Lecture 6: Flory-Huggins Theory

A. Introduction

* So far, we have only talked about very dilute polymer solutions. Today, we will talk about mixtures. This includes:
  - polymer solutions away from the dilute limit
  - polymer blends

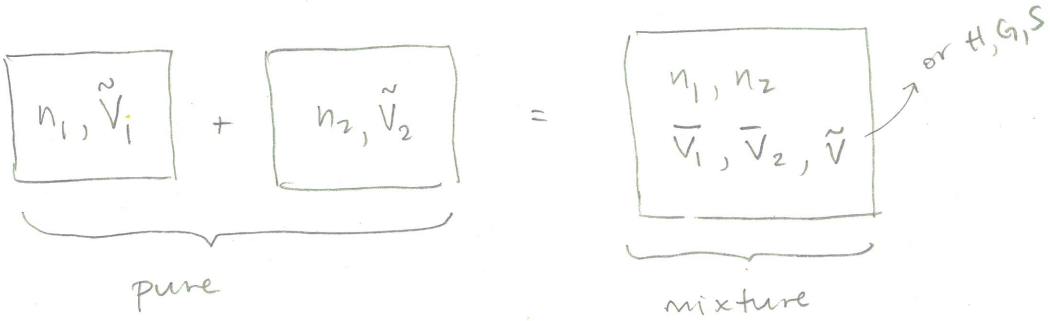
* This is a pretty big class of polymeric liquids. In fact, it covers most homopolymer liquids of interest.

* The theory we will talk about today is called Flory-Huggins theory. It is a mean-field theory, like our free energy expressions from before. There is more we could say about polymer solutions from scaling theories, but we don't have time today.

* The key to F-H theory is that we need to understand the mixture thermodynamics of polymers.
  - All solutions are a mixture of a polymer solute & a solvent. As we have seen, this is an important case for polymers
  - Polymer blends are mixtures of two different homopolymers with no solvent.

- If we know the mixing thermodynamics, we will be able to get:
  - 2nd virial coefficient for understanding polymer conformations
  - Miscibility and phase behavior

B. Review of Mixture Thermodynamics



n_i: moles of species i

$\tilde{V}_i$: molar volume of i, $\tilde{V}_i = \frac{V}{n_i}$ (pure only)

$\bar{V}_i$: partial molar volume of i, $\bar{V}_i = \left(\frac{\partial V}{\partial n_i}\right)_{n_j, P, T}$

$\tilde{V}$: total molar volume of mixture, $\tilde{V} = x_1 \bar{V}_1 + x_2 \bar{V}_2$

$$\Delta V_{mixing} = V_{mixture} - V_{pure}$$

$$= n_1 \bar{V}_1 + n_2 \bar{V}_2 - n_1 \tilde{V}_1 - n_2 \tilde{V}_2$$

* Same for H, G, S, etc.

* Partial molar free energy: chemical potential

$$\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_j}$$

* An "ideal solution" (or "ideal mixture") has the form:

$$\mu_i = \mu_i^*(P,T) + RT \ln x_i$$

$$\mu_i^*(P,T) = \tilde{G}_i(P,T)$$ pure species Gibbs free energy.

- An ideal mixture has the properties:

$$\bar{V}_i = \tilde{V}_i \leftarrow \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial \mu_i^*}{\partial P}\right)_{T,n_i}$$

$(\Delta \tilde{V}_{mix} = 0)$

$\bar{H}_i = \tilde{H}_i$ ← no interactions between molecules.

$(\Delta \tilde{H}_{mix} = 0)$

$$\tilde{G} = \sum_i x_i \mu_i \Rightarrow \Delta \tilde{G}_{mix} = RT \sum_i x_i \ln x_i$$ (<0 b/c $x_i < 1$)

(and using $\tilde{G} = \tilde{H} - T\tilde{S}$)

$$\Delta \tilde{S}_{mix} = -R \sum_i x_i \ln x_i$$

* For a non-ideal mixture, we can use the ideal mixture as a reference state:

$$\mu_i = \mu_i^*(P,T) + RT \ln a_i$$ (a_i: activity)

$$\mu_i - \mu_i^{(id)} = RT \ln (a_i/x_i)$$ ← Let $\gamma_i = \frac{a_i}{x_i}$, activity coefficient

$$\mu_i = \mu_i^{(id)} + RT \ln \gamma_i$$

- Define $\bar{G}_i^E = \mu_i - \mu_i^{(id)}$ $\bar{G}_i^E$: "excess" molar Gibbs energy of i

* In a lot of mixing thermodynamics, we look for an "equation of state" for γ_i.

* We can decompose $\tilde{G}^E = \tilde{H}^E + T\tilde{S}^E$

(recall $\tilde{G}^E = \sum_i x_i \bar{G}_i^E = RT \sum_i x_i \ln \gamma_i$)

- If $\tilde{S}^E = 0$, then it is a "regular solution"

$$\tilde{G}^E = \tilde{H}^E$$

$$\Delta\tilde{G}_{mix} = -T\Delta\tilde{S}_{mix}^{(id)} + \tilde{H}^E$$

↑ only deviation from ideal is interactions between molecules.

- Good for small molecules
- Example: Margules.

- If $\tilde{H}^E = 0$, then it is an "athermal solution."

$$\tilde{G}^E = -T\tilde{S}^E$$

no interactions, but configurations of molecules must be accounted for in entropy.

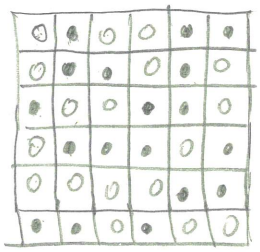
C. Mixing Entropy in a polymer solution

* Now, we need to come up with models for $\tilde{S}^E$ & $\tilde{H}^E$. We need statistical mechanics to come up with the model.

- Models are necessarily limited. Very useful though.

- we will use a lattice model that is based on mean-field arguments. Both assumptions can be removed, but the math is complicated. I'll talk more about this at the end.

* Mixing Entropy of small molecules



$n_1, n_2 \quad V, T$

$S = k_B \ln \Omega$

↑ # of microstates in system

$m_i = n_i N_A$ = # molecules ← avagadro's #.

mis a bit weird, but out of N's.

- each lattice site can be occupied by only 1 molecule
- each molecule has equal molar volumes:

$$\bar{V}_1 = \bar{V}_2$$

- cell size = molar volume
- lattice coordination number, z (how many neighbors) . e.g. z = 4 for square

- what is Ω?

- place m_2 particles: $\frac{m!}{(m-m_2)!}$
- indistinguishable: $\frac{1}{m_2!}$ (order is not significant)
- place m_1 particles (given m_2) $\frac{m_1!}{m_1!} = 1$

- # of configurations ${}_nC_k = \frac{n!}{k!(n-k)!}$

$n = m = m_1 + m_2 \qquad k = m_1 \ (\text{or } m_2)$

↑ place m_1 indistinguishable particles in the lattice

$$\Omega = \frac{m!}{m_1! \, m_2!}$$

- Calculate S, use Stirling's Approximation ↓

$S = k_B \ln \Omega \qquad \ln m! \approx m \ln m - m \quad , m \gg 1$

$$\ln\left(\frac{n!}{n_1!\,n_2!}\right) = \ln(n!) - \ln(n_1!) - \ln(n_2!)$$

$$= (n\ln n - n) - (n_1 \ln n_1 - n_1) - (n_2 \ln n_2 - n_2)$$

$$= (n_1+n_2)\ln(n_1+n_2) - (n_1+n_2) - n_1 \ln n_1 + n_1 - n_2 \ln n_2 + n_2$$

$$= n_1\left[\ln(n_1+n_2) - \ln n_1\right] + n_2\left[\ln(n_1+n_2) - \ln n_2\right]$$

$$= n_1 \ln\left(\frac{n_1+n_2}{n_1}\right) + n_2 \ln\left(\frac{n_1+n_2}{n_2}\right)$$

$$= -n_1 \ln x_1 - n_2 \ln x_2$$

$$S = k_B\left[-n_1 \ln x_1 - n_2 \ln x_2\right] \leftarrow \text{in \# molecules}$$

$$\boxed{\begin{aligned} S &= -R\left[n_1 \ln x_1 + n_2 \ln x_2\right] \\ \tilde{S} &= -R\left[x_1 \ln x_1 + x_2 \ln x_2\right] \end{aligned}}$$

- what is $\Delta\tilde{S}_{mix} = ?$

- why is this zero?
  - our reference state is the pure unmixed liquid. Essentially, we have a configurational density of states, ie. we have entropy of incompressible liquid already accounted for in reference.

$$S_1 = k_B \ln \Omega_1 = k_B \ln\left(\frac{n_1!}{n_1!}\right) = 0$$

$$S_2 = k_B \ln \Omega_2 = k_B \ln\left(\frac{n_2!}{n_2!}\right) = 0$$

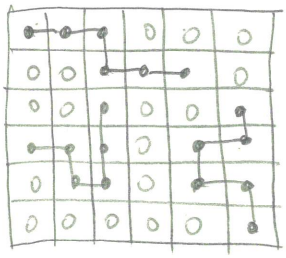
Similar to "dividing out" ideal gas partition function.

$$\boxed{\Delta\tilde{S}_{mix} = -R\left[x_1 \ln x_1 + x_2 \ln x_2\right]}$$

same as ideal!

- $\Delta\tilde{S}_{mix} > 0$ always ($x_i < 1$)
- Assumes no energetic interaction between molecules. Else need $e^{-\beta U}$

* Now, what happens if we connect one of the types of "monomers" to form chains:



○: 1, solvent
●: 2, polymer

n_i : # of molecules

Nn_2 : # of monomers

n_1 : # of solvent molecules.

- lattice site occupies one solvent molecule or one "monomer" (segment)
- $N \propto$ degree of polymerization

$$N = \frac{\bar{V}_{polymer}}{\bar{V}_{solvent}}$$

- use ϕ so we don't need to know M_W precisely when doing measurements.
- Is equivalent to a mass basis with $\bar{V}_{solvent} = \text{const}$, which is assumed.

$\bar{V}_{solvent} = v_0$

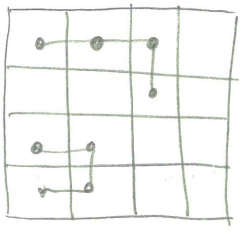
v_0: volume of a cell.

$$\phi_1 = \frac{n_1 v_0}{n_1 v_0 + n_2 N v_0} = \frac{n_1}{n_1 + N n_2} = \frac{n_1}{n}$$

$$\phi_2 = \frac{N n_2}{n_1 + N n_2} = \frac{N n_2}{n}, \quad n = n_1 + N n_2$$

- Now, how get mixing entropy? No longer a "regular solution". (Is athermal for now.)

- consider placing the $(i+1)^{th}$ chain



occupied sites: $i \cdot N$

available sites: $n - iN$

(i chains are already placed)

- number of ways to place the 1st monomer:

$m - iN$ •

- number of ways to place the 2nd monomer:

$z \times$ fraction available 

$z \times \frac{m - iN}{m}$ } mean-field approximation of available sites

- number of ways to place 3rd monomer

$(z-1) \times$ fraction available 

$(z-1) \times \frac{m - iN}{m}$

- 3rd, 4th..., N^{th} are the same.

$$\boxed{\star} \quad w_{i+1} = (m - iN) \times \left(z \frac{m - iN}{m}\right) \times \left[(z-1)\left(\frac{m - iN}{m}\right)\right]^{N-2}$$

• what is the total entropy?

$$\boxed{\star} \quad \Omega_{mix} = \frac{w_1 \cdot w_2 \cdots w_{m_2}}{m_2!} = \frac{1}{m_2!} \prod_{i=0}^{m_2 - 1} w_{i+1}$$

$m_2!$ ↑ indistinguishable

(what about monomers? Once the m_2 polymers are arranged, there are $\frac{m_1!}{m_1!} = 1$ ways of arranging the monomers.)

• Now, we need to do the math to simplify:

$$\Omega = \frac{1}{m_2!} \frac{z^{m_2} (z-1)^{m_2(N-2)}}{m^{m_2(N-1)}} \prod_{i=0}^{m_2 - 1} (m - iN)^N$$

(warning: detailed math)

- pull out another $N^{m_2 N}$

$$\Omega = \frac{z^{m_2}(z-1)^{m_2(N-2)} N^{m_2 N}}{m_2!\, m^{m_2(N-1)}} \underbrace{\prod_{i=0}^{m_2-1}\left(\frac{m}{N}-i\right)^N}$$

$$\left[\left(\frac{m}{N}\right)\left(\frac{m}{N}-1\right)\left(\frac{m}{N}-2\right)\cdots\left(\frac{m}{N}-m_2+1\right)\right]^N$$

$$= \left[\left(\frac{m}{N}\right)! \Big/ \left(\frac{m}{N}-m_2\right)!\right]^N$$

$$\frac{m}{N} = \frac{m_1}{N} + \frac{N m_2}{N} = \frac{m_1}{N} + m_2$$

$$= \left[\left(\frac{m}{N}\right)! \Big/ \left(\frac{m_1}{N}\right)!\right]^N$$

* This assumes that $\frac{m}{N} \gg i$ or $\frac{m}{N} \gg m_2$

recall that $m = m_1 + N m_2$,

so:

$$\frac{m_1}{N} + m_2 \gg m_2$$

$$\frac{m_1}{N} \gg 0$$

In other words, the solution is mostly solvent, i.e. a dilute polymer solution

$$\Omega = \frac{z^{m_2}(z-1)^{m_2(N-2)} N^{m_2 N}}{m_2!\, m^{m_2(N-1)}} \left[\frac{(m/N)!}{(m_1/N)!}\right]^N$$

- The Entropy is given by: $S = k_B \ln \Omega$

$$\frac{S}{k_B} = \ln\left\{ \frac{z^{m_2}(z-1)^{m_2(N-2)} N^{m_2 N}}{m_2!\, m^{m_2(N-1)}} \left[\frac{(m/N)!}{(m_1/N)!}\right]^N \right\}$$

$$\frac{S}{k_B} = m_2 \ln z + m_2(N-2)\ln(z-1) + m_2 N \ln N$$

$$- \ln(m_2!) - m_2(N-1)\ln m + N \ln[(m/N)!]$$

$$- N \ln[(m_1/N)!]$$

- use sterling's approximation: $\ln(x!) = x \ln x - x$

$$\frac{S}{k_B} = m_2 \ln z + m_2(N-2)\ln(z-1) + m_2 N \ln N$$

$$- m_2 \ln m_2 + m_2 - m_2(N-1)\ln m + N\left[\frac{m}{N}\ln\left(\frac{m}{N}\right) - \frac{m}{N}\right]$$

$$- N\left[\frac{m_1}{N}\ln\left(\frac{m_1}{N}\right) - \frac{m_1}{N}\right]$$

- recall: $n = n_1 + N n_2$

$$\frac{S}{k_B} = n_2 \ln z + n_2(N-2)\ln(z-1) + n_2 N \ln N$$
$$- n_2 \ln n_2 + n_2 - n_2 N \ln n + n_2 \ln n$$
$$+ n \ln\left(\frac{n}{N}\right) - n - n_1 \ln\left(\frac{n_1}{N}\right) + n_1$$

$$= n_2 \ln z + n_2(N-2)\ln(z-1) + n_2 N \ln N$$
$$- n_2 \ln n_2 + n_2 - n_2 N \ln n + n_2 \ln n$$
$$+ n_1 \ln\left(\frac{n}{N}\right) + N n_2 \ln\left(\frac{n}{N}\right) - n_1 - N n_2 - n_1 \ln\left(\frac{n_1}{N}\right) + n_1$$

$n_1 \ln n - n_1 \ln N$ $\quad N n_2 \ln n - N n_2 \ln N$ $\quad -n_1 \ln n_1 + n_1 \ln N$

$$= n_2 \ln z + n_2(N-2)\ln(z-1) + (1-N) n_2$$
$$+ n_2 \ln n - n_2 \ln n_2 + n_1 \ln n - n_1 \ln n_1$$

- Add and subtract: $n_2 \ln N - n_2 \ln N$
  (see why in a minute)

$$\frac{S}{k_B} = n_2 \ln z + n_2(N-2)\ln(z-1) + (1-N) n_2 + n_2 \ln N$$
$$+ n_2 \ln\left(\frac{n}{N n_2}\right) + n_1 \ln\left(\frac{n}{n_1}\right)$$

$$\boxed{S = -k_B\left[n_1 \ln\left(\frac{n_1}{n}\right) + n_2 \ln\left(\frac{n_2 N}{n}\right)\right]}$$
$$\boxed{+ k_B n_2\left[\ln z + (N-2)\ln(z-1) + (1-N) + \ln N\right]}$$

- what is ΔS_{mix}? Need pure component S.

- For pure solvent: $n = n_1 \quad n_2 = 0$

$$S_1 = -k_B \left[n_1 \ln\left(\frac{n_1}{n_1}\right) + 0 \right] + 0$$

$n_1/n_1 = 1$, $\ln(1) = 0$

$$\boxed{S_1 = 0}$$

- For pure polymer: $n = N n_2$, $n_1 = 0$

$$S_2 = -k_B \left[n_2 \ln\left(\frac{N n_2}{N n_2}\right)^{1} \right] \qquad \ln(1) = 0$$

$$+ k_B n_2 \left[\ln z + (N-2)\ln(z-1) + (1-N) + \ln N \right]$$

$$\boxed{S_2 = k_B n_2 \left[\ln z + (N-2)\ln(z-1) + (1-N) + \ln N \right]}$$

- This is why we needed to +/- $n_2 \ln N$. It gives the 2nd part as the entropy of 2. It would come out now if we hadn't.
- why is this not 0? Our reference state is a pure monomer. The configurational entropy is non-trivial
- we can actually make sense of the config entropy:

$$\lim_{N\to\infty} S_2 = k_B n_2 \left[N \ln(z-1) - N \right]$$

$$= \underbrace{k_B n_2 N}_{\text{extensive in \# of monomers}} \left[\underbrace{\ln(z-1) - 1}_{\text{mean-field config entropy of a monomer in self-avoiding chain}} \right]$$

Or $\lim_{N\to\infty} F_2 = k_B T n_2 N \left[1 - \ln(z-1) \right]$ ← like Rosenbluth weight

- Finally, $\Delta S_{mix} = S_{mixture} - S_1 - S_2$

$$\boxed{\Delta S_{mix} = -k_B\left[n_1 \ln\left(\frac{n_1}{n}\right) + n_2 \ln\left(\frac{n_2 N}{n}\right)\right]}$$

Remember: $\phi_1 = \frac{n_1}{n}$, $\phi_2 = \frac{n_2 N}{n}$

$$\Delta S_{mix} = -k_B\left[n_1 \ln\phi_1 + n_2 \ln\phi_2\right]$$

$n_1 = m_1/N_A$, $n_2 = m_2/N_A$, $R = kN_A$

$$\boxed{\Delta S_{mix} = -R\left[n_1 \ln\phi_1 + n_2 \ln\phi_2\right]}$$

or: $\frac{n_1}{n} = \phi_1$, $\frac{n_2}{n} = \frac{\phi_2}{N}$, $\Delta\tilde{S}_{mix} = \frac{\Delta S}{n}$

$$\boxed{\Delta\tilde{S}_{mix} = -k_B\left[\phi_1 \ln\phi_1 + \frac{\phi_2}{N} \ln\phi_2\right]}$$

- Comments:
  - Recover ideal $\Delta\tilde{S}_{mix}$ when $N = 1$.
  - The mixing entropy is always positive.

    $\phi_1 < 1$ & $\phi_2 < 1$ so $\ln\phi_1 < 0$ & $\ln\phi_2 < 0$.

    So, mixing is always favored.
  - The mixing entropy is smaller than ideal for the polymer component. Polymer conformations have less entropy than molecules that can freely move (makes sense).
  - Can generalize for system with 2 polymers:

$$\Delta\tilde{S}_{mix} = -k_B\left[\frac{\phi_1}{N_1} \ln\phi_1 + \frac{\phi_2}{N_2} \ln\phi_2\right]$$

$n = n_1 N_1 + n_2 N_2$

$\phi_i = \frac{n_i N_i}{n}$

D. Enthalpy of mixing

* the last section only considered entropy of mixing.
what happens if monomers & solvent can interact?

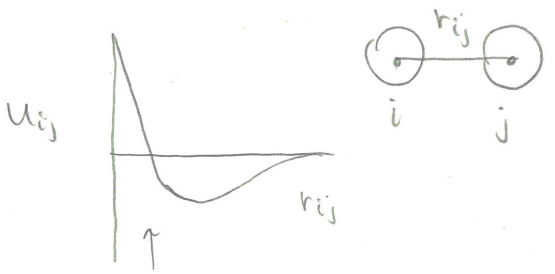
- Assume that there is no p-V work. We assumed the system is incompressible already, so

$$H_{mix} = U_{mix} \qquad (H = U + \cancel{PV}^{0})$$

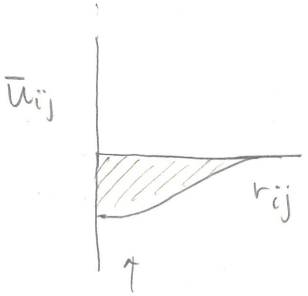
[This means
$G = H - TS$
$F = U - TS$
will be the same.
Gibbs & Helmholtz have same mixing free energy.]

- Assume the energy change (per monomer) is so small that S_{mixing} is not affected. In other words $e^{-\beta U}$ will not need to be counted in our prior derivation. (We did account for self-avoidance though w/ incompressibility & $\ln(Z-1)$, though in a weird mean-field way.)

- What is interaction?



did this part w/ incompressible lattice



attraction only.

$$w_{ij} = \frac{1}{V}\int \bar{u}_{ij}\, d\underline{r}_{ij}$$

↖ units of energy (average attraction)

- attraction only, due to dispersion forces (dipole-dipole, etc.). "van der Waals".

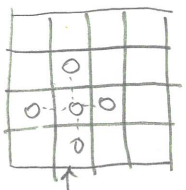
w_{11} : attraction between particles of type 1 (solvent-solvent)

w_{22} : " " " " " 2 (monomer-monomer)

w_{12} : " " " " " 1 & 2 (solvent-monomer)

- what is the mean-field energy in the pure states?

Pure solvent



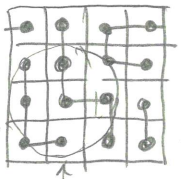
$$U_1 = m_1 \cdot z w_{11} \cdot \frac{1}{2} = \boxed{\frac{1}{2} m_1 z w_{11}}$$

m_1: # sites

$\frac{1}{2}$: avoid double counting (interactions are pairs, only count 1 pair)

energy per site: $z w_{11}$

Pure Polymer



$$U_2 = N m_2 \cdot z w_{22} \cdot \frac{1}{2} = \boxed{\frac{1}{2} N m_2 z w_{22}}$$

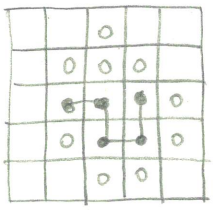
$N m_2$: # sites

$\frac{1}{2}$: avoid double counting

energy per site: $z w_{22}$

- connectivity doesn't change energy of interaction

- what is the mean-field energy of a mixture?



$$U_{11} = \frac{1}{2} m_1 z w_{11} \times \text{probability of a 1 being by a 1} \} P_{11}$$

$$U_{22} = \frac{1}{2} N m_2 z w_{22} \times P_{22} \leftarrow \text{prob of 2 by a 2}$$

$$U_{12} = \frac{1}{2} m_1 z w_{12} \times P_{12} \leftarrow \text{prob of 2 by a 1}$$

$$+ \frac{1}{2} N m_2 z w_{12} \times P_{21} \leftarrow \text{prob of 1 by a 2}$$

$\frac{1}{2} N m_2$: counting 2's

P_{21}: neighbor is a 1

- assume uniform distribution:

$$P_{11} = \frac{m_1}{m} = \phi_1 \quad , \quad P_{22} = \frac{N m_2}{m} = \phi_2$$

$$P_{21} = \frac{m_1}{m} = \phi_1 \quad , \quad P_{12} = \frac{N m_2}{m} = \phi_2$$

- Probability is determined by neighbors.
  (fixed self, what is neighbor)
- obviously the mean-field assumption here isn't quite right. You are more likely to find a monomer near you if you are a polymer. we are neglecting this.
- Add it all up:

$$U_{mix} = \frac{1}{2} m_1 z w_{11} \phi_1 + \frac{1}{2} N m_2 z w_{22} \phi_2 + \frac{1}{2} m_1 z w_{12} \phi_2 + \frac{1}{2} N m_2 z w_{12} \phi_1$$

$$U_{mix} = \frac{1}{2} m_1 z \left(w_{11} \frac{m_1}{m} + w_{12} \frac{N m_2}{m} \right) + \frac{1}{2} N m_2 z \left(w_{22} \frac{N m_2}{m} + w_{12} \frac{m_1}{m} \right)$$

- Now, what is ΔH_{mix}?

$$\Delta H_{mix} = \Delta U_{mix} = U_{mix} - U_1 - U_2$$

$$= \frac{z}{2} \left[w_{11} \frac{m_1 m_1}{m} + w_{12} \frac{m_1 N m_2}{m} + w_{12} \frac{m_1 N m_2}{m} + w_{22} \frac{N m_2 N m_2}{m} \right] - \frac{z}{2} w_{11} m_1 - \frac{z}{2} w_{22} N m_2$$

$$= \frac{z}{2} \left[w_{11} \left(\frac{m_1^2}{m} - m_1 \right) + 2 w_{12} \frac{N m_1 m_2}{m} + w_{22} \left(\frac{N^2 m_2^2}{m} - N m_2 \right) \right]$$

- what is $\frac{m_1^2}{m} - m_1$? $\frac{N^2 m_2^2}{m} - N m_2$?

$$\frac{m_1^2}{m} - m_1 = \frac{m_1 m_1 - m m_1}{m} = \frac{m_1 m_1 - (m_1 + N m_2) m_1}{m}$$

$$= -\frac{N m_1 m_2}{m}$$

$$\frac{N^2 m_2^2}{m} - N m_2 = \frac{N^2 m_2^2 - N m_2 m}{m} = \frac{N^2 m_2^2 - N m_2 (m_1 + N m_2)}{m}$$

$$= -\frac{N m_1 m_2}{m}$$

- Put it together:

$$\Delta H_{mix} = \frac{z}{2}\left[-w_{11}\frac{N m_1 m_2}{m} + 2w_{12}\frac{N m_1 m_2}{m} - w_{22}\frac{N m_1 m_2}{m}\right]$$

$$\boxed{\Delta H_{mix} = z\frac{N m_1 m_2}{m}\left[w_{12} - \frac{w_{11}}{2} - \frac{w_{22}}{2}\right]}$$

Define: $\Delta w = w_{12} - \frac{w_{11}}{2} - \frac{w_{22}}{2}$

"exchange energy" – cost to switch solvent & monomer positions.

$$\boxed{\Delta H_{mix} = \frac{m_1 N m_2}{m} z \Delta w}$$

$\frac{m_1 N m_2}{m}$: binary contacts

$z\Delta w$: exchange energy per molecule

- A couple of ways to re-write this that are equivalent:

recall $\phi_1 = \frac{m_1}{m}$ & $\phi_2 = \frac{N m_2}{m}$

$$\Delta H_{mix} = N m_2 \phi_1 z \Delta w = m_1 \phi_2 z \Delta w$$

- we want to get rid of the model dependence if we can, built into $z\Delta w$, so we define:

$$\chi = \frac{z\Delta w}{k_B T}$$

← dimensionless exchange energy. What fraction of kT to swap solvent & monomer.

- Now, ΔH_{mix} becomes:

$$\Delta H_{mix} = n_1 \phi_2 k_B T \chi = n_1 \phi_2 RT \chi$$

or, on a per site basis (per mole)

$$\Delta \tilde{H}_{mix} = \phi_1 \phi_2 \chi RT$$

E. Flory-Huggins Free Energy

* To get a total free energy of mixing, we now assume that

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

- Assumes that ΔS_{mix} is not affected by energy. Kinda already assumes this

$$\Delta H_{mix} = n_1 \phi_2 \chi RT$$

$$\Delta S_{mix} = -R\left[n_1 \ln \phi_1 + n_2 \ln \phi_2\right]$$

$$\Delta G_{mix} = RT\left[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi\right]$$

* Or, on a per-site basis

$$\frac{\Delta\tilde{G}_{mix}}{RT} = \phi_1 \ln\phi_1 + \frac{\phi_2}{N}\ln\phi_2 + \phi_1\phi_2\chi$$

* Comments:

- Remember, $\Delta\tilde{F}_{mix}$ will give the same as $\Delta\tilde{G}_{mix}$ because no PV work
- Entropy favors mixing: $-T\Delta S_{mix} < 0$ always.
- Enthalpy opposes mixing: $\Delta H_{mix} > 0$ always (when $\chi > 0$)
- $\chi > 0$ when "prefers itself over neighbor." less attracted to neighbor than self. All attraction though.
- Mean-field assumptions aren't very good, but theory is pretty good anyway! A lot of garbage gets buried into χ:

$$\chi_{eff} = \frac{\Delta\tilde{G}^{ex}_{mix}}{\phi_1\phi_2 RT} \qquad \Delta\tilde{G}^{ex}_{mix} = \Delta\tilde{G}_{mix} - \phi_1\ln\phi_1 - \frac{\phi_2}{N}\ln\phi_2$$

$$\chi_{eff} = \frac{\alpha}{T} + \beta \leftarrow \text{people fit } \chi_{eff} \text{ to this form.}$$

- Can get estimate for χ if we assume

$$w_{12} = (w_{11}w_{22})^{1/2} \quad \text{(mixing rule, geometric mean)}$$

- usually ok for non-polar molecules only
- Not very good normally

$$\longrightarrow \chi = \frac{\hat{V}_1}{RT}(\delta_1 - \delta_2)^2, \qquad \delta_i^2 \equiv -\frac{z}{2}\frac{N_A w_{ii}}{\hat{V}_i}$$

$\hat{V}_1$: molar volume of solvent, lattice size

δ_i: solubility parameter (tabulated)

- Summary of assumptions:
  - No ΔV_{mix}: $\bar{V}_1 = \hat{V}_1$, $\bar{V}_2 = \hat{V}_2$
  - ΔS_{mix} is combinatorial entropy of mixing.
    No energy of interaction ("ideal" in one sense of the word)
    ↑ not thermo of mixing "ideal" though
  - $\Delta H_m = \Delta U_m$
  - Mean-field assumptions all over the place. → local conc = average → random mixing
  - Interactions are short-ranged & pairwise & isotropic

It would be good to go over
- Osmotic Pressure
- Phase Diagrams,

But I am out of time

• Do show phase diagrams though.