Solutions to

Chem 664 | **Problem Set #9** (revised) | **Due: November 25, 2002**

A. 5.14

B. 5.15

C. 5.16

D. 5.17

E. 5.18

F. 5.19

G. 6.1

H. 6.3

I. 6.4

A (5.14)

(i) $r_n \approx b\phi^{-n/d}$ d-dimensions

(ii) Dense packing of ξ-blobs

$g b^d / \xi^d \approx \phi$

within a blob $g \approx (\xi/b)^2$

$\therefore$ Size of dense-packing blobs in d-dimensions

$\xi \approx b\phi^{-\frac{1}{(d-2)}}$

(iii) Ave distance between monomers in neighboring chain ξ is of the order of r_n

$r_n \approx \xi$, $b\phi^{-n/d} \approx b\phi^{-\frac{1}{d-2}}$

$\therefore n \approx \frac{d}{d-2}$

(iv) If $d=3$

3-body contact $3 \approx \frac{3}{3-2}$ QED!

If $d=4$, $\frac{4}{4-2} \approx 2 = n$ (two body contact)

$r_2 \approx b\phi^{-2/4} \approx b/\sqrt{\phi}$

B (5.15) Alexander-de Gennes brush in $\chi = 0.43$ medium

$N = 10^4$, $b = 3\text{Å}$, $\sigma = 10^{-4}\text{Å}^{-2}$, meaning one chain per $100\text{Å} \times 100\text{Å}$ area

(i) $\xi \approx \frac{1}{\sqrt{\sigma}} = 100\text{Å}$ (interchain distance)

(ii) $\xi_T \approx b^4/v$, $v = (1-2\chi)b^3 = 0.14(3\text{Å})^3 \cong 3.8\text{Å}^3$

$\approx \frac{3^4}{3.8}\text{Å} \cong \frac{9.9}{3.8} \cong 21\text{Å}$, Thus $\xi > \xi_T$, brushes are swollen

(iii) $g_T \approx \frac{b^6}{v^2} \approx \frac{1}{(1-2\chi)^2} \cong 51$

$\xi \approx v^{1/5} b^{2/5} g^{3/5}$, $g \approx \frac{\xi^{5/3}}{v^{1/3} b^{2/3}} \approx \frac{\sigma^{-5/6}}{(1-2\chi)^{1/3} \cdot b} \cong \frac{100^{5/3}}{3.8^{1/3}\, 3^{2/3}} \cong 665$

(iv) $N/g = 15$

(v) $H \approx \xi \frac{N}{g} \cong 100\text{Å} \cdot 15 = 1500\text{Å}$

C(5.16) H for brushes with $N = 10^3$, $b = 5\text{Å}$, $\sigma = 10^{-2}\text{Å}^{-2}$, $\chi = 0.3$

$\xi \approx \frac{1}{\sqrt{\sigma}} = 10\text{Å}$, $\xi_T \approx \frac{b}{1-2\chi} \cong \frac{5}{0.4} \cong 12.5\text{Å}$

$\xi_T > \xi$, no swelling of brushes

$g \approx \xi^2/b^2 \cong 10^2/25 = 4$, $H \approx \xi \frac{N}{g} \cong 10\text{Å}\,\frac{10^3}{4} \cong 2.5 \cdot 10^3\text{Å}$

D(5.17) From the figure given, $\xi \approx r/\sqrt{f}$ since cross-sectional area of f-arm star is $A \approx 4\pi r^2/f$, $\xi \approx \sqrt{A} \approx r/\sqrt{f}$

in θ-condition, $\xi \approx b/\phi$ $\therefore \phi(r) \approx b/\xi(r) \approx \frac{b\sqrt{f}}{r}$

As the mass conservation is added

$$N \approx \int_0^R \frac{\phi(r)}{b^3} 4\pi r^2 dr \approx \frac{1}{b^3}\int_0^R \frac{b\sqrt{f}}{r} r^2 dr \approx \frac{\sqrt{f}}{b^2}\frac{R^2}{2} \approx \sqrt{f}\left(\frac{R}{b}\right)^2$$

$\therefore R \approx b N^{1/2} f^{-1/4} \approx b\left(\frac{N}{f}\right)^{1/2} f^{1/4}$

Example: 8-arm star, arm d.p. $= N/f$

If $f = 8$, $f^{1/4} = 8^{1/4} = 1.68$ about 68% expansion

E.(5.18) athermal, $\xi \approx b/\phi^{3/4} \approx r/\sqrt{f}$, $\phi(r) \approx \left(\frac{b}{r}\right)^{4/3} f^{2/3}$

$N \approx \frac{1}{b^3}\int_0^R \frac{b^{4/3} f^{2/3}}{r^{4/3}} r^2 dr \approx \frac{f^{2/3}}{b^{5/3}} R^{5/3}$, $R \approx N^{3/5} b / f^{2/5} \approx b\left(\frac{N}{f}\right)^{3/5} \cdot f^{1/5}$

$\therefore f^{1/5}$ is the expansion factor, e.g., $f = 8$

$f^{1/5} = 1.52$, 52% expansion

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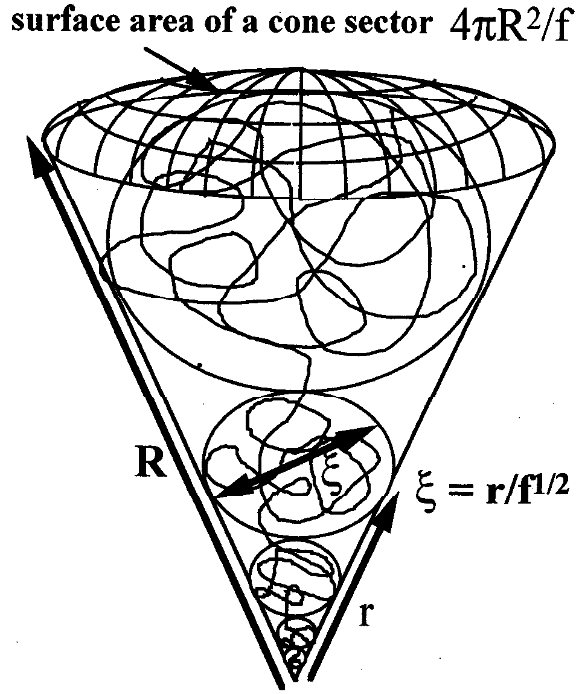

Figure 1

F(5.19) Density profile of f-arm star in good solvent

$R = f(N, b, v, f)$? Given that $\xi \approx r/\sqrt{f}$, $\xi_T \approx b^4/v$

As long as $\xi < \xi_T$, chain is ideal at $r < r_T \approx \xi_T \sqrt{f}$ from the branch point

$$\phi \approx \frac{g b^3}{\xi^3} \approx \frac{b}{\xi} \approx \frac{b\sqrt{f}}{r}$$

$\xi^2 = b^2 g$

$$\phi(r) \approx \frac{b\sqrt{f}}{r} \quad \text{at} \quad r \le \frac{b^4\sqrt{f}}{v}$$

When $\xi > \xi_T$, $\xi \approx v^{1/5} b^{2/5} g^{3/5}$

$$\phi(r) \approx \frac{g b^3}{\xi^3} \approx \frac{(\xi^{5/3}/v^{1/3} b^{2/3}) b^3}{\xi^3} \approx \frac{b^{7/3}}{\xi^{4/3} v^{1/3}} \approx \frac{b}{v^{1/3}}\left(\frac{b\sqrt{f}}{r}\right)^{4/3}$$

at $r > r_T \approx \dfrac{b^4\sqrt{f}}{v}$

Star size R:

a) If the star is small enough that $R \le r_T$, then

$$N \approx \frac{1}{b^3}\int_0^{r_T} \phi(r) r^2 dr \approx \frac{1}{b^3} b\sqrt{f} \int_0^{r_T} r\, dr \approx \sqrt{f}\left(\frac{r_T}{b}\right)^2$$

$$\approx \sqrt{f}\left(\frac{b^4\sqrt{f}}{b \cdot v}\right)^2 \approx \sqrt{f}\left(\frac{\sqrt{f}}{v}\right)^2 b^6 \approx \frac{f^{3/2} b^6}{v^2}$$

$R \approx b N^{1/2} f^{-\frac{1}{4}}$ if $N \le \dfrac{f^{3/2} b^6}{v^2}$

$$\approx \underline{\underline{b\left(\frac{N}{f}\right)^{1/2} f^{1/4}}}$$

b) If the star is large that $R \gg r_T$

$$N \approx \frac{1}{b^3}\int_{r_T}^{R} \phi(r) r^2 dr \approx \frac{1}{b^3}\int_0^R \frac{b}{v^{1/3}}\left(\frac{b\sqrt{f}}{r}\right)^{4/3} r^2 dr$$

$$\approx \frac{b(b\sqrt{f})^{4/3}}{b^3 v^{1/3}} \int_0^R r^{2/3} dr \approx \frac{b f^{2/3}}{v^{1/3}}\left(\frac{R}{b}\right)^{5/3}$$

$$\therefore R \approx \underline{\underline{v^{1/5} b^{2/5}\left(\frac{N}{f}\right)^{3/5} f^{1/5}}}$$

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G (6.1)

(i) - ergodic

(ii) - ergodic

(iii) - non-ergodic

(iv) - non-ergodic

H (6.3)

(i) 3-D kinetic gelation

(ii) 1-D percolation

(iii) 2-D percolation

(iv) 3-D percolation

I (6.4)

$$n(p,N) = p^{N-1}(1-p) \approx q e^{-qN}, \qquad q \equiv 1-p$$

$$N_n = \int_0^\infty N n(p,N)\, dN = q \frac{1}{q^2} = \frac{1}{q}$$

$$N_w \cong \frac{2}{q}, \qquad N_w / N_n \cong 2$$