ChE 530 Polymer Chemistry University of Rhode Island
Professor Greenfield Spring 2007

Homework 3
due April 11, 2007

If you find yourself without enough information, make and justify a reasonable approximation. Please answer all parts of a question! (This is good practice for an exam setting.)

1. Find a piece of string that is approximately 2 to 4 ft long. First, record the fully extended length of your piece of string. Next, drop it (from as high a place as possible; a balcony over a stairwell is great) onto a flat surface 10–20 times, and measure the end-to-end distance r each time. As a reminder, r equals the distance between the two ends of the piece of string.

   Then, calculate $\langle r^2 \rangle^{1/2}$ (the square root of the average of the square of the end-to-end distance, also called the "root-mean-square" or RMS) from your measured data, and plot the measured distribution $P(r)$. In other words, how many string measurements had r values within each range of r values? (See also note below.) Does the shape agree with the random-walk prediction

$$P(r,n)dr = \frac{2}{n\ell^2} r \exp\left(-\frac{r^2}{n\ell^2}\right) dr \qquad (1)$$

   of the two-dimensional chain distribution? For the parameter combination $n\ell^2$ in this equation, use the fact that the average mean-squared distance is $\langle r^2 \rangle = n\ell^2$ for this model, as in one and three dimensions. (That means that you set $n\ell^2$ equal to the value of $\langle r^2 \rangle$ that you measured.)

   How did $\langle r^2 \rangle^{1/2}$ compare with the fully extended length? What do you think would happen if similar lengths of rope or thread were used instead? (Hint: think about how they are more or less stiff.)

   Notes on how to plot a distribution: to calculate values of $P(r)$ from your data, divide up all the possible r's into domains, such as $a < r < b$. Then figure out the fraction of measured r's that fall into each domain. The value of $P(r)$ equals this fraction, DIVIDED BY the width of the domain, $(b - a)$. This division may seem artificial, but it's actually necessary. As an example, think about if you were guessing real numbers that fell between 0 and 10. Say you tried two bin sizes, either 1 or 2 wide (i.e. 10 or 5 bins). In the first case, you'd expect each bin to have 1/10 of the numbers. In the second case, you'd expect each bin to have 1/5 of the numbers, or twice as many per bin! Since these are both the same distribution, the way to compensate for the "extra" bin width in the second case is to divide each bin by its width, leading to (1/10) / 1 compared to (1/5) / 2 = 1/10.

   If you'd rather think about it in terms of math, consider it this way. The normalization has to be

$$1 = \int P(r)dr \approx \sum_{\text{bins } i} P_i \Delta r_i = \sum_{\text{bins } i} \text{fraction in bin } i$$

   where Δr_i is the width of bin i. (Not all bin widths have to be the same.) Comparing the individual terms in each of the last two sums,

$$P_i \Delta r_i = \text{fraction in bin } i$$

   so

$$P_i = (\text{fraction in bin } i)/\Delta r_i$$

   as described in words above.

2. This problem is from Painter and Coleman.

   (a) The characteristic ratio C_∞ for polyethylene is 6.8. What would be the root-mean-square end-to-end distance of a chain of degree of polymerization 100,000, if the chain is in a melt of other high molecular weight polyethylene chains? Use $\ell = 1.54$ Åfor the carbon–carbon bond distance.

   (b) What would be the radius of gyration in this circumstance?

   (c) Assuming that all constants of proportionality cancel out, what is the ratio of the root-mean-square end-to-end distance of the same chain in a good solvent compared to that in the melt?

3. Consider a situation in which a polymer gel is mechanically stable at a variety of polymer volume fractions. Assume that the chain shapes between junction points (sometimes called cross links, and equivalent for the purposes of this problem to entanglements in solution) follow the “blob” description of the semi-dilute scaling regime.

   Your objective is to use these solvent-swollen gels to separate different molecules. The first swollen polymer gel that you try has a polymer volume fraction of 0.01 (remainder is solvent) and tends to separate molecules with sizes larger than 16 nm from smaller molecules.

   (a) How would you adjust the initial polymer volume fraction to achieve a separation boundary for molecules of 10 nm size? For a 1 nm size?

   (b) Quantitatively, how does the relative number of chains that make up each blob vary among these three volume fractions?

4. Sun, problem 8.4. In part (a), calculate the values of both K and a, for the Mark-Houwink equation. Then continue the rest of the problem. Use the hint provided in the text!

5. Drug delivery devices can function in a few different ways. One possibility is that drug molecules diffuse out of the polymer matrix into the surrounding tissue, based on a combination of (1) chemical potential differences between the device and tissue and (2) a concentration gradient within the device. Another possibility is that the polymer matrix itself can degrade *in vivo*, releasing drug in the process.

   In this problem we will analyze overly simple models of each process. First consider a polymer matrix that does not degrade. For simplicity, picture a device that is thin in the x direction and has an area $A = 1$ cm in the other two directions. The boundaries of the device (i.e. the main contacts with tissue) are at $x = 0$ and $x = L$, where $L = 1$ mm is the thickness. The drug concentration in the device depends only on x and time t, and generally it will follow an equation like

$$c(x,t) = \sum_n c_n \sin(n\pi x/L) \exp\left(-\frac{Dn^2\pi^2}{L^2}t\right) \tag{2}$$

   where the sum over $n = 1, \infty$ is a *Fourier series* and allows for any initial concentration profile (uniform, gradient, etc) to be incorporated into the model. It also assumes that the concentration instantaneously reaches zero at the boundaries, where $x = 0$ or L. In this problem, we will set $c_1 = 0.01$ g/cm^3, and will set all other c_n equal to zero, i.e. only one term will appear in this equation.

   (a) We will consider a diffusion coefficient of order 10^{-10} cm^2/s for a moderate size molecule in a polymer matrix that is partially plasticized by contact with water. Calculate the rate that drug diffuses out of the device, assuming that “resistance is on the matrix side”. This means that we neglect the driving force for drug to enter the tissue and assume instead that reaching the surface of the delivery device is rate-limiting. The rate can be found by first calculating the *flux* (J[=] amount per area per time) of drug reaching the surfaces as

$$J = -D\frac{\partial c}{\partial x} \tag{3}$$

   and then multiplying by area to reach the release rate. The derivative can be found from equation 2 above for $c(x,t)$. Remember to include both the surfaces (i.e. $x = 0$ and $x = L$).

   (b) Calculate how your result from part (a) would change for a more elastomeric polymer, in which the diffusion coefficient of a small drug molecule is closer to 10^{-7} cm^2/s.

   (c) Now we will consider a polymer that *does* degrade over time. As the polymer degrades, the dissolved drug is introduced into the tissue. For simplicity, consider a uniform concentration in the device, and make it a factor of $2/\pi$ times the concentration above in order to have the same total amount of drug in the device. (Why $2/\pi$? That comes from integrating over the concentration profile $c(x,t)$ at time zero for a single term in the concentration equation; give it a try if you’d like.) Calculate the rate (volume per time) at which polymer must degrade in order to provide the same initial dissolution rate as in part b. Then convert this rate to a velocity (mm/s, by dividing by A) and finally to a characteristic time by dividing it into the thickness L.

   How fast must a diffusion process be (i.e. how big a diffusion coefficient D) for the characteristic diffusion time L^2/D to be comparable to this degradation time?