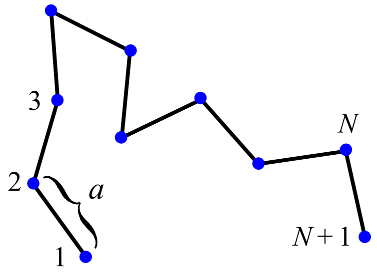
RG Methods in Statistical Field Theory: Problem Set 5

due: Friday, November 3, 2006

In lecture we showed that the scaling behavior of physical quantities near a critical point arises naturally from looking at the coarse-grained description of the system. In this problem set we will see that similar renormalization-group ideas can be used to derive some of the fundamental scaling characteristics of polymers. The beauty of this approach is that one can find a few basic results just from general arguments, without needing to know the details of the renormalization-group transformation. (Happily for us, this means no long, tedious calculations are necessary.)

Part I: The Ideal Chain



(a) Consider the simplest possible model for a polymer in d dimensions: a chain of $N+1$ molecules ("monomers") connected by N bonds of fixed length a, where the direction of each bond is completely random. We begin by looking at an "ideal chain", where there are no interactions between the monomers, so that every configuration of the chain has the same energy. Let $\mathbf{R}_i$ be the position of the ith atom, and $\mathbf{a}_i = \mathbf{R}_{i+1} - \mathbf{R}_i$ be the bond vector between ith and the $(i+1)$th atom. Each $\mathbf{a}_i$ vector has length a, and the randomness of the bond directions means that $\langle \mathbf{a}_i \rangle = 0$ and $\langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = 0$, for $i \neq j$, where $\langle\ \rangle$ denotes a thermodynamic average over all possible chain configurations. One way to characterize the total size of the polymer coil is by the end-to-end vector $\mathbf{R}$, defined as:

$$\mathbf{R} \equiv \mathbf{R}_{N+1} - \mathbf{R}_1 = \sum_{i=1}^{N} \mathbf{a}_i$$

Since $\langle \mathbf{a}_i \rangle = 0$, clearly $\langle \mathbf{R} \rangle = 0$, but $\langle \mathbf{R}^2 \rangle = \langle \mathbf{R} \cdot \mathbf{R} \rangle$ has a nonzero value. Show that:

$$\langle \mathbf{R}^2 \rangle = N a^2$$

Thus the root-mean-squared end-to-end distance $\bar{R} \equiv \langle \mathbf{R}^2 \rangle^{1/2}$ scales like $N^{1/2}$ for the ideal chain.

(b) We would like to replace the ideal chain with a coarse-grained model that has the same global properties. We can divide up the original chain into N/b subunits, with each subunit containing b consecutive monomers. If we assign a position $\mathbf{R}'_n$ to the nth subunit (for example, the center of mass of the b monomers in the subunit), then we can consider a new coarse-grained ("renormalized") polymer chain defined by the series of positions $\mathbf{R}'_n$ and the vectors $\mathbf{a}'_n = \mathbf{R}'_{n+1} - \mathbf{R}'_n$. Of course the $\mathbf{a}'_n$ will now have different lengths depending on the original chain configuration, but as a first approximation we can fix the length $|\mathbf{a}'_n| = a'$ for all n, where a' represents some average distance between the subunits. We would like the size $\bar{R}'$ of the new chain to equal $\bar{R}$ of the original. For this to be true, show that a' must satisfy:

$$a' = b^{1/2} a$$

Part II: The Interacting Chain

Note that in the ideal chain there is nothing preventing two monomers from occupying the same position. In real polymers, there are repulsive interactions: if two monomers come too close to each other, the energy of the configuration becomes large. We can represent this interaction by some short-ranged function, so that the energy of the system is $U = \frac{1}{2}\sum_{i,j} U_{ij}$, where the potential between the ith and jth monomer is written as $U_{ij} = k_B T F(\mathbf{R}_i - \mathbf{R}_j)$. Here we have factored out an energy $k_B T$, so that the function F is dimensionless. We assume that F is large only when $\mathbf{R}_i$ and $\mathbf{R}_j$ are close to each other, and nearly zero otherwise. More complicated three-body or higher-order interactions are ignored. In the limit of very short-ranged interactions, we can write $F(\mathbf{R}_i - \mathbf{R}_j) \approx v\delta^{(d)}(\mathbf{R}_i - \mathbf{R}_j)$, where v is a constant with dimensions of volume (note that the delta function has dimensions of volume^{-1}, since $\int d^d\mathbf{x}\, \delta^{(d)}(\mathbf{x}) = 1$). The constant v, which measures the strength of the interaction and can vary with temperature, is known as the *excluded volume.* When $v = 0$, we have an ideal chain.

The excluded volume interaction has a dramatic effect on the system. If $v > 0$ the polymer will "swell up": the size of the coil will be greater than for an equivalent ideal chain, because different parts of the polymer will repel each other. Exact calculations become impossible, but we can still say something about the system from renormalization-group arguments. Consider a coarse-grained model of the interacting polymer, made up of N/b subunits and described by constants a' and v'. The parameter a' must take into account all the interactions between monomers inside one subunit, and v' must account for interactions between any two subunits. Because of monomer-monomer repulsion, the distance a' should be larger than the ideal chain result of part (b). We can write it as:

$$a' = b^{1/2} a (1 + H_b(u))$$

where $H_b(u)$ is a positive, dimensionless function that depends on b and the dimensionless interaction parameter $u \equiv v/a^d$. (Since a and v are the only constants in the system, u is the only dimensionless parameter we can form.) We can write down a similar equation for v': if two subunits of the renormalized polymer could completely interpenetrate each other, then v' would equal $b^2 v$, because there are b^2 possible interactions between the b monomers of one subunit and the b monomers of the other. But because there is repulsion between the subunits, complete interpenetration does not happen, and the actual v' is smaller:

$$v' = b^2 v (1 - L_b(u))$$

where $L_b(u)$ is a positive dimensionless function. The exact forms of H_b and L_b could be found from a detailed renormalization group transformation. For our purposes, we only need to assume that they exist and are well-behaved. The transformation preserves the size of the coil, so that $\bar{R}' = \bar{R}$.

(c) Write down a renormalization-group equation for $u' = v'/(a')^d$. Now we can course-grain the renormalized system, repeating the transformation, giving us a new polymer with N/b^2 subunits and an interaction parameter u''. After n course-grainings, we have some parameter $u^{(n)}$ describing the interactions for a polymer with N/b^n subunits. Show that there exists a critical dimension d_c such that for $d > d_c$, the value $u^{(n)} \to 0$ as $n \to \infty$. Find d_c.

(d) Part (c) shows that $u^* = 0$ is a fixed point of the renormalization-group transformation for $d > d_c$. What does this mean for the size of the original system $\bar{R}$? For a polymer of N bonds of length a, we expect $\bar{R}$ to have the form:

$$\bar{R} = aD(N, u)$$

where D is some dimensionless function. Using the fact that $\bar{R}$ is preserved by the RG transformation, show that:

$$\bar{R} \propto N^{1/2} \quad \text{for } d > d_c$$

Thus the system behaves similar to an ideal chain.

(e) For $d < d_c$, $u^{(n)}$ will tend to a fixed point u^*, but u^* does not have to be zero. In fact, we expect that after n coarse-grainings, with n large, when each subunit corresponds a large polymer coil of b^n monomers in the original system, the subunits will behave like impenetrable spheres: the excluded volume will be proportional to the size of the coil itself, $v^{(n)} \sim (a^{(n)})^d$. Thus $u^{(n)} = v^{(n)}/(a^{(n)})^d$ goes to some nonzero constant u^* as $n \to \infty$. Show that in this case:

$$\bar{R} \propto N^{\nu} \quad \text{for } d < d_c$$

and find an equation for ν in terms of u^*, b, and the functions H_b, L_b. The *Flory exponent* ν has a universal value for all real polymers in a certain dimension. For $d = 3$, $\nu \approx 3/5$. As expected, $\nu > 1/2$ because the size of the polymer should grow faster with N compared to an ideal chain, due to the repulsive interactions.

Part III: The Polyelectrolyte Chain

(f) Finally, let us consider a chain with long-range interactions: one where each monomer has a charge e, and the monomers interact through Coulomb repulsion. Since the Coulomb force decays slowly with distance, the repulsive effects can be quite dramatic (as we will see later, in certain cases the chain can end up fully stretched into a rigid line, with each monomer trying to get as far from the others as possible). The potential between the ith and jth monomer now has the form:

$$U_{ij}(|\mathbf{R}_i - \mathbf{R}_j|) = k_d \frac{e^2}{|\mathbf{R}_i - \mathbf{R}_j|^{d-2}}$$

where k_d is some constant that depends on dimension d. For this system, if we want a dimensionless parameter u measuring the strength of the interaction, let us take the ratio of the Coulomb repulsion between neighboring monomers and the energy $k_B T$:

$$u \equiv \frac{k_d e^2}{k_B T a^{d-2}}$$

Assume that a' of the renormalized system has an RG equation of the same form as in Part II above, involving an unknown positive function $H_b(u)$. The equation for u' turns out to be simpler, since the charge e' of a subunit with b monomers is exactly $e' = be$. Find an equation for u' in terms of the physical parameters and $H_b(u)$.

(g) Show that there are three cases for the RG behavior:

$\underline{d > 6:}$ $u^{(n)} \to 0$ as $n \to \infty$. By the same reasoning as in part (d), this means that $\bar{R} \propto N^{1/2}$.

$\underline{4 < d < 6:}$ $u^{(n)} \to u^*$ as $n \to \infty$, where u^* is a nonzero constant. Prove that the size of the polymer behaves like $\bar{R} \propto N^{\nu}$, where ν is given by the simple equation:

$$\nu = \frac{2}{d-2}$$

$\underline{d < 4:}$ $u^{(n)} \to \infty$ as $n \to \infty$. Show that this means the polymer is maximally stretched out into a rigid line.