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Polymers in a random environment

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Abstract. Self-avoiding polymer chains in a random environment are considered by means of the renormalization group (RG) and without using the replica trick. The coupled differential equations of the RG for the excluded volume strength and for the strength of the disorder are derived and solved up to the first order of $\epsilon = 4 - d$. The quenched average of the number of states of a polymer chain is studied. In the case of finite volume the result obtained is in agreement with that derived earlier by Machta. The radius of the collapsed polymer derived by Edwards and Muthukumar is rederived within the RG method. The quenched average of the second virial coefficient of a solution of polymers in the random environment is considered.

The equilibrium properties of polymer chains in random environments have been studied by many authors in recent years [1–14]. Systems in random environments are usually studied by using the replica trick. In this article we consider polymers with Gaussian disorder without using the replica trick. The idea of our approach consists of the following. The random environment is considered at first as an inhomogeneous external field. Assuming that the field is weak we expand the physical quantities such as the normalized chain end-to-end correlation functions (CF) in powers of the external potential. The average over this potential then occurs within these perturbation expansions. We use the continuous model of a polymer chain described by Edwards. The vector $r(s)$ ($0 \leq s \leq L$, L is the contour length of the chain) describes the configuration of the chain. The probability of the configuration $r(s)$ is given by

$$P(\{r(s)\}) \simeq \exp \left\{ -\frac{d}{2l} \int_0^L ds \left(\frac{\partial r(s)}{\partial s} \right)^2 - \frac{1}{2} l^{-2} v_0 \int_0^L ds_1 \int_0^L ds_2 \delta^d(r(s_1) - r(s_2)) - l^{-1} \int_0^L ds U(r(s)) \right\} \quad (1)$$

where d is the dimension of space, l is the Kuhnian segment length, v_0 is the excluded volume strength, and $U(r(s))$ is the external potential. The non-normalized end-to-end chain correlation function is defined as follows

$$G_1(p_1, p_2) = \langle \exp(-ip_1 r(L) - ip_2 r(0)) \rangle \quad (2)$$

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where the average has to be carried out with (1). We will study the quenched average of the normalized end-to-end chain correlation function

$$g_1(p_1, p_2) = \langle G_1(p_1, p_2) / G_1(0, 0) \rangle_U \quad (3)$$

where the bracket with the subscript U in (3) means the quenched average over the random potential $U(r)$. For the annealed average the numerator and denominator in (3) are averaged over the disorder independently of each other. We note that in (2) and (3) the ends of the polymer are not fixed. At first we expand the CF (2) in powers of the external field $U(r)$. The latter can be represented by means of diagrams [15]. Examples of these diagrams are given in figure 1.



Figure 1. The diagrammatic expansion of $G_1(p_1, p_2)$ in powers of the external field. The broken lines are associated with the external potential $U(r(s))$.

Then we substitute the perturbation series of $G_1(p_1, p_2)$ into (3) and carry out the average over $U(r)$. The disorder is assumed to be Gaussian and is characterized by the correlator

$$\langle U(q_1)U(q_2) \rangle = (2\pi)^d \Delta_0 t^{-2} \delta^d(q_1 + q_2). \quad (4)$$

The consequence of this average is that the vertices associated with the external potential will be connected in pairs with each other by an interaction line which is associated with the factor given by equation (4). Because of the quenched average contractions appear between the numerator and denominator of the CF (3). However it can immediately be shown that such contractions contain the factor $1/V$ (V is the volume) and they disappear in the thermodynamic limit. The factor $1/V$ appears as follows. The first term of the perturbation expansion of the denominator is $(2\pi)^d \delta(0) = V$. We note that $\delta(0)$ appears as a result of the integration over $r(0)$. For a polymer with a fixed end such a factor does not appear. In order to expand the denominator in powers of the external potential we have to factor out the common factor V . Because of this the diagrams of the denominator contain the factor $1/V$. After carrying out the average over the disorder connected diagrams consisting of the diagrams of the numerator and the denominator appear. Because of the normalization of the denominator (the factor $1/V$) these diagrams are independent of V . The diagrams without such contractions contain the factor V . For this reason the contractions between the numerator and denominator do not appear in the thermodynamic limit. Therefore for infinite systems the quenched average reduces to the annealed one. We note that this is due to the fact that the end of the polymer is not fixed. It is interesting that the appearance of contractions between numerator and denominator is related to replica symmetry breaking. In the case where such contractions do not appear (a polymer with free ends) replica symmetry breaking does not appear. For a polymer with one end fixed contractions between the numerator and denominator appear and replica symmetry breaking takes place. It is easy to see that for $V \rightarrow \infty$ the interaction appearing as a consequence of the average over the disorder is of the same character as the excluded volume interaction with

the one distinction that the former is negative. Thus the only effect of the random environment is the 'renormalization' of the excluded volume strength: $\bar{v}_0 = v_0 - \Delta_0$. As is well known from the excluded volume problem the renormalization of the interaction constant in the one-loop approximation is given by [16]

$$\bar{v} = \bar{v}_0 \left(1 - \frac{8}{\epsilon} \bar{v}_0 L^{\epsilon/2} + \dots \right). \tag{5}$$

The factor $(d/2\pi l)^{d/2} l^{-4}$ is absorbed into \bar{v}_0 . The renormalization of the chain end-to-end distance is given by [15, 16] $R^2 = L'l$ with

$$L' = L \left(1 + \frac{2}{\epsilon} \bar{v}_0 L^{\epsilon/2} + \dots \right). \tag{6}$$

In order to obtain the differential equations of the renormalization group we introduce the cutoff λ by demanding that (5) and (6) remain finite in $d = 4$: $(2/\epsilon)L^{\epsilon/2} \rightarrow (2/\epsilon)(L^{\epsilon/2} - \lambda^{\epsilon/2})$. Considering λ as a parameter of the renormalization group and introducing the dimensionless interaction constant $g' = (v - \Delta)\lambda^{\epsilon/2}$ we obtain differential equations for g' and L' as follows

$$\partial g' / \partial x = \frac{1}{2}\epsilon g' - 4g'^2 \quad \partial \ln L' / \partial x = g' \tag{7}$$

with $x = \ln \lambda'$. The solution of the equation for L' is

$$L' = L \left(1 + \frac{8}{\epsilon} \bar{v}_0 \lambda_m^{\epsilon/2} \right)^{1/4}. \tag{8}$$

The mean square end-to-end distance of the polymer in the renormalized theory is given by

$$R^2 = L'l f_r(g) \tag{9}$$

where $f_r(g)$ takes into account the regularized part of the perturbation expansion. The final parameter of the RG, λ_m , has to be identified with L' (matching condition [17, 16]). In the excluded volume regime ($v_0 > 0$) equation (8) yields a power-like behaviour of $R^2 = L'l, R^2 \simeq L^{2\nu}$, with $\nu = 1/2 + \epsilon/16$. It is remarkable that equation (9) together with the matching condition has a non-zero solution for negative $v_0 = -\Delta_0$. For finite L this solution can only be obtained numerically. For $L \rightarrow \infty, L'_c$ approaches the value

$$R_c^2 \simeq L_c l = l \left(\frac{\epsilon}{8\Delta_0} \right)^{2/(4-d)}. \tag{10}$$

Besides the numerical prefactor the latter coincides with the result obtained by Edwards and Muthukumar [5] by using the replica trick. We note that in obtaining (10) we omit the function $f_r(g)$. This would be legitimate if the latter tends to a constant for large negative g . In the following we give an argument in support of this. Up to the first order in $g, f_r(g)$ is given by [16]

$$f_r(g) = 1 + c(-g) + \dots$$

with $c > 0$. According to this expansion $f_r(g)$ is an increasing function of $-g$. On the other hand an increase in f causes an increase in R^2 . However one would expect that R^2 would not increase with g . For this reason we expect $f_r(g)$ to have a

finite value for large negative g and not tend to zero for large g . The first correction to (10) is

$$R_c^2 \simeq L_c l \left(1 - \frac{2}{\epsilon} (L_c/L)^4 \right). \tag{11}$$

For $d = 4$ instead of (10) we obtain $R_c^2 = l \lambda \exp(1/(4\Delta_0))$, where λ is an ultraviolet cutoff (microscopic length) comparable with the statistical segment length.

Now we will consider the partition function of one polymer chain. The quenched average for the chain with one end fixed is more difficult and will be considered in a separate paper. The diagrammatic expansion of the difference $\delta Z = \ln\langle Z \rangle - \langle \ln Z \rangle$ is represented in figure 2

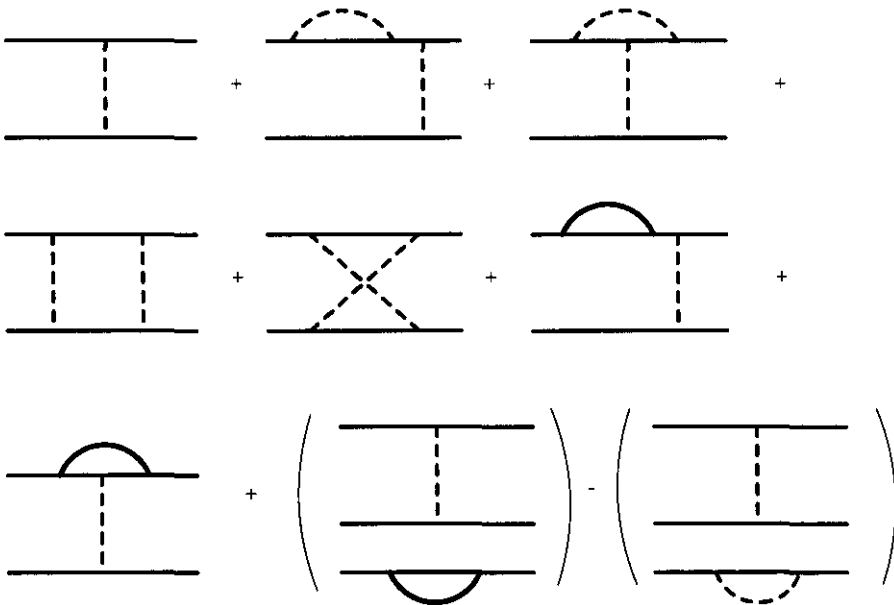


Figure 2. Diagrams contributing to δZ . The broken curves represent the interaction due to disorder. The thick curved lines represent the excluded volume interaction.

Analogously to the theory of polymer solutions [15, 16], the renormalization of the strength of the disorder is obtained from the diagrams in figure 2 as

$$\Delta = \Delta_0 \left(1 + \frac{8}{\epsilon} \Delta_0 L^{\epsilon/2} - \frac{4}{\epsilon} v_0 L^{\epsilon/2} + \dots \right). \tag{12}$$

Combining (5) and (12) we obtain the renormalization prescription of the excluded volume strength v_0 as follows

$$v = v_0 \left(1 - \frac{8}{\epsilon} v_0 L^{\epsilon/2} + \frac{12}{\epsilon} \Delta_0 L^{\epsilon/2} + \dots \right). \tag{13}$$

Using the cutoff λ as a parameter of the renormalization group and introducing the dimensionless quantities $g = v \lambda^{\epsilon/2}$ and $u = \Delta \lambda^{\epsilon/2}$ we obtain the differential

equations of the renormalization group as follows

$$\partial g / \partial x = \frac{1}{2} \epsilon - 4g^2 + 6gu \tag{14}$$

$$\partial u / \partial x = \frac{1}{2} \epsilon + 4u^2 - 2gu \tag{15}$$

with $x = \ln \lambda'$. The solutions of (14) and (15) are

$$v = \frac{\tilde{v}_0}{Q(\lambda')(1 - (\Delta_0/v_0)Q(\lambda')^{1/2})} \quad \Delta = \frac{v\Delta_0}{v_0} Q(\lambda')^{1/2} \tag{16}$$

where $Q(\lambda') = 1 + (8/\epsilon)v_0\lambda'^{\epsilon/2}$. The renormalization of δZ gives

$$\delta Z = \frac{1}{2} \Delta L^2 / V f_r(u, g) \tag{17}$$

where the function $f_r(u, g)$ takes into account the renormalized part of the perturbation expansion. In the strong self-avoiding limit, $v_0 \rightarrow \infty$, g tends to $g^* = \epsilon/8$ and u tends to zero as $v_0^{-1/2(1-\epsilon/4)}$. Thus, in this limit δZ is obtained as

$$\delta Z \simeq \Delta_0 L^2 / V.$$

In the limit $V \rightarrow \infty$ the annealed average coincides with the quenched one. In the opposite limit when the dimension of the chain becomes comparable with the volume, $V \simeq L^{vd}$, we get from the above equation

$$\delta Z \simeq L^{2-dv} \tag{18}$$

which agrees with the result obtained by Machta [10] and Machta and Kirkpatrick [11] for a polymer chain with a fixed end and for the disorder generated by the site dilution of the lattice. We note that in deriving (18) the end of the polymer was not fixed. The difference in the disorder (site dilution in [10, 11] and the Gaussian disorder here) does not appear to be significant for the behaviour of δZ in (18).

In order to study the behaviour of many polymer chains in the same environment we consider the quenched average of the osmotic pressure. In the case of dilute polymer solutions we can restrict ourselves to the second virial coefficient which is the quenched average of the usual definition of the latter [15, 16]. The result of the computation is

$$A_2 \simeq v L^2 f_A^r(u, g) \tag{19}$$

where $f_A^r(u, g)$ stands for the renormalized perturbation expansion of A_2 and u and g are given by (14)–(16). Equations (16) have a pole at the condition

$$\frac{8}{\epsilon} \Delta_0 \lambda'^{\epsilon/2} = 1 + \frac{v_0}{\Delta_0}. \tag{20}$$

As can be seen from the differential equations (14) and (15) even for $v_0 > \Delta_0$ the attraction caused by the disorder dominates the self-avoidance. This has the consequence that the excluded volume strength, being the positive quantity, will be renormalized as in the case of attraction. The pole is the consequence of this. If one approaches the pole, the effective interaction constants Δ and v tend to infinity. The renormalization has to be carried out up to a length that is smaller than the length leading to the pole. The pole gives the condition at which the attractive force due to the disorder begins to dominate the self-avoidance. In order to study the result of the interplay between these two interactions one must look for the behaviour

of the renormalized perturbation expansion A_2 . Because of the dominance of the attraction we expect the first-order correction to $f_A^f(u, g)$ to be negative and for large u and g the latter tends to zero. Therefore the attractive interaction caused by the disorder compensates for the bare excluded volume interaction between the chains and, as a result, the second virial coefficient becomes zero. We note that in the strong self-avoiding limit the disorder is still irrelevant.

In conclusion we have considered the polymers in a random environment by treating the disorder in the framework of the perturbation theory. For one polymer the disorder results a reduced excluded volume strength, and it becomes irrelevant when the self-avoidance is strong enough. The quenched average of the number of states of a polymer chain in a finite volume obtained is in agreement with the result of Machta, which was derived for self-avoiding walks on site diluted lattices. The radius of a collapsed polymer obtained earlier by Edwards and Muthukumar [5] has been rederived within the RG method. To study the behaviour of different polymer chains in random environment we have considered the quenched average of the second virial coefficient. We have shown that, for long polymer chains, disorder prevails over the excluded volume interaction between different chains. From this result we draw the conclusion that the disorder screens the bare excluded volume interaction between the chains. However, the self-avoidance of each polymer chain can still remain.

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