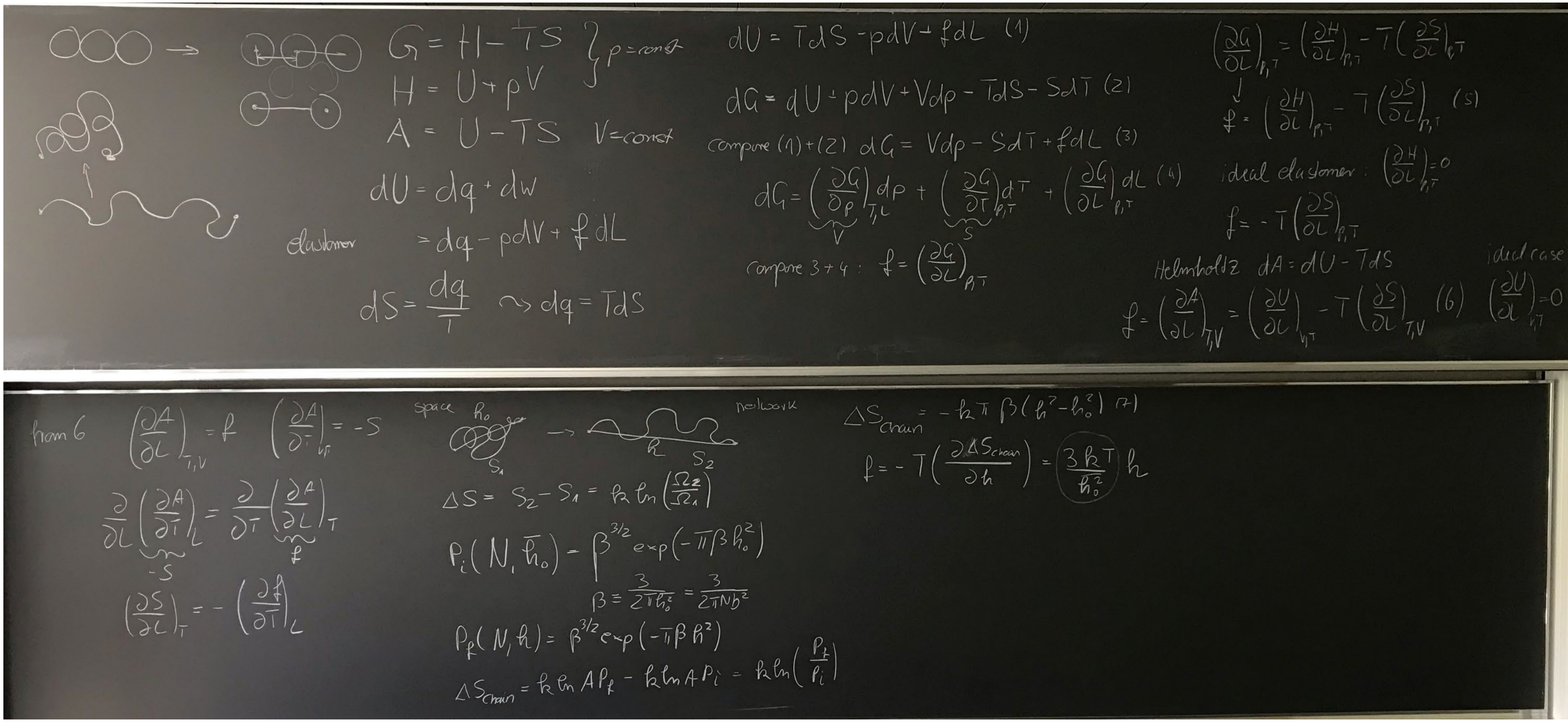
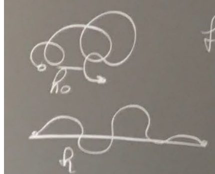
Network and Rubber Elasticity

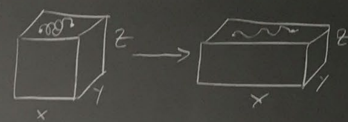


$$\left(\frac{\partial G}{\partial L}\right)_{p,T} = f = \left(\frac{\partial H}{\partial L}\right)_{p,T} - T\left(\frac{\partial S}{\partial L}\right)_{p,T} \quad (5)$$

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



$$f = \left(\frac{3kT}{h_0^2}\right) h$$



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

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

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

$$x_0 \rightarrow \alpha_x x_0$$

$$\Delta S_{strands} = k \ln\left(\frac{P_f}{P_i}\right) = -kT\beta(x^2+y^2+z^2) - (-kT\beta(x_0^2+y_0^2+z_0^2))$$

$$x_0 = \frac{N_x b^2}{3} \qquad \beta = \frac{3}{2 \pi N b^2}$$

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

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

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

$$\varepsilon = \frac{l - l_0}{l_0} \qquad \alpha = \frac{l}{l_0}$$

$$\alpha = 1 - \varepsilon$$

$$\alpha_x = \alpha \qquad \alpha_y = \alpha_z = \frac{1}{\sqrt{\alpha}}$$

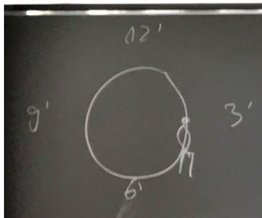
$$\Rightarrow \Delta S = -\frac{\nu_e k}{2}\left(\alpha^2 - \frac{2}{\alpha} - 3\right)$$

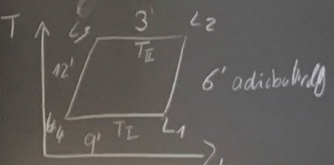
$$f = -T\left(\frac{\partial S}{\partial L}\right) = \frac{\nu_e k T}{L_0}\left(\alpha - \frac{1}{\alpha^2}\right)$$

$$\frac{f}{\underset{= L_0^2}{\text{surface }\Delta}} = \sigma = kT\frac{\nu_e}{V}\left(\alpha - \frac{1}{\alpha^2}\right)$$

$$\frac{\nu_e}{V} = n$$

$$\boxed{\sigma = nRT\left(\alpha - \frac{1}{\alpha^2}\right)}$$





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

x, y, z direction isotropic swelling

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

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

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

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

L_s: swollen but unstrained network

$$\sigma = \frac{f}{L_s^2} = kT\frac{\nu_e}{V} v_2^{-2/3}\left(\alpha - \frac{1}{\alpha^2}\right) = kT\frac{\nu_e}{V_0} v_2^{-2/3}\left(\alpha - \frac{1}{\alpha^2}\right)$$

equilibrium $\Delta G = \underset{RT(n_1 \ln v_1 + \chi n_1 v_2)}{\Delta G_m} + \underset{-T\Delta S_{el}}{\Delta G_{el}}$

$N \rightarrow \infty$

$$\Delta S_{el} = -\frac{k\nu_e}{2}\left(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \underbrace{\ln(\alpha_x\alpha_y\alpha_z)}_{\text{Flory}}\right)$$

Flory: additional gain of entropy by increasing volume