

Solutions to Problem Set #10
due 12/04/02

SPS 10/1

$$A(6.8) \quad \Sigma_2 = \frac{[1-p^2(f-1)]p}{(1-p)[1-p(f-1)]^3}, \quad \frac{\partial p}{\partial x} = \frac{p(1-p)}{x[1-p(f-1)]}$$

where $x \equiv p(1-p)^{f-2}$

$$\begin{aligned} \Sigma_3 &= x \frac{\partial \Sigma_2}{\partial x} = x \cdot \frac{\partial \Sigma_2}{\partial p} \cdot \frac{\partial p}{\partial x} \\ &= \frac{x p(1-p)}{x[1-p(f-1)]} \frac{\partial}{\partial p} \left\{ \frac{[1-p^2(f-1)]p}{(1-p)[1-p(f-1)]^3} \right\} \\ &= \frac{p\{[1-p^2(f-1)]^2 + 2p(f-1)(1-p)^2\}}{(1-p)[1-p(f-1)]^5} \end{aligned}$$

$$\begin{aligned} \therefore N_3 = \frac{\Sigma_3}{\Sigma_2} &= \frac{p\{[1-p^2(f-1)]^2 + 2p(f-1)(1-p)^2\}}{(1-p)[1-p(f-1)]^5} \cdot \frac{(1-p)[1-p(f-1)]^3}{[1-p^2(f-1)]p} \\ &= \frac{[1-p^2(f-1)]^2 + 2p(f-1)(1-p)^2}{[1-p(f-1)]^2 [1-p^2(f-1)]} \end{aligned}$$

$$\begin{aligned} \frac{N_3}{N_W} &= \frac{[1-p^2(f-1)]^2 + 2p(f-1)(1-p)^2}{[1-p(f-1)]^2 [1-p^2(f-1)]} \cdot \frac{[1-p(f-1)]^2}{[1-p^2(f-1)]} \\ &= 1 + \frac{2p(f-1)(1-p)^2}{[1-p^2(f-1)]^2} \end{aligned}$$

$$\begin{aligned} \lim_{p \rightarrow p_c} \frac{N_3}{N_W} &= 1 + \frac{2(\frac{1}{f-1})(f-1)(1-p_c)^2}{[1-p_c(\frac{1}{f-1})(f-1)]^2} = 1 + 2 = 3 \\ p_c &= \frac{1}{f-1} \end{aligned}$$

$$B(6.11) \quad f=4, \quad p_c = \frac{1}{f-1} = \frac{1}{3}$$

$$P_{sol}^{1/4} = 1-p+p \cdot P_{sol}^{3/4}$$

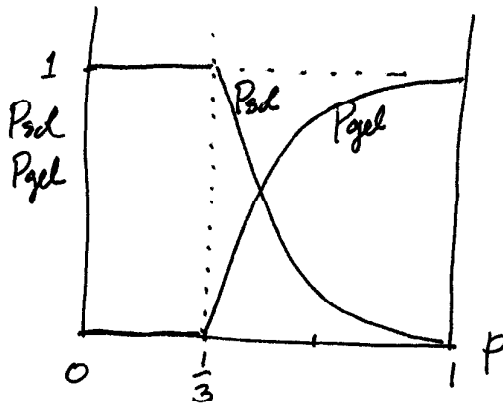
$$P_{sol}^{1/4} \equiv x$$

$$x = 1-p+p \cdot x^3, \quad px^3 - x - p + 1 = 0, \quad p(x^3-1) - (x-1) = 0$$

$$p(x-1)(x^2+x+1) - (x-1) = (x-1)[p(x^2+x+1) - 1] = 0$$

$$x=1 + px^2+px+(p-1)=0 \quad x = \frac{-p \pm \sqrt{p^2 - 4p(p-1)}}{2p}$$

$$\underline{P_{sol}^{1/4} = 1, \quad p < p_c = \frac{1}{3}}, \quad P_{sol} = \left(\frac{-p + \sqrt{4p-3p^2}}{2p} \right)^4, \quad p > p_c = \frac{1}{3}$$



C(6.14)

Lattice	f	$p_c = \frac{1}{f-1}$
i) Honeycomb	3	$1/2$
ii) Square	4	$1/3$
iii) triangular	6	$1/5$
iv) diamond	4	$1/3$
v) Simple cubic	6	$1/5$

vi) The gel points are less than those listed in Table 6.1 & the difference arises from the mean field approach for percolation not taking into account intramolecular bonds.

vii) $d=3$ closer to those in Table 6.1 ($f=6$) because they are less likely for intramolecular bonding

$$D(6.21) \quad n(N) \approx N^{-\tau}, \quad m_k = \int_0^\infty N^k n(N) dN \approx \int_0^\infty N^{k-\tau} dN \approx \frac{N^{k-\tau+1}}{k-\tau+1} \Big|_0^\infty$$

m_k is finite if & only if $k-\tau+1 < 0$, or $\tau > k+1$

(i) $N_m = m_1/m_0$ to be finite, $\tau > 2$

(ii) $N_w/N_m = \frac{m_2 m_0}{m_1^2} = \frac{\int_0^\infty N^{1-\tau} dN}{\left(\int_0^\infty N^{2-\tau} dN\right)^2}$ is finite if $\tau > 3$

(iii) $N_z = \frac{m_3}{m_2} = \frac{\int_0^\infty N^{3-\tau} dN}{\int_0^\infty N^{2-\tau} dN}$ is finite if $\tau > 4$

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

$$E(6.22) \quad \bar{z} = \frac{p - p_c}{p_c} = -0.01$$

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$$(i) \quad N^* \approx |\bar{z}|^{-1/\sigma} = \frac{1}{(10^{-2})^2} = 10^4 \quad \text{where } \sigma = 1/2 \text{ mean field theory}$$

$$(ii) \quad R_g \approx b(N^*)^{1/4} = 3 \text{ \AA} \cdot (10^4)^{1/4} = 30 \text{ \AA}$$

$$(iii) \quad R \approx b(N^*)^{2/5} \approx 3 \cdot (10^4)^{2/5} \approx 120 \text{ \AA}$$

$$(iv) \quad A_e \approx kT v \frac{(N^*)^2}{R^3}$$

$$A_s \approx kT \frac{R^2}{(N^*)^{1/2} b^2} \quad \left. \vphantom{\frac{R^2}{(N^*)^{1/2} b^2}} \right) A \approx kT \left[\frac{R^2}{(N^*)^{1/2} b^2} + v \frac{(N^*)^2}{R^3} \right]$$

$$\left(\frac{\partial A}{\partial R} \right) = 0 = \frac{2R}{((N^*)^{1/2} b)^2} - \frac{3v(N^*)^2}{R^4}$$

$$\frac{2R}{N^{*1/2} b^2} = \frac{3b^3 N^{*2}}{R^4}$$

$$, \quad R^5 \approx b^5 N^{*5/2}, \quad R \approx b N^{*1/2}$$

$$\approx 3 \cdot 10^2 \text{ \AA}$$

F(6.28) Ideal random branched chain

$$R_{g,0} \approx b N_0^{1/2}, \quad R_g \approx R_{g,0} \left(\frac{N}{N_0} \right)^{1/4} \approx b N_0^{1/4} N^{1/4}$$

$$(i) \quad R_g \approx 5 \text{ \AA} \cdot (10^2)^{1/4} (10^4)^{1/4} \approx 5 \cdot 10^{3/2} \approx 158 \text{ \AA}, \quad N_0 = 10^2$$

$$(ii) \quad R_g \approx 5 \text{ \AA} \cdot 10^{1/2} \cdot 10 \approx 89 \text{ \AA}, \quad N_0 = 10$$

$$(iii) \quad \phi \approx \left(\frac{10^4}{10^6} \right)^{1/4} \approx 0.32 \quad (i)$$

$$\phi \approx \left(\frac{10^4}{10^3} \right)^{1/4} \approx 1.78 \quad (ii)$$

For this chain $N > N_0^3$ $\phi > 1$

because the fractal dimension of ideal randomly branched polymer is 4, higher than 3-D space.

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

$$G(7.1) \quad dA = -SdT - PdV + fdL, \quad \left(\frac{\partial S}{\partial L} \right)_{T,V} = - \left(\frac{\partial f}{\partial T} \right)_{V,L}$$

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

$$H(7.7) \quad E = 2(1+\nu)G = 3(1-2\nu)K$$

$$(i) \quad E = 3(1-2\nu)K, \quad \nu = \frac{1}{2} \left[1 - \frac{E}{3K} \right] = \frac{1}{2} \left(1 - \frac{1.3 \cdot 10^6}{3 \cdot 2 \cdot 10^9} \right)$$

$$(ii) \quad G = \frac{E}{2(1+\nu)} = \frac{1.3 \cdot 10^6 \text{ Pa}}{2(1.4999)} \stackrel{=0.4999}{\approx} 4.334 \cdot 10^5 \text{ Pa}$$

$$(iii) \quad \frac{G}{K} = \frac{3}{2} \left(\frac{1-2\nu}{1+\nu} \right), \quad \text{if } K \gg G \quad \frac{1-2\nu}{1+\nu} \approx 0 \quad \text{or } \nu = \frac{1}{2}$$

$$(iv) \quad E = 3(1-2\nu)K, \quad E/K = 3-6\nu$$

$$\nu = \frac{1}{2} - \frac{E}{6K}, \quad \text{hence } \frac{E}{6K} \text{ is the correction factor for a compressible body } \nu < \frac{1}{2}$$

I(7.9)

$$mg\Delta h = mc_p\Delta T$$

$$(i) \quad \Delta T = \frac{g\Delta h}{c_p} \approx \frac{9.81 \frac{\text{m}}{\text{s}^2} \cdot 0.08 \text{ m}}{2200 \text{ J/kg} \cdot \text{K}} \approx 3.57 \cdot 10^{-4} \text{ K}$$

$$T + \Delta T = 300.150357 \text{ K}$$

$$(ii) \quad \frac{\Delta E}{E} = \frac{\Delta T}{T} = \frac{3.57 \cdot 10^{-4}}{3 \cdot 10^2} \approx 1.19 \cdot 10^{-6} \quad \text{hardly a change!}$$