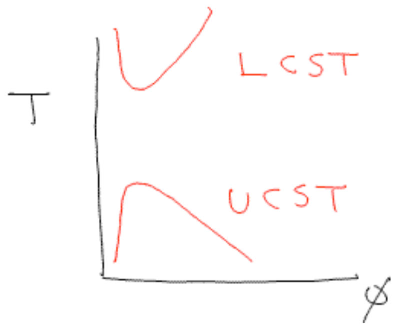
2.4. Additional remarks:

In general, chi parameter is experimentally found to be $\chi = \frac{a}{T} + b(T)$

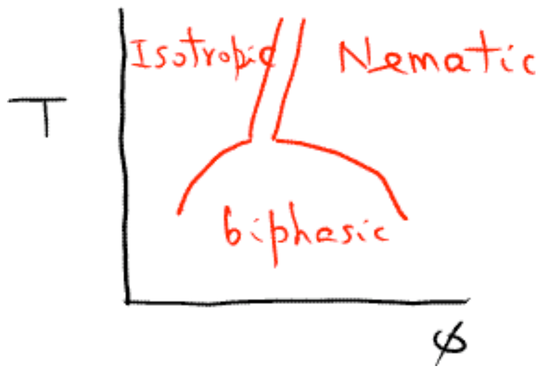
(a) Phase separation at higher temperatures:



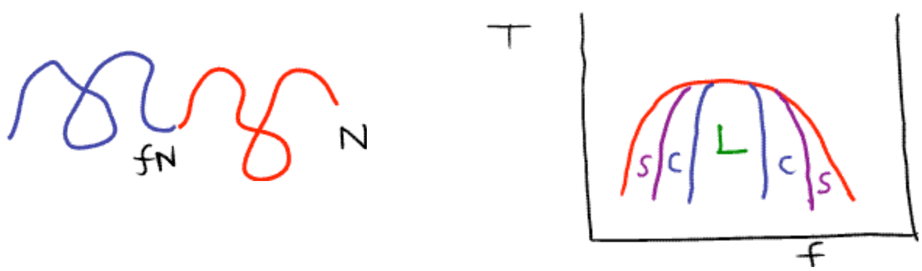
Lower Critical Solution Temperature

Upper Critical Solution Temperature

(b) Lyotropic liquid crystals:



(c) Diblock copolymers (microphase separation):

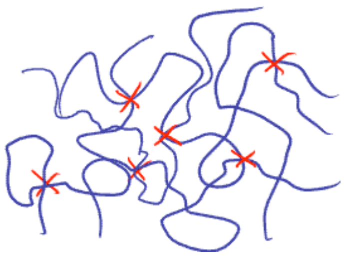


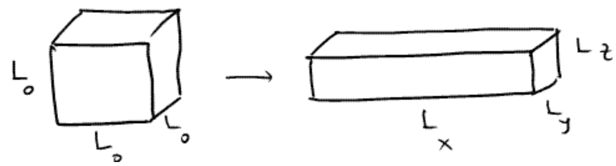
(L = lamellar, C = cylinder, and S = sphere morphologies)

3. RUBBER ELASTICITY

3.1. Stretching of an ideal network:

Consider a stretching of a crosslinked polymer network:





$$\lambda_x = \frac{L_x}{L_0}, \quad \lambda_y = \frac{L_y}{L_0}, \quad \lambda_z = \frac{L_z}{L_0}$$

If incompressible,

$$\lambda_x \lambda_y \lambda_z = 1$$

Recall, for a single Gaussian chain:

$$\Delta S = -\frac{3k_B}{2N\ell^2}\left(R^2 - R_0^2\right)$$

Therefore, the tensile force for stretching is:

$$f = -T\left(\frac{\partial \Delta S}{\partial R}\right) = \frac{3k_BT}{N\ell^2} R$$

For a network of Gaussian strands, per each strand,

$$\Delta S = -\frac{3k_B}{2N\ell^2}\left[\left(x_0^2\lambda_x^2 + y_0^2\lambda_y^2 + z_0^2\lambda_z^2\right) - \left(x_0^2 + y_0^2 + z_0^2\right)\right]$$

$$= -\frac{k_B}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

For ν_e elastically effective strands,

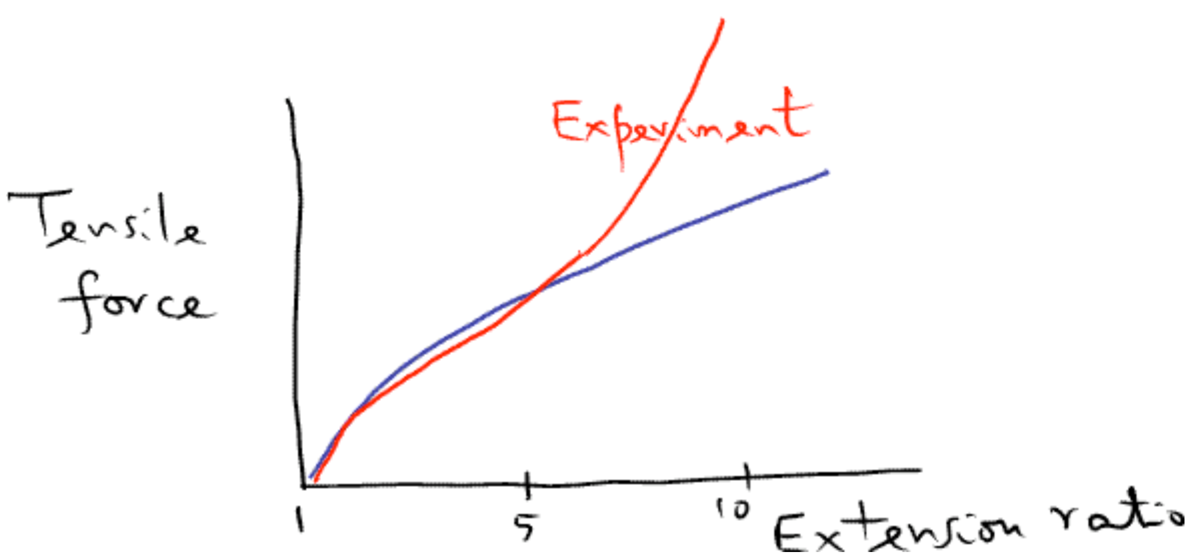
$$\Delta S = -\frac{\nu_e k_B}{2}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

For a uniaxial extension along x, $\lambda_x = \lambda\,,\quad \lambda_y = \frac{1}{\sqrt{\lambda}} = \lambda_z$

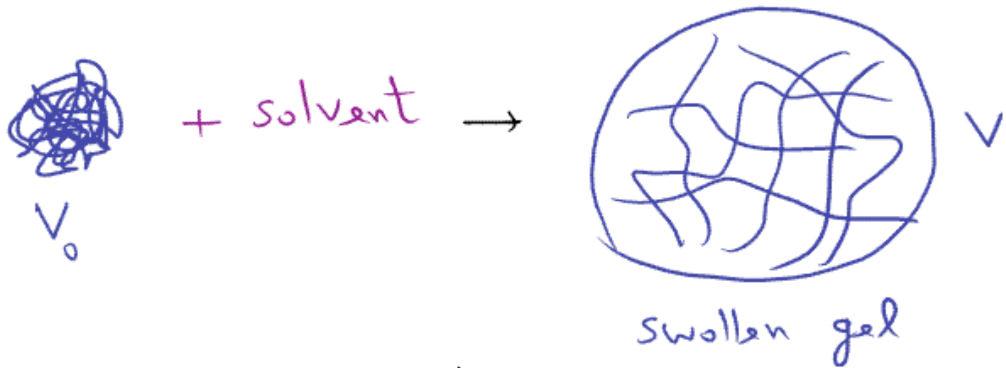
$$\Delta S = -\frac{\nu_e k_B}{2}\left(\lambda^2 + \frac{2}{\lambda} - 3\right)$$

Tensile force for stretching the rubber is:

$$f = -T\,\frac{\partial \Delta S}{\partial L} = -\frac{T}{L_0}\,\frac{\partial \Delta S}{\partial \lambda} = \frac{\nu_e k_B T}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$



3.2. Swelling of polymer gels:



Volume fraction of polymer: $\phi = \dfrac{V_0}{V}$

Free energy of the gel:

$$\frac{\Delta F}{k_B T} = \frac{\nu_e}{2}\left[\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln(\lambda_x \lambda_y \lambda_z)\right] + \frac{\Delta F_m[\phi, \chi]}{k_B T}$$

rubber elasticity   Flory-Huggins theory

For uniform swelling,

$$\lambda_x = \lambda_y = \lambda_z = \lambda = \phi^{-1/3}$$

osmotic pressure is:

$$\frac{\Pi}{k_B T} = (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) + \frac{3\phi}{N}\left(\phi^{-2/3} - 1\right) + \frac{\phi}{2N}\ln\phi$$

At equilibrium,

$$\Pi = 0 \Rightarrow \boxed{\phi^{-5/3} = N\left(\tfrac{1}{2} - \chi\right)}$$