

[pex46] Chemical potential in two-component system

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

$$G = V[p + f(T, \phi)],$$

where $V = N_p v_p + N_s v_s$ is the volume and p the pressure. The numbers of solute and solvent particles 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 standard thermodynamic relations $\mu_p = (\partial G / \partial N_p)_{T, p, N_s}$ and $\mu_s = (\partial G / \partial N_s)_{T, p, N_p}$, the following general expressions for the chemical potentials of the solute and solvent particles:

$$\mu_p(T, p, \phi) = v_p[p + f(T, \phi) + (1 - \phi)f'(T, \phi)], \quad \mu_s(T, p, \phi) = v_s[p + f(T, \phi) - \phi f'(T, \phi)],$$

where we use the convention $f' \doteq \partial f / \partial \phi$.

(b) If the profile of $f(T, \phi)$ permits the coexistence of two phases with volume fractions $\phi_a < \phi_b$ then the common-tangent conditions must be satisfied: $f'(T, \phi_a) = f'(T, \phi_b)$ and $f(T, \phi_a) + f'(T, \phi_a)[\phi_b - \phi_a] = f(T, \phi_b)$. Show that it follows that the chemical potentials must be the same in both phases: $\mu_p(T, \phi_a) = \mu_p(T, \phi_b)$ for the solute and $\mu_s(T, \phi_a) = \mu_s(T, \phi_b)$ for the solvent.

Solution: