Properties Quiz 1 040402

Polymers are best described by statistical features since they are disordered structures. For a system described by a large number of random events the Gaussian distribution is often used to approximate the average features.

a) Write the Gaussian distribution function for 1d and sketch the distribution curve (probability versus x or R).

b) The polymer coil in the theta state is often called both a Gaussian coil and a Brownian coil. What is the relationship between Brownian motion and the Gaussian distribution function?

c) If the Gaussian function is centered at 0, explain why the mean, <R> or <x> is zero. (This can be done mathematically or in words.

d) Polyethylene can be synthesized using ethylene (C_2H_4) or squalene ($C_{60}H_{120}$) as "monomer". A polymer of 70,000 g/mole molar mass would have $2n_{squalene} = 160$ and $2n_{ethylene} = 5{,}400$ (2n is the number of chemical bonds of length 2.54 Ang. for the C-C bond and 152 Ang for squalene). If the Gaussian end-to-end distance is 480 Ang, in both cases, calculate the statistical segment lengths.

e) Explain why the persistence length, 8.51 Ang, (compared to the statistical segment length) is a better description of this polymer. (You will need to define the persistence length and the statistical segment length, and calculate the number of persistence units, z, you would use to calculate entropy for this chain.)

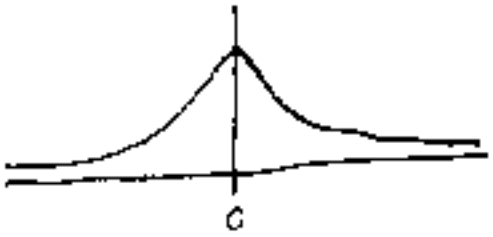
ANSWERS: **Properties Quiz 1 040402**

a)

$$P(x,\mu,\sigma) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\frac{(x-\mu)^2}{\sigma^2}\right]$$

or

$$P(R,n,b) = \frac{1}{(2\pi n b^2)^{3/2}} \exp\left[-\frac{1}{2}\frac{R^2}{nb^2}\right]$$



b) Brownian motion involves a continuous random motion of a particle. Such a continuous motion can be broken down into a series of small steps in approximation. For such a series of steps the direction of each step is chosen at random and would follow a 3-d Gaussian distribution, that is, the final distance traveled would be described by a 3-d Gaussian probability function which is composed of the second equation of part a) cubed using n/3 for n.

c) The sketch of part a) shows that the Gaussian function is symmetric about 0, that is there are equal probabilities for values -R and R. The mean value is 0 for any symmetric distribution function. Mathematically,

$$\langle R \rangle = \int_{R=-\infty}^{R=\infty} \frac{R}{\sqrt{2\pi n b^2}} \exp\left[-\frac{1}{2}\frac{R^2}{nb^2}\right] dR$$

$$dy = R\,dR \qquad y = \frac{R^2}{2} \qquad K = \frac{1}{nb^2}$$

$$= \frac{-1}{\sqrt{2\pi K}} \int_{y=+\infty,\ \frac{(-R)^2}{2}}^{y=+\infty} -K \exp(-Ky)\,dy = \frac{-1}{\sqrt{2\pi K}} \left[\exp -Ky\right]_{\infty}^{\infty} = 0$$

d) $\langle R^2 \rangle = (2n)\, l_{ssl}^2$

For ethylene l_{ssl} = 6.5 Ang

For squalene l_{ssl} = 38 Ang

e) The statistical segment length is a conversion factor that has units of length used to convert the degree of polymerization (n or 2n) to the mean end-to-end distance as noted in question d). The persistence length is a physical measure of the local rigidity of the chain. In this case, the persistence length is composed of about 3 ethylene units. The number of persistence units in this chain, z, is about 3,200, which is smaller than 2n using ethylene units but larger than 2n using squalene units. Calculations such as for the modulus of a single chain, $f \sim 1/z$, would result in different values depending on the physical unit used for the chain.