Solutions to

Chem 664 | Problem Set #11 | Due: November 26, 2003

A. 6.8

B. 6.21

C. 6.22

D. 6.28

E. 7.1

F. 7.2

G. 7.6

Solutions to PS#11

due 11/26/03

A(6.8) $\sum_2 = \frac{[1-p^2(f-1)]p}{(1-p)[1-p(f-1)]^3}$, let $x \equiv p(1-p)^{f-2}$, $\frac{\partial p}{\partial x} = \frac{p(1-p)}{x[1-p(f-1)]}$

$$\sum_3 = x\,\frac{\partial \sum_2}{\partial p}\left(\frac{\partial p}{\partial x}\right) = x\,\frac{\{[1-p^2(f-1)]^2+2p(f-1)(1-p)^2\}p}{(1-p)[1-p(f-1)]^5}$$

$$N_z = \sum_3/\sum_2 = \frac{[1-p^2(f-1)]^2+2p(f-1)(1-p)^2}{\cancel{(1-p)}[1-p(f-1)]^{\cancel{5}\,2}}\cdot\cancel{p}\,\frac{\cancel{(1-p)}[1-p(f-1)]^{\cancel{3}}}{[1-p^2(f-1)]\cancel{p}}$$

$$= \frac{[1-p^2(f-1)]^2+2p(f-1)(1-p)^2}{[1-p(f-1)]^2\,[1-p^2(f-1)]}$$

$$N_z/N_w = \frac{\dfrac{[1-p^2(f-1)]^2+2p(f-1)(1-p)^2}{[1-\cancel{p(f-1)]^2}\cdot[1-p^2(f-1)]}}{\dfrac{[1-p^2(f-1)]}{[1-\cancel{p(f-1)]^2}}}$$

$$= \frac{[1-p^2(f-1)]^2+2p(f-1)(1-p)^2}{[1-p^2(f-1)]^2} = 1 + \frac{2\cdot\cancel{\left(1-\frac{1}{f-1}\right)^2}}{\cancel{\left(1-\frac{1}{f-1}\right)^2}} = 3$$

N_w, N_z both diverge as $p \to p_c = \frac{1}{f-1}$ but the ratio remains const at 3.

B(6.21) The kth moment, $m_k = \int_1^\infty N^k n(N)\,dN = \int_1^\infty N^{k-\tau}\,dN$

$$\approx \frac{1}{k-\tau+1} N^{k-\tau+1}\Big|_1^\infty \approx N^{(k+1)-\tau}\Big|_1^\infty$$

$$= \text{finite if } \tau > k+1$$

(i) # Ave d.p. is finite if m_1 is finite, $\tau > 2$

(ii) PDI is finite if m_2 is finite, $\tau > 3$

(iii) z-ave d.p. is finite if m_3 is finite, $\tau > 4$

(iv) $P_{sol} = m_1$, hence $\tau > 2$

C(6.22) Randomly branched chain in 3D percolation limit $\nu = 0.88$ & $D = 2.53$

$$\sigma = \frac{1}{D\nu} \cong 0.45$$

(i) $N^* \approx |\varepsilon|^{-\frac{1}{\sigma}} \cong (0.01)^{-1/0.45} \cong 2.8\cdot 10^4$

(ii) Ideal size, $R \approx b(N^*)^{1/4} \cong 3\mathring{A}(2.8\cdot 10^4)^{1/4} \cong 39\mathring{A}$

(iii) Size in the reactor, $R \approx b(N^*)^{2/5} \cong 180\mathring{A}$

(iv) $F \approx kT\left[\frac{R^2}{[b(N^*)^{1/4}]^2} + v\frac{(N^*)^2}{R^3}\right]$

Minimum free energy, swollen branched chain

$$R \approx b(N^*)^{1/2} \cong 3\mathring{A}(2.8\cdot 10^4)^{1/2} \cong 500\mathring{A}$$

D(6.28) Precursor $N_0 = 100$ & 10, $b = 5\mathring{A}$, $N = 10^4$

$$R \approx bN_0^{1/2}\left(\frac{N}{N_0}\right)^{1/4} \approx b(N_0 N)^{1/4}$$

(i) $R \approx 5\mathring{A}(10^6)^{1/4} \cong 5\cdot 10^{3/2} \cong 158\mathring{A}$

(ii) $R \approx 5\mathring{A}(10^5)^{1/4} \cong 5\cdot 10^{5/4} \cong 50\cdot 10^{1/4} \cong 89\mathring{A}$

(iii) $\phi \approx Nb^3/R^3 \approx (N/N_0^3)^{1/4}$

i) $\phi \cong \left(\frac{10^4}{10^6}\right)^{1/4} \cong 0.3$

ii) $\phi \cong \left(\frac{10^4}{10^3}\right)^{1/4} \cong 1.78$ larger than 1 since $N > N_0^3$

$D = 4 > d = 3$

E(7.1) $\left(\frac{\partial A}{\partial T}\right)_{V,L} = -S$, $\left(\frac{\partial A}{\partial V}\right)_{T,L} = -P$, $\left(\frac{\partial A}{\partial L}\right)_{T,V} = f$

$$\because dA = -SdT - PdV + fdL$$

$$\frac{\partial^2 A}{\partial V \partial L} = \frac{\partial^2 A}{\partial L \partial V}, \quad -\left(\frac{\partial P}{\partial L}\right)_{T,V} = \left(\frac{\partial f}{\partial V}\right)_{T,L}$$

Similarly, $\left(\frac{\partial^2 A}{\partial T \partial V}\right) = \left(\frac{\partial^2 A}{\partial V \partial T}\right)$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_{T,L} = \left(\frac{\partial P}{\partial T}\right)_{V,L}$$

F(7.2) $\quad f = f_E + f_S = a + \left(\frac{\partial f}{\partial T}\right)_{V,L} T$

$$a = f_E = 1.7 \cdot 10^3\ N$$

$$f = 1.48 \cdot 10^4 \text{ at } 300K$$

f_E / f

$= \frac{1.7}{14.8} = \underline{\underline{0.11}}$

G(7.6) $\quad \varepsilon_{xx} = \lambda_x - 1 = \lambda - 1$

$$\varepsilon_{yy} = \lambda_y - 1 = \frac{1}{\sqrt{\lambda}} - 1$$

$\nu \equiv -\varepsilon_{yy}/\varepsilon_{xx} = \frac{1 - \frac{1}{\sqrt{\lambda}}}{\lambda - 1}$ → needs to be differentiated to apply L'Hopital's rule

$$\lim_{\lambda \to 1} \nu = \frac{\frac{1}{2\lambda^{3/2}}}{1} = \frac{1}{2}$$

At larger deformation $\nu \downarrow$ as $\lambda \uparrow$

$\nu = 1/6$ when $\lambda = 4$

$\nu = 1/12$ " $\lambda = 9$