# Chemical Potential [pln29]

Gibbs free energy (from [pln26]): $G(T,p,N_\mathrm{p},N_\mathrm{s}) = V\big[p + f(T,\phi)\big]$.

Thermodynamic functions from first derivatives:

- entropy and volume: $S \doteq -\left(\dfrac{\partial G}{\partial T}\right)_{p,N_\mathrm{p},N_\mathrm{s}}, \quad V \doteq \left(\dfrac{\partial G}{\partial p}\right)_{T,N_\mathrm{p},N_\mathrm{s}},$
- chemical potentials: $\underbrace{\mu_\mathrm{p} \doteq \left(\dfrac{\partial G}{\partial N_\mathrm{p}}\right)_{T,p,N_\mathrm{s}}}_{\text{solute}}, \quad \underbrace{\mu_\mathrm{s} \doteq \left(\dfrac{\partial G}{\partial N_\mathrm{s}}\right)_{T,p,N_\mathrm{p}}}_{\text{solvent}}$

▷ Heat tends to flow, diffuse, or radiate from regions of high $T$ to regions of low $T$.

▷ Fluid tends to flow from regions of high $p$ to regions of low $p$.

▷ Solute (solvent) tends to migrate from regions of high $\mu_\mathrm{p}$ ($\mu_\mathrm{s}$) to regions of low $\mu_\mathrm{p}$ ($\mu_\mathrm{s}$).

Expressions for the chemical potentials from part (a) of [pex46].

- solute: $\mu_\mathrm{p}(T,p,\phi) = v_\mathrm{p}\big[p + f(T,\phi) + (1-\phi)f'(T,\phi)\big]$,
- solvent: $\mu_\mathrm{s}(T,p,\phi) = v_\mathrm{s}\big[p + f(T,\phi) - \phi f'(T,\phi)\big]$,

where $\phi = N_\mathrm{p}v_\mathrm{p}/V$, $V = N_\mathrm{p}v_\mathrm{p} + N_\mathrm{s}v_\mathrm{s}$.

Chemical potential of solvent depends on osmotic pressure (from [pln28]):

$$\mu_\mathrm{s}(T,p,\phi) = \mu_\mathrm{s}^{(0)}(T) + v_\mathrm{s}\big[p - \pi(T,\phi)\big], \quad \mu_\mathrm{s}^{(0)}(T) \doteq v_\mathrm{s} f(T,0).$$

Dependence of chemical potentials on volume fraction of solute:

$$\frac{\partial \mu_\mathrm{p}}{\partial \phi} = v_\mathrm{p}(1-\phi)f''(T,\phi), \quad \frac{\partial \mu_\mathrm{s}}{\partial \phi} = -v_\mathrm{s}\phi f''(T,\phi).$$

▷ $f''(T,\phi) > 0 \quad \Rightarrow \dfrac{\partial \mu_\mathrm{p}}{\partial \phi} > 0, \quad \dfrac{\partial \mu_\mathrm{s}}{\partial \phi} < 0,$
$\Rightarrow$ solute migrates from high to low $\phi$ and solvent from low to high $\phi$,
$\Rightarrow$ homogeneous state favored.

▷ $f''(T,\phi) < 0 \quad \Rightarrow \dfrac{\partial \mu_\mathrm{p}}{\partial \phi} < 0, \quad \dfrac{\partial \mu_\mathrm{s}}{\partial \phi} > 0,$
$\Rightarrow$ solute migrates from low to high $\phi$ and solvent from high to low $\phi$,
$\Rightarrow$ phase-separated state favored.