

[pex13] Swelling equilibrium of polymer gel I

The swelling equilibrium of a polymer gel is a combination of thermal, chemical, and mechanical equilibrium. We take the expression for the free-energy density,

$$f_{\text{gel}}(\phi) = \frac{3}{2}G_0 \left[\left(\frac{\phi_0}{\phi} \right)^{2/3} - 1 \right] + \frac{\phi_0}{\phi} f_{\text{sol}}(\phi), \quad f_{\text{sol}}(\phi) = \frac{k_B T}{v_c} [(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)],$$

from [pln65] and implement the equilibrium condition at constant temperature, $\partial f_{\text{gel}}/\partial \phi = 0$. Show that the result becomes

$$G_0 \left(\frac{\phi}{\phi_0} \right)^{1/3} = \pi_{\text{sol}}(\phi), \quad \pi_{\text{sol}}(\phi) = \frac{k_B T}{v_c} [-\ln(1 - \phi) - \phi - \chi \phi^2],$$

where we use the expression for osmotic pressure derived in [pln28] in the slightly adapted rendition,

$$\pi_{\text{sol}}(\phi) \doteq \phi f'_{\text{sol}}(\phi) - f_{\text{sol}}(\phi).$$

[adapted from Doi 2013]

Solution: