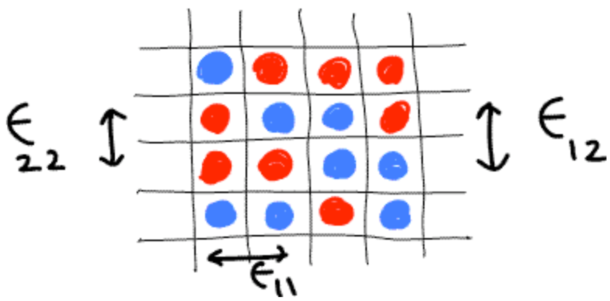
2. PHASE EQUILIBRIA

2.1. Lattice theory of small molecules:

Assume random mixing:



$$n_1 + n_2 = n_0$$

$$\phi_1 = \frac{n_1}{n_0}$$

$$\phi_2 = \frac{n_2}{n_0} = 1 - \phi_1$$

The free energy of mixing, ΔF_m:

$$\frac{\Delta F_m}{k_B T} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_0 \phi_1 \phi_2$$

entropy of mixing   enthalpy of mixing

where the chemical mismatch parameter, "chi parameter" is

$$\chi = \frac{z}{k_B T}\left[\epsilon_{12} - \frac{1}{2}\left(\epsilon_{11} + \epsilon_{22}\right)\right]$$

(z = effective coordination number)

Now, the Bragg-Williams theory for binary alloys:

$$\left.\frac{\Delta F_m}{k_B T}\right|_{\text{molecule}} = \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \chi \phi_1 \phi_2$$

2.2. Lattice theory of polymer solutions and blends:

$$\begin{pmatrix} n_1 \text{ molecules} \\ \text{with } N_1 \text{ segments} \end{pmatrix} + \begin{pmatrix} n_2 \text{ molecules} \\ \text{with } N_2 \text{ segments} \end{pmatrix}$$

$$\downarrow$$

BLEND

Volume fraction of component1 is:

$$\phi_1 = \frac{n_1 N_1}{(n_1 N_1 + n_2 N_2)}$$

Assuming random mixing, FLORY-HUGGINS THEORY:

$$\frac{\Delta F_m}{k_B T} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + \chi n_0 \phi_1 \phi_2$$

$$\left.\frac{\Delta F_m}{k_B T}\right|_{site} = \frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \chi \phi_1 \phi_2$$

For a symmetric blend, $N_1 = N = N_2$,

$$\left.\frac{\Delta F_m}{k_B T}\right|_{molecule} = \phi_1 \ln \phi_1 + \phi_2 \ln \phi_2 + \chi N \phi_1 \phi_2$$

"Higher molecular weight is equivalent to lower temperature"

Chemical potentials:

$$\frac{\mu_1(\phi_2) - \mu_1(0)}{k_B T} = \left.\frac{\partial \left(\Delta F_m / k_B T\right)}{\partial n_1}\right|_{n_2, T}$$

$$= -\frac{\Pi v_1}{k_B T}$$

Π is osmotic pressure and v_1 is molecular volume of solvent.

For polymer solutions:

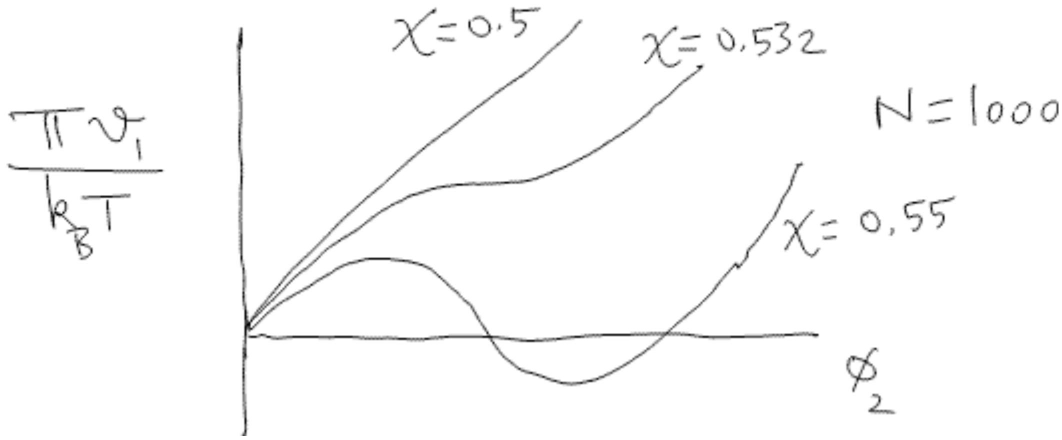
For $N_1 = 1, \quad N_2 = N$

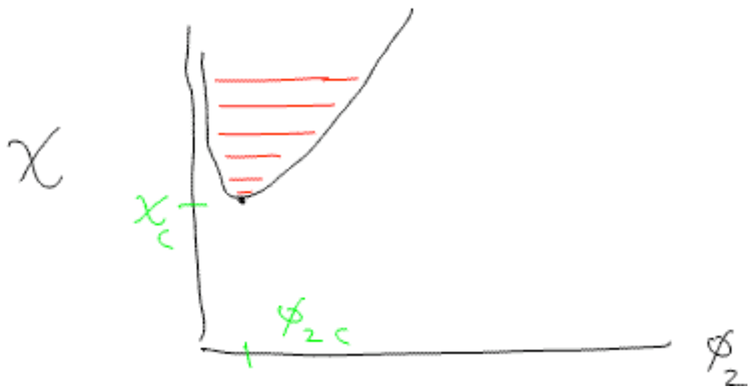
$$\frac{\Pi v_1}{k_B T} = \frac{\phi_2}{N} + \left(\frac{1}{2} - \chi\right) \phi_2^2 + \cdots$$

Note that the second virial coefficient is predicted to be independent of N, according to the Flory-Huggins theory.

Similarly, chemical potential of the second component can be derived.

2.3. Stability and phase behavior:





Critical point:

$$\chi_c = \frac{\left(\sqrt{N_1} + \sqrt{N_2}\right)^2}{2 N_1 N_2}$$

$$\phi_{2c} = \frac{\sqrt{N_1}}{\left(\sqrt{N_1} + \sqrt{N_2}\right)}$$

For polymer solutions

$$\chi_c = \frac{1}{2} + \frac{1}{\sqrt{N}} + \ldots$$

$$\phi_{2c} = \frac{1}{\sqrt{N}}$$