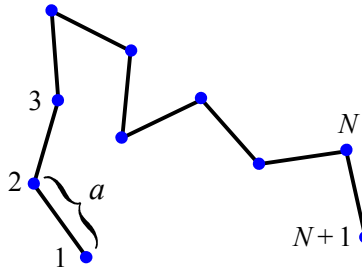


# RG Methods in Statistical Field Theory:

## Problem Set 5 Solution

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  $i$ th atom, and  $\mathbf{a}_i = \mathbf{R}_{i+1} - \mathbf{R}_i$  be the bond vector between  $i$ th 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:

$$\langle \mathbf{R}^2 \rangle = Na^2$$

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.

**Answer:**

$$\langle \mathbf{R}^2 \rangle = \left\langle \sum_{i,j=1}^N \mathbf{a}_i \cdot \mathbf{a}_j \right\rangle = \sum_{i=1}^N \langle \mathbf{a}_i \cdot \mathbf{a}_i \rangle + \sum_{i \neq j}^N \langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = Na^2$$

where we have used the fact that

$$\langle \mathbf{a}_i \cdot \mathbf{a}_j \rangle = \begin{cases} 0 & i \neq j \\ a^2 & i = j \end{cases}$$

(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  $n$ th 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:

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

**Answer:** We would like  $\bar{R}' = N'^{1/2}a'$  to equal  $\bar{R} = N^{1/2}a$ . Since  $N' = N/b$ , this implies  $a' = b^{1/2}a$ .

## 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  $i$ th and  $j$ th 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<sup>-1</sup>, 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  $b^2v$ , 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:

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

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  $u^{(n)} \rightarrow 0$  as  $n \rightarrow \infty$ . Find  $d_c$ .

**Answer:** Putting together the RG equations for  $a$  and  $v$  we find:

$$u' = \frac{v'}{(a')^d} = \frac{b^2v(1 - L_b(u))}{b^{d/2}a^d(1 + H_b(u))^d} = b^{2-d/2}u \frac{(1 - L_b(u))}{(1 + H_b(u))^d}$$

Since  $1 - L_b(u) < 1$  and  $1 + H_b(u) > 1$ , the factor  $\frac{(1-L_b(u))}{(1+H_b(u))^d} < 1$ . When  $2 - d/2 < 0$ , or  $d > 4$ , all the factors multiplying  $u$  on the right-hand side will be smaller than 1. Iterating the RG equation, we can determine that  $u^{(n)} < b^{n(2-d/2)}u$ . Thus  $u^{(n)} \rightarrow 0$  as  $n \rightarrow \infty$  for dimensions  $d > d_c = 4$ .

**(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.

**Answer:** The condition  $\bar{R} = \bar{R}'$  implies that:

$$\bar{R} = aD(N, u) = a'D(N', u') = \dots = a^{(n)}D(N^{(n)}, u^{(n)})$$

From the RG equation for  $a$  we know that:

$$a^{(n)} = b^{1/2}a^{(n-1)}(1 + H_b(u^{(n-1)})) = \dots = b^{n/2}a \prod_{i=0}^{n-1} (1 + H_b(u^{(i)}))$$

Taking the limit of large  $n$  we know that  $u^{(n)} \rightarrow u^* = 0$ , so we can simplify the product above as follows: choose a large integer  $n_0$  such that for  $n \geq n_0$  we can make the replacement  $u^{(n)} \approx u^*$ . (The exact value of  $n_0$  is unimportant, so long as we keep it fixed in the derivation below.) Then  $a^{(n)}$  in the limit  $n \rightarrow \infty$  can be written as:

$$\begin{aligned} a^{(n)} &= b^{n/2} a \prod_{i=0}^{n_0-1} (1 + H_b(u^{(i)})) \prod_{i=n_0}^{n-1} (1 + H_b(u^{(i)})) \\ &\approx b^{n/2} a (1 + H_b(u^*))^{n-n_0} \prod_{i=0}^{n_0-1} (1 + H_b(u^{(i)})) \\ &= C b^{n/2} a (1 + H_b(u^*))^{n-n_0} \end{aligned}$$

where the constant  $C \equiv \prod_{i=0}^{n_0-1} (1 + H_b(u^{(i)}))$ . The value of  $H_b(u^*)$  at  $u^* = 0$  must be zero, since the RG equation for  $a$  in the noninteracting limit  $u = 0$  must give back the ideal chain result of part (b):  $a' = b^{1/2} a (1 + H_b(0)) = b^{1/2} a$ . Thus  $a^{(n)} \approx C b^{n/2} a$ . Plugging this along with  $N^{(n)} = b^{-n} N$  into the equation for  $\bar{R}$  above we get:

$$\bar{R} = a^{(n)} D(N^{(n)}, u^{(n)}) \approx C b^{n/2} D(b^{-n} N, u^*)$$

Choose  $n$  large enough so that  $b^n \approx N$ . Then:

$$\bar{R} \approx C N^{1/2} D(1, u^*)$$

Thus we have the result that  $\bar{R} \propto N^{1/2}$  for  $d > d_c$ .

(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  $n \rightarrow \infty$ . Show that in this case:

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

and find an equation for  $\nu$  in terms of  $u^*$ ,  $b$ , and the functions  $H_b$ ,  $L_b$ . The *Flory exponent*  $\nu$  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.

**Answer:** We can proceed exactly like in the answer to part (d). The only difference will be that since  $u^* \neq 0$  for  $d < d_c$ ,  $H_b(u^*) \neq 0$  and the factor  $(1 + H_b(u^*))^{n-n_0} \neq 1$ . Thus the result for  $\bar{R}$  is:

$$\begin{aligned} \bar{R} &\approx C b^{n/2} (1 + H_b(u^*))^{n-n_0} D(b^{-n} N, u^*) \\ &= \tilde{C} b^{n\nu} D(b^{-n} N, u^*) \end{aligned}$$

where:

$$\tilde{C} \equiv C (1 + H_b(u^*))^{-n_0}, \quad \nu \equiv \frac{1}{2} + \frac{\ln(1 + H_b(u^*))}{\ln b}$$

Here we have used the fact that we can write a quantity  $x$  as  $x = b^y$  where  $y = \ln x / \ln b$ . If we choose  $n$  large enough that  $b^n \approx N$  we have:

$$\bar{R} \approx \tilde{C} N^\nu D(1, u^*)$$

so  $\bar{R} \propto N^\nu$ . Note that for  $d \leq d_c$ , when  $u^* = 0$  and  $H_b(u^*) = 0$ , the equation for  $\nu$  gives the answer  $\nu = 1/2$  you found in part (d).

### 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  $i$ th and  $j$ th 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  $H_b(u)$ .

**Answer:**

$$u' = \frac{k_d (e')^2}{k_B T (a')^{d-2}} = \frac{k_d b^2 e^2}{k_B T b^{(d-2)/2} a^{d-2} (1 + H_b(u))^{d-2}} = b^{3-d/2} u (1 + H_b(u))^{2-d}$$

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

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

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

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

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

**Answer:** From the RG equation of part (f) we see that for  $d > 6$  we have  $b^{3-d/2} < 1$  and  $(1 + H_b(u))^{2-d} < 1$ , so  $u^{(n)} \rightarrow 0$  as  $n \rightarrow \infty$ . For  $d < 6$  the factor  $b^{3-d/2} > 1$ , so we need to understand the behavior of the other factor  $(1 + H_b(u))^{2-d}$  in order to determine the RG flow of  $u$ . Up to this point in the problem set, the only facts about the function  $H_b(u)$  we have used is that it is positive and  $H_b(0) = 0$ . Is there anything else we can say? We know that in the limit  $u \rightarrow \infty$  the Coulomb repulsion becomes infinitely strong: physically, we expect the charged monomers to get as far away from each other as possible, stretching the polymer into a rigid line. But when the polymer is a straight line,  $\bar{R} = Na$ , and the renormalization of the segment length  $a$  is trivial:  $a' = ba$  for a coarse-grained system with  $N' = N/b$  segments. Since  $a' = b^{1/2}a(1 + H_b(u))$ , this implies that when  $u = \infty$  we have:  $1 + H_b(\infty) = b^{1/2}$ .

Now we are ready to make an RG argument. Let us be in a dimension  $d < 6$ . If our original system has a very small  $u$ , we can say that  $1 + H_b(u) \approx 1$ , so

$$u' \approx b^{3-d/2}u$$

Clearly  $u$  will flow to a larger value. If our original system has a very large  $u$ , we can say that  $1 + H_b(u) \approx b^{1/2}$ , so

$$u' \approx b^{3-d/2}b^{(2-d)/2}u = b^{4-d}u$$

If  $d < 4$  we see that in this case also  $u$  will flow to a larger value. From these two limiting cases we can say that the fixed point  $u^* = \infty$  when  $d < 4$ .

On the other hand when  $4 < d < 6$ , we find that a large  $u$  will flow to a smaller value, and a small  $u$  will flow to a larger value. Hence the fixed point must be some  $u^* \neq 0, \infty$ . The fixed point equation is:

$$u^* = b^{3-d/2}u^*(1 + H_b(u^*))^{2-d}$$

which implies that  $(1 + H_b(u^*)) = b^{(d/2-3)/(2-d)}$ . Doing the same analysis as in part (e), we get exactly the same expression for  $\nu$ , but now we can plug in the value of  $(1 + H_b(u^*))$ :

$$\nu = \frac{1}{2} + \frac{\ln(1 + H_b(u^*))}{\ln b} = \frac{1}{2} + \frac{d/2 - 3}{2 - d} = \frac{2}{d - 2}$$