Brilliant FH Success #1 : Phase Sep'n

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

$$\frac{\partial}{\partial n_1} \Delta G_{mix} = \mu_1 - \mu_1^\circ$$

Need: $\dfrac{\partial \phi_1}{\partial n_1} = \dfrac{\partial}{\partial n_1}\left[\dfrac{n_1}{n_1 + \sigma n_2}\right] = \dfrac{\phi_2}{n_1 + \sigma n_2}$

Ask them to prove it

$$\frac{\partial \phi_2}{\partial n_1} = \frac{\partial}{\partial n_1}\left[\frac{\sigma n_2}{n_1 + \sigma n_2}\right] = \frac{-\phi_2}{n_1 + \sigma n_2}$$

☆ The result is: $\mu_1 - \mu_1^\circ = RT\left[\ln(1-\phi_2) + \phi_2\left(1 - \frac{1}{\sigma}\right) + \chi \phi_2^2\right]$

This equation has the partner $\mu_2 - \mu_2^\circ = RT\left[\ln \phi_2 + (1-\phi_2)(1-\sigma) + \chi\sigma(1-\phi_2)^2\right]$

Phase Sep'n. occurs when 2 compositions exist at which μ_1 <u>and</u> μ_2 are the same in both phases.

e.g. $\mu_1^\alpha = \mu_1^\beta$

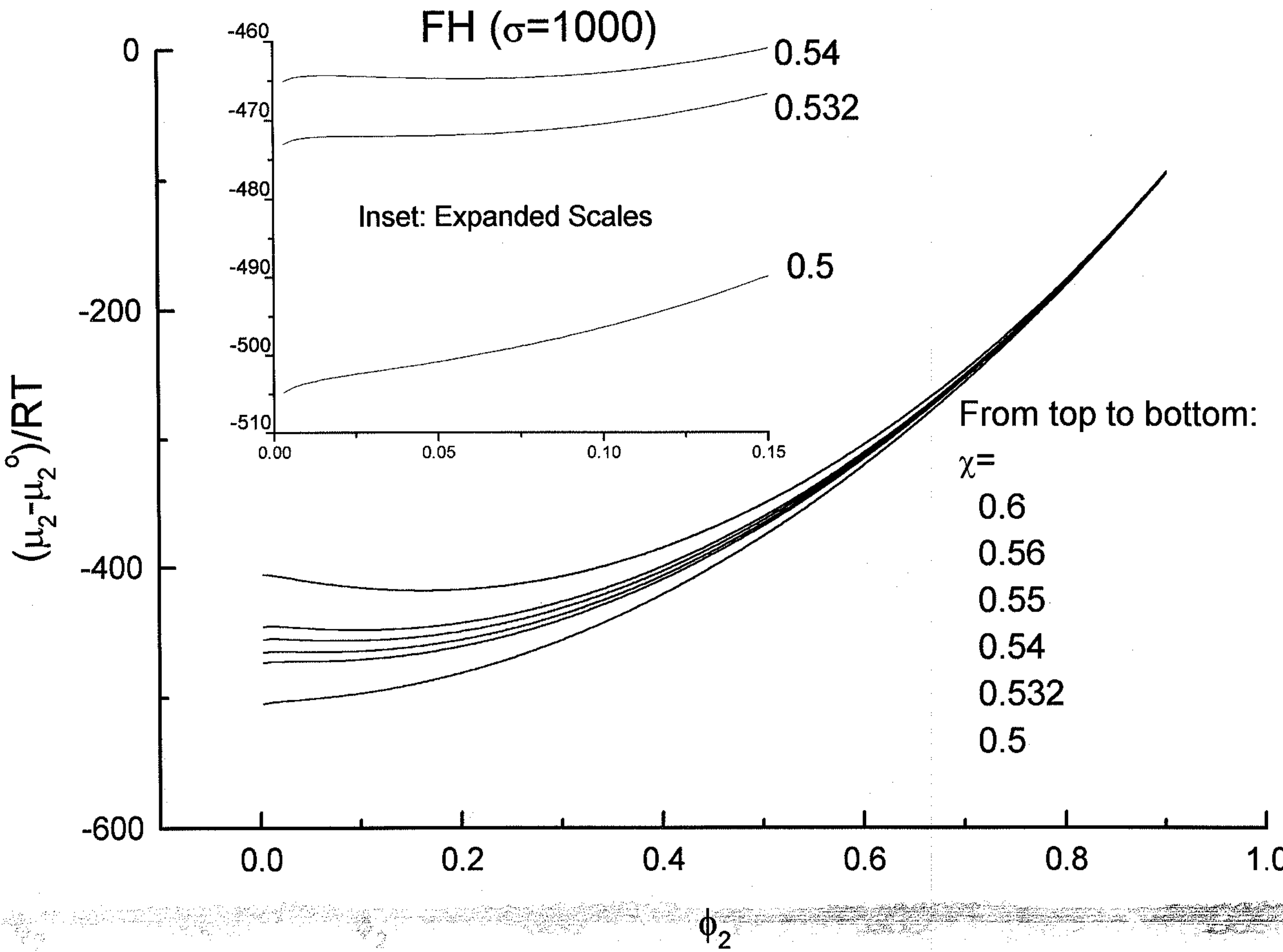
$\mu_2^\alpha = \mu_2^\beta$

The following plots show that this happens only above a certain χ_{crit}. Now we develop the theory.

☆ Try as an exercise!

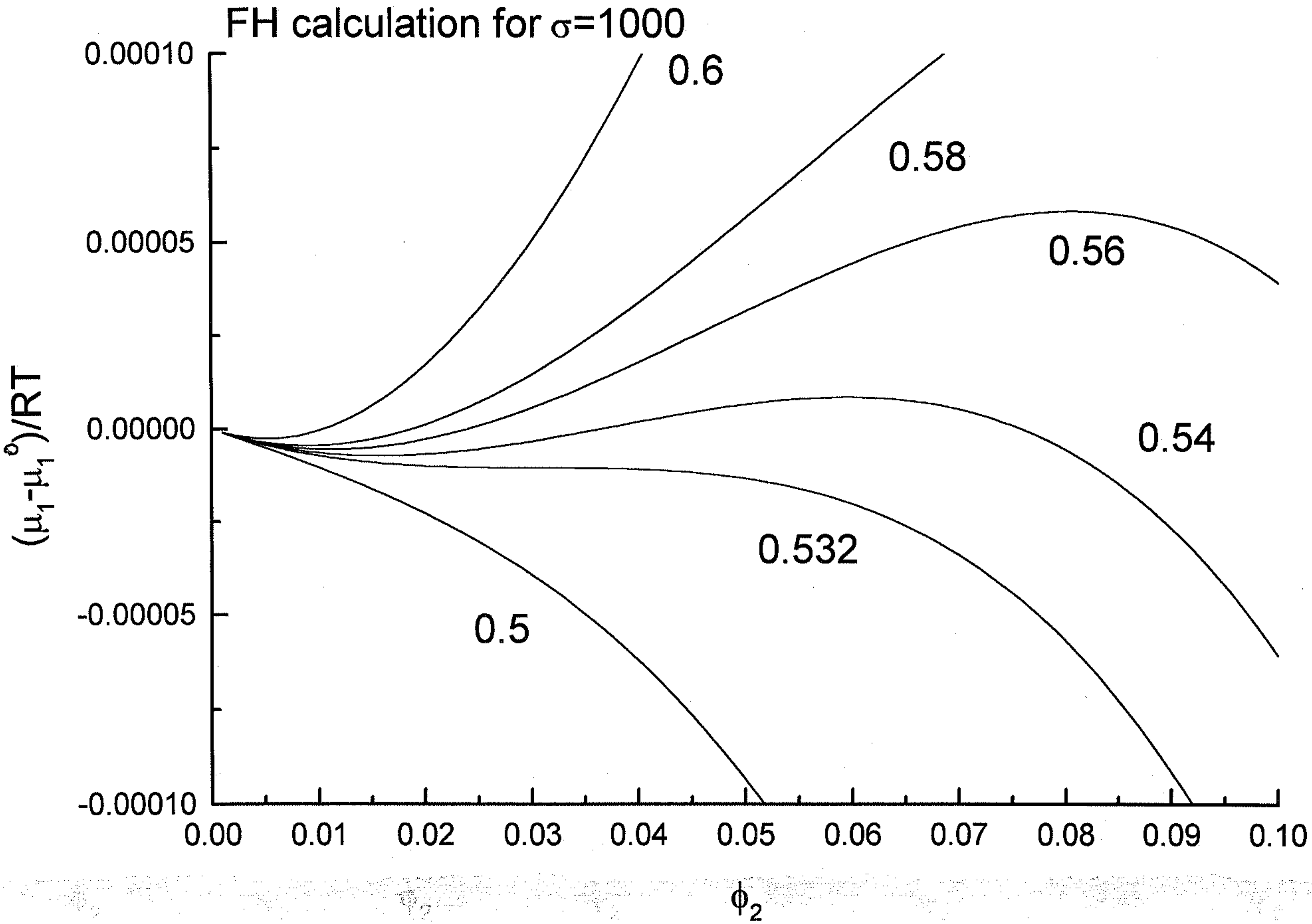
FH65, 2

4595--FHmu.opj



FHB 5.3

4595--FHM[illegible]pj



Old Flory p. 544

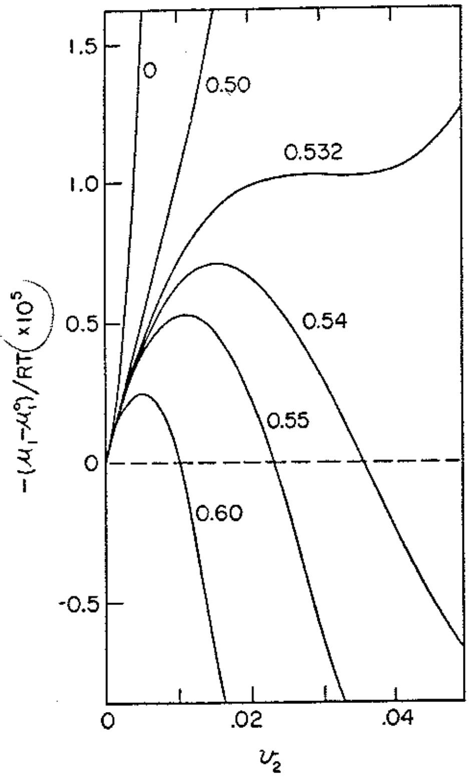


FIG. 120.—The chemical potential of the solvent in a binary solution containing polymer at low concentrations (v_2). Curves have been calculated according to Eq. (XII-26) for $x=1000$ and the values of χ_1 indicated with each curve.[1]

Can we find the critical condition?

$$\mu_1 - \mu_1^0 = RT\left[\ln(1-\phi_2) + \phi_2\left(1-\frac{1}{\sigma}\right) + \chi\phi_2^2\right]$$

Occurs at $\dfrac{\partial\mu_1}{\partial\phi_2} = 0 = \dfrac{\partial^2\mu_1}{\partial\phi_2^2}$

$\dfrac{d\mu_1}{\partial\phi_2} \Rightarrow \quad \dfrac{1}{1-\phi_2}(-1) + \left(1-\dfrac{1}{\sigma}\right) + 2\chi_{crit}\phi_2 = 0 \qquad$ A

$\dfrac{d^2\mu_1}{\partial\phi_2^2}$ and $\quad \dfrac{-1}{(1-\phi_2)^2} + 2\chi_{crit} = 0 \qquad$ B

$\Rightarrow \chi_{crit} = \dfrac{1}{2(1-\phi_2)^2} = \dfrac{1}{2\phi_{1,crit}^2} \qquad$ C

Put (C) into (A)

$$-\frac{1}{\phi_1} + \left(1 - \frac{1}{\sigma}\right) + \cancel{2}\left(\frac{1}{\cancel{2}\phi_1^2}\right)\phi_2 = 0$$

$$\Downarrow$$

$$\frac{1}{\phi_1} - \left(\frac{\sigma-1}{\sigma}\right) - \frac{\phi_2}{\phi_1^2} = 0$$

Multiplying thru by ϕ_1^2 $\Rightarrow$

$$\phi_1 - \phi_1^2\left(\frac{\sigma-1}{\sigma}\right) - \phi_2 = 0$$

or.....

$$\phi_1^2\left(\frac{1-\sigma}{\sigma}\right) + \phi_1 - \phi_2 = 0$$

$$\boxed{\phi_2 = 1 - \phi_1}$$

$$\Rightarrow \quad \phi_1^2\left(\frac{1-\sigma}{\sigma}\right) + 2\phi_1 - 1 = 0$$

1ST GUESS AT SOLUTION

MAYBE SKIP

let σ = very large

$$\Rightarrow \quad -\phi_1^2 + 2\phi_1 - 1 = 0 \Rightarrow \phi_1^2 - 2\phi_1 + 1 = 0$$

$$\Rightarrow \quad (\phi_1 - 1)^2 = 0 \Rightarrow \boxed{\phi_{1,crit} \approx 1} \xrightarrow[\text{eq. C}]{\text{Plug into}} \boxed{\chi_{crit} \approx 1/2}$$

In more exact form, we leave in $\left(\frac{1-\sigma}{\sigma}\right)$ and write:

$$\phi_1^2\left(\frac{1-\sigma}{\sigma}\right) + 2\phi_1 - 1 = 0$$

$$\phi_{1,crit} = \frac{-2 \pm \sqrt{4 + 4\left(\frac{1-\sigma}{\sigma}\right)}}{2\left(\frac{1-\sigma}{\sigma}\right)}$$

$$= \frac{-2 \pm 2\sqrt{1 + \frac{1-\sigma}{\sigma}}}{\frac{2(1-\sigma)}{\sigma}}$$

$$= \frac{-2\sigma \pm 2\sigma\sqrt{\frac{1}{\sigma}}}{2(1-\sigma)}$$

$$\phi_{1,crit} = \frac{-\sigma \pm \sqrt{\sigma}}{1-\sigma} = \frac{\sigma \pm \sqrt{\sigma}}{\sigma - 1}$$

$\phi_{1,crit}$ <u>cannot</u> be >1, so choose $(-)$ term only

$$\boxed{\phi_{1,crit} = \frac{\sigma - \sqrt{\sigma}}{\sigma - 1}}$$

$$\phi_{2,crit} = 1 - \phi_{1,crit} = 1 - \frac{\sigma - \sqrt{\sigma}}{\sigma - 1} = \frac{\cancel{\sigma} - 1 - \cancel{\sigma} + \sqrt{\sigma}}{\sigma - 1}$$

$$\boxed{\phi_{2,crit} = \frac{\sqrt{\sigma} - 1}{\sigma - 1}}$$

But $\sigma - 1 = (\sqrt{\sigma}-1)(\sqrt{\sigma}+1)$

So... $\phi_{2,crit} = \dfrac{\sqrt{\sigma}-1}{(\sqrt{\sigma}-1)(\sqrt{\sigma}+1)} = \dfrac{1}{\sqrt{\sigma}+1}$

* easily remembered $\boxed{\phi_{2,crit} \simeq \dfrac{1}{\sqrt{\sigma}}}$ D

Put D into C

$$\chi_{crit} \simeq \frac{1}{2\left(1-\frac{1}{\sqrt{\sigma}}\right)^2} = \frac{\sigma}{2(\sqrt{\sigma}-1)^2} \quad *$$

If instead put $\phi_{2,crit} = \dfrac{1}{\sqrt{\sigma}+1}$ into C then you get a more accurate estimate:

$$\chi_{crit} = \frac{1}{2(1-\phi_{2,crit})^2} = \frac{1}{2\left(1-\frac{1}{\sqrt{\sigma}+1}\right)^2} = \frac{1}{2\left(\frac{\sqrt{\sigma}}{\sqrt{\sigma}+1}\right)^2}$$

$$\chi_{2,crit} = \frac{(\sqrt{\sigma}+1)^2}{2\sigma}$$

---

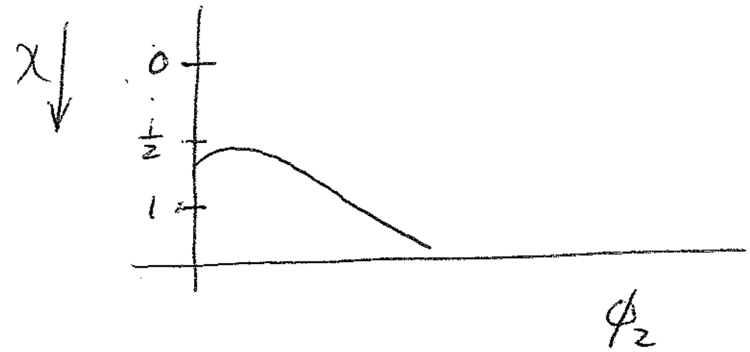
* This equation doesn't exactly match Hiemenz because our eq. D is approximate.

Now typically $\sigma \simeq 100$ or more

So... $\phi_{2,crit} \simeq 0$

$\chi_{crit} \simeq \frac{1}{2}$ (aha! we predicted we would see this $\frac{1}{2}$ business!)

So.... phase boundary is shifted to low ϕ_2



- The great shift to low ϕ_2 matches experiment: a brilliant success.

- Recall that $\chi \leq 0$ corresponds to good solvents. Polymers don't phase separate until χ becomes quite positive $(+\frac{1}{2})$. Reason is that it takes considerable "badness" to quench out all that configurational entropy. One could guess (correctly) that rigid polymers do not tolerate such high χ values – i.e. they phase separate at $\chi \simeq 0$.

- By inference, any rodlike polymer (of real size & genuine stiffness) that has dissolved has done so in a good solvent.

- Since χ_{crit} depends on σ, you can fractionate polymers!

Brilliant Success #2 : α^2 revisited

Recall we already did an α^2 calculation de Gennes style. That calculation gave us the good solvent limit (i.e. $\nu = 3/5$) but made no connection to thermodynamics.

Feynman: any important problem can be solved several ways... one of which should be simple. The de Gennes approach is simple. Now we do something a bit harder. We should again get $\nu = 3/5$ BUT also thermo info.

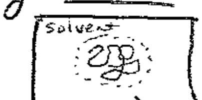
2 heroes

The following calculation is due to S. Prager. Some years after he did this (w/o notes, as always) in our polymer physics class, a paper appeared by another author: See E.A. De Marzio, Macromolecules 1984, 17, 969. (as cited in the Painter & Coleman text).

General idea: treat a single polymer coil as a small chunk of solution. Knowing the volume of that solution we connect $\langle r^2 \rangle$ to thermodynamics.

1) Imagine a polymer to be the very first one placed on a lattice.

2) After polymer is placed, let us put a confining balloon around it, or a loose "sac"



3) Polymer must stay in the sac; solvent can permeate it.

On average, the dimensions of the polymer are those of the sac. But we choose the sac to have dimensions that are not too restrictive – i.e. about $\sqrt{\langle r^2 \rangle}$

Strategy

1) Calculate ΔG_{mix} for polymer constrained this way, as a function of r_{sac}
2) Minimize to find equilibrium

Compute # of configurations:

<u>Consider unbagged chain</u>

$$W \simeq N_0 z (z-1)^{\sigma - 2}$$

{ assume $R_I = 0$ in Flory-Huggins Calculation since this is first chain on lattice }

Now, W counts <u>ALL</u> possible configurations, including some that won't fit in bag. We want a <u>reduced</u> count, W_R = # configurations subject to constraint that $\sqrt{\langle r^2 \rangle} = R$. This also ensures molecule is in an internally concentrated enough form that FH will work.

penalizes conformations that are larger than σl^2

$$W_R = P(R)\, W \sim e^{\boxed{\frac{-3R^2}{2\sigma l^2}}} N_0 z(z-1)^{\sigma-2}$$

$$S_r = k \ln W_r = \underbrace{-\frac{3}{2}\frac{R^2}{\sigma l^2}}\; + \left\{ \begin{array}{l} \text{Usual Flory} \\ \text{Huggins Result} \\ \text{which should be} \\ \text{valid inside the chain,} \end{array} \right\}$$

as $\phi_{2,\text{internal}}$ is large

i.e., entropy is <u>reduced</u> because we constrain the molecule so it can't have all possible conformations, but only those where rms end to end length = R.

$$\frac{\Delta G_{mix}}{kT} = \frac{3}{2}\frac{r^2}{\sigma l^2} + \underbrace{\left[N_1 \ln \phi_1 + N_2 \ln \phi_2 + \chi N_1 \phi_2 \right]}$$

N_i are molecules not moles

$\Rightarrow$ this term is $\dfrac{\Delta G_{FLORY-HUGGINS}}{kT}$

Now minimize w/res. r:

$\Rightarrow$ FIRST TERM IS EASY

$\Rightarrow$ 2ND TERM CAN BE DONE BY CHAIN RULE

$$\frac{\partial}{\partial r} = \frac{\partial N_1}{\partial r} \frac{\partial}{\partial N_1}$$

Taking $\dfrac{\partial}{\partial N_1}\left(\dfrac{\Delta G_{FH}}{kT}\right)$ will give same answer as $\dfrac{\partial}{\partial m_1}\left(\dfrac{\Delta G_{FH}}{RT}\right)$ which we obtained already: $\dfrac{\mu_1 - \mu_1^\circ}{RT} = \ln(1-\phi_2) + \phi_2\left(1 - \frac{1}{\sigma}\right) + \chi \phi_2^2$

$$\Rightarrow 0 = \frac{3r}{\sigma l^2} + \left(\frac{\partial N_1}{\partial r}\right)\left(\ln(1-\phi_2) + \phi_2\left(1-\frac{1}{\sigma}\right) + \chi\phi_2^2 \right)$$

$V_{sac} \approx \frac{4}{3}\pi r^3$

V of solvent $= (1-\phi_2) V_{sac}$

$$\Rightarrow \boxed{N_1 = \frac{(1-\phi_2)\,\frac{4}{3}\pi r^3}{(V_1^\circ / N)}} = \frac{\text{volume of solvent in sac}}{\text{volume per molecule of solvent}}$$

Thus $\dfrac{\partial N_1}{\partial r} = \dfrac{(1-\phi_2)\,4\pi r^2}{(V_1^0/N)} \simeq \dfrac{4\pi r^2}{V_1^0/N}$

$$\therefore \quad 0 = \frac{3r}{\sigma l^2} + \frac{4\pi r^2}{(V_1^0/N)}\left[\ln(1-\phi_2) + \phi_2\left(1-\frac{1}{\sigma}\right) + \chi\phi_2^2\right]$$

$$0 \simeq \frac{3r}{\sigma l^2} + \underbrace{\frac{4\pi r^2}{(V_1^0/N)}}\underbrace{\left[\cancel{-\phi_2} - \frac{\phi_2^2}{2} + \cancel{\phi_2} - \frac{\phi_2}{\sigma} + \chi\phi_2^2\right]}_{\phi_2\left\{\phi_2\left(\chi-\frac{1}{2}\right)-\frac{1}{\sigma}\right\}}$$

now $\phi_2 = \dfrac{\sigma(V_1^0/N)}{\frac{4}{3}\pi r^3} = \dfrac{\text{volume of } \sigma \text{ polymer segments}}{\text{volume of sac}}$

rearrange: $\dfrac{4\pi r^2}{(V_1^0/N)} = \dfrac{3\sigma}{\phi_2 r}$

$$\therefore \quad 0 \simeq \frac{3r}{\sigma l^2} + \frac{3\sigma}{\cancel{\phi_2} r}\left[\cancel{\phi_2}\left\{\phi_2\left(\chi-\frac{1}{2}\right)-\frac{1}{\sigma}\right\}\right]$$

$$0 \simeq \frac{3r}{\sigma l^2} + \frac{3\sigma}{r}\left(\phi_2\left(\chi-\frac{1}{2}\right)-\frac{1}{\sigma}\right)$$

Now use $\phi_2 = \dfrac{\sigma(V_1^0/N)}{\frac{4\pi R^3}{3}}$ again & expand

$$0 \simeq \frac{3r}{\sigma l^2} + \frac{9\sigma}{r}\left(\frac{\sigma(V_1^0/N)}{4\pi r^3}\right)\left(\chi-\frac{1}{2}\right) - \frac{3}{r}$$

remove all r's from denominator } $\boxed{\frac{9}{4\pi}\frac{v_c}{N}}$
(mult. by r^4

$$\Rightarrow 0 = \frac{3r^5}{\sigma l^2} + K\sigma^2\left(\chi - \tfrac{1}{2}\right) - 3r^3$$

$$\text{Now } r^2 = \alpha^2 \sigma l^2$$
$$r^5 = \alpha^5 \left(\sigma l^2\right)^{5/2}$$
$$r^3 = \alpha^3 \left(\sigma l^2\right)^{3/2}$$

$$\Rightarrow \quad 3\alpha^5 \left(\sigma l^2\right)^{3/2} + K\sigma^2\left(\chi - \tfrac{1}{2}\right) - 3\alpha^3\left(\sigma l^2\right)^{3/2} = 0$$

$\div$ both sides by $3(\sigma l^2)^{3/2}$ $\Rightarrow$ $$\alpha^5 - \alpha^3 = \frac{-K\sigma^2\left(\chi - \tfrac{1}{2}\right)}{3\left(\sigma l^2\right)^{3/2}}$$

absorb "3" into K and l^3 $\Rightarrow$ $K' \sigma^{1/2} \left(\tfrac{1}{2} - \chi\right)$

OBSERVATION #1

At large σ, $\alpha^5 \gg \alpha^3$, so.....

$$\alpha^5 \sim \sigma^{1/2}$$

$$\Rightarrow \boxed{\alpha \sim \sigma^{1/10} = \sigma^{0.1}}$$

Consistent with de Gennes "spring"/"repulsion" approach

e.g. Suppose $\alpha = 2$
$\frac{2^5}{2^3} = \frac{32}{8} \simeq 4$
if $\alpha = 3$
$\frac{3^5}{3^3} = \frac{243}{27} \approx 9$

Virial coefficient in FH formulation: finding $\chi = \frac{1}{2}$

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

Compute $\mu_1 - \mu_1^\circ$ from $\frac{\partial}{\partial n_1}$

$$\Rightarrow \quad \mu_1 - \mu_1^\circ = RT\left[\ln(1-\phi_2) + \phi_2\left(1 - \frac{1}{\sigma}\right) + \chi \phi_2^2\right]$$

use $\ln(1+x) \simeq x - \frac{x^2}{2} + \dots$

$$\Rightarrow RT\left[-\phi_2 - \frac{\phi_2^2}{2} + \phi_2 - \frac{\phi_2}{\sigma} + \chi \phi_2^2\right]$$

group ϕ_2 & ϕ_2^2 terms

take out − sign $\Rightarrow$ $-RT\left[\frac{\phi_2}{\sigma} + \phi_2^2\left(\frac{1}{2} - \chi\right)\right]$

$$= -RT\phi_2\left[\frac{1}{\sigma} + \phi_2\left(\frac{1}{2} - \chi\right)\right]$$

Convert ϕ_2 to c_2

$$\phi_2 = \frac{\sigma n_2}{\sigma n_2 + n_1} \simeq \frac{\sigma n_2}{n_1} = \frac{\sigma g_2}{n_1 M_2} = \frac{\sigma g_2}{\left(\frac{V}{V_1^\circ}\right) M_2} = \frac{\sigma c_2 V_1^\circ}{M_2}$$

$$n_2 = \frac{g_2}{M_2}$$

$$n_1 V_1^\circ = V$$

$$g_2/V = c_2$$

$$\Rightarrow \quad \mu_1 - \mu_1^\circ = -RT c_2 V_1^\circ\left[\frac{1}{M_2} + \frac{\sigma^2 V_1^\circ}{M_2^2}\left(\frac{1}{2} - \chi\right) c_2\right]$$

Thus, $$A_2 = \frac{\sigma^2 V_1^\circ}{M_2^2}\left(\tfrac{1}{2} - \chi\right)$$

Now $\sigma V_1^\circ = \overline{V_2}$

and $\dfrac{\overline{V_2}}{M_2} \cong \tilde{v}_2$

So $$A_2 = \frac{(\tilde{v}_2)^2}{V_1^\circ}\left(\tfrac{1}{2} - \chi\right) = 0 \quad @ \ \chi = \tfrac{1}{2}$$

Note that if $\chi = 0$, A_2 is positive: repulsion

$\chi \ll 0$, A_2 gets large: ionic interaction in polyelectrolytes might cause this.

As usual, use $\pi = \dfrac{-(\mu - \mu_1^\circ)}{V_1^\circ}$

$$\frac{\pi}{c} = RT\left[\frac{1}{M} + \underbrace{\left(\tfrac{1}{2} - \chi\right)\frac{\tilde{v}_2^{\,2}}{V_1^\circ}}_{A_2} c + \cdots\right]$$

Note: this predicts A_2 independent of M.
Recall that this is the same as rods, while spheres gave $A_2 = \dfrac{4\tilde{v}_2}{M} \simeq M^{-1}$

☆ Turns out that experiments show $A_2 \sim M^{-0.2}$

– The first big failure of FH