Dilute Solutions [pln30]

Criterion: $\phi \ll 1$.

Expansion of osmotic pressure in powers of volume fraction:

$$\pi(T,\phi) = \frac{k_\mathrm{B}T}{v_\mathrm{p}}\phi \;+\; A_2\phi^2 \;+\; A_3\phi^3 \;+\; \cdots \tag{1}$$

▷ A_2, A_3: virial coefficients.

▷ Leading *van't Hoff* term, $nk_\mathrm{B}T$, with number density, $n \doteq N_\mathrm{p}/V = \phi/v_\mathrm{p}$, is independent of molecular interactions.

▷ $A_2 > 0$ is realized for repulsive solute interaction; $A_2 < 0$ is possible if solute interaction is attractive.

Consistent expansion of free energy function $f(T,\phi)$ (from [pln26]):

$$f(T,\phi) = f(T,0) + k_0\phi + \frac{k_\mathrm{B}T}{v_\mathrm{p}}\phi\ln\phi + A_2\phi^2 + \frac{1}{2}A_3\phi^3 + \cdots \tag{2}$$

with T-dependent k_0, A_2, A_3.

To prove consistency use $\pi(\phi) = f(0) + \phi f'(\phi) - f(\phi)$ from [pln28] and convert the rhs into $f(0) + \phi^2[f(\phi)/\phi]'$.

Chemical potentials inferred from (2):

- solvent

$$\mu_\mathrm{s}(T,\phi) = \mu_\mathrm{s}^{(0)}(T) + v_\mathrm{s}p - \frac{v_\mathrm{s}}{v_\mathrm{p}}k_\mathrm{B}T\phi - v_\mathrm{s}\big[A_2\phi^2 + A_3\phi^3 + \cdots\big],$$

- solute

$$\mu_\mathrm{p}(T,\phi) = \mu_\mathrm{p}^{(0)}(T) + v_\mathrm{p}p + k_\mathrm{B}T\ln\phi + v_\mathrm{p}\left[\left(2A_2 - \frac{k_\mathrm{B}T}{v_\mathrm{p}}\right)\phi + \left(\frac{3}{2}A_3 - A_2\right)\phi^2 + \cdots\right].$$

[extracted from Doi 2013]