Drift of a polymer chain in disordered media

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(November 20, 2018)

Abstract

We consider the drift of a polymer chain in a disordered medium, which is caused by a constant force applied to the one end of the polymer, under neglecting the thermal fluctuations. In the lowest order of the perturbation theory we have computed the transversal fluctuations of the centre of mass of the polymer, the transversal and the longitudinal size of the polymer, and the average velocity of the polymer. The corrections to the quantities under consideration, which are due to the interplay between the motion and the quenched forces, are controlled by the driving force and the degree of polymerization. The transversal fluctuations of the Brownian particle and of the centre of mass of the polymer are obtained to be diffusive. The transversal fluctuations studied in the present Letter may also be of relevance for the related problem of the drift of a directed polymer in disordered media and its applications.

PACS numbers: 05.40.+j., 36.20.C, 61.41.+e.
The behaviour of a polymer chain in disordered media is of interest for different applications such as gel electrophoresis of biopolymers (see [1]-[8] and references therein). It is also expected that the study of the behavior of a polymer in a disordered medium may be useful for a better understanding such a fundamental problem as reptation [7]-[8]. Despite the large interest in this problem in the last decade [4]-[5] no complete quantitative understanding of the behaviour of the polymer chain has been achieved so far. The reason is the quenched nature of the disorder, which after the average results in an effective attraction between the polymer segments and is responsible that the problem under consideration becomes a strong coupling problem. The standard theoretical tools such as perturbation theories and also the renormalization group method break down in a number of interesting cases for these kind of problems due to the runaway of the effective coupling constant. Thus, the polymer in a disordered media is characterized by a nontrivial interplay between the thermal effects and the disorder, which so far is beyond of a quantitative analytical treatment. The interplay between disorder and thermal effects is also of great importance for different kind of creep phenomena [16]-[17] (and references therein).

In the present Letter we will present the results of the study of the simpler problem of the drift of a polymer chain in disordered media under the action of a constant force applied to one end of the polymer by neglecting the thermal effects. The motivation of the present problem is the electrophoresis of biopolymer molecules in porous media. The drift of a polymer in disordered media can be considered as a further example of the driven dynamics of manifolds (flux lines, interfaces, etc.) in disordered media, where a considerable progress was achieved in last years [18]. One of the interesting aspects of the driven dynamics of the polymer chain in a disordered medium is the generation of the transversal fluctuations, which is due to the interplay between the motion and the quenched random forces. This effect, which to our knowledge have not been studied previously, appears already in the case of a Brownian particle (at zero temperature). We will argue in this Letter that the transversal fluctuations of the centre of mass of the polymer chain (and of the Brownian particle) generated due to the interplay between the disorder and motion are diffusive. We
expect that such transversal fluctuations may be of interest for directed manifolds (flux lines, crack propagation, etc.).

We start the consideration with the Langevin equation for a discrete polymer chain \[8\]

\[
f \frac{\partial r_i}{\partial t} = \zeta (r_{i+1} + r_{i-1} - 2r_i) + F_i(r_i) + \eta_i, \tag{1}\]

where \(r_i^\alpha\) give the positions of monomers \((i = 1, ..., N)\) in \(d\)-dimensional space \((\alpha = 1, ..., d)\), \(f\) is the monomer friction coefficient. The elastic forces are associated with the potential \(U = \frac{\zeta}{2} \sum_{i=1}^{N} (r_i - r_{i-1})^2\). Notice that the elasticity constant \(\zeta\) is given by \(\zeta = dkT/l^2\), \(l\) is the statistical segment length, and \(N = L/l\) is the number of monomers. In the following we will consider the drift of the polymer chain at zero temperature, so that we will consider \(\zeta\) as a constant, which is temperature independent. The force \(F_i(r) = F\delta_{i1} + g(r)\) with \(F\) being the constant driving force acting on the 1st segment of the polymer, and \(g(r)\) is the random quenched force. We assume that the latter is Gaussian distributed with the zero mean and the correlator

\[
[g^\alpha(r)g^\beta(r')] = C^{\alpha\beta}(r - r'). \tag{2}\]

The Fourier transform of \(C^{\alpha\beta}(r)\), \(C^{\alpha\beta}(q)\), is assumed to decay exponentially for large \(q\) with a width \(a\). In particular \(C^{x\alpha}(q)\) has the shape \(C^{x\alpha}(q) = \Delta \exp(-a^2q^2)\) with \(\alpha = x, y, z\) in \(3d\). The thermal forces are Gaussian distributed with the correlator given by

\[
< \eta_i^\alpha(t)\eta_j^\beta(t') > = 2\delta^{\alpha\beta}\delta_{ij}fkT\delta(t - t'). \tag{3}\]

The Langevin equation (1) can be formulated in a standard way by using the path integrals, which in the limit of a continuous chain results in the following expression for the transition probability density for a polymer configuration \(r(s, t)\)

\[
P(r(s), t; r_0(s), t_0) = \int_{r(s, t_0) = r_0(s)}^r Dr(s, t) \int Dp(s, t) \exp(-S), \tag{4}\]

where the action for the continuous polymer chain reads
\[ S = D \mu^2 \int_0^L ds \int_{s_0}^s dt' p(s, t')^2 - i \int_0^L ds \int_{s_0}^s dt' p(s, t') \left( \frac{\partial r(s, t')}{\partial t'} - \gamma \mu \nabla_s^2 r(s, t') - \mu g_k(r(s, t')) \right) \]

(5)

with \( D = f kT/l, \mu^{-1} = f/l, \gamma = \kappa l, \) and \( l \) being the statistical segment length. The generating functional of the non-interacting polymer, \( Z_0(j, \tilde{j}) = \int_{r(s,t_0)=r^0(s)} Dr(s,t) \int Dp(s,t) \exp(-S + i \int_0^L ds \int_{s_0}^s dt'(r(s,t')j(s,t') + p(s,t')\tilde{j}(s,t')) \), is given by

\[
Z_0(j, \tilde{j}) = \exp(-i \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 j_k(t_1)G^0_k(t_1 - t_2)\tilde{j}_k(t_2) + i \int_{t_0}^t dt_1 j_k(t_1)G^0_k(t_1 - t_2)\xi_k^0 + i \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 j_k(t_1)G^0_k(t_1 - t_2)\mu g_k - \frac{D\mu^2}{2\gamma \mu k^2} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 j_k(t_1)(G^0_k(t_1 - t_2) + G^0_k(t_2 - t_1) - G^0_k(t_1 + t_2 - 2t_0))j_k(t_2),
\]

(6)

where the Fourier transform of a quantity \( a(s) \) is defined as follows \( a(s) = \sum_{k=0}^\infty Q_{sk} a_k \) with \( Q_{sk} = \sqrt{2/L} \cos(\pi sk/L) \), and \( Q_{s0} = 1/\sqrt{L} \), \( G^0_k(t) = \exp(-\gamma \mu k^2 t)\theta(t) \) with \( \theta(t) \) being the Heaviside function, and \( \xi_k^0 \) is the Fourier transform of \( r(s, t = 0) \). The last term in the exponential of Eq.(6) disappears for zero temperatures. The generating functional \( Z(j, \tilde{j} = 0) \) at zero temperature can be written in the symbolic form as

\[
Z(j) = \exp \left( \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \int_0^L ds_1 \int_0^L ds_2 \sum_q j^a_k(t_1)C^a_k(t_1 - t_2)Q_{sk}C^{a3}(q)Q_{sk}Q_{sk}C^0_k(t_2 - t_1)j^b_k(t_2) + i \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 j_k(t_1)G^0_k(t_1 - t_2)\mu g_k \right),
\]

(7)

where the source \( j_k(t) \) in Eq.(7) has to be modified in each order of the perturbation expansion as follows: \( j_k(t) \rightarrow j_k(t) + qQ_{sk}\delta(t - t_1) - qQ_{sk}\delta(t - t_2) \), where \( q, s_1, s_2, t_1, \) and \( t_2 \) are variables associated with the disorder correlator, in the 1st order, \( j_k(t) \rightarrow j_k(t) + q_1Q_{sk}\delta(t - t_1) - q_1Q_{sk}\delta(t - t_2) + q_2Q_{sk}\delta(t - t_3) - q_2Q_{sk}\delta(t - t_4) \) in the 2nd order and so on.

We now will study the behaviour of the ideal polymer chain under the action of the force acting at one end of the polymer under neglecting thermal fluctuations. Due to the modification of \( j_k(t) \) the last term in (7) gives rise (in the steady state limit) to the sum...
\[ \sum_{k=1}^{\infty} (Q_{s_{1k}} - Q_{s_{2k}})/(\pi k/L)^2 = \sqrt{L/2}(s_2 - s_1)\left(1 - (s_1 + s_2)/2L\right). \]

Both the transversal fluctuations of the centre of mass and the transversal size of the polymer can be expressed by the quantity

\[ \left[ \xi_{k_1}^\alpha(t) \xi_{k_2}^\beta(t) \right] = \frac{1}{\iota^2} \delta^2 Z(j)/\delta j_{k_1}^\alpha(t) \delta j_{k_2}^\beta(t). \]  
(8)

The transversal size of the polymer is obtained from Eq.(8) with \( k_1 \) and \( k_2 \) nonzero and \( \alpha, \beta \neq z \). The analytical expression associated with Eq.(8) reads

\[ \mu^2 l^{-2} \int_0^L ds_1 \int_0^L ds_2 \int_0^{t_2} dt_2 \int_0^{t_1} dt_1 \int_q C^{\alpha\beta}(q)Q_{s_{1k_1}}Q_{s_{2k_2}}(t - t_2)G_{k_1}(t - t_1) \exp(iq_2g_k(t_1 - t_2) + iq'(s_2 - s_1)\left(1 - (s_1 + s_2)/2L\right)), \]  
(9)

where \( g_k = \mu F/L \) and \( q' = q_z F/(\sqrt{2}\gamma) \). Due to the fact that we are interested in large \( t \), we have neglected the time dependent part associated with the second term in the exponential of Eq.(8). Integrations over times in (9) can be performed straightforwardly. The integrals over \( s_1 \) and \( s_2 \) in (9) can also be computed analytically. It appears that the main contribution in the latter originates from \( k_1 = k_2 \) (the term with \( k_1 \neq k_2 \) vanishes for large \( F \)), so that we obtain

\[ A(k, q) = \int_0^L ds_1 \int_0^L ds_2 \cos(k s_1) \cos(k s_2) \exp(iq(s_2 - s_1)\left(1 - (s_1 + s_2)/2L\right)) = \]
\[ \left(\pi L/4q\right)((C(\sqrt{L/\pi q}(q + k)) + C(\sqrt{L/\pi q}(q - k))^2 + \]
\[ (S(\sqrt{L/\pi q}(q + k)) + S(\sqrt{L/\pi q}(q - k))^2), \]  
(10)

where \( C(x) \) and \( S(x) \) are Fresnel functions. In the limit of large \( L \) the function \( A(k, q) \) tends to the function \( (\pi L/2q)(\theta(|| q | - | k ||) \). After performing the integrations over \( t_i \) and \( s_i \ (i = 1, 2) \) in Eq.(8) and using the property of \( A(k, q) \) for large \( L \), the mean-square transversal size of the polymer chain is obtained to the first order in disorder strength as

\[ [\Delta r_{tr}^2] = \frac{(d - 1)a \sqrt{2L^3}}{4\gamma l^2 F}\pi^{d-1}\Delta/a^d + O(\Delta^2). \]  
(11)

The fluctuations of the centre of mass of the polymer chain to the first order in disorder strength can be studied by using (8,9) with \( k_1 = k_2 = 0 \). The mean-square transversal...
displacement of the centre of mass of the polymer chain is obtained after performing the integrations over times $t_1, t_2$ and $s_1, s_2$ as
\[
[\Delta r_c^2(t)] = \frac{(d-1)atL\mu}{F^2} \pi^{d-1} \Delta/a^d + O(\Delta^2)
\] (12)

Setting $L = l$ in Eq. (12) yields the mean-square transversal displacement for a Brownian particle.

We now will derive Eq. (12) for a Brownian particle in a qualitative way. Due to the motion in the direction of the force $F$, the particle experiences the random force in the transversal directions too. The transversal fluctuations can be estimated according to the Langevin equation of the particle as $f^2 x^2_{tr}/t^2 \simeq \delta F^2$ with $\delta F^2 \simeq a\Delta/a^d/l_F$ being the square of the typical value of the random force and $l_F = \mu F t$ being the characteristic length.

It follows from Eq. (12) and from the above qualitative consideration that the transversal behaviour of the centre of mass of the polymer chain and of the Brownian particle is diffusive. The analysis of higher-order corrections to (12) shows that they are linear in $t$, so that the transversal fluctuations of the particle are expected to be diffusive. Rewriting (12) in terms of the unperturbed velocity $v_{c,0} = \mu F/L$ yields that the mean-square transversal displacements for both the Brownian particle and the polymer chain coincide.

Excluding the time $t$ in (12) in favor of the arc length $L$ by using the relation $\mu \gamma t \sim L^2$, which is obtained from the unperturbed response function $\exp(-\gamma \mu (\pi k/L)^2 t)$ or from the relation $v_c t \simeq \delta r^z$ with $v_c$ and $\delta r^z$ given by Eqs. (11,18) up to order $O(\Delta^0)$, we find that Eq. (12) is compatible with Eq. (11). To our knowledge the transversal fluctuations given by (11-12) have not been studied before. Notice that the temperature is zero and the transversal fluctuations are due to the interplay between the motion and the frozen in random forces.

To study the average velocity of the polymer we will consider the quantity
\[
[\xi^z_k(t)] = i^{-1} \delta Z(j)/\delta j_k^z(t)
\] (13)

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1The latter argument was suggested by one of the referee.
in the limit \( k = 0 \). The analytical expression associated with (13) is given by
\[
[\xi_0^z(t)] = \sqrt{Lg} \exp \left[ \mu^2 l^{-2} \sum_{k=1}^{\infty} \left( -iq \right)^2 C^{zz}(q) \int_{0}^{L} ds_1 \int_{0}^{L} ds_2 \int_{0}^{t_2} dt_1 \int_{0}^{t_2} dt_1 Q_{s_2} Q_{s_1} Q_{s_2} \right] G_0^0(t_2 - t_1) \exp \left( iqg_k(t_1 - t_2) + iq'(s_2 - s_1)(1 - (s_1 + s_2)/2L) \right). \quad (14)
\]

After performing in (14) the integrations over times and arc lengths we arrive at
\[
v_c(t) = \mu F/L \left( 1 - \sqrt{2\gamma a L^{3/2}/(l^2 F^{3/2})} \left( \int_{0}^{L} \frac{C^{zz}(q) \sqrt{\gamma a L^{3/2}/(l^2 F^{5/2})}}{dx/(x^4 + 1)} \right) dx + \ldots \right). \quad (15)
\]

The upper limit in the integration over \( x \) can be put to infinity for large driving force \( F \), so that (15) simplifies to
\[
v_c(t) = \mu F/L \left( 1 - c_v \sqrt{\gamma a L^{3/2}/(l^2 F^{5/2})} \right) \left( \Delta/a^d \right) + \ldots, \quad (16)
\]
with \( c_v = \pi^2/\sqrt{2\Gamma(3/4)} \). Eq.(16) gives the first-order correction to the velocity, so that the correction term in (16) is expected to be small. This condition is fulfilled for large driving force \( F \). For finite \( F \) and large \( L \) the disorder drastically affects the behaviour of the polymer chain. According to Eq.(16), the validity of the perturbation expansion for a given force \( F \) is restricted to the arc length of the polymer \( L, L \leq F^{5/3} \).

Let us compare Eq.(15) with the driven motion of an interface in disordered media \[18\]. The expansion parameter of the perturbation expansion (10), \( \sqrt{\gamma a L^{3/2}/(l^2 F^{5/2})} \left( \Delta/a^d \right) \), depends on \( F \) as \( F^{-5/2} \) instead of \( F^{-3/2} \) as it is the case for interfaces in \( d = 1 \). The additional factor \( 1/F \) for the polymer problem is a consequence of nontrivial integrations over \( s_1 \) and \( s_2 \), which are due to the absence of the factor \( \delta(d)(x_1 - x_2) \) in the disorder correlator (2) and to the fact that the driving force acts on the extremity of the polymer. The additional factor \( 1/F \) has the consequence that the expansion parameter cannot be expressed in terms of the force density \( F/N \). The latter expresses the nontrivial carrying over of the driving force \( F \) to the monomers of the polymer chain.

To study the longitudinal size of the polymer we consider Eq.(13) with \( k \neq 0 \). The analytical expression associated with the latter is
\[
\left[ \xi^z_p(t) \right] = \frac{\sqrt{Lg_p}}{(\gamma \mu p^2)} + \mu^2 l^{-2} \sum_{k=1}^{\infty} \int_q (-iq^a)C^{z\alpha}(q) \int_0^L ds_1 \int_0^L ds_2 \int_0^{t_2} dt_2 \int_0^{t_2} dt_1 Q_{s_{2p}} Q_{s_{1k}} Q_{s_{2k}}
\]

\[
C^0_p(t - t_1)C^0_k(t_2 - t_1) \exp(iq_gk(t_1 - t_2) + iq'(s_2 - s_1)(1 - (s_1 + s_2)/2L)). \tag{17}
\]

The average value \([r^z(0) - r^z(L)] \equiv [\delta r^z(L)]\) is obtained in terms of the normal coordinates as \(2 \sqrt{2/L} \sum_{k=1}^{\infty} \left[ \xi^z_{2k-1} \right]\). Performing the integrations over the times and arc lengths results in

\[
[\delta r^z(L)] = \frac{\sqrt{2}\mu F L}{4\mu \gamma} (1 - \frac{\pi}{2\Gamma(3/4)} \frac{L^3/2}{F^{5/2}} (\Delta/a^d) + ... \tag{18}
\]

with \(c_r = \pi^2/(2\Gamma(3/4))\). Notice that the disorder weakens the stretching of the polymer. This can be understood as follows. It is evident that the effect of the disorder results in a decrease of the unperturbed velocity \(\mu F/L\). The decrease of the velocity due to disorder can be interpreted as the unperturbed motion due to a smaller force, which in virtue is accompanied by a less stretching of the polymer. Thus, this argument supports the non evident result of Eq.(18) that the stretching of the polymer in the longitudinal direction will be diminished due to disorder.

To conclude, we have considered the drift of a polymer chain in disordered media under the action of a constant force applied to one of the extremities of the polymer by neglecting the thermal effects. The dynamics of the polymer is governed by the interplay between the motion and the quenched random forces. One of the significant effects of this interplay is the generation of transversal fluctuations of the polymer chain. The latter take also place for a Brownian particle. We have also found that disorder results in a weakening of the elongation of the polymer in the longitudinal direction, which is caused by the friction of the polymer with the surrounding medium. Due to the specific dependence of the quantities under investigation on the driving force \(F\) and the length of the polymer \(L\), the fluctuations induced by the drift of the polymer may compete with thermal fluctuations. An interesting question is the experimental manifestation of these fluctuations. However, the first-order corrections studied in the present Letter do not allow us to make predictions on the total effect of the disorder on the quantities under consideration. The only conclusion we may
drawn on this matter is that for finite driving force the effect of disorder increases with the polymer length. The transversal fluctuations studied in the present Letter may be also of relevance for the related problems of the drift of a directed polymer in disordered media, crack propagation in disordered media etc. To our knowledge, the transversal fluctuations in these problems have not been studied so far.

ACKNOWLEDGMENTS

A support from the Deutsche Forschungsgemeinschaft (SFB 418) is gratefully acknowledged. Useful comments and suggestions of the Referee are also acknowledged.
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