Problems Self-assembly, HS2 2023

1a. $x_n = e^{-\epsilon} \lambda^n$

$$\sum_{n=1}^{\infty} x_n = e^{-\epsilon} \sum_{n=1}^{\infty} \lambda^n = e^{-\epsilon} \frac{\lambda}{1-\lambda}$$

$$\sum_{n=1}^{\infty} n x_n = e^{-\epsilon} \sum_{n=1}^{\infty} n \lambda^n$$

$$= e^{-\epsilon} \cdot \lambda \cdot \frac{d}{d\lambda}\left(\frac{\lambda}{1-\lambda}\right)$$

$$= e^{-\epsilon} \lambda \cdot \left[\frac{1}{1-\lambda} + \frac{\lambda}{(1-\lambda)^2}\right] = e^{-\epsilon} \frac{\lambda}{(1-\lambda)^2}$$

$$\rightarrow \langle n \rangle = \frac{\sum x_n}{\sum n x_n} = \frac{1}{1-\lambda}$$

b. Repeat $\rightarrow \frac{d}{dx} \sum_{n=1}^{\infty} n x^n = \sum_{n=1}^{\infty} n^2 x^{n-1}$

So $\sum_{n=1}^{\infty} n^2 x^n = x \cdot \frac{d}{dx} \sum_{n=1}^{\infty} n x^n$

$$\rightarrow \sum_{n=1}^{\infty} n^2 x_n = e^{-\epsilon} \sum_{n=1}^{\infty} n^2 \lambda^n = e^{-\epsilon} \lambda \cdot \frac{d}{d\lambda}\left(\frac{\lambda}{(1-\lambda)^2}\right)$$

$$= e^{-\epsilon} \lambda \left[\frac{1}{(1-\lambda)^2} + \frac{2\lambda}{(1-\lambda)^3}\right] = e^{-\epsilon} \cdot \frac{\lambda(1+\lambda)}{(1-\lambda)^3}$$

$$\rightarrow \langle n \rangle_w = \frac{1+\lambda}{1-\lambda}$$

So $\dfrac{\langle n \rangle_w}{\langle n \rangle} = 1+\lambda \longrightarrow 2$ for $\lambda \to 1$ (long polymers)

c) $$\sum_{n=1}^{\infty} n x_n = e^{-\epsilon} \frac{\lambda}{(1-\lambda)^2} = \phi \text{ (see a)}$$

$$\rightarrow \frac{\lambda}{(1-\lambda)^2} = \phi e^{\epsilon}$$

Also $\langle n \rangle = \dfrac{1}{1-\lambda} \rightarrow \lambda = 1 - \dfrac{1}{\langle n \rangle}$

$$\rightarrow \frac{\lambda}{(1-\lambda)^2} = \langle n \rangle^2 \cdot \left(1 - \frac{1}{\langle n \rangle}\right) = \langle n \rangle^2 - \langle n \rangle$$

$$\rightarrow \langle n \rangle^2 - \langle n \rangle = \phi e^{\epsilon}$$

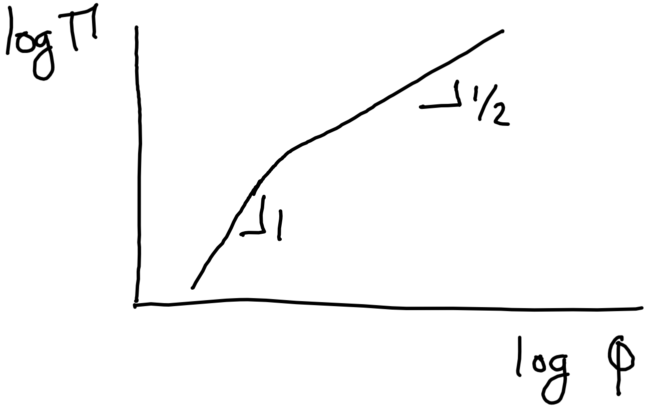
$$\langle n \rangle^2 - \langle n \rangle - \phi e^{\epsilon} = 0$$

$$\langle n \rangle = \frac{1 \pm \sqrt{1 + 4\phi e^{\epsilon}}}{2} \rightarrow \frac{1}{2} + \frac{1}{2}\sqrt{1+4\phi e^{\epsilon}}$$

d) $$\sum_{n=1}^{\infty} C_n = \sum_{n=1}^{\infty} X_n = \frac{\phi}{\langle n \rangle}$$

For $\phi e^{\epsilon} \ll 1 \rightarrow \langle n \rangle = 1 \rightarrow \Pi \sim \phi$

$\phi e^{\epsilon} \gg 1 \rightarrow \langle n \rangle \simeq \sqrt{\phi e^{\epsilon}} \rightarrow \Pi \sim \sqrt{\phi}$



2. Cylinders:

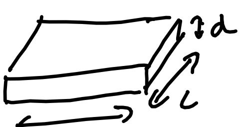
$$V = \pi R^2 L = n v$$

$$A = 2\pi R L = n a_0$$

$$\frac{V}{A} = \frac{v}{a_0} = \frac{R}{2}$$

$$\to R = \frac{2v}{a_0} < l_c \to P < 1/2$$

Bilayer



$$V = L^2 d$$
$$A = L^2$$

$$\to \frac{V}{A} = d = \frac{v_0}{a_0} < l_c$$

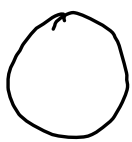
$$\to P < 1$$

3a. $m = 10 \rightarrow v = 296.4 \cdot 10^{-3}\ nm^3$

$l_c = 1.419\ nm$

$a_0 = 0.65\ nm^2$

$\rightarrow P = \frac{v}{a_0 l_c} = 0.32 < \frac{1}{3} \rightarrow$ spheres!

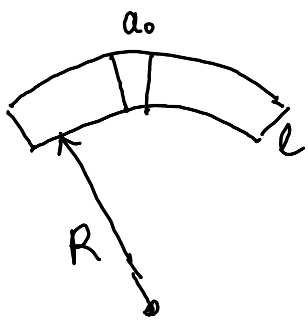
b. 

$V = \frac{4}{3}\pi R^3 = N v$

$A = 4\pi R^2 = N a_0$

$R = 3\, v/a_0 = 1.37\ nm$

$N = \frac{4\pi R^2}{a_0} = 36$

4. 

Cylinder:

$V_{shell} = \pi L\left[(R+l)^2 - R^2\right]$

$= \pi L\left(l^2 + 2lR\right) = n v_0$

$A_{shell} = 2\pi R L = n a_0$

$\rightarrow \frac{L}{n} = \frac{a_0}{2\pi R}$

$\Leftrightarrow$

$\rightarrow v_0 = \frac{\pi a_0}{2\pi R}\left(l^2 + 2lR\right)$

$$v_0 = \frac{\cancel{\pi} a_0}{2\cancel{\pi} R}\left(\ell^2 + 2\ell R\right)$$

$$= a_0 \ell \left[1 + \frac{\ell}{2R}\right]$$

Cylinder $\rightarrow$ $H = \frac{1}{2R}$; $K = 0$

So $a_0 \ell \left[1 + \ell H + \frac{1}{3}\ell^2 K\right] = a_0 \ell \left(1 + \frac{\ell}{2R}\right)$

Sphere : $V_{shell} = \frac{4\pi}{3}\left((R+\ell)^3 - R^3\right)$

$$= \frac{4\pi}{3}\left[3\ell R^2 + 3\ell^2 R + \ell^3\right] = n v_0$$

$A_{shell} = 4\pi R^2 = n a_0$

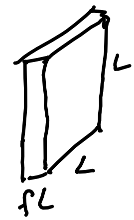
$$\rightarrow n = \frac{4\pi R^2}{a_0}$$

$$\rightarrow v_0 = \frac{a_0}{4\pi R^2} \cdot \frac{4\pi}{3}\left[3\ell R^2 + 3\ell^2 R + \ell^3\right]$$

$$= a_0 \ell \left[1 + \frac{\ell}{R} + \frac{1}{3}\ell^2 \frac{1}{R^2}\right]$$

Sphere $\rightarrow H = 1/R$, $K = 1/R^2$

5. * Lamellar phase



$V_A = fL^3$

$A_L = 2L^2$

* Cylindrical (cubic):

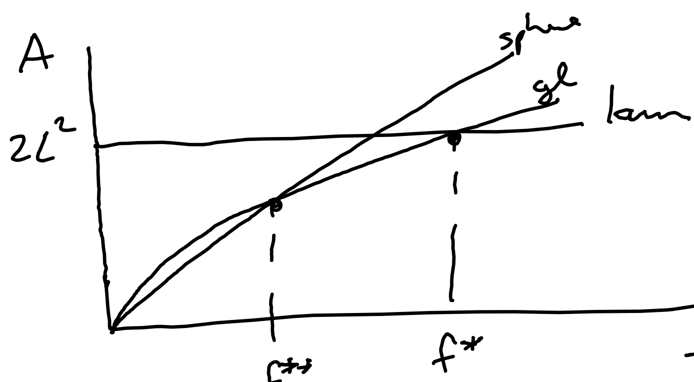
$V_A = \pi R_c^2 L = fL^3 \rightarrow R_c = L\left(\frac{f}{\pi}\right)^{1/2}$

$A_c = 2\pi R_c L = 2(\pi f)^{1/2} L^2$

* Spheres (cubic)

$V_A = \frac{4\pi}{3} R_s^3 = fL^3 \rightarrow R_s = L\left(\frac{3f}{4\pi}\right)^{1/3}$

$A_s = 4\pi R_s^2 = (36\pi)^{1/3} f^{2/3} L^2$



$f^* \to A_c = A_L \to 2L^2 (\pi f^*)^{1/2} = 2L^2$

$\to f^* = \frac{1}{\pi} \approx 0.32$

$f^{**} \to A_c = A_s \to 2L^2 (\pi f)^{1/2} = L^2 (36\pi)^{1/3} f^{2/3}$

$\left[2 (\pi f)^{1/2}\right]^3 = \left[(36\pi)^{1/3} f^{2/3}\right]^3$

$8 \pi^{3/2} f^{3/2} = 36\pi f^2$

$\to f^{1/2} = \frac{8\pi^{1/2}}{36} \to f^{**} = \frac{4\pi}{81} \approx 0.16$