J04T.3

a)

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

$$F_0(R, N) = -TS_c = \text{const} + k_B T \frac{3R^2}{2Nb^2}$$  \hspace{1cm} (1)

where $R = |R|$. Knowing that $F = -k_B \ln Z$, the partition function can be written

$$Z(R, N) = A \exp \left( \frac{-3R^2}{2Nb^2} \right).$$  \hspace{1cm} (2)

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

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

$$= -4\pi A \frac{\partial}{\partial \alpha} \sqrt{\frac{\pi}{\alpha}} = 2\pi^{3/2} \alpha^{-3/2}$$  \hspace{1cm} (3)

The expectation value of $R^2$ is thus

$$\langle R^2 \rangle = Z^{-1} 4\pi A \int_0^\infty R^4 \exp \left( \frac{-3R^2}{2Nb^2} \right) dR = 3Z^{-1} \pi^{3/2} \alpha^{-5/2} = \alpha^{-1} = Nb^2$$  \hspace{1cm} (4)
b) With the probability density of \( R \) given by
\[
\rho_R = R^2 \exp\left( -\frac{3R^2}{2Nbh^2} \right)
\]
we take the derivative with respect to \( R \) to find the most probable value,
\[
2R \exp\left( -\frac{3R^2}{2Nbh^2} \right) - \frac{3R^3}{Nbh^2} \exp\left( -\frac{3R^2}{2Nbh^2} \right) = 0
\]
or
\[
2 - 3 \frac{R^2}{Nbh^2} = 0 \Rightarrow R = \sqrt{\frac{2N}{3}} b
\]
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
\[
vU(R, N) \propto \frac{v}{Nv - R^3}
\]
To make the dimensions correct, simply multiply by \( k_B T \).
\[
vU(R, N) = \frac{Nvk_B T}{Nv - R^3} = \frac{Nvk_B T}{R^3 \left( 1 - \frac{Nv}{R^3} \right)}.
\]
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
\[
vU(R, N) \approx \frac{Nvk_B T}{R^3} \left( 1 + \frac{Nv}{R^3} \right).
\]
d) To lowest order, the probability density is now
\[ \rho_R = R^2 \exp \left( -\frac{3R^2}{2Nb^2} - \frac{Nv}{R^3} \right) \]  \hspace{1cm} (11)

Taking the derivative, we get

\[ 2R - R^2 \left( \frac{3R}{Nb^2} - \frac{3Nv}{R^4} \right) = 0 \]  \hspace{1cm} (12)

or

\[ \frac{2}{3} - \frac{R^2}{Nb^2} + \frac{Nv}{R^3} = 0 \]  \hspace{1cm} (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,

\[ 1 - \frac{R^2}{Nb^2} + \frac{v}{N^{1/2} b^3} = 0 \]  \hspace{1cm} (14)

which gives the approximate solution

\[ R = \sqrt{\frac{2}{3} Nb^2 + \frac{vN^{1/2}}{b}} . \]  \hspace{1cm} (15)

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2 thoughts on “J04T.3”

D
December 15, 2013 at 11:59 pm

Yeah. It should just be \( R^2 \). I’ll fix that.
(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 $R^3 e^{-\alpha}$ for the probability density instead of $R^2 e^{-\alpha}$ for some reason.