Solutions

Chem 664 **Problem Set #7** (to) **Due: November 11, 2002**

A. Graph P_1/P_1^o vs. ϕ_1 for $\chi_1 = 0, 0.25, 0.50, 0.75$ and 1.0 at $N=100$ and at $N=1000$. Overlay on each of the two graphs that of ideal solution prediction, given by (2)

$$P_1 / P_1^o = \phi_1 \cdot \exp\left[(1-\frac{1}{N})(1-\phi_1) + \chi_1 (1-\phi_1)^2 \right] \tag{1}$$

$$P_1 / P_1^o = X_1 = \frac{N\phi_1}{N\phi_1 + (1-\phi_1)} \tag{2}$$

B. Plot $-\frac{\mu_1 - \mu_1^o}{RT}$ vs. ϕ_2 for a range of $0 \le \phi_2 \le 0.05$ for $\chi_1 = 0, 0.50, 0.532, 0.54, 0.55$ and 0.56 at $N=1000$. Find the inflection point by setting

$$\left(\frac{\partial \mu_1}{\partial \phi_1}\right)_{T,P} = 0, \text{ and} \left(\frac{\partial^2 \mu_1}{\partial {\phi_1}^2}\right)_{T,P} = 0$$

and determine $\chi_{1,C}$ and $\phi_{2,C}$ at the inflection point.

$$-\frac{\mu_1 - \mu_1^o}{RT} = -[\ln(1-\phi_2) + (1-\frac{1}{N})\phi_2 + \chi_1\phi_2^2] \tag{3}$$

C. 3.15

D. 3.18

E. 3.21

F. 3.24

G. 3.25

H. 3.26

I. 3.27

A.

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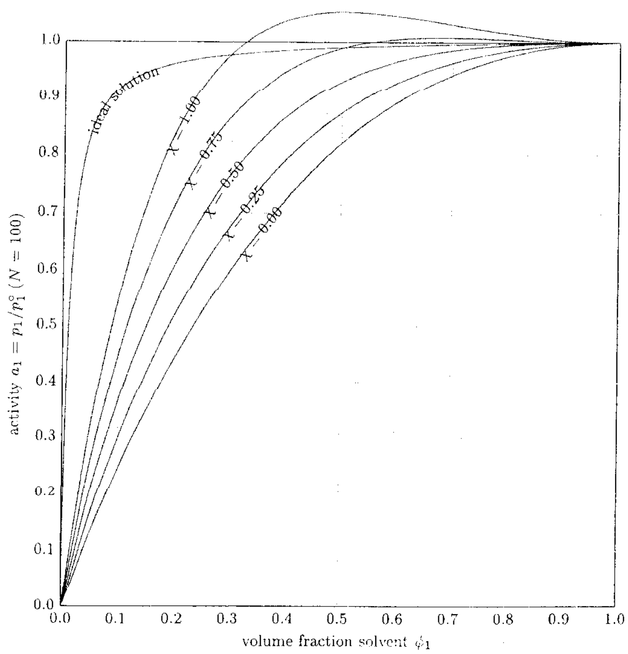
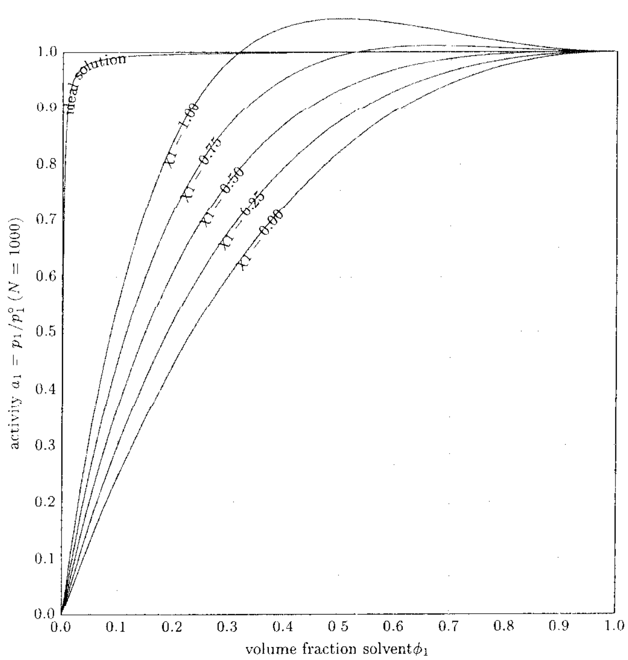


ideal solution
χ = 1.00
χ = 0.75
χ = 0.50
χ = 0.25
χ = 0.00
activity $a_1 = p_1/p_1^\circ$ ($N = 100$)
volume fraction solvent ϕ_1



ideal solution
χ1 = 1.00
χ1 = 0.75
χ1 = 0.50
χ1 = 0.25
χ1 = 0.00
activity $a_1 = p_1/p_1^\circ$ ($N = 1000$)
volume fraction solventϕ_1

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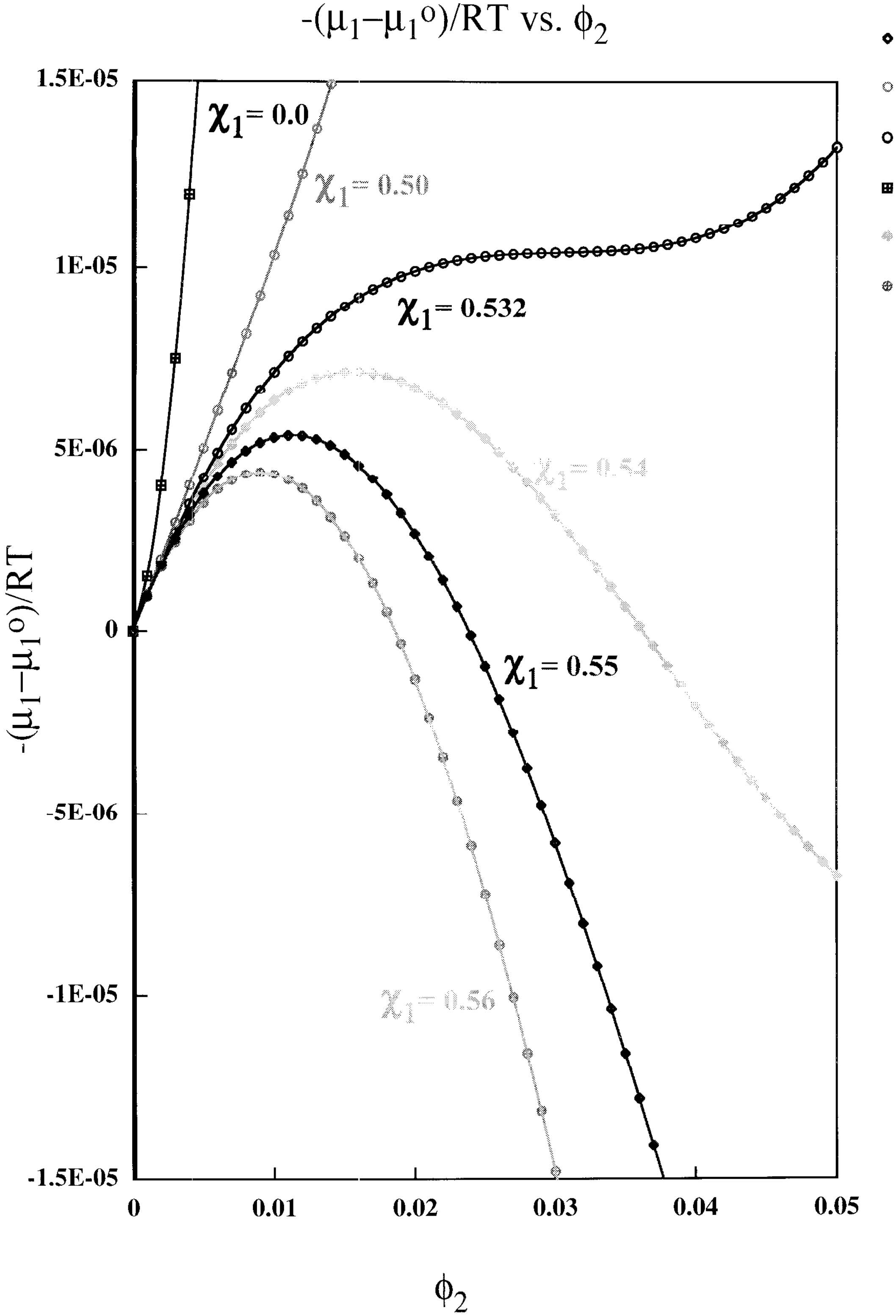
B.



$$\phi_{2,c} = \frac{1}{1+N^{1/2}} \cong 0.031$$

$$\chi_{1,c} = \frac{(1+N^{1/2})^2}{2N} = 0.532$$

C. (3.15)

Helmholtz Free Energy and force for stretching a chain with an arbitrary scaling exponent ν with $R_\nu = bN^\nu$

Follow the procedure similar to those for $R_F = bN^{3/5}$

$$\xi \approx bg^\nu, \quad R_f \approx \xi \frac{N}{g} \approx \xi \frac{N}{(\xi/b)^{1/\nu}} \approx bN\left(\frac{b}{\xi}\right)^{(1-\nu)/\nu}$$

$$g \approx (\xi/b)^{1/\nu}$$

$$\therefore \xi \approx \frac{(bN)^{\frac{\nu}{1-\nu}} \cdot b}{R_f^{\frac{\nu}{1-\nu}}} \approx b\left(\frac{bN}{R_f}\right)^{\frac{\nu}{1-\nu}}$$

$$A(N, R_f) \approx kT\frac{N}{g} \approx kTN\left(\frac{b}{\xi}\right)^{1/\nu} \approx kTN\left(\frac{R_f}{bN}\right)^{\frac{1}{1-\nu}}$$

$$f \approx \frac{kT}{\xi} \approx \frac{kT}{b}\left(\frac{R_f}{bN}\right)^{\frac{\nu}{1-\nu}} \approx \frac{kT}{R_\nu}\left(\frac{R_f}{R_\nu}\right)^{\nu/(1-\nu)}$$

$$\begin{aligned} b(bN)^{\frac{\nu}{1-\nu}} &= bN^\nu N^{-\nu}(bN)^{\frac{\nu}{1-\nu}} \\ &= bN^\nu [N^{-\nu\left(\frac{1-\nu}{\nu}\right)} bN)^{\frac{\nu}{1-\nu}} \\ &= bN^\nu [N^{-1+\nu} bN]^{\frac{\nu}{1-\nu}} \\ &= R_\nu \cdot R_\nu^{\frac{\nu}{1-\nu}} \end{aligned}$$

D. (3.18) D, thickness of an adsorbed chain with $R_\nu = bN^\nu$ with the interaction energy per monomer in contact with the surface ε.

$$A_{int} \approx -\varepsilon kTN\frac{b}{D}, \quad A_{confinement} \approx kTN\left(\frac{b}{D}\right)^{1/\nu} \text{ (Eq. 3.49)}$$

$$A_{total} \approx -\varepsilon kTN\left(\frac{b}{D}\right) + kTN\left(\frac{b}{D}\right)^{1/\nu}, \quad \left(\frac{\partial A_{total}}{\partial D}\right)_T = 0$$

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$$+\varepsilon kTN\frac{b}{D^2} - \frac{1}{\nu}kTN\frac{b^{1/\nu}}{D^{1+\frac{1}{\nu}}} = 0$$

$$\varepsilon\frac{b}{D^2} = \frac{1}{\nu}\frac{b^{1/\nu}}{D^{1+\frac{1}{\nu}}}, \quad \frac{D^2}{D\cdot D^{\frac{1}{\nu}}} \approx \frac{\varepsilon\nu b}{b^{1/\nu}}$$

$$D^{1-\frac{1}{\nu}} \approx \varepsilon\nu\, b^{1-\frac{1}{\nu}}, \quad D \approx (\varepsilon\nu)^{\frac{\nu}{\nu-1}}\cdot b$$

$$\approx \frac{b}{(\nu\varepsilon)^{\nu/(1-\nu)}} \approx \frac{b}{\varepsilon^{\nu/(1-\nu)}}$$

$$A_{confinement} \approx kTN\left(\frac{b}{D}\right)^{1/\nu} \approx kTN(\nu\varepsilon)^{\frac{1}{1-\nu}} \approx kTN\varepsilon^{1/(1-\nu)}$$

$$\frac{b}{D} \approx (\nu\varepsilon)^{\frac{\nu}{1-\nu}}$$

E.(3.21) Polymer adsorption from good solvent

$-\varepsilon kT$ attractive energy

(i) $D \approx b/\varepsilon^{3/2}$ (eq. 3.59)

(ii) $N = 10^3$, $b = 3\,\text{Å}$, $\varepsilon = 0.4$

$$\xi_{ads} \approx D \approx \frac{b}{\varepsilon^{3/2}} \approx 12\,\text{Å}$$

(iii) Minimal force to pull away at r.t.

$$f \approx \frac{kT}{\xi_{ads}} \cong \frac{1.38\cdot 10^{-23}\cdot 300}{1.2\cdot 10^{-9}} \cong 3.45\cdot 10^{-12}\,N$$

$$= 3.45\,pN$$

(iv) $2f = 6.9\,pN$, pull out 2 blobs at a time

(v) $D \approx b/\varepsilon \approx \xi_{ads}$, $f \approx \frac{kT}{(b/\varepsilon)} \approx \frac{1.38\cdot 10^{-23}\cdot 300\cdot 0.4}{0.3\cdot 10^{-9}}$

$\approx 5.52\,pN$

Adsorption is stronger.

F. (3.24)

$$R_F \to 4R_F = R_f$$

$$f \approx \frac{kT}{R_F}\left(\frac{R_f}{R_F}\right)^{3/2} \quad (\text{Eq. } 3.38), \quad R_F \approx v^{1/5} b^{2/5} N^{3/5} \approx 20 \cdot 10^{-9} m$$

$$kT \cong 4.14 \cdot 10^{-21} \text{ J/molecule}$$

$$f \cong \frac{kT}{R_F}\left(\frac{4\cancel{R_F}}{\cancel{R_F}}\right)^{3/2} \cong \frac{8kT}{R_F} \cong 1.65 pN$$

which is valid because $\xi_{tension} \cong 6.3b > \xi_T \cong 3.3b$

G. (3.25)

(i) $\xi_T \approx b^4/v$, $g_T \approx b^6/v^2$

(ii) Size of compression blob $\approx$ slit dimension D

(iii) $D \approx v^{1/5} b^{2/5} g^{3/5}$ for $D > \xi_T \approx b^4/v$

Thus, $g_{con} \approx D^{5/3}/v^{1/3} b^{2/3}$ if $D > \xi_T$

$g'_{con} \approx (D/b)^2$ if $D < \xi_T \approx b^4/v$

(iv) With $D > \xi_T \approx b^4/v$

$$A_{confinement} \approx kT\frac{N}{g_{con}} \approx kTN\frac{v^{1/3} b^{2/3}}{D^{5/3}} \approx kT\left(\frac{v^{1/5} b^{2/5} N^{3/5}}{D}\right)^{5/3}$$

$$\approx kT\left(\frac{R_F}{D}\right)^{5/3}$$

With $D < \xi_T$

$$A_{confinement} \approx kT\frac{N}{g'_{con}} \approx kTN\left(\frac{b}{D}\right)^2 \approx kT\left(\frac{R_0}{D}\right)^2$$

(v) The crossover from $D > \xi_T$ to $D < \xi_T$ should be at $D \approx \xi_T \approx b^4/v \cong \frac{(5\mathring{A})^4}{20\mathring{A}^3} \cong \frac{25\cdot 25}{20}\mathring{A} \cong 31\mathring{A}$

H. (3.26)

For randomly branched polymer in solution

(i) $A \approx kT\left(\frac{3}{2}\frac{R^2}{R_0^2} + v\frac{N^2}{R^3}\right)$ (Eq. 3.19)

where $R_0 = bN^{1/4}$ for this polymer

$$\left(\frac{\partial A}{\partial R}\right)_T = kT\left[\frac{3}{2}\cdot 2\left(R/R_0^2\right) - 3vN^2/R^4\right] = 0$$

$$\frac{3R}{R_0^2} \approx vN^2/R^4, \quad R^5 \approx vN^2 b^2 N^{1/2} \approx vb^2 N^{5/2}$$

$$\boxed{R \approx v^{1/5} b^{2/5} N^{1/2}}$$

(ii) $\xi_T \approx b g_T^{1/4}$, g_T can be estimated from

$$\underbrace{kTv\frac{g_T^2}{\xi_T^3}}_{\text{analog of } \frac{vN^2}{R^3}} \approx kT, \quad g_T^2 \approx \frac{\xi_T^3}{v} \approx \frac{b^3 g_T^{3/4}}{v}$$

$$g_T \approx \left(\frac{b^3}{v}\right)^{4/5} \cong \left(\frac{3^3\mathring{A}^3}{2.7\mathring{A}^3}\right)^{4/5} \cong 6.3$$

Linear chains,

$g_T \approx \left(\frac{b^3}{v}\right)^2$ which is substantially different from $(b^3/v)^{4/5}$

(iii) $\xi_T \approx b g_T^{1/4} \approx b\cdot\left(\frac{b^3}{v}\right)^{1/5}$ branched

$\xi_T \approx b^4/v$ linear

(iv)

$$R_0 \approx b N^{1/4}$$

$$R \approx v^{1/5} b^{2/5} N^{1/2} \approx (2.7\,Å^3)^{1/5} (3\,Å)^{2/5} (10^3)^{1/2}$$

$$\cong (1.22)(1.55)(31.6) \cong 60\,Å$$

(v) $R \approx (v b^2 N^3)^{1/5} \cong (2.7\,Å^3 \cdot 3^2\,Å^2 \cdot 10^9)^{1/5} \cong 119\,Å$

(vi) $\xi_T \approx b\left(\frac{b^3}{v}\right)^{1/5} \cong 3\left(\frac{3^3\,Å^3}{2.7\,Å^3}\right)^{1/5} Å \cong 3 \cdot 10^{1/5}\,Å \cong \underline{\underline{4.8\,Å}}$

$g_T \cong 6.3$

(vii) $\xi_T \approx b^4/v = \left(\frac{3^4\,Å^4}{2.7\,Å^3}\right) \cong \underline{\underline{30\,Å}}, \quad g_T \cong \left(\frac{b^3}{v}\right)^2 \cong \underline{\underline{100}}$

I.(3.27) $\quad v = \left(1 - \frac{\theta}{T}\right) b^3$

$N = 10^3, \quad b = 3\,Å, \quad \theta = 303\,K$

$$R_F \approx v^{1/5} b^{2/5} N^{3/5} \approx \left(1 - \frac{\theta}{T}\right)^{1/5} b^{3/5} \cdot b^{2/5} \cdot N^{3/5}$$

$$\approx \left(1 - \frac{\theta}{T}\right)^{1/5} b N^{3/5}$$

$T = 60°C$, $\quad R_F \approx \left(1 - \frac{303}{333}\right)^{1/5} (3\,Å)(10^{9/5})$

$$\cong 117\,Å$$

$T = 30°C \qquad R \approx b N^{1/2} \cong 95\,Å$

$T = 10°C$ (poor solvent)

$$R_{gl} \approx b^2 \left(\frac{N}{|v|}\right)^{1/3} \approx b^2 \frac{10}{|(1 - \frac{\theta}{T}) b^3|^{1/3}} \approx \frac{b \cdot 10}{\left(\frac{303}{283} - 1\right)^{1/3}}$$

$$\cong \frac{30\,Å}{0.41} \cong 73\,Å$$

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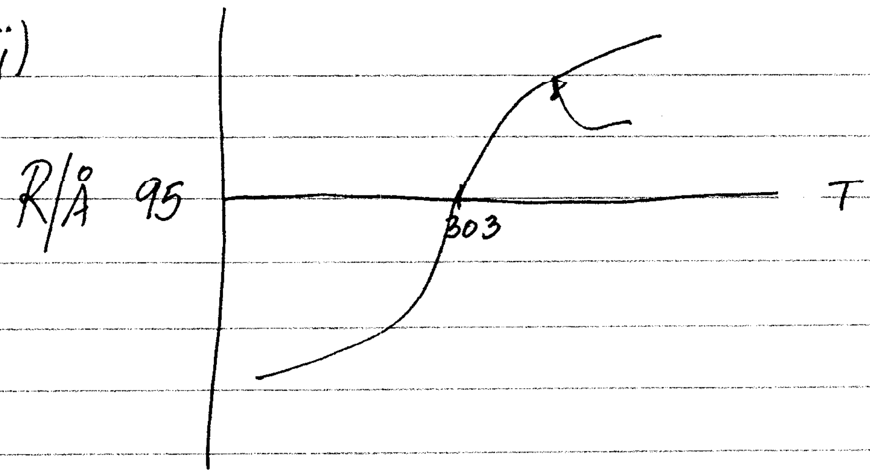
(ii)



(iii) at 60°C $\quad g_T \approx (b^3/v)^2 \approx \left(1 - \frac{\theta}{T}\right)^{-2} \triangleq 123$

(iv) at 10°C $\quad g_T \approx \left(\frac{b^3}{|v|}\right)^2 \triangleq \left(\frac{\theta}{T} - 1\right)^{-2} \triangleq 200$