[pex48] Osmotic pressure in two-component fluid system

Consider a two-component fluid system with Helmholtz free energy,

$$F = Vf(T, \phi) + (V_{tot} - V)f(T, 0),$$

where $V = N_p v_p + N_s v_s$ is the volume of the solution on one side of a semi-permeable membrane and $V_{tot} - V$ the volume of the pure solvent on the other side. The numbers of solute and solvent particles in the solution are N_p and N_s, respectively. Their specific volumes are v_p and v_s, respectively. The free-energy density $f(T, \phi)$ is an unspecified function of temperature T and volume fraction $\phi = N_p v_p / V$ of solute particles.

(a) Derive, via the standard thermodynamic relation $\pi = -(\partial F/\partial V)_T$, the following general expression of the osmotic pressure in a two-component fluid:

$$\pi(T, \phi) = -f(T, \phi) + \phi f'(T, \phi) + f(T, 0), \qquad f' \doteq \partial f/\partial\phi.$$

(b) Apply this expression to the explicit free-energy density $f(T, \phi)$ used in [pex47] for a two-component fluid in a single compartment (no membrane). Plot $\pi(T, \phi)$ thus obtained in explicit form versus ϕ for three parameter values $\chi > \chi_c$, $\chi = \chi_c$, and $\chi > \chi_c$. Identify the number of coexisting phases and their volume fractions ϕ in each case. Expand the expression to second order in powers of ϕ and interpret the physical significance of the first two terms.

Solution: