Chemistry 276 - Autumn 2009-10 - Advanced Physical Chemistry

Problem Set 1 (due 10/1/09 in class)

Random walk models of self-diffusion

The problem set is concerned with simple mathematical models for diffusion that are based on the concept of a random walk. For the moment, don't be concerned about how realistic or unrealistic the models are. Let's just use them to illustrate some of the mathematical features of random processes and of diffusion.

There are some notes on probability theory posted on the website for this course. You should download those notes and study them. They may be useful in solving the following problems.

A. Random walk on a one-dimensional lattice of sites. Suppose a particle moves along one dimension (in the x direction) and at any time its position is on one of various lattice sites. The sites are evenly spaced, with a spacing of ℓ. Then the nth site has an x coordinate $n\ell$, where $-\infty < n < \infty$. Suppose that time is divided into discrete intervals of length τ, with $t_m = m\tau$ for $0 \leq m \leq \infty$, where m takes on integer values.

At $t = t_0 = 0$, the particle is on the origin lattice site. At each subsequent t_m, it hops one site to the left or right, with it being equally likely to go in either direction. The hop directions for hops at different times are statistically uncorrelated. If d_i is the distance jumped at time t_i, then $\langle d_i \rangle = 0$, $\langle d_i^2 \rangle = \ell^2$. Note that $\langle d_i d_j \rangle = \langle d_i \rangle \langle d_j \rangle = 0$ if $i \neq j$, because the hops at different times are statistically independent. Here the angular brackets denote the expectation value or average over the relevant probability distribution function.

Let x_m be the coordinate of the particle just after time t_m. It is clear that

$$x_m = \sum_{i=1}^{m} d_i$$

x_m is a random variable.

1. As a function of m, what is the value of $\langle x_m \rangle$, the average of x_m?

2. As a function of m, what is the value of $\langle x_m^2 \rangle$, the average of x_m^2?

3. As a function of m, what is the value of $\langle x_m^3 \rangle$, the average of x_m^3?

4. As a function of m, what is the value of $\langle x_m^4 \rangle$, the average of x_m^4?

5. What is the maximum possible value of x_m (i.e. the largest value that has a nonzero probability)? What is the smallest possible value (i.e. the most negative value)?

6. $x_m - x_n$, the displacement associated with the motion from just after t_n to just after t_m, is also a random variable. Evaluate $\langle x_m - x_n \rangle$ and $\langle (x_m - x_n)^2 \rangle$

7. x_m and d_m are random variables. Are they statistically independent?

8. x_m and d_{m+1} are random variables. Are they statistically independent?

9. For long times (large m), it can be shown that the probability distribution function is a gaussian function of the form

$$P_{x_m}(x) = A \exp(-ax^2).$$

   A can be expressed in terms of a using the normalization condition. I won't ask you to prove the gaussian result, but I do want you to confirm it, in the following way. Calculate $\langle x_m^2 \rangle$ and $\langle x_m^4 \rangle$ in terms of a from this formula. Use the results to find a relationship between these two moments. Then verify that this relationship holds (for large m), using your answers to parts 2 and 4.

10. The equation just above is a solution of the diffusion equation, and for long times the motion of the random walk is diffusive. It follows from the diffusion equation that the mean square displacement $\langle x_m^2 \rangle$ should be equal to $2Dt_m$ for large t_m. (This result is appropriate for one dimensional diffusion. Here D is the self-diffusion coefficient.) What is the explicit formula for D in terms of the fundamental parameters of this random walk model? What are the dimensions of D?

B. Random walk on a three dimensional lattice of sites. Suppose a particle moves on a three dimensional cubic lattice. The sites are evenly spaced, with a spacing of ℓ. Each site is labeled by three integers n_x, n_y, n_z, where $n_x\ell$ is the x coordinate of the site, $n_y\ell$ is the y coordinate, and $n_z\ell$ is the z coordinate. Time is divided into discrete intervals of length τ, with $t_m = m\tau$ for $0 \le m \le \infty$.

At $t = t_0 = 0$, the particle is at the origin lattice site. At each subsequent t_m, it hops in one of 6 randomly picked directions $\pm x, \pm y, \pm z$ to the next site. Each of the six directions is equally likely, and hops at different time are uncorrelated with one another.

Let $\mathbf{r}_m$ be the location of the particle just after time t_m. It is clear that

$$\mathbf{r}_m = \sum_{i=1}^{m} \mathbf{d}_i.$$

where $\mathbf{d}_i$ is the vector distance traveled in the ith jump.

1. Calculate $\langle d_{ix} \rangle$, the average of the x component of $\mathbf{d}_i$.

2. d_{ix} and d_{iy} are random variables. Are they statistically independent?

3. d_{ix} and $d_{i+1,y}$ are random variables. Are they statistically independent?

4. The motion on a long time scale and long distance scale is diffusive (i.e. satisfies a diffusion equation), and the mean square displacement $\langle |\mathbf{r}_m|^2 \rangle$ is equal to $6Dt_m$ for large t_m. (This result is appropriate for three dimensional diffusion. Here D is the self-diffusion coefficient.) What is the formula for D in terms of the fundamental parameters of the model? What are the dimensions of D?

C. Random walk in continuous three dimensional space. Suppose a particle undergoes a random walk in continuous three dimensional space. At each t_m, defined as in the previous problems, the particle picks a random direction in three dimensional space and moves a distance ℓ in that direction. All directions are equally likely (i.e. all solid angles in three dimensional space are equally likely), and jumps at different times are uncorrelated.

What is the formula for the diffusion constant in terms of the fundamental parameters of the model?