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Diffusion of polymer chains in disordered media

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Abstract. — The diffusion of a polymer chain in a random environment is studied by means of the RG method. Below the critical dimension of the disorder considered ($d_c = 2$) the anomalous diffusion takes place and the results for the polymer chain follows from that of the Brownian particle by an appropriate rescaling of the strength of the disorder and the bare diffusion coefficient. The results of the RG study of the anomalous diffusion below the critical dimension are used to compute the renormalized diffusion coefficient above the critical dimension.

The diffusion of polymers in melts and in concentrated solutions is of current interest in the literature (see [1] and the Refs. therein). One expects that the reptation of polymers in melts and in concentrated polymer solutions is caused by the restriction of the conformations of the polymer due to the surrounding polymers. A simple model to study the effect of the surrounding polymers is the polymer in a disordered medium. Such a model has been investigated in recent years by Muthukumar and Baumgärtner mainly by using the Monte Carlo simulations. So far there are only few analytical works on this subject [3-5]. In recent years there is an interest in the behavior of Brownian particles in random environments [6-12]. It was established [8, 9] that there exists a critical dimension, which depends on the disorder, below of which an anomalous dimension appears. In this connection one appears the question how these results change in case of polymer chains.

In this article we consider the diffusion of a polymer chain in random environment. We use the formalism, which is an extension of the formalism developed recently for Brownian particles [15]. In order to describe the dynamics of a polymer chain in an external field it is convenient instead of the position $r(s)$ ($s \in [0, L]$, L is the contour length of the polymer) to introduce its Fourier transform as follows

$$r(s) = \sum_{k=0}^{\infty} Q_{sk} \xi_k$$

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where

$$Q_{s0} = L^{-1/2}, \quad Q_{sk} = \left(\frac{2}{L}\right)^{1/2} \cos\left(\frac{\pi sk}{L}\right)$$

The Smoluchowski equation in terms of ξ_k is given by [13]

$$\partial P(\{\xi_k\})/\partial t = (D_0 \nabla_k^2 + \nabla_k D_0 \lambda_{(k)} \xi_k) P + D_0 \nabla_k (\nabla_k F_{ex}) P \quad (1)$$

The Einstein sum convention is assumed in (1). The transition probability $P(\xi, t; \xi^0, t^0)$ ($\xi = \{\xi_k\}$) can be represented as a path integral in the configurational space as follows

$$P(\xi, t; \xi^0, t^0) = \int D\xi(t) \exp \left\{ -\frac{1}{4D_0} \int_0^t dt' \dot{\xi}_k(t')^2 + D_0 \int_0^t \nabla_k^\mu \lambda_{(k)} \xi_k^\mu(t') + \int_q f(q) a(q) \right\} \quad (2)$$

where $f(q)$ is the Fourier transform of the force $F_{ex}(r)$ and

$$a(q) = D_0 \int_0^t dt' \nabla_{\xi_k}(t') \int_0^L ds Q_{sk} \exp(iq Q_{sk} \xi_k(t'))$$

The path integral (2) can be derived in the following way. By using the propagator method (1) can be rewritten as an integral equation. Iterating the latter with respect to the external force F_{ex} we obtain the perturbation expansion of the transition probability in powers of the external force. After symmetrising the ordered time integrations we can represent this series as a path integral (2).

Now we consider $f(q)$ to be a random force with the correlation function

$$\langle f^\mu(q) f^\nu(q') \rangle = \delta(q + q') C^{\mu\nu}(q)$$

The average of the transition probability over the random force yields

$$\begin{aligned} \bar{P}(\xi, t; \xi^0, t^0) = \int D\xi(t) \exp \left\{ -\frac{1}{4D_0} \int_0^t dt' \dot{\xi}_k(t')^2 \right. \\ \left. + D_0 \int_0^t dt' \nabla_k \lambda_{(k)} \xi_k(t') + \frac{1}{2} \int_q a^\mu(q) a^\nu(-q) C^{\mu\nu}(q) \right\} \quad (3) \end{aligned}$$

The transition probability \bar{P} describes the displacement of the polymer chain and on that account it does not tend to the equilibrium distribution in the limit $t \rightarrow \infty$ (or $t^0 \rightarrow -\infty$). The situation changes if we integrate over the zero modes $\xi_0(t)$. The latter is proportional to the centre of mass of the polymer. The transition probability of the internal modes tends to the equilibrium distribution for large time. In order to study the diffusion of the polymer chain it is convenient instead of (3) to consider the correlation function

$$\begin{aligned} G(p_1, p_2) = \langle\langle \langle \exp(-ip_1 \xi_0(t) - ip_2 \xi_0(0)) \rangle \rangle \rangle \\ = \langle\langle \int D\xi(t) \int D\xi(0) \exp(-ip_1 \xi_0(t) - ip_2 \xi_0(0)) P(\xi, t; \xi^0, 0) P'(\xi(0), 0; \xi^0, -\infty) \rangle \rangle \quad (4) \end{aligned}$$

where $\langle \dots \rangle$ and $\langle\langle \dots \rangle\rangle$ denote respectively the conformational average and the average over the disorder. The prime at P in (4) means that the zero modes is excluded from it. $P'(\xi(0), 0; \xi^0, -\infty)$ is the normalized steady-state probability for the internal modes ($\xi_k(0)$,

$k = 1, 2, \dots$) in the external field. The perturbation expansion of (4) in powers of the disorder can be represented by means of diagrams. The rules for computing the diagrams are as follows.

1) The diagrams consist of continuous and wavy lines. The wavy lines are associated with the correlation function $C^{\mu\nu}(q)$. A momentum q is associated with each wavy line. The integration over the momenta have to be carried out. The continuous lines represent the polymer chains.

2) The external momentum is directed from the left to the right.

3) The intersections of the wavy lines with the continuous lines (vertices) are numbered from the right to the left. The following integrations are associated with the vertex k

$$\int_0^{t_k} dt_k \int_0^L ds_k \sum_m$$

The summation occurs over all modes.

4) The parts of the continuous lines between the vertices m and $m - 1$ and the first part from the left are associated with the propagator

$$ip_k^\mu a_{(k)}(t_m - t_{m-1}) Q_{s_m k} e^{-p_k^2 f_{(k)}(t_m - t_{m-1})}$$

with $a_{(k)}(t) = e^{-D_0 \lambda_{(k)} t}$,

$$f_{(k)}(t) = \frac{1 - a_{(k)}(t)^2}{2\lambda_{(k)}},$$

and

$$\lambda_{(k)} = \frac{d}{l} \left(\frac{\pi k}{L} \right)^2.$$

5) The first part of the continuous line on the right is associated with the propagator

$$P_0(p_k) = \exp\{-p_k^2 f_{(k)}(t_1 - t_0) + ip_k a_{(k)}(t_1 - t_0) \xi_k(t_0)\}.$$

6) The momentum conservation. The momentum of the propagator between the vertices $m - 1$ and m is defined as follows

$$p_k = p'_k a_k(t_{m+1} - t_m) + q_m Q_{s_m k}$$

where p'_k is the momentum of the propagator that is posed on the left from the considered propagator. q_m is the momentum associated with the wavy line which enter into the vertex m .

7) The zero mode begins at time t and ends at time 0. We note that the formalism described is a generalization of the formalism for a Brownian particles [15] to the system (polymer) with internal degrees of freedom. This formalism is equivalent to the Siggia-Martin-Rose formalism. However the present formalism enables one to represent the perturbation expansion in a diagram form that is familiar with the diagram technique of the ϕ^4 -theory.

In the following we will consider two models of the disorder:

$$C^{\mu\nu}(q) = \begin{cases} \Delta_0 \frac{q^\mu q^\nu}{q^2} & \text{model I} \\ \Delta_0 \delta^{\mu\nu} & \text{model II} \end{cases} \quad (5)$$

The mean-square displacement of the polymer chain up to the first order in the disorder strength is computed as

$$r_c^2(t) = \frac{2dD_0 t}{L} + \frac{2}{L^2} \Delta_0 D_0^2 \int_0^L ds_1 \int_0^L ds_2 \int_0^t \tau \{(d-2)t + (4-d)\tau\} \times \\ \times \left[\frac{l}{2d} (s_2 - s_1) + \frac{1}{\lambda_{(k)}} Q_{s_1 k} Q_{s_2 k} (1 - e^{-D_0 \lambda_{(k)} \tau}) \right]^{-d/2} \quad (6)$$

where d in braces in (6) has to be put to one for the model II. In case of a Brownian particle, (6) reduces to the corresponding result for the Brownian particle [8, 9]. It can be seen from (5) that for large times the zero mode dominates and the internal modes can be dropped. The only difference to the case of a Brownian particle consists in the following change of the parameter Δ_0 and D_0

$$\begin{aligned} \Delta_0 &\rightarrow \Delta_0 L^2 \\ D_0 &\rightarrow D_0/L \end{aligned} \tag{7}$$

On that account we can obtain the mean-square displacement for the polymer chain using the results for the Brownian particle [8, 9]. Below we will outline the proceeding in a brief form. To carry out the renormalization of the mean-square displacement we need the renormalization prescription of the strength of the disorder Δ_0 . The latter can be derived from the two-chain correlation function, which is defined analogously to (4). The computation of two particle (chain) diagrams occurs on the basis of the diagram rules 1),...,7). As a result we obtain

$$\Delta = \Delta_0 \tag{I} \tag{8}$$

$$\Delta = \Delta_0 \left(1 - \frac{1}{\epsilon} \Delta_0 (D_0 t)^{2/\epsilon}\right) \tag{II} \tag{9}$$

The $1/\epsilon$ terms in the perturbation expansion of $r_c^2(t)$ with respect to the strength of the disorder renormalizes D_0 . The result up to the first order in Δ_0 is

$$D = D_0 \left(1 - \frac{1}{\epsilon} \Delta_0 (D_0 t)^{\epsilon/2} + \dots\right) \tag{I} \tag{10}$$

$$D = D_0 \left(1 - \frac{1}{\epsilon} \Delta_0^2 (D_0 t)^\epsilon + \dots\right) \tag{II} \tag{11}$$

In order to obtain the differential equations of the renormalization group we introduce the cutoff λ by demanding that (7) - (10) remain finite in $d = 2$. Then the equations for D and the dimensionless interaction constant $g = \Delta \lambda'^{\epsilon/2}$ are obtained as

$$\lambda' \frac{\partial \ln D}{\partial \lambda'} = -\frac{1}{2} g \tag{12}$$

$$\lambda' \frac{\partial g}{\partial \lambda'} = \frac{\epsilon}{2} g \tag{13}$$

for the model I and

$$\lambda' \frac{\partial \ln D}{\partial \lambda'} = -g^2 \tag{14}$$

$$\lambda' \frac{\partial g}{\partial \lambda'} = \frac{\epsilon}{2} g - \frac{1}{2} g^2 \tag{15}$$

for the model II.

Below we give the result for the mean-square displacement for the polymer chain in case of model II

$$r_c^2(t) = 2d \frac{1}{L^{1-\epsilon^2+4\epsilon}} (D_0 t)^{1-\epsilon^2} \left(\frac{g^*}{\Delta_0}\right)^{2\epsilon} e^{2g^*} \tag{16}$$

where the fixed point value of g , $g^* = \epsilon$. ϵ is assumed to be positive. From (15) it follows that the diffusion of the polymer chain is slow down by the factor $L^{1-\epsilon^2+4\epsilon}$ in comparison to the Brownian particle. The solution of (13) - (14) gives in $d = 2$

$$r_c^2(t) = 4 \frac{D_0}{L} t \exp\left(-\Delta_0^2 \frac{\ln(\lambda'/\lambda)}{1 + \frac{1}{2} \Delta_0 \ln(\lambda'/\lambda)}\right) \tag{17}$$

For large values of the logarithm (16) yields $r_c^2(t) = 4Dt$ where the diffusion constant D is obtained as

$$D = (D_0/L)\exp(-\Delta_0 L^2) \quad (18)$$

To avoid the misunderstanding we note that the measuring unit of the strength of the disorder Δ_0 is different for polymer chain and for Brownian particle. The argument of the exponent in (17) is dimensionless. Equation (17) is the result of summing up the main logarithms of the perturbation series, which are leading in the limit $\lambda' \rightarrow \infty$. In this limit we conclude that (17) is exact.

In case of the model I the effective coupling constant remains unchanged under the RG transformation [9]. The mean-square displacement is obtained for the model I as

$$r_c^2(t) = 4 \frac{D_0}{L} t \exp(-2\Delta_0 L^2 \frac{(D_0 t/L)^{\epsilon'/2} - \lambda^{\epsilon'/2}}{\epsilon}) \quad (19)$$

For the model I the anomalous diffusion takes place in $d = 2$

$$r_c^2(t) = 4 \frac{D_0 t}{L} \exp(-2\Delta_0 L^2 \ln(\frac{D_0 t}{L\lambda})) \quad (20)$$

We now turn to the consideration of the effect of the disorder on the diffusion of the polymer chain above the critical dimension $d_c = 2$. In case of a Brownian particle the disorder leads to the anomalous diffusion below the critical dimension $d_c = 2$. Above the critical dimension the disorder is irrelevant and the diffusion with the bare diffusion coefficient takes place. However, above the critical dimension there appear the ultraviolet singularities in the perturbation expansions of the quantities under consideration. In order to regularise the perturbation expansions a microscopic cutoff, which is used as parameter of the renormalization group, has to be introduced. It is well known that this cutoff can be used as parameter of the renormalization group. This cutoff is of the order of magnitude of the dimension of the Brownian particle. The situation changes if we consider a polymer chain. Above d_c the disorder is also irrelevant for large times. But in contrast to the Brownian particle the ultraviolet behavior is now controlled by a microscopic length that is of the order of magnitude of the dimension of the polymer chain. To the first order in the disorder this ultraviolet cutoff is given by

$$\lambda \simeq R^2 \simeq Ll \quad (21)$$

But the disorder influences the coil dimension too. To obtain the renormalized coil dimension the high-order calculations are necessary. At first we will ignore the influence of the disorder and the self-avoidance of the polymer on the gyration radius and accept (21). Later we will discuss the effect of the self-avoidance and the effect of the disorder on the coil dimension. The model I and the model II will be considered below in a separate way. The solution of the RG equations (14, 15) gives for the mean square displacement of the center of mass of the polymer chain for the model II

$$r_c^2(t) = \frac{2dtD_0}{L} \exp(-2\Delta_0 \lambda^{-\epsilon'/2}) \lambda^{-\epsilon'^2} (\Delta_0/\epsilon')^{2\epsilon'} \quad (22)$$

where $\epsilon' = d - 2 > 0$ is introduced. By using (14), (15) and (21) the diffusion coefficient is obtained as

$$D = (D_0/L) \exp(-2 \Delta_0 l^{-\epsilon'/2} L^{3-d/2}) L^4 \epsilon'^{-\epsilon'^2} l^{-\epsilon'^2}$$

In case of model I the renormalized diffusion coefficient is obtained as

$$D = \frac{D_0}{L} \exp(-\Delta_0 l^{-\epsilon'/2} / (d-2) L^{3-d/2}) \quad (23)$$

Equation (23) corresponds to the disorder characterized by the correlation function (5). By studying the behavior of the gyration radius of a polymer in disordered media one considers the disorder characterized by the delta-correlated potential [16]. The critical dimension in this case is $d_c = 0$. The diffusion constant for this disorder can be obtained from (23) by identifying ϵ' with d . Then, instead of (23) we obtain

$$D = \frac{D_0}{L} \exp(-\Delta_0 / d L^{2-d/2}) \quad (24)$$

The latter coincides with the result obtained by Machta for Gaussian chains. We now turn to consider how (23),(24) will be changed by taking into account the effect of the disorder and the self-avoidance on the gyration radius. The interplay between the disorder and the self-avoidance is only studied for Gaussian disorder [20, 16 – 19]. Therefore we start the discussion with (24). Because of the Harris argument [20], there is no influence of the disorder on the coil dimension and the cutoff in equation (21) is proportional to the dimension of the swollen coil. Then instead of (24) we obtain

$$D = \frac{D_0}{L} \exp(-\Delta_0 / d L^{2-\nu d}) \quad (25)$$

The latter coincides with the result obtained by Machta in a different way [5]. The polymer chain without self-avoidance collapses in the disordered medium [16] and the coil dimension does not depend on L . In this case we obtain from (21)

$$D = \frac{D_0}{L} \exp(-\Delta_0 / d L^2) \quad (26)$$

We obtain the surprising result that the diffusion constant for the collapsed polymer is smaller in comparison to that of the coil.

In conclusion we considered the diffusion of a polymer chain in a random environment. The analysis of the perturbation expansion showed that the result for the polymer chain can be obtained from that for the Brownian particle by only rescaling the strength of the disorder and the bare diffusion constant of the particle (Eqs.(7)). Below the critical dimension ($d_c = 2$ for the disorder considered) the behavior of the chain does not differ qualitatively from that of the particle. The situation changes for $d > 2$. The infrared behavior ($t \rightarrow \infty$) is the same in both cases. In case of a Brownian particle the normal diffusion with the bare diffusion constant takes place when the disorder is weak. The diffusion, which takes place above the critical dimension of the disorder, is studied by using the results of the RG investigation of the anomalous diffusion of Brownian particles below the critical dimension. Our results show that the random environment affects the diffusion in a much stronger way than predicted by the reptation theory of de Gennes [14].

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