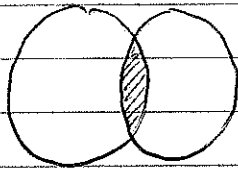


Flory-Krigbaum Theory patches up the M dependence of A_2

Ref. Richards 3.17

Yamakawa Ch. 4



1) $\Delta G_{\text{overlap}} = \Delta G(2\phi_2, \text{internal}) - 2\Delta G(\phi_2, \text{whole})$

2) lens-like geometry to get the overlap volume

3) Assumptions about segment distribution at periphery

4) "Introduce" interpenetration parameters"

\Downarrow

$A_2 \sim M^{-0.2}$ in good solvents
in agreement with experiments.

A_2 still $\propto (\frac{1}{2} - \chi)$ so $\rightarrow 0$ at $\chi = \frac{1}{2}$

(chains can't interpenetrate)

Perturbation Theories - extend small molecule

Two-parameter Theories - e.g. Yamakawa

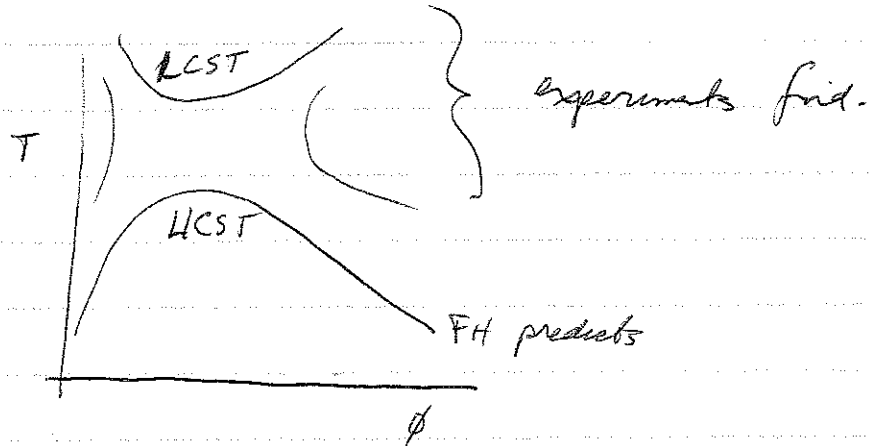
(any theory with short range (ζ_0) and long range (α^2))

V.V. Simple proof of $A_2 \sim M^{-0.2}$

$$A_2 \sim \frac{N u}{2M^2} \xrightarrow[\text{constants}]{\text{ignore}} \frac{R_g^3}{M^2} \rightarrow \frac{(M^{0.6})^3}{M^2} = M^{-0.2}$$

from simple deGennes argument
found in Chen 4810

Additional failure of FH model (Painter & Coleman)



Why FH misses the LCST is the assumption that segment/solvent sizes ~~and~~ neglect free volume. Of course, there is free volume, and the temp. dependence of it ~~varies~~ differs polymers vs. solvents.

Two kinds of models try to deal with this: one has physical insight and much math; the other has trial & error approach.

~~Why FH misses the LCST is the assumption that segment/solvent sizes and neglect free volume.~~

Sometimes people write $\chi = a + \frac{b}{T}$ (Patterson, 1970)

A look at polymer solutions.

$$\Delta G \Rightarrow RT \left(\frac{\phi_A}{\nu_A} \ln \phi_A + \frac{\phi_B}{\nu_B} \ln \phi_B + \phi_A \phi_B \chi \right)$$

If ν_A & ν_B are both large, the entropic contribution is made smaller. This results in enhanced importance of the enthalpic terms. ~~Especially~~, for any positive χ mixing will be much less favorable, so it is hard to get polymers to mix. Enormous consequences - e.g. for polymer recycling.

FH 85 18

Also, if one does find missile blands That is very special.

Solubility Parameters

We have seen that χ can be measured by osmometer.
 But we may wish to identify or estimate when
 a good solvent ($\chi \leq 0$) condition exists... without experimenting.

Recall that $\chi = \frac{z\epsilon}{kT}$

where $\epsilon = \frac{1}{2} (2E_{12} - E_{11} - E_{22})$

Switch to enthalpy (ignore entropy)

$\Rightarrow h = \frac{1}{2} (2H_{12} - H_{22} - H_{11})$

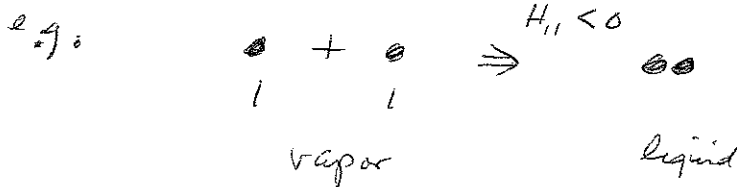
Big approximation

Use geometric mean (Hildebrand) approximation

$H_{12} = \sqrt{H_{22} H_{11}}$

Then (try it!) $h = \frac{1}{2} (\sqrt{-H_{11}} + \sqrt{-H_{22}})^2$

(H_{11} and H_{22} must be < 0 which makes sense @ They are combination energies)



Let $H_{11} \propto -\Delta H_{vap, 1}$

$H_{22} \propto -\Delta H_{vap, 2}$

define: $\delta_1 = \text{"solubility parameter"} = \sqrt{\frac{\Delta H_{vap, 1}}{V_1^0}}$ } Widely tabulated!
 or calculate:
 $\delta \approx \frac{\rho}{M_0} \sum_i G_i$

Then $h \approx (\delta_1 - \delta_2)^2 = 0$ @ $\delta_1 = \delta_2$

$\chi \approx 0$ (ignoring entropy!) at $\delta_1 = \delta_2$

↑ sum over atoms in monomer.