

FT Theory in  
2 hours

HPC warming demo  
 $\Delta S_{mix}$  plot  
FT.exe

Why we learn polymer thermo

- The equilibrium counterpart to dynamic phenomena.
- controls when polymers stay in solution - HPC demo
- guides/controls MWT determination
- polymer miscibility - how nice it would be to blend rather than synthesizing.

Start at ideal gas & get down the general method

1 = solvent  
2 = solute



$N = 3 \times 3$   
 $N_2 = 3$

p. 2

$$W = \frac{N}{N_2} \cdot \frac{N-1}{N_2-1} \cdot \frac{N-2}{N_2-2} \dots \text{etc.}$$

$$= \frac{N!}{N_2! N_1!}$$

Then  $S = +k \ln W = k [\ln N! - \ln N_2! - \ln N_1!]$

Use  $\ln N! = N \ln N - N$  Stirling Approximation

$\ln N!$  is extensive, but  $W$  is not  
That is why Boltzmann proposed  $k \ln W$ .

Now we want  $\Delta S_{mix} = S_{mixed} - S_{pure 1} - S_{pure 2}$

$$= k \ln S_{mixed} - k \ln(1) - k \ln(1)$$

$\downarrow$                        $\downarrow$   
 $0$                        $0$

} left as exercise  
↓

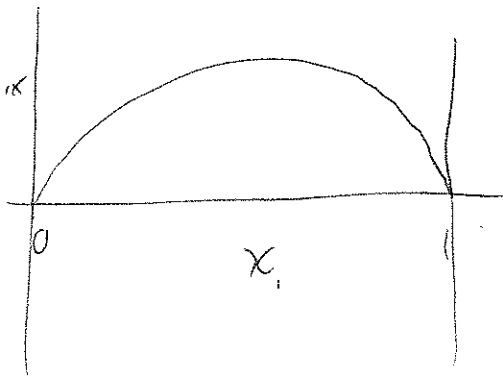
$$S = -k [N_1 \ln x_1 + N_2 \ln x_2]$$

where  $x = \text{mole fraction} = \frac{N_i}{N_1 + N_2}$

$$\equiv -k (N_1 + N_2) [x_1 \ln x_1 + x_2 \ln x_2]$$

$\Delta S_{\text{mix}} \equiv -R n [x_1 \ln x_1 + x_2 \ln x_2]$	$n = \text{moles total}$ $= \frac{N_1 + N_2}{N_{\text{Avogadro}}}$
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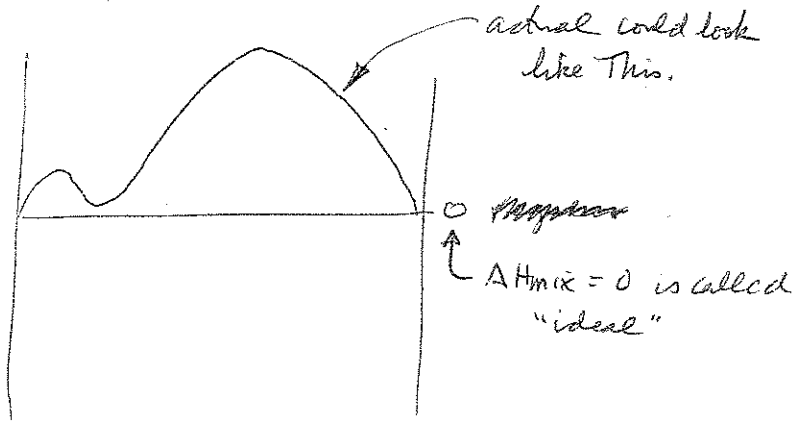
Plot This  $T\Delta S_{mix}$



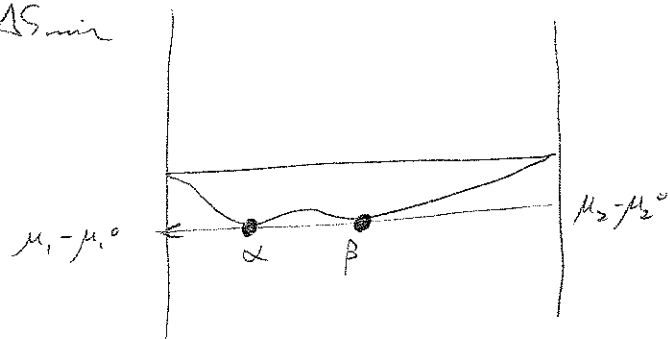
Everything should mix!

Why doesn't it?

$\Delta H_{mix}$



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



See partial Molar

Quantities, p. 8 of Thermo.

↖ Introduced with volume (partial molar volume)  
 but really we are after partial molar free energy a.k.a. chemical potential  
 a.k.a. "escape potential"

↖ The serious student will at this point look into Lewis Randall Pitzer & Brewer's text on Thermo. Yes, that Lewis.

We are going to assume  $\Delta H_{mix}$  is no weirder for polymers than regular solutions  $\Rightarrow$  "Regular Solution Theory"

So what to do about  $\Delta S_{mix}$ ?


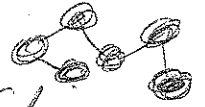
Consider Huggins' & Flory's landscape. Ideal gases have been patched up to include two small-molecule effects

Small Molecules are Nonideal Because:

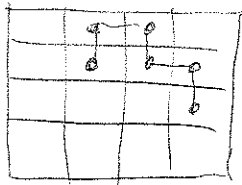
- 1. They have finite size
- 2. They may attract or repel

Large chains add to this connectivity - if we

think of our monomers as solutes then the solutes cannot be put any old place - must go near attached chains.

	Ideal	Small 	Chain 
size	N	Y	Y
attract-repel	N	Y	Y
connectedness	N	N	Y

Refer to Ch 12 VB (Virtual Book) p 3.4



$Z = 4$   
 $N_1 = 10$   
 $N_2 = 1$   
 $\sigma = 6$

$Z =$  site neighbors = 4 here (in 2D)

$N_1 =$  # solvent molecules

$N_2 =$  # chains

$\sigma N_2 =$  # monomers ( $\sigma =$  size = D.P.)

$N_0 =$  total lattice size =  $N_1 + \sigma N_2$

~~let~~

let  $W_{I+1} =$  # of ways to put in the ~~the~~  $(I+1)^{th}$  chain after  $I$  chains are in already.

let  $R_I = \frac{\sigma I}{N_0} =$  probability a given site is already occupied

( $1 - R_I =$  prot. a site is open)

Strategy: compute  $W_{I+1}$  for  $I = 0$  to  $I = N_2 - 1$   
 multiply all these together to get the total ways to put chains in lattice

Then  $\Delta S_{mix}$  as above.

I polymers already placed

⑥

1. Put in chain end first

$$\text{Ways} = (1 - r_I) N_0 = \text{ways to put chain end on}$$

2. Second segment

$$\text{Ways} = z(1 - r_I) \quad \text{Wow!}$$

Went down from  $(1 - r_I) N_0$  to  $z(1 - r_I)$

That's the huge effect of connectedness.

People who are married ~~and~~ understand this difference very well.

3. 3rd segment

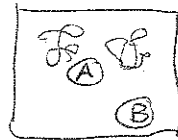
$$\text{Ways} = (z - 1)(1 - r_I)$$

4. 4th segment Same Thing

OK... what's wrong?

1. We are not adjusting  $r_I$  as each segment goes in. This is trivial.
2. We are assuming occupancy is  $r_I$  independent of where first segment goes. Not true in dilute solutions. FH Theory will be invalid for dilute solutions.

For a 3rd chain to go



in, the situation at (A) is different than at (B)

FH works when most of the chains go into an already-crowded lattice. IE when you "build" a conc. solution.

So for our  $(I+1)^{\text{th}}$  chain we have

$$W_{I+1} = N_0 (1-r_I) z (1-r_I) \left[ (z-1)(1-r_I) \right]^{\nu-2}$$

let  $z \approx z-1$   $\rightarrow$

$z$  should disappear anyway

$$\approx N_0 (1-r_I)^{\nu} (z-1)^{\nu-1}$$

$$\equiv N_0 \left( \frac{N_0 - \cancel{\nu} \nu I}{N_0} \right)^{\nu} (z-1)^{\nu-1}$$

But that's just one chain.

$$W_{\text{TOTAL}} = W_{\text{ALL CHAINS}} = \prod_{I=0}^{N_2-1} W_{I+1}$$

$N_2!$

degeneracy term: all chains are indistinguishable

(See Ch 12 notes, p. 3.9)

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

Then  $S = k \ln W_{TOT}$  as before

$$\Delta S_{mix} = k \ln W_{TOT, mix} - k \ln W_{TOT, \text{pure solvent}} - k \ln W_{TOT, \text{pure polymer}}$$

$\downarrow$  pure solvent  $\rightarrow 0$ 
 $\downarrow$  pure polymer  $\rightarrow ?$

\* See p. 3.11 to 3.14 where one sum is replaced by  $\int$

\* again use  $N \ln N \approx \ln N!$

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

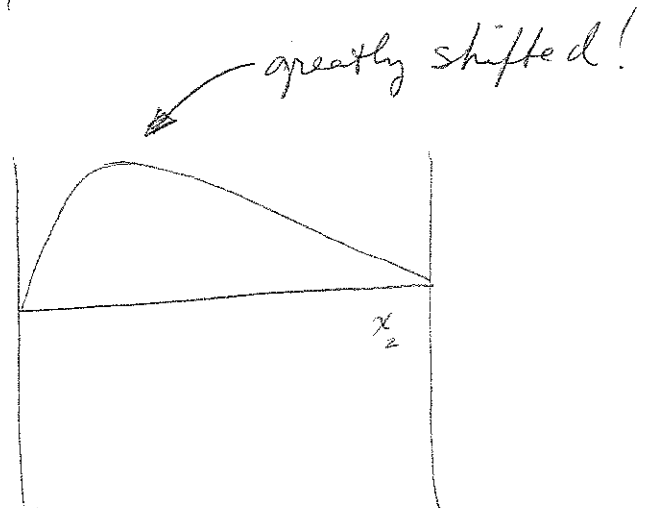
$$\phi_1 = \frac{N_1}{N_1 + \sigma N_2}$$

$$\phi_2 = \frac{N_2 \sigma}{N_1 + \sigma N_2}$$

like ideal gas!  
except  $\phi$  not  $x$

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

$$= -k N_0 \left\{ x_1 \ln \phi_2 + x_1 \ln \phi_1 \right\}$$



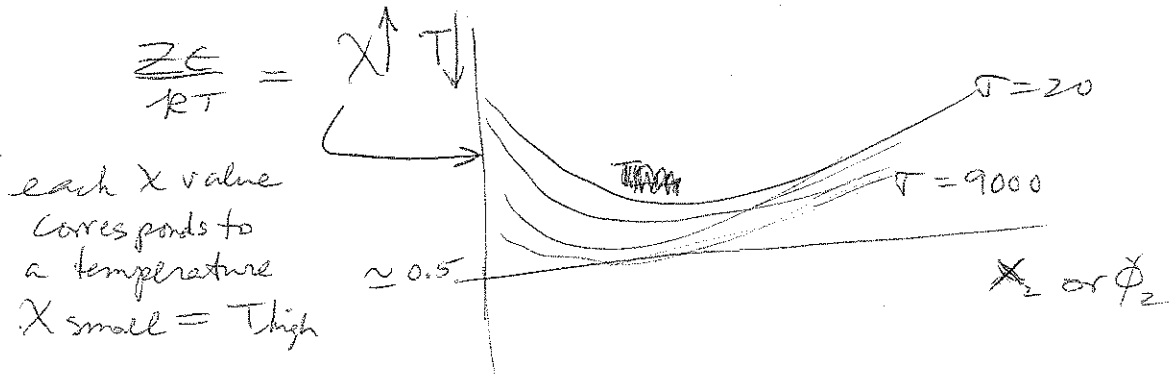
or... 
$$\Delta S_{mix} = -k(N_1 + \sigma N_2) \left\{ \frac{N_2}{N_1 + \sigma N_2} \ln \phi_2 + \frac{N_1}{N_1 + \sigma N_2} \ln \phi_1 \right\}$$

$$= -k N_0 \left\{ \frac{\phi_2}{\sigma} \ln \phi_2 + \phi_1 \ln \phi_1 \right\}$$

Show / Discuss F11. EXE



Note That  $X_{critical} = \frac{1}{2}$  @ large  $f$  polymers



$\epsilon =$  site mixing energy

$\epsilon > \frac{1}{2} kT$  means there is enough badness to the solvent that a large chain will begin to stick to itself, forming a concentrated phase ( $\beta$ ). Because you have skewed the phase diagram so much, the other phase ( $\alpha$ ) contains only a little polymer.

You can think of  $X_{crit}$  as how much badness it takes to rob the chains of enough entropy of mixing that they prefer not to mix uniformly in space, but form one phase with almost no polymer & another with lots.