Polymer Gel [pln65]

Mixture of polymer network and solvent. Swelling or shrinking of gel described quantitatively via deformation free-energy density.

Deformation free energy

Volume increase: $V_\mathrm{g} \;\to\; V_\mathrm{g}\lambda_1\lambda_2\lambda_3, \quad \lambda_i > 1.$

Free-energy density:

$$f_\mathrm{gel}(\lambda_1,\lambda_2,\lambda_3) = f_\mathrm{ela}(\lambda_1,\lambda_2,\lambda_3) + f_\mathrm{mix}(\lambda_1,\lambda_2,\lambda_3). \tag{1}$$

- Elastic part is an application of [pln63] [pln64].

$$f_\mathrm{ela}(\lambda_1,\lambda_2,\lambda_3) = \frac{1}{2}G_0\big(\lambda_1^2+\lambda_2^2+\lambda_3^2-3\big). \tag{2}$$

- Mixing part is worked out in [pex14].

$$f_\mathrm{mix}(\lambda_1,\lambda_2,\lambda_3) = \frac{\phi_0}{\phi}f_\mathrm{sol}(\phi), \tag{3}$$

$$f_\mathrm{sol}(\phi) = \frac{k_\mathrm{B}T}{v_\mathrm{c}}\big[(1-\phi)\ln(1-\phi)+\chi\phi(1-\phi)\big], \quad \frac{\phi_0}{\phi} = \lambda_1\lambda_2\lambda_3,$$

  - v_c: is the volume of solvent molecules,
  - $\chi > 0$: interaction constant controlling phase separation [pln32].

Swelling equilibrium

Application to isotropically swelling gel: $\lambda_1 = \lambda_2 = \lambda_3 \doteq \lambda = (\phi_0/\phi)^{1/3}$.

$$f_\mathrm{gel}(\phi) = \frac{3}{2}G_0\left[\left(\frac{\phi_0}{\phi}\right)^{2/3} - 1\right] + \frac{\phi_0}{\phi}f_\mathrm{sol}(\phi). \tag{4}$$

Equilibrium condition, $\partial f_\mathrm{gel}/\partial\phi = 0$, is worked out in [pex13]:[1]

$$G_0\left(\frac{\phi}{\phi_0}\right)^{1/3} = \pi_\mathrm{sol}(\phi), \quad \pi_\mathrm{sol}(\phi) = \frac{k_\mathrm{B}T}{v_\mathrm{c}}\big[-\ln(1-\phi)-\phi-\chi\phi^2\big]. \tag{5}$$

Balance of forces:

- osmotic pressure (right) represents expanding force,
- gel elasticity (left) represents restoring force.

[1] Note that swelling is associated with a decrease in polymer volume fraction ϕ.