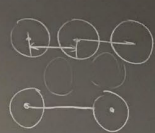
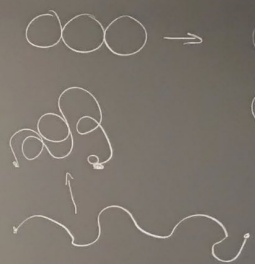


Network and Rubber Elasticity



$$\left. \begin{aligned} G &= H - TS \\ H &= U + pV \\ A &= U - TS \end{aligned} \right\} p = \text{const}$$

$$V = \text{const}$$

$$\begin{aligned} dU &= dq + dw \\ &= dq - pdV + f dL \end{aligned}$$

$$dS = \frac{dq}{T} \leadsto dq = T dS$$

$$dU = T dS - p dV + f dL \quad (1)$$

$$dG = dU - p dV + V dp - T dS - S dT \quad (2)$$

$$\text{compare (1) + (2)} \quad dG = V dp - S dT + f dL \quad (3)$$

$$dG = \left(\frac{\partial G}{\partial p} \right)_{T,L} dp + \left(\frac{\partial G}{\partial T} \right)_{p,L} dT + \left(\frac{\partial G}{\partial L} \right)_{p,T} dL \quad (4)$$

$$\text{compare 3 + 4: } f = \left(\frac{\partial G}{\partial L} \right)_{p,T}$$

$$\left(\frac{\partial G}{\partial L} \right)_{p,T} = \left(\frac{\partial H}{\partial L} \right)_{p,T} - T \left(\frac{\partial S}{\partial L} \right)_{p,T}$$

$$f = \left(\frac{\partial H}{\partial L} \right)_{p,T} - T \left(\frac{\partial S}{\partial L} \right)_{p,T} \quad (5)$$

$$\text{ideal elastomer: } \left(\frac{\partial H}{\partial L} \right)_{p,T} = 0$$

$$f = -T \left(\frac{\partial S}{\partial L} \right)_{p,T}$$

$$\text{Helmholtz } dA = dU - T dS$$

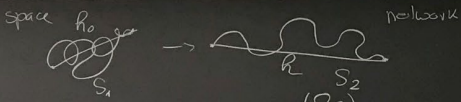
ideal case

$$f = \left(\frac{\partial A}{\partial L} \right)_{T,V} = \left(\frac{\partial U}{\partial L} \right)_{T,V} - T \left(\frac{\partial S}{\partial L} \right)_{T,V} \quad (6) \quad \left(\frac{\partial U}{\partial L} \right)_{T,V} = 0$$

from 6 $\left(\frac{\partial A}{\partial L} \right)_{T,V} = f \quad \left(\frac{\partial A}{\partial T} \right)_{L,V} = -S$

$$\frac{\partial}{\partial L} \left(\frac{\partial A}{\partial T} \right)_L = \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial L} \right)_T$$

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



$$\Delta S = S_2 - S_1 = k_B \ln \left(\frac{R_0^2}{L^2} \right)$$

$$P_i(N, R_0) = \beta^{3/2} \exp(-\pi \beta R_0^2)$$

$$\beta = \frac{3}{2\pi R_0^2} = \frac{3}{2\pi N b^2}$$

$$P_f(N, R) = \beta^{3/2} \exp(-\pi \beta R^2)$$

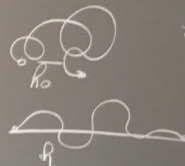
$$\Delta S_{\text{chain}} = k_B \ln A P_f - k_B \ln A P_i = k_B \ln \left(\frac{P_f}{P_i} \right)$$

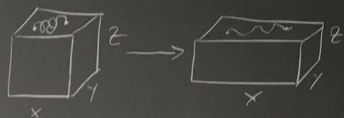
$$\Delta S_{\text{chain}} = -k_B \pi \beta (R^2 - R_0^2) \quad (7)$$

$$f = -T \left(\frac{\partial \Delta S_{\text{chain}}}{\partial R} \right) = \left(\frac{3 k_B T}{R_0^2} \right) R$$

$$\left(\frac{\partial G}{\partial L}\right)_{P,T} = f = \left(\frac{\partial H}{\partial L}\right)_{P,T} - T \left(\frac{\partial S}{\partial L}\right)_{P,T} \quad (5)$$

$$\left(\frac{\partial A}{\partial L}\right)_{V,T} = f = \left(\frac{\partial U}{\partial L}\right)_{V,T} - T \left(\frac{\partial S}{\partial L}\right)_{V,T} \quad (6)$$

$$f = \left(\frac{3kT}{2l_0}\right) \alpha$$




assumption N_x : const no volume change $\gamma = 1/2$

$$V = L_x L_y L_z = V_0 = L_0^3 \quad \alpha_x \alpha_y \alpha_z = 1$$

$$\text{extension ratio } \alpha_x = \frac{L_x}{L_0}$$

$$x_0 \rightarrow \alpha_x x_0$$

$$\Delta S_{\text{stretch}} = k \ln \left(\frac{f}{f_0} \right) = -k \ln \left(\beta (x^2 + y^2 + z^2) \right) - (-k \ln \beta (x_0^2 + y_0^2 + z_0^2))$$

$$x_0 = \frac{N_x b^2}{3} \quad \beta = \frac{3}{2 + N b^2}$$

$$\Delta S = -\frac{k}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$$

$$\Delta S = -\frac{v_e k}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (8)$$

$$\text{number of strands per unit volume } n = \frac{S N_A}{M_x}$$

$$\epsilon = \frac{l - l_0}{l_0} \quad \alpha = \frac{l}{l_0}$$

$$\alpha = 1 + \epsilon$$

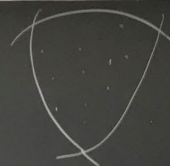
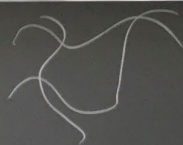
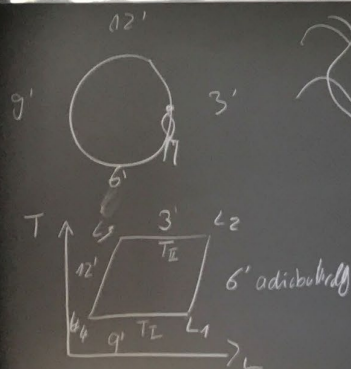
$$\alpha_x = \alpha \quad \alpha_y = \alpha_z = \frac{1}{\alpha}$$

$$\Delta S = -\frac{v_e k}{2} \left(\alpha^2 - \frac{2}{\alpha} - 3 \right)$$

$$f = -T \left(\frac{\partial S}{\partial L} \right) = \frac{v_e k T}{L_0} \left(\alpha - \frac{1}{\alpha^2} \right)$$

$$\frac{f}{L_0^2} = \sigma = k T \frac{v_e}{V} \left(\alpha - \frac{1}{\alpha^2} \right)$$

$$\frac{v_e}{V} = n \quad \sigma = n R T \left(\alpha - \frac{1}{\alpha^2} \right)$$



$$v_2 = \frac{V_0}{V}$$

x, y, z direction isotropic swelling

$$\left(\frac{V}{V_0} \right)^{1/3} = v_2^{1/3}$$

$$\Delta S = -\frac{v_e}{2} v_2^{2/3} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$$

elastic force in x-direction $\alpha_x = \alpha \quad \alpha_y = \alpha_z = \frac{1}{\alpha}$

$$f = -T \left(\frac{\partial \Delta S}{\partial L} \right) = -\frac{T}{L_0} \left(\frac{\partial \Delta S}{\partial \alpha} \right) = \frac{v_e k T}{L_0} v_2^{1/3} \left(\alpha - \frac{1}{\alpha^2} \right)$$

Swollen but unstrained network

$$G = \frac{f}{L_0^2} = k T \left(\frac{v_e}{V} \right) v_2^{1/3} \left(\alpha - \frac{1}{\alpha^2} \right) = k T \left(\frac{v_e}{V_0} \right) v_2^{-1/3} \left(\alpha - \frac{1}{\alpha^2} \right)$$

$$\text{equilibrium } \Delta G = \Delta G_m + \Delta G_{el}$$

$$RT(n_1 \ln v_1 + n_2 \ln v_2) - T \Delta S_{el}$$

$$N \rightarrow \infty$$

$$\Delta S_{el} = -\frac{k v_e}{2} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) - k \ln (\alpha_x \alpha_y \alpha_z)$$

Flory additional gain of entropy by increasing volume