Free Energy of Solutions [pln26]

Two-component incompressible fluid system: solute (p) and solvent (s).

Terms of specification:

- $N_\mathrm{p}, N_\mathrm{s}$; $m_\mathrm{p}, m_\mathrm{s}$: numbers and masses of molecules,
- $v_\mathrm{p}, v_\mathrm{s}$; $\rho_\mathrm{p} \doteq m_\mathrm{p}/v_\mathrm{p}, \rho_\mathrm{s} \doteq m_\mathrm{s}/v_\mathrm{s}$: specific volumes[1] and mass densities,
- $V = N_\mathrm{p}v_\mathrm{p} + N_\mathrm{s}v_\mathrm{s}$: volume,
- $c \doteq \dfrac{N_\mathrm{p}m_\mathrm{p}}{V}$: weight concentration of solute,
- $x_m \doteq \dfrac{N_\mathrm{p}}{N_\mathrm{p}+N_\mathrm{s}}$: molar fraction of solute,
- $\phi_m \doteq \dfrac{N_\mathrm{p}m_\mathrm{p}}{N_\mathrm{p}m_\mathrm{p}+N_\mathrm{s}m_\mathrm{s}}$: mass fraction of solute,
- $\phi \doteq \dfrac{N_\mathrm{p}v_\mathrm{p}}{N_\mathrm{p}v_\mathrm{p}+N_\mathrm{s}v_\mathrm{s}} = \dfrac{N_\mathrm{p}v_\mathrm{p}}{V}$: volume fraction of solute.

Relation : $c = \rho_\mathrm{p}\phi$.

Helmholtz free energy: $F(T, N_\mathrm{p}, N_\mathrm{s}) = U - TS$,

▷ internal energy U to be constructed from interactions,
▷ entropy S to be derived from combinatorics,
▷ volume V via $N_\mathrm{p}, N_\mathrm{s}$ (see above).

Extensivity: $F(T, \alpha N_\mathrm{p}, \alpha N_\mathrm{s}) = \alpha F(T, N_\mathrm{p}, N_\mathrm{s})$.

Set $\alpha = v_\mathrm{p}/V \quad \Rightarrow \; F\left(T, \dfrac{N_\mathrm{p}v_\mathrm{p}}{V}, \dfrac{N_\mathrm{s}v_\mathrm{p}}{V}\right) = \dfrac{v_\mathrm{p}}{V}F(T, N_\mathrm{p}, N_\mathrm{s})$.

$$\Rightarrow \; F(T, N_\mathrm{p}, N_\mathrm{s}) = \frac{V}{v_\mathrm{p}}F\left(T, \phi, \frac{v_\mathrm{p}}{v_\mathrm{s}}(1-\phi)\right) \doteq V f(T, \phi).$$

Gibbs free energy: $G(T, p, N_\mathrm{p}, N_\mathrm{s}) = F + pV = V\big[p + f(T, \phi)\big]$.

The function $f(T, \phi)$ has yet to be determined from molecular interactions and the combinatorics of molecular configurations.

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[1] In the fluids considered here all volume is taken up by either solute or solvent particles. In gases the specific volume, V/N, is unrelated to the size of the particles.