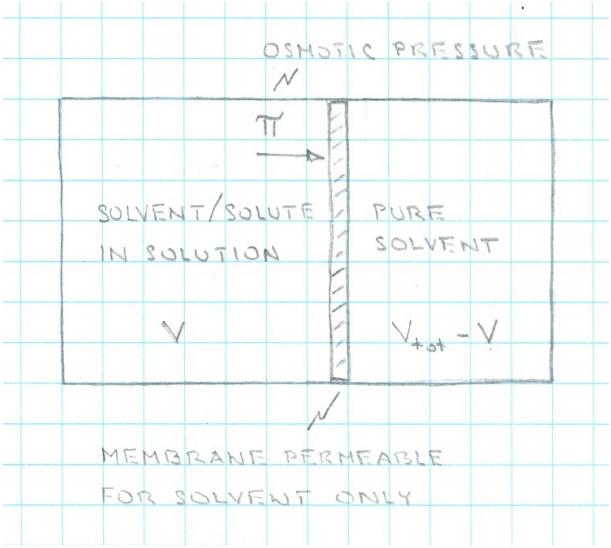
Osmotic Pressure [pln28]

Mixing solute and solvent raises the entropy S. If molecular interactions make the internal energy U either increase by an amount smaller than TS or decrease then the free energy $F = U - TS$ decreases.

Mixing is thermodynamically favorable in these conditions. This tendency can be converted into a thermodynamic force that acts, for example, on a semi-permeable wall.



Helmholtz free energy: $F_{\rm tot} = V f(T,\phi) + (V_{\rm tot} - V) f(T,0)$,

Definition of osmotic pressure: $\pi \doteq -\left(\dfrac{\partial F_{\rm tot}}{\partial V}\right)_T$.

Use $\phi = \dfrac{N_{\rm p} v_{\rm p}}{V}$ from [pln26] and infer $\dfrac{\partial \phi}{\partial V} = -\dfrac{\phi}{V}$.

General expression for osmotic pressure:

$$\pi(T,\phi) = -f(T,\phi) + \phi f'(T,\phi) + f(T,0), \quad f' \doteq \frac{\partial f}{\partial \phi}.$$