040423 Quiz 4 Polymer Properties

For a symmetric distribution function the mean, median and most probable values are identical. This is not true for a skewed distribution (single mode but asymmetric) such as the log-normal and Lorentzian distributions. The function $R^2 P_G(R)$ is asymmetric despite the symmetry of $P_G(R)$, the 3d Gaussian distribution.

a) Show that the generic probability P(R) is given by $P(R) = -\dfrac{R_{mp,R^2}\dfrac{dP(R)}{dR}}{2}$, where $R_{mp,R2}$ is the most probable "R" value of the function $R^2 P(R)$.

b) Use this expression for P(R) to calculate $\langle R^2 \rangle$, the mean value of R^2 in terms of $R_{mp,R2}$. Assume that P(R) is symmetric. You will need to use integration by parts, $udv = uv - \int vdu$. (Also, note that a normalized P(R) has units of inverse size.)

c) How does the result in "b" support or detract from the Flory-Krigbaum approach to the calculation of the scaling behavior for an isolated polymer coil in a good solvent? (If successful you have shown that $R_{mp,R2} \sim <R^2>^{1/2}$)

d) The consideration of excluded volume as a generic description of and as an equivalent statement of long-range interactions in analogy to our previous consideration of short range interactions in the context of prohibiting local chain backtrack is the basis of segregation of the study of polymers into local persistence effects and global chain scaling effects. Describe briefly how such conceptual segregation might be used to describe a polyelectrolyte (charged polymer) in a good solvent such as sulfonated polystyrene in water as a function of chain charge.

e) An expression for the free energy of an isolated chain in a theta or in a good solvent can be obtained from the Flory Krigbaum approach and the Boltzmann principle. Give the expressions for the free energy of these two cases showing how the expressions relate to the conformational probability functions discussed in class.

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a) Calculate $R_{mp,R2}$:

$$0 = \frac{d\left(R^2 P(R)\right)}{dR} = 2R_{mp,R^2}P(R) + R_{mp,R^2}^2\frac{d\left(P(R)\right)}{dR}$$

solve for P(R) to obtain the expression.

b) $\langle R^2 \rangle = \int_{-L}^{L} R^2 P(R)dR = \frac{-R_{mp,R^2}}{2}\int_{-L}^{L} R^2 \frac{d\left(P(R)\right)}{dR}dR$

use integration by parts with $u = R^2$ and $dv = \frac{d\left(P(R)\right)}{dR}dR$, so, v = P(R), then

$$\langle R^2 \rangle = \frac{-R_{mp,R^2}}{2}\left[R^2 P(R) - 2\int_{-L}^{L} RP(R)dR\right] = R_{mp,R^2}\left[L^2 P(L)\right]$$

c) The equality in "b" shows that the maximum probability value is proportional to the rms value if the distribution function is symmetric. This is assumed for the Flory-Krigbaum derivation, meaning that the derivation of the scaling behavior of the end-to-end distance is reasonable except for the implicit assumption that it is a perturbation from the Gaussian symmetric distribution.

d) For a charged polymer the short range interactions between like charged groups lead to repulsion and are well known to significantly increase the chain persistence, sometimes by an order of magnitude! On the other hand, the Flory-Krigbaum theory states that once the polymer shows strong affinity for the solvent the global chain scaling should display a dimension of 5/3 for a self-avoiding walk, as long as the persistence length is smaller than the overall chain size. In polyelectrolytes it is possible for the entire chain to be persistent so that no coil dimension is observed at all. Without an understanding of segregation between coil scaling and chain persistence (long and short range interactions) it is impossible to understand the structural manifestations of electrostatic charge on polymer coils.

e) The Boltzmann distribution function states that the probability of a physical state (conformation), P(R), is related to the free energy of the conformation, E,

$$P(R) = K\exp\left(-\frac{E}{kT}\right)$$

Through comparison of the Gaussian probability for a Brownian chain,

$$W_0(R) = Z^N 4\pi R^2 \left(\frac{2\pi R_F^2}{3}\right)^{-3/2} \exp\left(-\frac{3R^2}{2R_F^2}\right) dR$$

we can obtain an expression for the free energy of an isolated chain by comparison,

$$E \sim kT \frac{3R^2}{2R_F^2}$$

For the Flory-Krigbaum expression we have similarly,

$$E \sim kT \left[\frac{3R^2}{2R_F^2} - \frac{N^2 V_c(1-2\chi)}{2R^3}\right]$$