Solutions to

Chem 664 **Problem Set #10** **Due: November 19, 2003**

A. 5.20

B. 5.21

C. 5.22

D. 6.4

E. 6.11

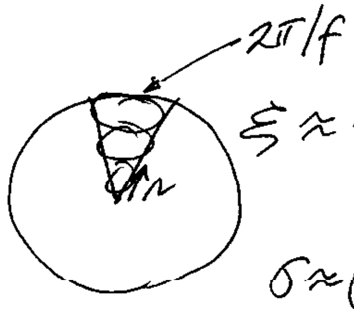
F. 6.14

G. 6.20

H. 6.23

/ SPS 10/1

A(5.20) f-arm star on 2D



$\xi \approx r/f$, $\xi \approx b g^{3/4}$, $\sigma \approx \dfrac{g b^2}{\xi^2} \approx \dfrac{1}{\sqrt{g}}$

area fraction

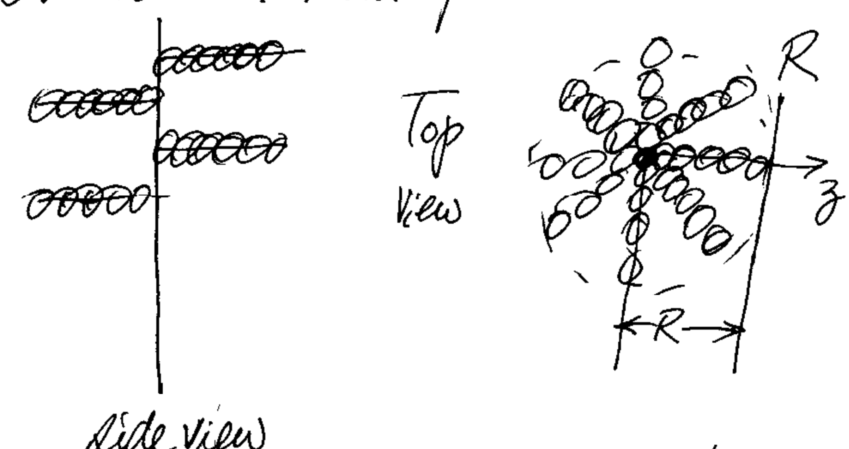
$\sigma \approx \left(\dfrac{\xi}{b}\right)^{-2/3} \approx \left(\dfrac{bf}{r}\right)^{2/3}$

$g \approx (\xi/b)^{4/3}$

$$N \approx \int_b^R \frac{\sigma(r)}{b^2} 2\pi r\,dr \approx \frac{1}{b^2}\int_0^R \left(\frac{bf}{r}\right)^{2/3} r\,dr \approx f^{2/3}\left(\frac{R}{b}\right)^{4/3}$$

$$R \approx \frac{b N^{3/4}}{f^{1/2}}$$

B(5.21) Correction. Hint provided is not correct!



$$\xi \approx \frac{1}{\sigma} \quad g \approx (\xi/b)^{5/3} \approx \left(\frac{1}{b\sigma}\right)^{5/3}$$

$$R \approx \xi\left(\frac{N}{g}\right) \approx \frac{1}{\sigma}(b\sigma)^{5/3} N \approx N b^{5/3} \sigma^{2/3}$$

$$\phi \approx \begin{cases} b^3 g/\xi^3 \approx (b\sigma)^{4/3} & z < R \\ 0 & z > R \end{cases}$$

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C(5.22)

Conc in the core $\phi_A \approx \frac{|v_A|}{b^3} \approx 2\chi_A - 1$

(i) Core volume, $V_{core} \approx \frac{f N_A b^3}{\phi_A} \approx \frac{f N_A b^3}{2\chi_A - 1}$

Core size, $R_{core} \approx V_{core}^{1/3} \approx b\left(\frac{f N_A}{2\chi_A - 1}\right)^{1/3} \approx f^{1/3} R_{gl}$

Constrasted to $\underline{R_{gl} \approx b\left(\frac{N}{2\chi - 1}\right)^{1/3}}$

(ii) $\gamma \approx \frac{kT}{\xi^2} \approx \frac{kT}{b^2}(2\chi - 1)^2$

$R_{core}^2 \approx f^{2/3} R_{gl}^2$ $\quad\therefore$ surface energy of the core $= f^{2/3} \cdot$ surface energy of globule of each block

$\gamma R_{core}^2 \approx f^{2/3} \gamma R_{gl}^2$

Surface energy per arm $\frac{\gamma R_{core}^2}{f} \approx f^{-\frac{1}{3}} \gamma R_{gl}^2$

(iii) Each block is confined to a cone with $4\pi/f$ solid angle

Cross sectional area at r from the center $= r^2/f$

Correlation length $\xi \approx r/\sqrt{f} \approx b\phi^{-3/4}$ ← athermal

$\therefore \phi \approx \left(\frac{\xi}{b}\right)^{-4/3} \approx \left(\frac{b\sqrt{f}}{r}\right)^{4/3}$

$$f N_B = \int \frac{\phi(r)}{b^3} dV \approx \frac{1}{b^3}\int_{R_{core}}^{R_{micelle}} \phi(r) r^2 dr \approx \frac{1}{b^3}\int_{R_{core}}^{R_{micelle}} \left(\frac{b\sqrt{f}}{r}\right)^{4/3} r^2 dr$$

$$\approx f^{2/3}\left[\left(\frac{R_{micelle}}{b}\right)^{5/3} - \left(\frac{R_{core}}{b}\right)^{5/3}\right]$$

$$R_{micelle} \approx b\left[\left(\frac{R_{core}}{b}\right)^{5/3} + f^{1/3} N_B\right]^{3/5}$$

$$\approx f^{1/5} b\left[f^{2/9}\left(\frac{N_A}{2\chi - 1}\right)^{5/9} + N_B\right]^{3/5}$$

D(6.4)

$n(p,N) = p^{N-1}(1-p)$ which is just a MPD problem

$m_0 = \sum n(p,N) = 1$

$m_1 = \sum N\, p^{N-1}(1-p) = (1-p)(1+2p+3p^2+\dots) = \frac{1-p}{(1-p)^2} = \frac{1}{1-p}$

$m_2 = \sum N^2 p^{N-1}(1-p) = (1-p)(1+4p+9p^2+16p^3+\dots)$

$= (1-p)\frac{(1+p)}{(1-p)^3} = \frac{1+p}{(1-p)^2}$ (see Handout #5)

$N_n = \frac{1}{1-p} = 100$

$N_W = \frac{1+p}{1-p} = 199$

$\Big\}\ p = 0.99,\quad N_W/N_n = 1.99 \cong 2$

E(6.14) $p_c = \frac{1}{f-1}$

(i) honeycomb, $f=3$, $p_c = 1/2$

(ii) square lattice, $f=4$, $p_c = 1/3$

(iii) ~~diamond~~ triangular, $f=6$, $p_c = 1/5$

(iv) diamond, $f=4$, $p_c = 1/3$

(v) Cubic, $f=6$, $p_c = 1/5$

(vi) The predictions are sligtly lower than the values in Table 6.1. The mean field theory does not let the loops formed whereas they are counted in those in the table. The loops do not contribute to the global connectivity hence the more is wasted than the mean field theory predicts.

(vii) The higher the dimension, the more likely the mean field theory is correct because of fewer loops. Note that $d=6$, the mean field theory is exact

exchange

F.(6.11) $f=4$, $P_{sol}^{1/4} = 1-p+p\,P_{sol}^{3/4}$

let $x \equiv P_{sol}^{1/4}$, $px^3 - x + (1-p) = 0$

$x=1$ is a solution

$[px + px - (1-p)](x-1) = 0$

Thus $px^2 + px - (1-p) = 0$

$$x = \frac{-p \pm \sqrt{p^2 + 4p(1-p)}}{2p}$$, the positive solution $$x = \frac{\sqrt{4p-3p^2} - p}{2p}$$

$\therefore$ $P_{sol} = 1$ for $p \le p_c = \frac{1}{3}$

$$P_{sol} = x^4 - \left(\frac{\sqrt{4p-3p^2}-p}{2p}\right)^4 \quad \text{for } p > p_c = \frac{1}{3}$$

$P_{gel} = 0$ for $p \le p_c = \frac{1}{3}$

$$P_{gel} = 1 - \left(\frac{\sqrt{4p-3p^2}-p}{2p}\right)^4 \quad \text{for } p > p_c = \frac{1}{3}$$

At $p = 0.4$, $P_{sol} = 0.458$

G(6.20) (i) $1 - p + p(1 - P_{gel}) = 1 - pP_{gel}$ – probability for not crosslinked or not a part of the gel even if crosslinked.

$$P_{sol} = 1 - P_{gel} = (1 - pP_{gel})^N$$

(ii) $\ln(1 - P_{gel}) = N \ln(1 - pP_{gel}) \cong -NpP_{gel}$ $\quad pP_{gel} \ll 1$

$$\ln(1-x) = -x - \tfrac{1}{2}x^2 \dots$$

$$1 - P_{gel} \cong e^{-NpP_{gel}}$$

H(6.23) $N_0 = 10^3$

(i) $\varepsilon_G \approx N_0^{-1/3} \cong 0.1$

(ii) $N = N_0 \varepsilon_G^{-2} \approx N_0^{5/3} = 10^5$

(iii) $\xi = bN_0^{1/2}\left(\frac{N}{N_0}\right)^{1/4} = b(N/N_0)^{1/4} \approx bN_0^{2/3} \cong 300\text{Å}$

(iv) $\phi \approx \frac{b^3 N}{\xi^3} \simeq \left(\frac{N}{N_0}\right)^{1/4} \cong 0.1$

(v) $\varepsilon_G \approx P_{gel} \cong 0.1$ $\quad P_{gel}$ at ε_G

(vi) $\phi \approx P_{gel}$, $P \cong 1$