

Thermo 3 - Origin of Nonideality in Polymer Systems

Outline

Athermal systems (entropy only)

Concentrated: Flory-Huggins Theory for ΔS_{mix}

Dilute: a general excluded volume formalism
& expressions for A_2 of rigid particles

Enthalpic Systems

Add van Laar ΔE_{mix} to get full FH model

Successes of FH model

- Phase separation
- χ^2

Failures of FH model

- Virial coefficient

Thermo 3 Origin of nonideality in polymer systems

The two usual effects

- enthalpic interaction
- finite size

One additional effect

- Connectivity

Even if you ignore the first two, or arrange for them to cancel out, you cannot get past the connectivity problem. In this sense, polymers are intrinsically non-ideal

We will want ΔG_{mix} eventually. But let's focus first on this connection problem - i.e. let's consider systems for which ΔH_{mix} is zero

↳ Athermal systems

Then we can build a theory for ΔS_{mix} , which is the heart of the problem. ΔH_{mix} can be added in later.

3-A) Athermal Systems (Richards Ch. 3 or Tanford Ch. 4)

- No single theory covers all concentration ranges
- The connectivity problem is approached via a lattice treatment
 - we'll see that this is only valid at high concentrations
- a separate calculation (no lattice) helps for globular solutes, like proteins. It also gives us a handle on interaction terms like the virial coefficient.

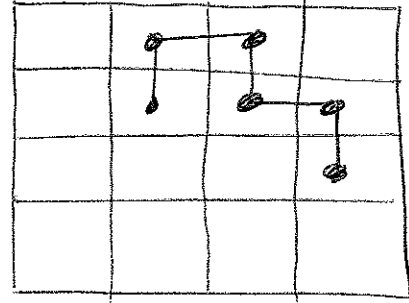
Flory-Huggins Calculation of ΔS_{mix}

Synopsis: a calculation valid for high concentrations
lattice calculation

Lattice jargon

- $Z = \#$ sites adjacent to any given cell.
= "lattice parameter"

$Z = 4$ for square lattice in 2D
 $Z = 6$ " cubic " " 3D



- $N_1 = \#$ of solvent molecules
- $N_2 = \#$ of polymer molecules
- $\sigma =$ degree of polymerization - i.e. # of monomer repeats on each polymer.
(what we have previously called n)
- Suppose that solvent & polymer segment are the same size. (If not, re-scale the segment - i.e., just redefine it).
- $N_0 = N_1 + \sigma N_2 =$ total lattice sites

For the lattice above: $Z = 4$
 $N_1 = 10$
 $N_2 = 1$
 $\sigma = 6$

Volume fractions: Probably More Dramatic NOT to introduce volume fractions until end

$$\left\{ \begin{aligned} \phi_1 &= \frac{N_1}{N_0} = \frac{N_1}{N_1 + nN_2} ; & \phi_2 &= \frac{nN_2}{N_1 + nN_2} \end{aligned} \right\}$$

Initial Condition of lattice & Strategy

1) Imagine there are already I polymers in lattice (occupying I sites). Now, compute # ways to put on $(I+1)^{\text{th}}$ polymer.

2) Then total ways to place polymers is product of the # of ways at each and every step from $I=0$ (placement of first chain) to $I=N_2-1$ (placement of last chain).

Def: let W_{I+1} = # ways to place $(I+1)^{\text{th}}$ chain, given that there are already I on lattice.

Def: let $r_I = \frac{I}{N_0}$ = fraction of sites consumed by polymers.

Note: $1 - R_I =$ fraction of sites remaining open

Now compute $W_{I+1} =$ ways to place $(I+1)^{\text{th}}$ polymer

Chain end $(1 - R_I) N_0$ sites on which to place end of $(I+1)$
(1st repeat unit)

Next repeat $Z(1 - R_I)$
(2nd unit)

Can go in any of Z sites adjacent to first chain.

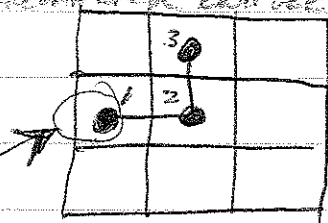
Prob. that the site is free

★ THIS IS THE BIG APPROXIMATION, AND IT RECURS IN TERMS BELOW. THIS WILL ONLY BE TRUE WHEN I IS SO LARGE

THAT SOLUTION IS CONCENTRATED.
(delink solution)
In general, even though internal concentration (inside a chain) is high, there are huge regions where the sites are mostly vacant. Treating the probability R_I as uniform throughout solution

is an approximation because R_I is really much higher near another polymer & much lower in other regions. — unless the solution is concentrated \Rightarrow Mean Field Theory.
 (Another way to say it: we need restrict ourselves to solutions where most of the chains go into already concentrated lattices, so these terms dominate)

3rd Repeat Unit



★ Another big approx: Assume R_I doesn't change much as each segment is put on or i.e. $R_I \rightarrow N_0$. This is fine, but what about intramolecular effects?

This site is disallowed $\Rightarrow Z-1$ sites
 Again, let $(1-R_I) = \text{prob. that one of the } (Z-1) \text{ sites is vacant.}$

$(Z-1) (1-R_I)$ ways
 # possible cells fraction open

Average # of Open Cells for 3rd Segment
 \Rightarrow MEAN FIELD AVG.

4th ; 5th ; 6th ; etc... is same as 3rd.

$$W_{I+1} = \underbrace{N_0 (1-R_I)}_{\text{1st segment}} \underbrace{Z (1-R_I)}_{\text{2nd}} \underbrace{\left[(Z-1) (1-R_I) \right]^{I-2}}_{\text{3rd - } I^{\text{th}} \text{ segments}}$$

$$= N_0 (1-R_I)^I Z (Z-1)^{I-2}$$

To a fair approximation: ($z \approx z-1$)

$$W_{I+1} \approx N_0 (1 - r_I)^\sigma (z-1)^{\sigma-1}$$

But $1 - r_I = \frac{\text{fraction of sites free}}{N_0} = 1 - \frac{\sigma I}{N_0} = \frac{N_0 - \sigma I}{N_0}$

~~$\therefore W_{I+1}$~~

$$\therefore (1 - r_I)^\sigma = \left(\frac{N_0 - \sigma I}{N_0} \right)^\sigma$$

$$W_{I+1} \approx N_0 \left(\frac{N_0 - \sigma I}{N_0} \right)^\sigma (z-1)^{\sigma-1}$$

Total ways for placing all chains is :

discuss why this limit:
 $I = \# \text{ chains before this one}$

$$W_{TOT} = \prod_{I=0}^{N_2-1} W_{I+1}$$

$$= \prod_{I=0}^{N_2-1} N_0 \left(\frac{N_0 - \sigma I}{N_0} \right)^\sigma (z-1)^{\sigma-1}$$

Factor out

$$= \frac{N_0^{N_2} (z-1)^{(\sigma-1)N_2} \prod_{I=0}^{N_2-1} (N_0 - \sigma I)^\sigma}{N_0^\sigma N_2}$$

Take $N_0^{N_2}$ numerator into denominator of denominator

$$= \frac{(z-1)^{(\sigma-1)N_2}}{\left(\frac{N_0^\sigma N_2}{N_0^{N_2}} \right)} \prod_{I=0}^{N_2-1} (N_0 - \sigma I)^\sigma$$

$$\Rightarrow \left(\frac{z-1}{N_0} \right)^{N_2(\sigma-1)} \prod_{I=0}^{N_2-1} (N_0 - \sigma I)^\sigma$$

Now, we need to make a correction to account for the fact that chains are indistinguishable. The above scheme counts the ways to place distinguishable chains on the lattice. If all chains are the same, e.g. colored

are same, then we must reduce our count e.g. gray

by $N_2!$ { i.e., N_2 way to select 1st chain
 N_2-1 " " " 2nd "
 N_2-2 " " " 3rd "
 etc...

$$W_{TOT} = \frac{1}{N_2!} \left(\frac{Z-1}{N_0} \right)^{N_2} \prod_{I=0}^{N_2-1} (N_0 - I)^I$$

$$S = k \ln W_{TOT}$$

$$= k \left\{ N_2 (\sigma - 1) \ln \left(\frac{z-1}{N_0} \right) + \sum_{I=0}^{N_2-1} \sigma \ln (N_0 - \sigma I) \right\} - \ln N_2!$$

To evaluate this, replace \sum by \int

$$\sum_{I=0}^{N_2-1} \sigma \ln (N_0 - \sigma I) \approx \int_0^{N_2-1} dI \sigma \ln (N_0 - \sigma I)$$

$$\text{let } u = N_0 - \sigma I$$

$$du = -\sigma dI$$

$$\text{or... } dI = -\frac{du}{\sigma}$$

$$\Rightarrow \int_{I=0}^{I=N_2-1} \left(-\frac{du}{\sigma} \right) \sigma \ln u = \int_{I=0}^{I=N_2-1} -du \ln u$$

get limits: @ $I=0$, $u = N_0 - \sigma(0) = N_0$

@ $I=N_2-1$, $u = N_0 - \sigma(N_2-1) = N_0 - \sigma N_2 + \sigma$

But $N_0 - \sigma N_2 = N_1$ and $N_1 \gg \sigma$

So upper limit is $\approx N_1$

$$\Rightarrow \int_{u=N_0}^{u=N_1} -du \ln u = - (u \ln u - u) \Big|_{N_0}^{N_1}$$

$$= - (N_1 \ln N_1 - N_1 - N_0 \ln N_0 + N_0)$$

$$\text{let } S_p = S_{\text{polymer}} = S @ N_1 = 0 \quad (N_0 = \sigma N_2)$$

$$S_p = k \left\{ \begin{array}{l} \cancel{\sigma N_2 \ln(z-1)} - \cancel{N_2 \ln(z-1)} - \cancel{\sigma N_2 \ln(\sigma N_2)} + \boxed{N_2 \ln(\sigma N_2)} \\ - 0 + \cancel{\sigma N_2 \ln \sigma N_2} \\ - \underset{*}{N_2 \ln N_2} + \underset{*}{N_2} \end{array} \right.$$

Sole Survivor!

Note: * terms cancel with * terms in the general expression for S.

Two other terms $|\sigma N_2 \ln(\sigma N_2)|$ cancel out
only the circled term will survive

$$\text{let } S_s = S_{\text{solvent}} = S @ N_2 = 0 \quad (N_0 = N_1)$$

$$= k \left\{ \begin{array}{l} 0 - 0 - 0 + 0 \\ \cancel{-N_1 \ln N_1} + \cancel{N_1 \ln N_1} \\ - 0 \end{array} \right.$$

$$= 0 \quad \text{as it must!}$$

$$\Delta S_{\text{mix}} = S - S_p - S_s$$

$$= k \left\{ \begin{array}{l} \cancel{-N_2 \sigma \ln N_0} + N_2 \ln N_0 \\ - N_1 \ln N_1 + \boxed{N_0 \ln N_0} \\ - N_2 \ln(\sigma N_2) \end{array} \right.$$

write as $N_1 \ln N_0 + \sigma N_2 \ln N_0$
(since $N_0 = N_1 + \sigma N_2$)

$$\Delta S_{mix} = k \left\{ \begin{aligned} N_2 \ln N_0 - N_1 \ln N_1 \\ + N_1 \ln N_0 - N_2 \ln(\nabla N_2) \end{aligned} \right\}$$

$$= k \left\{ N_2 \ln \frac{N_0}{\nabla N_2} + N_1 \ln \frac{N_0}{N_1} \right\}$$

$$= -k \left\{ N_2 \ln \frac{\nabla N_2}{N_0} + N_1 \ln \frac{N_1}{N_0} \right\}$$

But now we realize that $\frac{\nabla N_2}{N_0} = \frac{\text{total volume of polymer}}{\text{total volume}}$

$\frac{N_1}{N_0} = \frac{\text{solvent volume}}{\text{total volume}}$

define: $\phi_2 = \text{polymer volume fraction} = \nabla N_2 / N_0$

$\phi_1 = \text{solvent volume fraction} = N_1 / N_0$

$$\Delta S_{mix} = -k \left\{ N_2 \ln \phi_2 + N_1 \ln \phi_1 \right\}$$

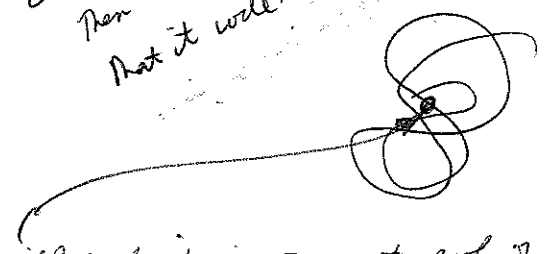
SAME FORM AS IDEAL GAS, BUT
 SWITCH FROM MOLE FRACTIONS
 TO VOLUME FRACTIONS !!

Unfortunately, The ΔS_{mix} expression just obtained is limited to high concentrations.

Why? — Because we assumed that probability of neighbors in lattice being unoccupied was given by $(1 - r_1)$ where $r_1 = \frac{v_1}{N_0}$. This is OK if the distribution of monomer segments is \approx uniform in solution.

However, in dilute solution the distribution of monomer is not uniform. The intermolecular distances are so long that there are large regions of solvent with no polymer segments at all. The $(1 - r_1)$ factor is obviously wrong in these regions and there is unit probability of adjoining segments being empty if a chain end begins in one of these regions.

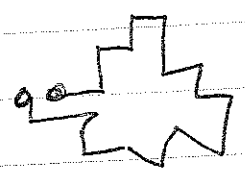
↓ If put first chain segment here, then there is unit probability that it will be surrounded by solvent



Also... if both at interior segment, prob. of

Moreover, the only intra-chain interactions we included were nearest neighbor.

That is, as we place, say, the 50th segment on the chain, it could be excluded from entering a lattice site occupied by the first segment of its own chain.



~~the use of a mean field value Ω_I is a~~

- The use of a mean field value Ω_I is a 2-edged sword:
- 1) it is unnecessarily restrictive on conformations where the 1st side is far from any other chain
 - 2) It does not allow us to compute changes in the # of free sites due to intramolecular effects. In this sense, it is not restrictive enough.

BOTH OF THESE PROBLEMS GO AWAY IF A LOT OF POLYMERS ARE ULTIMATELY PLACED ON THE LATTICE, SO THAT W_{TOT} is dominated by terms where I was large enough that the ~~site~~ fraction of sites open or closed ~~is~~ really is determined by intermolecular (many chain) interactions.

I.E. FOR CONC. SOLUTIONS

Note: The F-H calculation is different as far as excluded volume goes, from our DeBennes description of χ^2 :

F-H is entirely intermolecular (except nearest neighbor)
 DeBennes is intra.

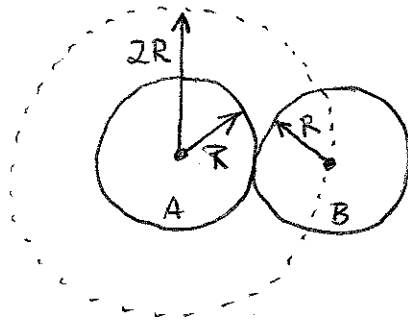
Athermal dilute calculation for globular solutes - no lattice!

Ref: Richards

Purpose: we reinforce what we learned from Flory-Huggins ΔS_{mix} by designing a calculation appropriate for the dilute regime. We use globular solutes, but some of what we do will apply to coils in good solvents. Calculation is again athermal.

Practical Outcome: we will get surprising info from an osmometry experiment.

Imagine 2 spheres, A & B. B cannot penetrate the zone defined by $2R$ from sphere A.



Center of mass of B is excluded from a volume $\frac{4}{3}\pi(2R)^3$ centered on A.

define: $u = \text{excluded volume} = \frac{4}{3}\pi(2R)^3 = 8V_A$

The calculation is sort of a less-constrained approach but has some similarities to the lattice method.

Consider a container of volume $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$

ways to place 1st solute = $K V$

↑ some const. of proportionality
{ K would go down as $(\text{radius})^3$ }

ways to place 2nd solute = $K(V-u)$

$u =$
 $=$ excl. volume

ways for 3rd solute = $K(V-2u)$

⋮
etc.

$$W_{TOT} = \frac{1}{N_2!} \prod_{j=0}^{N_2-1} K(V-j u)$$

$$S = k \ln W_{TOT} \Rightarrow \frac{S}{k} = -\ln N_2! + \sum_{j=0}^{N_2-1} \ln(K(V-j u))$$
$$= -(N_2 \ln N_2 - N_2) + \sum_{j=0}^{N_2-1} [\ln K + \ln(V-j u)]$$

$$= -(N_2 \ln N_2 - N_2) + N_2 \ln K + \sum_{j=0}^{N_2-1} \ln \left(V \left(1 - \frac{j u}{V} \right) \right)$$

$$= -(N_2 \ln N_2 - N_2) + N_2 \ln K + \sum_{j=0}^{N_2-1} \ln V + \sum_{j=0}^{N_2-1} \ln \left(1 - \frac{j u}{V} \right)$$

$$\approx -(N_2 \ln N_2 - N_2) + N_2 \ln K + N_2 \ln V - \sum_{j=0}^{N_2-1} \frac{j u}{V}$$

can expand $\ln(1 - \frac{j u}{V})$
 since, for dilute solutions,
 $j u \ll V$. Keep only
 1st term.

$$= -(N_2 \ln N_2 - N_2) + N_2 \ln K + N_2 \ln V - \frac{u}{V} \left(\sum_{j=0}^{N_2-1} j \right)$$

$$\sum_{j=0}^{N_2-1} j = 0 + 1 + 2 + 3 + 4 + \dots + N_2 - 1$$

$$= \sum_{j=1}^{N_2-1} j$$

look up this
 sum

$$\Rightarrow \frac{(N_2 - 1)(N_2)}{2}$$

We calculate it
 in 4010
 now!

$$\frac{S}{k} = -(N_2 \ln N_2 - N_2) + N_2 (\ln K + \ln V) - \frac{u}{V} \left(\frac{(N_2 - 1)(N_2)}{2} \right)$$

$$\approx \frac{N_2^2}{2}$$

Writing $N_2 = \sqrt{N} n_2$ and $V = n_1 \bar{V}_1 + n_2 \bar{V}_2$ (general)
 $\approx n_1 \bar{V}_1^0 + n_2 \bar{V}_2$ (dilute solution)

$$\Rightarrow \frac{S}{k} = -N \overset{*}{(n_2 \ln N n_2 - n_2)} + n_2 \overset{*}{N \ln K} \\ + n_2 N \ln (n_1 \bar{V}_1^0 + n_2 \bar{V}_2) - \frac{(N n_2)^2 u}{2 (n_1 \bar{V}_1^0 + n_2 \bar{V}_2)}$$

The $*$ terms will go away when we compute ΔS_{mix}

$$\Delta S_{mix} = S - \underbrace{S(@n_2=0)}_{\text{pure solvent}} - \underbrace{S(@n_1=0)}_{\text{pure solute}}$$

$$S(@n_2=0) = 0 \text{ (of course)}$$

$$S(@n_1=0) = -N \overset{*}{(n_2 \ln N n_2 - n_2)} + n_2 \overset{*}{N \ln K} \\ + n_2 N \ln (\cancel{n_1 \bar{V}_1^0} + n_2 \bar{V}_2) - \frac{(N n_2)^2 u}{2 (\cancel{n_1 \bar{V}_1^0} + n_2 \bar{V}_2)}$$

$$\neq 0$$

Amazing! Both solvent & solute are just little spheres. But

$S(\text{solvent}) = 0$ while $S(\text{solute})$ is not. What gives?

- It's an example of one of those hypothetical standard states
- in computing $S(@n_1=0)$ we are violating the dilute assumptions of the development. The $S(\text{solute})$ that we obtain is the entropy of a solvent-free system that is imagined to still obey this dilute equation for S .

$$\frac{\Delta S_{mix}}{k} = n_2 N \ln(n_1 \bar{V}_1^0 + n_2 \bar{V}_2) - n_2 N \ln(n_2 \bar{V}_2) - \frac{(n_2 N)^2 u}{2} \left[\frac{1}{n_1 \bar{V}_1^0 + n_2 \bar{V}_2} - \frac{1}{n_2 \bar{V}_2} \right]$$

$$\Rightarrow -n_2 N \ln\left(\frac{n_2 \bar{V}_2}{n_1 \bar{V}_1^0 + n_2 \bar{V}_2}\right) - \frac{(n_2 N)^2 u}{2} \left[\frac{-n_1 \bar{V}_1^0}{n_2 \bar{V}_2 (n_1 \bar{V}_1^0 + n_2 \bar{V}_2)} \right]$$

$$\frac{\Delta S_{mix}}{k} \Rightarrow -n_2 N \ln \phi_2 + \frac{(n_2 N)^2 u \phi_1}{2 n_2 \bar{V}_2}$$

$$\boxed{\frac{\Delta S_{mix}}{k} \Rightarrow -n_2 N \ln \phi_2 + \frac{n_2 N^2 u \phi_1}{2 \bar{V}_2}}$$

⊙ \div both sides by N to get

$$\boxed{\frac{\Delta S_{mix}}{R} = -n_2 \ln \phi_2 + \frac{n_2 N u \phi_1}{2 \bar{V}_2}}$$

$$\begin{aligned} \Delta G_{mix} &= \Delta H_{mix} - T \Delta S_{mix} \\ &= 0 + n_2 RT \ln \phi_2 - \frac{n_2 R u N T}{2 \bar{V}_2} \phi_1 \end{aligned}$$

$$\mu_1 - \mu_1^0 = \frac{d\Delta G_{mix}}{dn_1} = n_2 RT \frac{1}{\phi_2} \frac{d\phi_2}{dn_1} - \frac{n_2 R u N T}{2 \bar{V}_2} \frac{d\phi_1}{dn_1}$$

$$\text{Now... } \phi_2 = \frac{n_2 \bar{V}_2}{n_1 \bar{V}_1^0 + n_2 \bar{V}_2} \quad \frac{d\phi_2}{dn_1} = \frac{-n_2 \bar{V}_2 \bar{V}_1^0}{(n_1 \bar{V}_1^0 + n_2 \bar{V}_2)^2} \approx -\frac{\phi_2}{n_1}$$

$$\text{Then... } \frac{d\phi_1}{dn_1} = -\frac{d\phi_2}{dn_1} = \frac{+\phi_2}{n_1}$$

↑
because $\phi_1 = 1 - \phi_2$

$$\text{So... } \mu_1 - \mu_1^0 = n_2 RT \frac{1}{\phi_2} \left(\frac{-\phi_2}{n_1} \right) - \frac{n_2 R_u NT}{2 \bar{V}_2} \frac{\phi_2}{n_1}$$

$$\Rightarrow -\frac{n_2 RT}{n_1} - \frac{n_2}{n_1} \frac{R_u NT}{2} \left[\frac{\phi_2}{\bar{V}_2} \right]$$

$$\left[\frac{\left(\frac{n_2 \bar{V}_2}{n_1 V_1^0 + n_2 \bar{V}_2} \right)}{\bar{V}_2} \right] \approx \frac{n_2}{n_1 V_1^0}$$

$$\Rightarrow -\frac{n_2 RT}{n_1} - \frac{n_2^2}{n_1^2} \frac{R_u NT}{2 V_1^0}$$

~~but $n_2 \approx \frac{V}{V_1^0}$ so... $-\frac{n_2 RT V_1^0}{V} - \frac{n_2^2 V_1^0}{V^2} \frac{R_u NT}{2}$~~

The problem with this is that we may not know n_2 ; indeed, one purpose of the theory is to get Molecular weights so we could get n_2 . So, let's give the theory some grab handles.

$$\textcircled{1} \quad n_1 \approx \frac{V}{V_1^0} \quad \text{so } \mu_1 - \mu_1^0 \Rightarrow -\frac{n_2 RT V_1^0}{V} - \frac{n_2^2 V_1^0}{V^2} \frac{R_u NT}{2}$$

$$\textcircled{2} \quad n_2 = \frac{g_2}{M} \quad \text{so } \mu_1 - \mu_1^0 \Rightarrow -\frac{g_2 RT V_1^0}{M V} - \frac{g_2^2 V_1^0}{M^2 V^2} \frac{R_u NT}{2}$$

$$\textcircled{3} \quad \frac{g_2}{V} = c \text{ by definition, so finally}$$

$$\mu_1 - \mu_1^0 = -\frac{c RT}{M} V_1^0 - \frac{c^2}{M^2} V_1^0 \frac{R_u NT}{2}$$

The final grab handle is to replace μ with π

$$\pi = -\left(\frac{\mu_1 - \mu_1^0}{V_1^0}\right) = \frac{cRT}{M} + \frac{c^2 RT u \mathcal{N}}{M^2 2}$$

or...
$$\pi = cRT \left(\frac{1}{M} + \frac{c}{2M^2} u \mathcal{N} \right)$$

defini: $A_2 = 2^{\text{nd}} \text{ osmotic virial coefficient} = \frac{u \mathcal{N}}{2M^2}$

What is u for rigid ~~macromolecules?~~ macromolecules?

Sphere: $u = \frac{4}{3}\pi(2R)^3 = 8 \cdot \frac{4}{3}\pi R^3 = \frac{32\pi R^3}{3}$

$A_2 = \frac{N u}{2M_2} \Rightarrow \frac{16\pi R^3}{3} \frac{N}{M_2}$

* use osmometer to get size { If you knew M_2 from intercept of π/c vs. c plot and if you knew A_2 from slope, and if you knew particle was a sphere, you could calculate R

Can also write $\tilde{N}_2 = \left(\frac{\partial u}{\partial g_2}\right)_{T,P,g_1} \approx \frac{1}{S_2} = \frac{\frac{4}{3}\pi R^3}{\left(\frac{M}{N}\right)}$

So in the RHS above ~~we can use:~~ we can use:

$\frac{16\pi}{3} R^3 = 4 \cdot \frac{4}{3}\pi R^3 = 4\tilde{N}_2 \frac{M}{N}$ ~~$\frac{16\pi}{3} R^3 = 4\tilde{N}_2 \frac{M}{N}$~~

Note: $A_2 \downarrow$ as $M \uparrow$

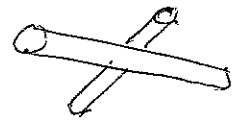
$A_2 = 4\tilde{N}_2 \left(\frac{M}{N}\right) \frac{N}{M_2} = \frac{4\tilde{N}_2}{M_2}$

$A_2 = \frac{4\tilde{N}_2}{M_2}$

Units $\left(\frac{ml}{gm}\right) = \frac{ml \text{ mol}}{gm^2}$
 $\left(\frac{gm}{mol}\right)$

Caution A_2 & B_2 are used interchangeably. Some books have $A_2 = 2B_2$

Calculation for rod much more difficult



What is excluded volume, averaged over orientations and relative distances?

Answer: Onsager, 1949

$$u = \frac{\pi d L^2}{2}$$

$$A_2 = \frac{N u}{2 M_2^2} = \frac{N \pi d L^2}{4 M_2^2}$$

indep. of $M_2!$
(Can use osmometer to tell shape of polymer solute!)

~~the A_2 is $\frac{N \pi d L^2}{4 M_2^2}$ in the book~~

Note that we can write this as: (multiply & divide by d)

$$A_2 = \frac{N \pi d L^2}{4 d M_2^2} = \frac{N \left(\frac{\pi d L^2}{4} \right) L}{d M_2^2}$$

$$= \frac{\text{rod (volume)} L}{d \left(\frac{M_2}{N} \right) M_2}$$

A rod mass

$$A_2 = \frac{\tilde{v}_2 L}{M_2 d}$$

This equation appears in Tomford

Again, you can estimate A_2 based on M_2 and \tilde{v}_2 and d (often, d is known).

You can also use to solve for d !

Calculation for flexible chain is deferred until later.

It is easier than rod (so we do it, not quote result) but hard enough that we will postpone until other stuff is ready.

Also... physicists (Theorists) don't like c .

Instead they like V , as in # density

$$\Pi = V k T (1 + A_{2,V} V + \dots)$$

Thermo 3-B. Enthalpic Systems

We are finally ready to allow that $\Delta H_{\text{mix}} \neq 0$ in most systems. In uncharged systems, this will often mean that we can include attractive terms between 2 polymers. Sometimes these can balance out the natural repulsive terms (leading to theta solvents). In charged systems, we can have big repulsive terms.

Our main goal is to fix up the Flory-Huggins treatment to include these ΔH_{mix} terms. To do that, we return to lattice picture.

Let V_{11} = energy of interaction of a pair of solvent molecules.

Sign convention: $V_{11} < 0$ means molecules attract.

V_{22} = energy of interaction of a pair of polymer SEGMENTS

V_{12} = interaction energy between solvent & solute.

Overall Goal: we can treat dissolution a bit like a reaction:



Immediate Goal: compute total energies of solvent, polymer & mixture.

Solvent:

$$U_{\text{solvent}} = \text{energy of solvent} = \frac{N_1 z}{2} \left[\phi_2 V_{12} + (1 - \phi_2) V_{11} \right]$$

Explanation: $\frac{N_1 z}{2}$ pairs to consider

ϕ_2 = probability of neighboring site containing polymer segment

V_{12} = energy associated with that occurrence

$1 - \phi_2$ = probability of neighboring site containing another solvent molecule

V_{11} = energy associated....

Polymer:

$$U_{\text{polymer}} = \frac{\sigma N_2 z}{2} \left[\phi_2 V_{22} + (1 - \phi_2) V_{12} \right]$$

(similar reasoning)

The total energy is then:

$$U = \frac{N_1 z}{2} [\phi_2 V_{12} + \phi_1 V_{11}] \\ + \frac{\sigma N_2 z}{2} [\phi_2 V_{22} + \phi_1 V_{12}]$$

$$\Delta U_{\text{mix}} = U - U(@N_1=0, \phi_2=1, \phi_1=0) - U(@N_2=0, \phi_2=0, \phi_1=1)$$

\downarrow $\frac{\sigma N_2 z}{2} V_{22}$ \downarrow $\frac{N_1 z V_{11}}{2}$

Group all the $\frac{N_1 z}{2}$ and $\frac{\sigma N_2 z}{2}$ terms together

$$\frac{N_1 z}{2} [\phi_2 V_{12} + V_{11} (\phi_1 - 1)] \\ + \frac{\sigma N_2 z}{2} [\underbrace{\phi_2 V_{22} - V_{22}}_{V_{22}(\phi_2 - 1)} + \phi_1 V_{12}]$$

i.e.

$$\Delta U_{\text{mix}} = \frac{N_1 z}{2} (\phi_2 V_{12} - \phi_2 V_{11}) \\ + \frac{\sigma N_2 z}{2} (\phi_1 V_{12} - \phi_1 V_{22})$$

But $N_1 = \phi_1 N_0$

$N_2 = \phi_2 N_0$

$$\Rightarrow \Delta U_{mix} = \frac{N_0 z}{2} \left\{ \begin{aligned} &\phi_1 [\phi_2 V_{12} - \phi_2 V_{11}] \\ &+ \phi_2 [2\phi_1 V_{12} - \phi_1 V_{22}] \end{aligned} \right\}$$

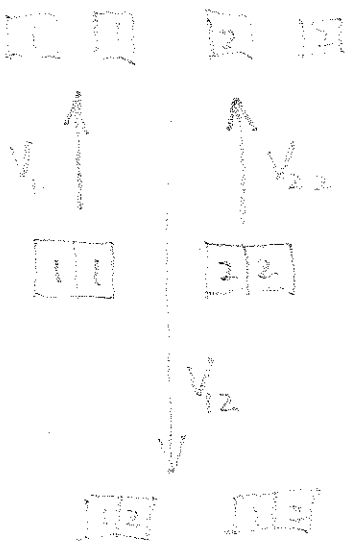
~~$$= \frac{N_0 z}{2} \phi_1 \phi_2 [2V_{12} - V_{11} - V_{22}]$$~~

joint probability that a pair of sites involves mixing of solvent & segment.

$$\Delta U_{mix} = \frac{N_0 z \phi_1 \phi_2}{2} [2V_{12} - V_{11} - V_{22}]$$

term due to interactions among 1,2 components in mixture

terms due to "breaking" solvent-solvent and solute-solute interactions



The meaning of $2V_{12} - V_{11} - V_{22}$ is related to Hess' law: take apart the solvent. Take apart the polymer segments. Put them together in mixture.

Interaction Parameter χ (also called β)

$$\text{let } \chi = \frac{z N_0 \phi_1 (2V_{12} - V_{11} - V_{22})}{2RTn_1} \quad \boxed{\text{eq. A}}$$

It is easily verified that

$$\Delta U_{\text{mix}} = RT\phi_2 \chi n_1$$

← Assign as exercise for Wed. Night at start of I.E.

χ has a simpler form, too.....

$$\text{let } \frac{1}{2}(2V_{12} - V_{11} - V_{22}) = \epsilon \quad \leftarrow$$

Has significance of energy of "site mixing"

use $N_0 \phi_1 = N_1$ in numerator of eq A

$Rn_1 = kN_1$ in denominator of eq A

$$\Rightarrow \chi = \frac{z\epsilon}{kT}$$

χ inversely proportional to temperature, if ϵ constant

Recall $H = U + PV$

$$\Delta H = \Delta U + \Delta(PV)$$

assume = 0

The consequence is that we should really treat χ as a free energy term. If we allow that χ is really a free energy term not associated with lattice mixing, ~~this~~ this assumption doesn't matter.

Then

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

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

↑ use Flory-Huggins result

$$\Delta G_{\text{mix}} = RT\phi_2 n_1 \chi - T[-R(n_1 \ln \phi_1 + n_2 \ln \phi_2)]$$

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

This is the full Flory-Huggins Eqn.
Remember, the entropy part is only valid at high concentrations.

Note that Z is gone - buried in χ .

The dimensionless χ interaction parameter was derived from the van Laar treatment of ΔU_{mix} , with assumptions about $\Delta(PV) = 0$. Flory knew this would only be approximate. For example, stuffing monomer segments and solvent into lattice cells of the same size may incur some entropy reductions. Also, solvent - monomer structure near the polymer, or the polymer may actually form entropy-reducing complexes with the solvent.

Thus, Flory knew that χ would not be purely enthalpic - e.g. it would not scale as $\frac{1}{T}$.

A whole formalism about this has actually evolved, and we shall introduce it briefly and then see how it came into existence later.

Forecast: The number $\frac{1}{2}$ appears a lot!

Ref: D.K. Carpenter, *Encyclopedia of Polymer Science & Engineering*
 Vol. 15, 2nd. ed. pp 419-482 (1989).

Flory knew the problem & proposed separation of χ into
 enthalpy + entropy parts.

(A)

$$\text{let } \chi = \kappa - \left(\psi - \frac{1}{2}\right) = \kappa - \psi + \frac{1}{2}$$

\uparrow enthalpy \uparrow entropy (both dimensionless)

(B)

also: define $\theta = \frac{\kappa T}{\psi} = \text{theta temp.}$

The condition $\psi = \frac{1}{2}$

Note: if $\psi = \frac{1}{2}$ then χ is purely enthalpic,
 meaning a clean separation between
 enthalpy & entropy in the
 Flory-H theory.

$$\chi = \kappa \text{ at } \psi = \frac{1}{2}$$

But $\kappa = \psi \frac{\theta}{T}$ so... at $\psi = \frac{1}{2}$!

$$\chi = \psi \frac{\theta}{T} = \frac{\theta}{2T}$$

Note also: if $T = \Theta$ then $\chi = \frac{1}{2}$.

Sneak Preview Special Things about $T = \Theta$

1) $\alpha \Rightarrow 1$

2) $A_2 \Rightarrow 0$

3) System is very near phase sep'n to form 2 liquid phases.

$\chi > \frac{1}{2}$ poor solvent

$\chi = \frac{1}{2}$ ideal (see above)

$\left\{ \chi < \frac{1}{2} \right.$ good solvent
including negative χ especially!

Now we must prove some of these things. Let's call this ~~the~~ next section:

"Brilliant Successes of FH Theory"