Homework 7

On the Typical Shape of an Ideal Chain[1]

Let us consider an ideal chain made of N monomers connected by bonds of length b. If $\vec{R}$ is the end-to-end vector, it is well-known that $\left\langle \vec{R}^2 \right\rangle \sim Nb^2$, where $\langle \cdots \rangle$ denotes an average over all the possible chain conformations. Now, suppose we fix once and for all the vector $\vec{R}$: naturally, this vector alone is not enough to define uniquely a conformation, but it rather corresponds to an ensemble of conformations. Let us consider a reference frame whose x axis has the same orientation of $\vec{R}$, i.e. in this frame $\vec{R} \equiv (R, 0, 0)$ (we are also taking the position of the first monomer as origin). Let $\langle \cdots \rangle_{\vec{R}}$ denote an average over the ensemble of conformations corresponding to a given $\vec{R}$. Show that the average projections of the radius of gyration (see reminder below) along the three direction of the reference frame we introduced are (hint: use the results of Homework 6):

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

In other words, the typical ideal chain realization is more likely to be represented by an ellipsoid rather than by a simple sphere, its projection along the end-to-end vector being strecthed according to the formula above. Finally, show that averaging over all the possible end-to-end vectors the correct expression $R_g^2 = Nb^2/6$ is recovered. What are the projections of the most likely ellipsoid to be observed?
Reminder: by definition, the radius of gyration is given by

$$R_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} \left(\vec{R}_i - \vec{R}_{CM} \right)^2$$

where $\vec{R}_i$ is the position vector of monomer i and

$$\vec{R}_{CM} \equiv \frac{1}{N} \sum_{i=1}^{N} \vec{R}_i$$

is the so-called center of mass of the chain. Notice that, by some algebraic manipulations, a useful formula can be obtained:

$$R_g^2 = \frac{1}{2N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left(\vec{R}_i - \vec{R}_j \right)^2$$

The average projections are obtained by suitably taking only some components of the position vectors. For example

$$X_g^2 \equiv \frac{1}{N} \sum_{i=1}^{N} (X_i - X_{CM})^2$$

[1] Adapted from M. Rubinstein and R. H. Colby, *Polymer Physics*, Oxford University Press.