Solution 7

On the Typical Shape of an Ideal Chain

If we fix the end-to-end vector of an ideal chain, from Homework 6 we know that each point far enough from the two ends of the chain still follows gaussian statistics with "renormalized" parameters. For the s^{th} monomer we have:

$$P_s\left(\vec{R}\right) = \left(\frac{3}{2\pi K_s b^2}\right)^{\frac{3}{2}} e^{-\frac{3(\vec{R}-\vec{R}_s)^2}{2K_s b^2}} \tag{1}$$

where

$$K_s \equiv \frac{s(N-s)}{N} \qquad\qquad \vec{R}_s \equiv \frac{N-s}{N}\vec{R}_1 + \frac{s}{N}\vec{R}_2$$

By looking at the one-dimensional projections, we will have

$$P_s\left(X\right) = \left(\frac{3}{2\pi K_s b^2}\right)^{\frac{1}{2}} e^{-\frac{3(X-X_s)^2}{2K_s b^2}} \tag{2}$$

and analogue formulas for the Y, Z components. While the K_s are equal for the three projections, an asymmetry arises for the average values:

$$X_s = \frac{s}{N}R \qquad\qquad Y_s = Z_s = 0 \tag{3}$$

Before starting any computation, let us introduce some useful notation. Since we will have to manipulate many gaussians, it is useful to define

$$G\left(\mu, \sigma^2\right)\big|_x \equiv \left(\frac{1}{2\pi\sigma^2}\right)^{\frac{1}{2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \tag{4}$$

In this way, for example eqn (2) can be simply written as

$$P_s(X) = G\left(X_s, \frac{K_s b^2}{3}\right) \tag{5}$$

Now, let us focus on the X component. The corresponding projection of the radius of gyration is given on average by

$$\left\langle X_g^2\right\rangle_{\vec{R}} = \frac{1}{2N^2}\sum_{i=1}^{N}\sum_{j=1}^{N}\left\langle (X_i - X_j)^2\right\rangle_{\vec{R}} = \frac{1}{N^2}\sum_{i=1}^{N}\sum_{j=i}^{N}\left\langle (X_i - X_j)^2\right\rangle_{\vec{R}} \tag{6}$$

We now propose to calculate the generic $(i,j)^{th}$ term $(i<j)$ of the previos sum[1]. The probability distribution (2) has here to be used with some caution: indeed, while the probability density of obtaining x_i can be obtained by blindly substituting the formula, in the case of j we have already

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[1] Rigorously speaking, in our calculation we would be allowed to use gaussian statistics only (see steps below) for $1 \ll i \ll j \ll N$. However, it turns out that the terms which do not satisfy this constraint give negligible contribution for large N, so that in our calculation we will "forget" about this detail.

fixed the position of i. Equation (2) has thus to be used by considering the $(j-i)^{th}$ monomer of a polymer of size $N-i$, where the two ends are fixed at positions x_i, R. In other words, in the case of j the renormalized mean and variance are

$$\frac{(N-i)-(j-i)}{N-i}x_i+\frac{j-i}{N-i}R=\frac{N-j}{N-i}x_i+\frac{j-i}{N-i}R$$

$$\frac{1}{3}\frac{(j-i)\left[(N-i)-(j-i)\right]}{N-i}b^2=\frac{(j-i)(N-j)}{3(N-i)}b^2$$

We thus have

$$\begin{aligned}\left\langle (X_i-X_j)^2\right\rangle_{\vec{R}} &= \int_{-\infty}^{+\infty}da_i\int_{-\infty}^{+\infty}da_j P\left(x_i=a_i\right)P\left(x_j=a_j|x_i=a_i\right)\left(a_i-a_j\right)^2= \\ &= \int da_i\int da_j\; G\left(\frac{i}{N}R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{a_i} G\left(\frac{N-j}{N-i}a_i+\frac{j-i}{N-i}R,\frac{(j-i)(N-j)}{3(N-i)}b^2\right)\Bigg|_{a_j}\left(a_i-a_j\right)^2\end{aligned}$$

By performing the change of variable $w\equiv a_j-a_i$, the previous expression becomes

$$\begin{aligned}\left\langle (X_i-X_j)^2\right\rangle_{\vec{R}} &= \int_{-\infty}^{+\infty}da_i\; G\left(\frac{i}{N}R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{a_i}\int_{-\infty}^{+\infty}dw\; G\left(\frac{N-j}{N-i}a_i+\frac{j-i}{N-i}R-a_i,\frac{(j-i)(N-j)}{3(N-i)}b^2\right)\Bigg|_{a_j}w^2= \\ &= \int_{-\infty}^{+\infty}da_i\; G\left(\frac{i}{N}R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{a_i}\int_{-\infty}^{+\infty}dw\; G\left(\frac{j-i}{N-i}(R-a_i),\frac{(j-i)(N-j)}{3(N-i)}b^2\right)\Bigg|_{a_j}w^2\end{aligned}$$

Now, it is well-known that for any distribution the variance can be obtained by the formula $\sigma^2=\left\langle x^2\right\rangle-\left\langle x\right\rangle^2$, so that $\left\langle x^2\right\rangle=\sigma^2+\left\langle x\right\rangle^2$. The second integral in our calculation is exactly the computation of $\left\langle w^2\right\rangle$ with the given gaussian distribution. We thus have:

$$\begin{aligned}\left\langle (X_i-X_j)^2\right\rangle_{\vec{R}} &= \int_{-\infty}^{+\infty}da_i\; G\left(\frac{i}{N}R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{a_i}\left\{\frac{(j-i)(N-j)}{3(N-i)}b^2+\left[\frac{j-i}{N-i}(R-a_i)\right]^2\right\}= \\ &= \frac{j-i}{3(N-i)}(N-j)b^2+\frac{(j-i)^2}{(N-i)^2}\int_{-\infty}^{+\infty}da_i\; G\left(\frac{i}{N}R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{a_i}\left(R-a_i\right)^2= \\ &= \frac{j-i}{3(N-i)}(N-j)b^2+\frac{(j-i)^2}{(N-i)^2}\int_{-\infty}^{+\infty}d\xi\; G\left(\frac{i}{N}R-R,\frac{i(N-i)}{3N}b^2\right)\Bigg|_{\xi}\xi^2= \\ &= \frac{j-i}{3(N-i)}(N-j)b^2+\frac{(j-i)^2}{(N-i)^2}\frac{i(N-i)}{3N}b^2+\frac{(j-i)^2}{(N-i)^2}\frac{(N-i)^2}{N^2}R^2= \\ &= \frac{j-i}{3(N-i)}(N-j)b^2+\frac{i(j-i)^2}{3N(N-i)}b^2+\frac{(j-i)^2}{N^2}R^2\end{aligned}$$

where in the third step we made use of the substitution $\xi\equiv a_i-R$. Now, if we substitute in eqn

(6) we obtain

$$\begin{aligned}
\left\langle X_g^2 \right\rangle_{\vec{R}} &= \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=i}^{N} \left\{ \frac{j-i}{3(N-i)}(N-j)b^2 + \frac{i(j-i)^2}{3N(N-i)}b^2 + \frac{(j-i)^2}{N^2}R^2 \right\} \to \\
&\to \frac{1}{N^2} \int_0^N di \int_i^N dj \left\{ \frac{j-i}{3(N-i)}(N-j)b^2 + \frac{i(j-i)^2}{3N(N-i)}b^2 + \frac{(j-i)^2}{N^2}R^2 \right\} = \\
&= \frac{1}{N^2} \int_0^N di \int_0^{N-i} dj \left\{ \frac{j}{3(N-i)}(N-j-i)b^2 + \frac{ij^2}{3N(N-i)}b^2 + \frac{j^2}{N^2}R^2 \right\} = \\
&= \frac{1}{N^2} \int_0^N di \int_0^{N-i} dj \left\{ \frac{jb^2}{3} - \frac{j^2}{3N}b^2 + \frac{j^2}{N^2}R^2 \right\} = \\
&= \frac{1}{N^2} \int_0^N di \left\{ \frac{(N-i)^2}{6}b^2 - \frac{(N-i)^3}{9N}b^2 + \frac{(N-i)^3}{3N^2}R^2 \right\} = \\
&= \frac{1}{N^2} \int_0^N di \left\{ \frac{i^2}{6}b^2 - \frac{i^3}{9N}b^2 + \frac{i^3}{3N^2}R^2 \right\} = \\
&= \frac{1}{18}Nb^2 - \frac{1}{36}Nb^2 + \frac{1}{12}R^2 = \\
&= \frac{1}{36}Nb^2 \left(1 + \frac{3R^2}{Nb^2} \right)
\end{aligned}$$

which is the formula reported in the text. As for the Y and Z components, we should repeat the same calculation we just went through, but with $R = 0$. We thus have

$$\left\langle Y_g^2 \right\rangle_{\vec{R}} = \left\langle Z_g^2 \right\rangle_{\vec{R}} = \frac{Nb^2}{36}$$

By averaging over all the possible end-to-end vectors, one finds:

$$\left\langle X_g^2 \right\rangle = \frac{Nb^2}{36} \left(1 + \frac{3\left\langle R^2 \right\rangle}{Nb^2} \right) \qquad \left\langle Y_g^2 \right\rangle_{\vec{R}} = \left\langle Z_g^2 \right\rangle_{\vec{R}} = \frac{Nb^2}{36}$$

so that

$$\left\langle R_g^2 \right\rangle = \left\langle X_g^2 \right\rangle + \left\langle Y_g^2 \right\rangle + \left\langle Z_g^2 \right\rangle = \frac{Nb^2}{12} \left(1 + \frac{\left\langle R^2 \right\rangle}{Nb^2} \right)$$

Since in the case of an ideal chain one has $\left\langle R^2 \right\rangle = Nb^2$, we obtain $\left\langle R_g^2 \right\rangle = Nb^2/6$, as expected. Note that in the case of an ideal chain the X projection of the radius of gyration is $\left\langle X_g^2 \right\rangle = Nb^2/9 = 4\left\langle Y_g^2 \right\rangle$, so that the typical ellipsoid is indeed quite asymmetric.