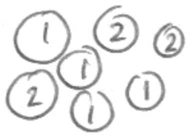
ME 3007
DERIVATION OF WILSON'S EQN



Binary Solution: For Type 1 Molecule –
x_{11} = probability that type 1 is a neighbor
x_{12} = " " " 2 " " "

$$\left.\right\} \quad x_{11} + x_{12} = 1, \qquad x_{21} + x_{22} = 1$$

$$\frac{x_{12}}{x_{11}} = \frac{x_2 \exp\left[-\frac{\lambda_{12}}{RT}\right]}{x_1 \exp\left[-\lambda_{11}/RT\right]}, \qquad \frac{x_{21}}{x_{22}} = \frac{x_1 \exp\left[-\lambda_{12}/RT\right]}{x_2 \exp\left[-\lambda_{22}/RT\right]},$$

"λ_{ij}" are pair interaction energies

So, local volume fractions are:

$$\xi_1 = \frac{x_1 v_1^L \exp(-\lambda_{11}/RT)}{x_1 v_1^L \exp(-\lambda_{11}/RT) + x_2 v_2^L \exp\left(-\frac{\lambda_{12}}{RT}\right)}$$

(volume fraction of type 1s around a type 1)

$$\xi_2 = \frac{x_2 v_2^L \exp(-\lambda_{22}/RT)}{x_1 v_1^L \exp(-\lambda_{12}/RT) + x_2 v_2^L \exp(-\lambda_{22}/RT)}$$

(Note that $\xi_1 + \xi_2 \neq 1$)

Plug these into the Flory-Huggins Equation to find:

$$\frac{G^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_1 \Lambda_{21} + x_2), \text{ where}$$

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} \exp\left[-\frac{(\lambda_{12} - \lambda_{11})}{RT}\right] \quad \text{and} \quad \Lambda_{21} = \frac{v_1^L}{v_2^L} \exp\left[-\frac{(\lambda_{12} - \lambda_{22})}{RT}\right]$$

Note: ① $(\lambda_{12} - \lambda_{11})$ and $(\lambda_{12} - \lambda_{22})$ are assumed to be constants
② $\lambda_{12} = \lambda_{21}$ but $\Lambda_{12} \neq \Lambda_{21}$

The resulting activity coefficients are:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2}\right]$$

$$\ln \gamma_2 = -\ln(x_1 \Lambda_{21} + x_2) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{x_1 \Lambda_{21} + x_2}\right]$$