## [pex51] Phase separation in polymer solution

Consider a monodisperse polymer composed of $N$ monomers in solution. Under the assumption that the volume of monomers and solvent particles are of very similar size we can adapt the mean-field lattice model used in [pex47] to this case. The free-energy density then reads

$$f(T,\phi,N) = \frac{k_BT}{v_c}\left[\frac{1}{N}\phi\ln\phi + (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi)\right], \quad \chi = -\frac{z\Delta\epsilon}{2k_BT} > 0,$$

where $\phi$ is the volume fraction of the polymer, $v_c$ is the specific volume of monomer and solvent particles, $z$ is the coordination number, and $\Delta\epsilon$ is a measure of the (attractive) interaction between solute particles and between solvent particles.

(a) Plot the function $f(T,\phi,N)$ vs $\phi$ across the range $0 \leq \phi \leq 1$ for $N = 100$ with appropriately scaled curves for $\chi = 0.5, 0.75, 1.0, 1.25$. Describe the physical meaning of the main features identified in these curves.

(b) Use the general expression for the osmotic pressure derived in part (a) of [pex48] to produce a specific expression $\pi(T,\phi,N)$ for the case of a polymer solution. Then plot this result for $N = 100$ as a function of $\phi$ using vertical and horizontal scales that highlight the features of interest. Describe those features.

(c) Identify the critical point by determining its coordinates $\phi_c(N)$ and $\chi_c(N)$ in the phase diagram. Show that your result is consistent with the result obtained in [pex47] for $N = 1$.

(d) Show that the spinodal line in the phase diagram, the locations of inflection points in the free-energy-density, has the following dependence on $\phi$ for any given $N$:

$$\chi_{sp}(\phi,N) = \frac{1}{2}\left[\frac{1}{1-\phi} + \frac{1}{N\phi}\right].$$

Verify that this result is consistent with the result for $N = 1$ derived in [pex47]. Plot $\chi_{sp}(\phi,100)$ with the vertial scale ranging from 0.5 to 1.0 and the horizontal scale ranging from zero to 0.5.

(e) Identify the coexistence line from the following construction. For a given value of $\chi > \chi_c$ the curve of $f(T,\phi,N)$ touches a tangent at two point with volume fractions $\phi_a < \phi_b$. These values are the solutions of the two equations $f'(\phi_a) = f'(\phi_b)$, $f(\phi_a) + f'(\phi_a)[\phi_b - \phi_a] = f(\phi_b)$. Produce some data for the coexistence line and include them into the phase diagram of part (d).

**Solution:**