Polymer Blends [pln48]

Both solute and solvent are polymers.

Adaptation of lattice model for two-component fluid from [pln32] assumes that both kinds of polymers are monodisperse.

Degrees of polymerization:

- solute: $N_{\rm A}$ (with volume fraction ϕ),
- solvent: $N_{\rm B}$ (with volume fraction 1ϕ).

Modified expression for free-energy density:

$$f(T,\phi,N_{\rm A},N_{\rm B}) = \frac{k_B T}{v_c} \Big[\frac{1}{N_{\rm A}} \phi \ln \phi + \frac{1}{N_{\rm B}} (1-\phi) \ln(1-\phi) + \chi \phi (1-\phi) \Big],$$

where $\chi = -z\Delta\epsilon/2k_BT$. For specificity we assume $N_{\rm A} \ge N_{\rm B}$.

The coordinates in the phase diagram of the critical point are [pex52]

$$\phi_{\rm c}(N) = \frac{1}{\sqrt{N_{\rm A}/N_{\rm B}} + 1}, \quad \chi_{\rm c}(N) = \frac{\left(\sqrt{N_{\rm A}} + \sqrt{N_{\rm B}}\right)^2}{2N_{\rm A}N_{\rm B}}.$$

Spinodal line [pex52]:

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

Special case: $N_{\rm A} = N_{\rm B} \doteq N$ [pex52]:

• critical point: $\phi_{\rm c} = \frac{1}{2}, \quad \chi_{\rm c} = 2/N,$

• spinodal line:
$$\chi_{sp}(\phi, N, N) = \frac{1}{2N} \frac{1}{\phi(1-\phi)},$$

• coexistence line: $\chi_{co}(\phi, N, N) = \frac{1}{2N} \frac{\operatorname{Artanh}(1-2\phi)}{1-2\phi}$

For large $N_{\rm A}$, $N_{\rm B}$ the spinodal line touches down to a value close to zero, implying that polymer blends have a strong tendency to phase separate. Interfaces tend to be weak, which makes plastic recycling problematic. The entropy of mixing is small compared to that of small molecules. Polymer blends that mix experience a strong mutual attraction.

[extracted from Doi 2013]