Problem Set #5

Due in class on Thursday, March 18

Here you will consider the simplest models for conformational fluctuations of a long chain molecule. The first is an ideal gas of $N$ polymer segments connected end to end. Each segment $i = 1, 2, \ldots, N$ (perhaps comprising many chemical units) has a fixed length $\ell$ and an orientation $\hat{b}_i$ that is parallel to one of $d$ Cartesian axes ($\hat{x}$, $\hat{y}$, or $\hat{z}$ in 3 dimensions). In other words the molecular configuration traces a random walk on a $d$-dimensional cubic lattice:

1. First imagine that the orientations of different segments are statistically independent, and that there is no preferred orientation, $\langle \hat{b}_i \rangle = 0$ and $\langle \hat{b}_i \cdot \hat{b}_j \rangle = \delta_{ij}$. Compute the mean squared end-to-end distance of the chain molecule, $\langle |\mathbf{R}|^2 \rangle$, where $\mathbf{R} = \ell \sum_{i=1}^{N} \hat{b}_i$. How does your result depend on dimensionality $d$?

2. Point to a possibly major flaw in neglecting correlations between segment orientations. If these correlations were considered more carefully, how would the dependence of $\langle |\mathbf{R}|^2 \rangle$ on $N$ change (qualitatively)?

3. Now imagine that there is an energetic bias for segments to point in a particular direction $\hat{a}$, described by a potential energy $u = -\gamma \hat{b}_i \cdot \hat{a}$ for each segment $i$. Compute the mean segment orientation $\overline{\mathbf{b}} = \langle \hat{b}_i \rangle$. (Assume that fluctuations in orientations of different segments remain uncorrelated, $\langle (\hat{b}_i - \overline{\mathbf{b}})(\hat{b}_j - \overline{\mathbf{b}}) \rangle = 0$ for $i \neq j$.) Then compute $\langle |\mathbf{R}|^2 \rangle$ and sketch its dependence on the bias strength $\gamma$.

4. For $\gamma = 0$ (no orientational bias), calculate $\langle |\mathbf{R}|^4 \rangle$. Show that in the limit of very large $N$, the ratio $\langle |\mathbf{R}|^4 \rangle / \langle |\mathbf{R}|^2 \rangle^2$ is consistent with a Gaussian distribution of the end-to-end vector $\mathbf{R}$. You may restrict your attention to $d = 3$. 
5. Assuming that $\mathbf{R}$ is in fact a Gaussian random variable, estimate the size of its fluctuations by computing

$$\frac{\sqrt{\langle|\mathbf{R}|^2\rangle - \langle|\mathbf{R}|\rangle^2}}{\langle|\mathbf{R}|\rangle}.$$

How does your result differ from the size of fluctuations in extensive quantities of typical macroscopic systems? Speculate on the origin of this difference.

6. If we imagine that the energy $U$ of repulsions between polymer segments depends only on the overall size of the molecule ($|\mathbf{R}|$), then the distribution of $\mathbf{R}$ should be multiplied by $e^{-\beta U(|\mathbf{R}|)}$. Estimate this interaction energy as you would in considering corrections to ideal gas behavior. Specifically, assume that the interaction energy for each segment is a constant $B$ times the density of segments in a sphere with radius $|\mathbf{R}|$. By locating the peak of your modified distribution, determine the most probable molecular size. Interpret the dependence of your result on dimensionality $d$. 