = -\frac{mkT}{x_o}\left(\lambda_x - \frac{1}{\lambda_x^2}\right)$