18.366 Random Walks and Diffusion, Spring 2006, M. Z. Bazant.

Problem Set 5

Due at lecture on Tu Dec 5.

1. **Restoring force of highly stretched polymers.** Consider modeling a polymer in a dilute solution as Rayleigh's isotropic random walk in three dimensions with IID displacements of length, a. Recall the formula for the PDF of the end-to-end displacement (from PSet 1),

$$P_N(\vec{x}) = \frac{1}{2\pi^2 r}\int_0^\infty u\,\sin(ur)\left[\frac{\sin(ua)}{ua}\right]^N du$$

   (a) Use the saddle-point method to derive a globally valid asymptotic approximation for $P_N(\vec{x})$ for $N \gg 1$ with $\xi = |\vec{x}|/Na \leq 1$ fixed, leaving your answer in terms of the inverse L^{-1} of the Langevin function,

$$L(z) = \coth z - \frac{1}{z}$$

   (b) Use this result to compute and plot the entropic contribution to the free energy, $F = -TS = -T\log P_N$, as well as the effective *nonlinear* force $f(R;T,N,a) = -dF/dR$, and compare to the approximation in the central region $R = |\vec{x}| = O(a\sqrt{N})$.

2. **Linear Polymer Structure.** Consider a chain of N monomers, each of length a, in $d=3$ dimensions. Let R_N be the end-to-end distance, with PDF, $P(R,N)$. In the absence of correlations, we have the usual scaling, $\overline{R}_N = \sqrt{\langle R_N^2\rangle} = a\sqrt{N}$. Now suppose that monomers also tend to be aligned linearly at each link, with an energy, $\varepsilon(\theta) = -\alpha\,\vec{\Delta x}_n \cdot \vec{\Delta x}_{n+1} = -\alpha a^2\cos\theta$, for $1 \leq n \leq N-1$, which yields a PDF, $p(\theta) \propto e^{-\varepsilon(\theta)/kT}$, for each angle, θ.

   (a) Normalize $p(\theta)$ and calculate the mean total energy, $\langle E_N\rangle = (N-1)\alpha a^2\rho$, where $\rho(T) = \langle\vec{\Delta x}_n \cdot \vec{\Delta x}_{n+1}\rangle/a^2$, is the correlation coefficient between 'steps' (monomer vectors).

   (b) Show that the same scaling holds,

$$\overline{R}_N \sim a_{eff}(T)\sqrt{N}$$

   as $N \to \infty$, with an effective monomer size, $a_{eff}(T)$. Sketch $a_{eff}(T)$, and discuss its asymptotics for $T \to 0, \infty$.

3. **A persistent Lévy flight**. Consider the Cauchy random walk with IID displacements, $\Delta x_n'$, $n = 1, ..., N$, with PDF, $p(x) = a/\pi(a^2+x^2)$. From this flight, construct another Cauchy random flight with *non-independent* steps,

$$\Delta x_1 = \Delta x_1', \quad \Delta x_{n+1} = (1-\rho)\Delta x_{n+1}' + \rho\Delta x_n', \quad n \geq 2$$

where $|\rho| < 1$ plays the role of a correlation coefficient between successive steps (although here correlations cannot be defined since the variance is infinite)[1]. Find the exact distribution of the final position, $X_N = \sum_{n=1}^N \Delta x_n$. Does the scaling of the half-width depend on ρ?

[1]This could model the effect of inertia in the problem of finding the tangential displacement of a particle in a dilute gas bouncing between rough parallel plates, separated by much less than the mean free path. It could also model positive short-time correlations in volatile stock prices.

4. **A continuous-time random walk.** Derive the exact PDF of the position, $P_N(n,t)$, of an unbiased CTRW on the integer lattice $n = 0, \pm 1, \pm 2, ...$ starting at the origin (with nearest-neighbor hopping) with waiting time PDF, $\psi(t) = e^{-t}$.

5. **Self-Avoiding Walk.** (Extra credit) Simulate self-avoiding walks on a cubic lattice in three-dimensions[2], and try to determine the scaling of the root-mean-square end-to-end length

$$R_n =< |\vec{X_N}|^2 >^{1/2} \sim N^\nu$$

by plotting $\log R_N$ versus $\log N$ and getting the slope of a (hopefully) straight line. How does your result compare with the Fisher-Flory estimate $\nu = 3/(d+2) = 3/5$ and the recent numerical result 0.5877 ± 0.0006?

[2]It is nontrivial to generate large SAW (because most end up "trapped"), so to see the scaling above, you may need to think about more sophisticated sampling algorithms!