J04T.3

a)

The free energy of the polymer for a distance R is given by

$$F_0(\mathbf{R}, N) = -TS_c = \mathrm{const} + k_B T \frac{3R^2}{2Nb^2} \qquad (1)$$

where $R = |\mathbf{R}|$.
Knowing that $F = -k_B lnZ$, the partition function can be written

$$Z(R, N) = A \exp\left(\frac{-3R^2}{2Nb^2}\right). \qquad (2)$$

To eliminate the R dependence, we integrate over all possible R, find the most probably value of R, we can integrate

$$Z(N) = 4\pi A \int_0^\infty R^2 \exp\left(\frac{-3R^2}{2Nb^2}\right) dR = -4\pi A \frac{\partial}{\partial\alpha} \int_0^\infty e^{-\alpha R^2}\, dR = \qquad (3)$$
$$-4\pi A \frac{\partial}{\partial\alpha} \sqrt{\frac{\pi}{\alpha}} = 2\pi^{3/2} \alpha^{-3/2}$$

The expectation value of R^2 is thus

$$\left\langle R^2 \right\rangle = Z^{-1} 4\pi A \int_0^\infty R^4 \exp\left(\frac{-3R^2}{2Nb^2}\right) dR = 3Z^{-1} \pi^{3/2} \alpha^{-5/2} = \alpha^{-1} = Nb^2 \quad (4)$$

b)

With the probability density of R given by

$$\rho_R = R^2 \exp\left(\frac{-3R^2}{2Nb^2}\right) \tag{5}$$

we take the derivative with respect to R to find the most probable value,

$$2R\exp\left(\frac{-3R^2}{2Nb^2}\right) - \frac{3R^3}{Nb^2}\exp\left(\frac{-3R^2}{2Nb^2}\right) = 0 \tag{6}$$

or

$$2 - 3\frac{R^2}{Nb^2} = 0 \Rightarrow R = \sqrt{\frac{2N}{3}}b \tag{7}$$

c)

Since U deals with the excluded volume, we expect a singularity when $Nv \approx R^3$, similar to that of the Van Der Waals correction to the ideal gas. To wit, we want

$$vU(\mathbf{R}, N) \propto \frac{v}{Nv - R^3} \tag{8}$$

To make the dimensions correct, simply multiply by $k_\mathrm{B}T$.

$$vU(\mathbf{R}, N) = \frac{Nvk_\mathrm{B}T}{Nv - R^3} = \frac{Nvk_\mathrm{B}T}{R^3\left(1 - \frac{Nv}{R^3}\right)}. \tag{9}$$

Since we expect R^2 to go as N in low order, the term Nv/R^3 should be small when v is small. This can we expanded as

$$vU(\mathbf{R}, N) \approx \frac{Nvk_\mathrm{B}T}{R^3}\left(1 + \frac{Nv}{R^3}\right). \tag{10}$$

d)

To lowest order, the probability density is now

$$\rho_R = R^2 \exp\left(-\frac{3R^2}{2Nb^2} - \frac{Nv}{R^3}\right) \tag{11}$$

Taking the derivative, we get

$$2R - R^2\left(\frac{3R}{Nb^2} - \frac{3Nv}{R^4}\right) = 0 \tag{12}$$

or

$$\frac{2}{3} - \frac{R^2}{Nb^2} + \frac{Nv}{R^3} = 0 \tag{13}$$

This is a polynomial of order five, which is generally unsolvable. However, we can substitute out previous solution for $\langle R \rangle$ into the lowest order term,

$$1 - \frac{R^2}{Nb^2} + \frac{v}{N^{1/2}\,b^3} = 0 \tag{14}$$

which gives the approximate solution

$$R = \sqrt{\frac{2}{3}Nb^2 + \frac{vN^{1/2}}{b}}\,. \tag{15}$$

2 thoughts on “J04T.3”

D

December 15, 2013 at 11:59 pm

Yeah. It should just be R^2. I'll fix that.

December 11, 2013 at 9:07 pm

(a) -- OK. Except that in (3): $\int_0^\infty e^{-x^2}\,dx = \frac{\sqrt{\pi}}{2}$, not just $\sqrt{\pi}$, but fortunately it didn't change your answer.
(b) -- why do you take $\rho_R = R^3 e^{-\alpha R^2}$? Your formula (3) suggests that it should be $R^2 e^{-\alpha R^2}$.
(c) -- looks OK. There is a sign-related typo in (9). Also, is low density important to you?
(d) -- looks OK except that in (11) you use $R^3 e^{\cdots}$ for the probability density instead of $R^2 e^{\cdots}$ for some reason