Homogeneous State vs Phase-Separated State [pln27]

When we mix solutions of the same solute and solvent materials in different amounts and concentrations the system equilibrates either in a *homogeneous* state or in a *phase-separated* state.

Initial state: (V_1, ϕ_1), (V_2, ϕ_2) with $\phi_1 < \phi_2$.

Amounts expressed by $x \doteq \dfrac{V_1}{V_1 + V_2}, \quad 1 - x = \dfrac{V_2}{V_1 + V_2}$.

Concentrations expressed by volume fractions of solute: ϕ_1, ϕ_2.

Homogeneous state: (V, ϕ) with $V = V_1 + V_2$ and $\phi = x\phi_1 + (1-x)\phi_2$.

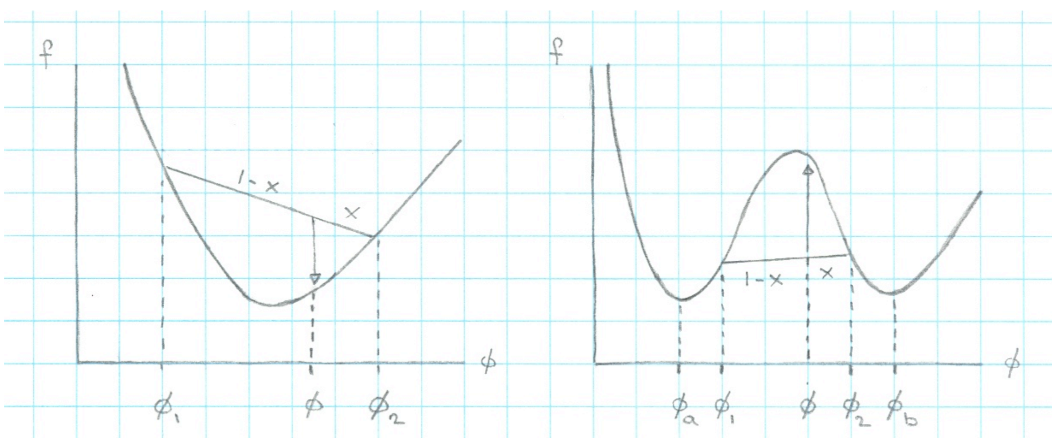
Stability criterion for homogeneous state:

$$(V_1 + V_2) f(T, \phi) < V_1 f(T, \phi_1) + V_2 f(T, \phi_2)$$

$$\Rightarrow \; f\big(T, x\phi_1 + (1-x)\phi_2\big) < x f(T, \phi_1) + (1-x) f(T, \phi_2)$$

$$\Rightarrow \; \frac{\partial^2 f}{\partial \phi^2} > 0, \quad \phi_1 < \phi < \phi_2.$$

Free energy minimized at $F = V f(T, \phi)$.



Phase-separated state: (V_a, ϕ_a), (V_b, ϕ_b) with $V = V_a + V_b$ and $\phi_a < \phi_b$.

$$\phi(V_a + V_b) = \phi_a V_a + \phi_b V_b \quad \Rightarrow \; V_a = V \frac{\phi_b - \phi}{\phi_b - \phi_a}, \quad V_b = V \frac{\phi - \phi_a}{\phi_b - \phi_a}.$$

Free energy minimized at $F = V_a f(T, \phi_a) + V_b f(T, \phi_b)$.