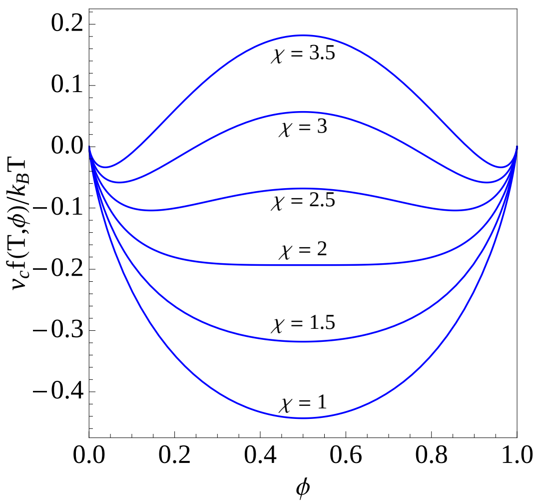
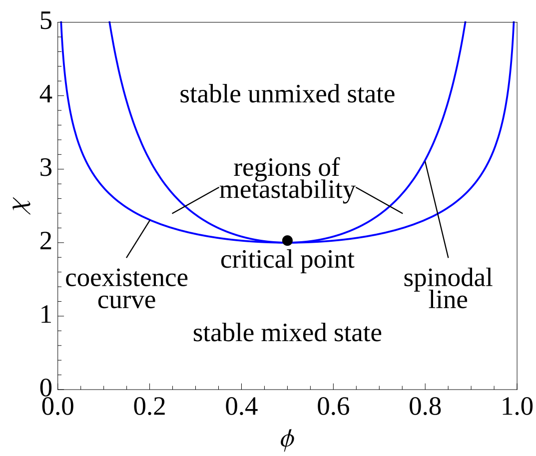
Mixing-Unmixing Transition [psl4]

Helmholtz free energy density (scaled) versus volume fraction ϕ for selected values of interaction parameter χ:



- $\chi \leq 2$: convex function with zero slope at $\phi = \frac{1}{2}$,
- $\chi = 2$: zero curvature at $\phi = \frac{1}{2}$ in addition to zero slope,
- $\chi > 2$: concave portion centered at $\phi = \frac{1}{2}$ gradually grows.

Phase diagram in the (ϕ, χ)-plane:



Critical point: Lowest value of χ for which phase separation exists.

▷ Criterion: $f'(\phi) = f''(\phi) = 0$.

▷ Solution: $\phi_c = \frac{1}{2}$, $\chi_c = 2$.

Spinodal line: Boundary of region of stable phase-separated states.

- ▷ Criterion: $f''(\phi) = 0$ at $\phi \neq \frac{1}{2}$ (inflection points).
- ▷ Solution: $\chi_{\mathrm{sp}} = \dfrac{1}{2\phi(1-\phi)}$ [pex47].

Coexistence line: Boundary of region of stable mixed states.

- ▷ Criterion: $f'(\phi) = 0$ at $\phi \neq \frac{1}{2}$ (local minima).
- ▷ Solution: $\chi_{\mathrm{co}} = \dfrac{1}{1-2\phi} \ln \dfrac{1-\phi}{\phi}$ [pex47].

Osmotic pressure:

General expression from [pln28]:

$$\pi(T,\phi) = -f(T,\phi) + \phi f'(T,\phi) + f(T,0).$$

Prediction of mean-field model [pex48]:

$$\pi(T,\phi) = \frac{k_{\mathrm{B}}T}{v_{\mathrm{c}}}\big[-\ln(1-\phi) - \chi\phi^2\big] \overset{\phi\ll 1}{\leadsto} \frac{k_{\mathrm{B}}T}{v_{\mathrm{c}}}\left[\phi + \left(\tfrac{1}{2}-\chi\right)\phi^2\right].$$

Interpretation of last expression:

- ▷ First term represents van't Hoff osmotic pressure,
- ▷ Second term with 2nd virial coefficient $A_2 = \frac{1}{2} - \chi$ represents correction with opposite trends due to hardcore repulsion ($\frac{1}{2}$) and nearest-neighbor coupling (χ).

Stability criterion for osmotic pressure: $\pi'(T,\phi) > 0$.

- ▷ $\chi < \chi_{\mathrm{c}}$: π is stable for exactly one value of ϕ,
- ▷ $\chi > \chi_{\mathrm{c}}$: π is stable for two distinct values of ϕ.

[extracted in part from Doi 2013]