Polymer drift in a solvent by force acting on one polymer end

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Abstract. We investigate the effect of hydrodynamic interactions on the non-equilibrium drift dynamics of an ideal flexible polymer pulled by a constant force applied at one polymer end using the perturbation theory and the renormalization group method. For moderate force, if the polymer elongation is small, the hydrodynamic interactions are not screened and the velocity and the longitudinal elongation of the polymer are computed using the renormalization group method. Both the velocity and elongation are nonlinear functions of the driving force in this regime. For large elongation we found two regimes. For large force but finite chain length $L$ the hydrodynamic interactions are screened. For large chain lengths and a finite force the hydrodynamic interactions are only partially screened, which in three dimensions results in unusual logarithmic corrections to the velocity and the longitudinal elongation.

Keywords: renormalization group, driven diffusive systems (theory), polymer elasticity and dynamics
1. Introduction

Understanding the dynamics of polymers in solutions is of great importance in many biochemical and industrial processes. In dilute solution, hydrodynamic interaction between different parts of the polymer chain plays a crucial role in the determination of dynamic properties [1]. In the classical theories which go back to Kirkwood and Zimm [2, 3], the main focus of research was to study the quantities such as the diffusion constant, the dynamic intrinsic viscosity and the dynamic structure factor of the polymer. Recent advances in experimental techniques make it possible to explore the motion of individual polymers under hydrodynamic flow, thermal noise or external fields. For instance, Chu et al [4]–[6] experimentally studied the behavior of polymers in different flow conditions with the emphasis on biological applications. See also related theoretical studies [7]–[9].

In this paper we study drift of an ideal flexible polymer pulled by a constant driving force applied at one polymer end. Classical theory of dragging objects dates back to Einstein’s Brownian motion and Stokes’ theory in the hydrodynamic medium, which yields the velocity of the dragged object, \( v_B = F / f_0 \) with \( f_0 = C \eta s R \). Unlike the drag of these simple objects, the dynamics of the polymer pulled at the polymer end is more complicated due to the interplay between the internal degrees of freedom of the polymer, hydrodynamic interactions and inhomogeneity of the chain configurations, which is due to the pulling force acting at the polymer end. The drift by a force applied at the polymer end is different from the case, if the external force is homogeneous and acts on all monomers of the chain.

In neglecting the hydrodynamic interactions, i.e. in the Rouse theory, the average \( z \) components of the velocity and the chain elongation are given by the expressions

\[
  v_z \simeq \frac{F}{f_0 N},
\]

(1)

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\[ \langle r_z(0, t) - r_z(L, t) \rangle = \frac{FLl}{2dk_BT}, \]  

where \( d \) is the dimensionality, \( F = F^z \) is the pulling force directed along the \( z \) axes and \( f_0 \) denotes the monomer friction coefficient. For small forces the polymer is expected to have the shape of a coil with the consequence that the hydrodynamic interaction is not screened (Zimm regime) and the velocity is described by the Stokes formula

\[ v^z \simeq \frac{1}{6\pi\eta_s R_h}F, \]  

with \( R_h \simeq l\sqrt{N} \) being the hydrodynamic radius of the polymer and \( \eta_s \) is the solvent viscosity. The Zimm behavior (3) is described in the framework of the renormalization group method as due to the renormalization of the friction coefficient, which becomes scale-dependent in the regime of strong hydrodynamic interaction [10]–[12].

For moderate forces a crossover between (1) and (3) as well as a nonlinear dependence on the pulling force is expected to apply. For large forces the effect of the hydrodynamic interaction is expected to be weak due to polymer stretching, so that a Rouse-type behavior should be observed.

In the present work we calculate the first-order corrections to the velocity and the longitudinal elongation. The renormalization group method allows us to establish the behavior of the quantities under consideration for moderate forces. We also show that in \( d = 3 \) the first-order corrections to the velocity and the longitudinal size of the polymer in powers of the hydrodynamic interactions logarithmically depend on the parameter \( \beta F\sqrt{lL/2d} \), which demonstrates that hydrodynamic interactions are only partially screened for a long polymer pulled at finite force.

This paper is organized as follows. After an introduction to the formalism in section 2, we perform the perturbational computation of the average velocity in section 3 and the longitudinal polymer size under the drift in section 4. In section 5, the velocity and the longitudinal size are analyzed for small and large force using renormalization group analysis. This work is summarized in section 6.

2. The formalism

The drift dynamics of a polymer chain is described by the Kirkwood diffusion equation, which in the continuum limit is given by [1]

\[ \frac{\partial P \{\{r(s)\}, t\}}{\partial t} = \int_0^L ds_2 \int_0^L ds_1 \frac{\delta}{\delta r(s_1)} [D_0 \delta^{\mu\nu} \delta(s_1 - s_2) + T^{\mu\nu}(r(s_1) - r(s_2))] \times \left[ \frac{\delta H_0}{\delta r(s_2)} - \beta F_{\text{ext}}(r(s_2)) + \frac{\delta}{\delta r(s_2)} \right] P. \]  

The Oseen tensor (multiplied by \( k_BT \)) in \( d \) dimensions is defined through its Fourier transform as

\[ T^{\mu\nu}(r(s_1) - r(s_2)) = \frac{k_BT}{\eta_s} \int \frac{d^d q}{(2\pi)^d q^2} \left( \delta^{\mu\nu} - \frac{q^\mu q^\nu}{q^2} \right) e^{i(q(r(s_1) - r(s_2)))}. \]
The free energy (multiplied by $k_B T$) and the pulling force applied in the $z$ direction are given by

$$H_0 = \frac{d}{2L} \int_0^L ds \left( \frac{d\mathbf{r}(s)}{ds} \right)^2, \quad F^\mu_{ext}(\mathbf{r}(s)) = \delta^{\mu z} F \delta(s). \tag{5}$$

The Rouse modes $\xi_k$ are the Fourier coefficients in the expansion of the position vector $\mathbf{r}(s)$ ($0 \leq s \leq L$) according to $\mathbf{r}(s) = \sum_{k=0}^\infty Q_{s k} \xi_k$ where the basis functions

$$Q_{s k} = \begin{cases} \frac{1}{\sqrt{L}}, & k = 0 \\ \sqrt{\frac{2}{L}} \frac{\pi s k}{L}, & k = 1, 2, 3, \ldots \end{cases} \tag{6}$$

are orthogonal and complete in the interval $(0, L)$.

The Kirkwood diffusion equation can be rewritten in terms of the normal coordinates

$$\frac{\partial P(\xi, t; \xi^0, t_0)}{\partial t} = L_0 P + L_i P, \tag{7}$$

where $\xi$ is an abbreviation for $\xi_0, \xi_1, \ldots$, and the operators $L_0$ and $L_i$ are given by

$$L_0 = D_0 \nabla \Sigma_k \nabla \xi_k^\mu - D_0 \beta F^\mu Q_{0k} \nabla \xi_k^\mu, \tag{8}$$

$$L_i = \nabla \Sigma_k T_{km} \nabla \xi_m^\nu + \lambda_m \xi_m^\nu - \nabla \Sigma_k T_{0k} \beta F^\nu, \tag{9}$$

with abbreviations $\nabla \equiv \delta/\delta \xi_k$, $T_{km} = \int_0^L ds \int_0^L ds_1 Q_{s k} T_{km}(s_1) Q_{s m}(s_2)$, and $\mathbf{r}^\mu(1) - \mathbf{r}^\mu(2) = \sum_{n=0}^\infty (Q_{s n} - Q_{s m}) \xi_n^\mu$. The summation convention over the indices $k$, $m$, $\mu$, and $\nu$ is implied in the above expressions.

In the following we consider the hydrodynamic interaction as a perturbation and use the Rouse chain pulled by a force at one end as a reference state. The solution of equation (7) with $L_i = 0$ gives the transition probability density of the reference Rouse state:

$$P_0(\xi, t; \xi^0, t_0) = \prod \frac{1}{(4\pi f_k(t - t_0))^{d/2}} \exp \left( -\frac{(\xi_k^\mu - \beta F^\mu Q_{0k}/\lambda_k - \xi_k^0 a_k(t - t_0))^2}{4f_k(t - t_0)} \right) \times \prod \frac{1}{(4\pi D_0 t)^{d/2}} \exp \left( -\frac{(\xi_0^\mu - D_0 \beta F^\mu Q_{00} t - \xi_0^0 a_0^2)^2}{4D_0 t} \right), \tag{10}$$

with $a_k(t) = \exp(-D_0 \lambda_k t), \quad f_k(t) = \frac{1 - \exp(-2D_0 \lambda_k t)}{2\lambda_k}$. 

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where $D_0 = k_B T l / f_0$ is the monomer self-diffusion coefficient and $\lambda_k = (d/l)(\pi k/L)^2$ are the Rouse eigenvalues.

To perform perturbational computations of the velocity, the longitudinal size, etc., of the polymer chain under the pulling force, we rewrite the Kirkwood diffusion equation as an integral equation:

$$P(\xi,t;\xi^0,t_0) = P_0(\xi,t;\xi^0,t_0) + \int_{t_0}^{t} dt' \int D\xi' P_0(\xi,t;\xi',t') L_i(\xi') P(\xi',t';\xi^0,t_0). \quad (11)$$

Iteration of (11) results in the perturbation expansions in powers of the hydrodynamic interaction, which is symbolically written as

$$P = P_0 + P_0 L_i P = P_0 + P_0 L_i P_0 + P_0 L_i P_0 L_i P_0 + \cdots.$$  

3. Perturbational computation of the velocity

Our aim is now to calculate the velocity of the polymer chain up to first order in the hydrodynamic interaction using equation (11). The center of mass $r_c$ of the polymer chain is expressed through the center-of-mass Rouse mode $\xi_{k=0}$ according to $r_c = \xi_{k=0}/\sqrt{L} = (1/L) \int_0^L ds \mathbf{r}(s)$. Hence, the computation of the average velocity reduces to the computation of the expectation value of the zero mode $\langle r_c(t) \rangle = \langle v_c(t) \rangle t$:

$$\langle \xi_{k=0}(t) \rangle = \int D\xi \xi_{k=0} P(\xi,t;\xi^0,t_0). \quad (12)$$

The computation of (12) to the zeroth order in powers of the hydrodynamic interaction (i.e. in the Rouse model) using the unperturbed distribution function (10) yields in the steady state

$$\langle \xi_{k=0}(t) \rangle_0 = \frac{LF}{f\sqrt{L}} t.$$  

For the velocity we obtain the expression $\langle v_c^z(t) \rangle_0 = F/(fN)$, which is in agreement with the Rouse theory. The first-order correction is derived from equation (11) by replacing $P$ on the right-hand side by $P_0$ as

$$\langle \xi_{k=0}^z(t) \rangle_1 = \int_{t_0}^{t} dt' \int_0^L ds_2 \int_0^L ds_1 \int \frac{d^d q}{(2\pi)^d} Q_{s_2 0} T^{zz}(q) Q_{s_1 0} \times \beta F Q_{00} \langle \xi_{k=0}^z(t) \rangle_0 - \xi_{0}^z - D_0 \beta F Q_{00}(t' - t_0), \quad \beta F Q_{00} = \frac{1}{(k_B T/\eta_0)(1/q^2)(\delta^{uu} - q^2 q^u/q^2)}.$$  

where $T^{uu}(q) = (k_B T/\eta_0)(1/q^2)(\delta^{uu} - q^2 q^u/q^2)$. The integrations over $\xi'$ yield

$$\langle \xi_{k=0}^z(t) \rangle_1 = \beta F Q_{00} \int_{t_0}^{t} dt' \int_0^L ds_2 \int_0^L ds_1 \int \frac{d^d q}{(2\pi)^d} Q_{s_2 0} T^{zz}(q) Q_{s_1 0} \times \exp \left( i q^z F \beta \sum_{n=1}^{\infty} Q_{s_1 n} - Q_{s_2 n} \lambda_n - q^2 \sum_{n=1}^{\infty} \frac{(Q_{s_1 n} - Q_{s_2 n})^2}{2 \lambda_n} \right). \quad (14)$$

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The evaluation of the sums in equation (14) gives

\[
\langle \xi^z_{k=0}(t) \rangle_1 = \int_0^t dt' \int_0^L ds_2 \int_0^L ds_1 \int \frac{d^d q}{(2\pi)^d} Q_{s_10} \times T^{zz}(q)Q_{s_10}\beta F Q_{s_00} \exp \left( iq_z F z b(s_1, s_2) - a q^2 \right),
\]

where the quantities \( a \) and \( b \) are defined as follows:

\[
a = \sum_{n=1}^{\infty} \frac{(Q_{s_1n} - Q_{s_2n})^2}{2\lambda_n} = \frac{l}{2d} |s_1 - s_2|,
\]

\[
b = \sum_{n=1}^{\infty} \frac{Q_{s_1n} - Q_{s_2n}}{\lambda_n} Q_{0n} = \frac{l}{d} (s_2 - s_1) \left( 1 - \frac{s_1 + s_2}{2L} \right).
\]

Performing the straightforward integration over \( q \) we finally obtain

\[
v^c_x(t) = \frac{F}{f_0 N} \left( 1 + \frac{1}{2^d} f_0 \left( \frac{d}{2\pi t} \right)^{d/2} I^{2-d/2} \int_0^1 dx_2 \int_0^{x_2} dx_1 \frac{A(y)}{(x_2 - x_1)^{d/2-1}} + \cdots \right),
\]

where the function \( A(y) \) and its argument \( y \) are respectively given by

\[
A(y) = \frac{(d-1)(d-2)}{y^4} e^{-y^2} - \frac{(d-1)(d-2-2y^2)}{y^d}
\times \left( 4 - d \Gamma \left( \frac{d-4}{2}, y^2 \right) + \Gamma \left( \frac{d-2}{2} \right) \right),
\]

\[
y = \beta F \sqrt{\frac{IL}{2d}} (x_2 - x_1)^{1/2} \left( 1 - \frac{x_2 + x_1}{2} \right),
\]

where \( \Gamma(a, z) = \int_0^\infty dt t^{a-1} e^{-t} \) is the incomplete gamma function. The function \( A(y) \) behaves for small and large arguments as

\[
A(y) \approx \begin{cases} 
\frac{8(d-1)}{d(d-2)} \frac{8(d-1)}{d(d+2)} y^{2+} + \frac{4(d-1)}{(d+2)(d+4)} y^4 + \cdots, & y \ll 1, \\
\frac{(d-1)(2y^2 + 2 - d)}{y^d} \Gamma \left( \frac{d-2}{2} \right) + \frac{2(d-1)}{y^4} e^{-y^2} + \cdots, & y \gg 1.
\end{cases}
\]

Integrations over \( x_1 \) and \( x_2 \) in equation (16), which can be carried out in the limit \( F \to 0 \), yield

\[
\int_0^1 dx_2 \int_0^{x_2} dx_1 \frac{A(0)}{(x_2 - x_1)^{d/2-1}} = \frac{4}{(6-d)(4-d)} A(0) \frac{2}{d-4} A(0).
\]

Note that the behavior of the first-order correction to the velocity in the vicinity of four dimensions, which is given by the last expression, plays an important role in the renormalization group analysis of the velocity.
4. Perturbational computation of the longitudinal size of the polymer

In this section we calculate the longitudinal size of the polymer up to first order in the hydrodynamic interaction. The longitudinal size of the polymer is expressed through the Rouse modes according to

$$\langle r^z(0, t) - r^z(L, t) \rangle = \sqrt{\frac{2}{L}} \sum_{k=1}^{\infty} \left(1 - (-1)^k\right) \langle \xi^z_k(t) \rangle. \quad (21)$$

The computation to zeroth order in the hydrodynamic interaction (i.e. in the Rouse model) in the steady state yields

$$\langle r^z(0, t) - r^z(L, t) \rangle_0 = \frac{FLl^2}{2dk_BT}.$$ (22)

The first-order correction to $$\langle \xi^z_k(t) \rangle$$ is obtained using equation (11) as

$$\langle \xi^z_k(t) \rangle_1 = \beta F \int_{t_0}^{t} dt' a_k(t - t') \int_0^L ds_2 \int_0^L ds_1 \int \frac{d^d q}{(2\pi)^d} Q_{s_2k} T^{zz}(q) Q_{s_1m} Q_{0n} \big|_{m=0}$$

$$\times \exp \left( i q^z F \beta \sum_{n=1}^{\infty} \frac{S_{s_1n} - S_{s_2n}}{\lambda_n} \frac{Q_{0n} - q^2 \sum_{n=1}^{\infty} (Q_{s_1n} - Q_{s_2n})^2}{2\lambda_n} \right).$$

The longitudinal elongation is

$$\delta r_z = \frac{FLl}{2dk_BT} \left( 1 - \frac{1}{2^2} \frac{f_0}{2\pi l} \int_0^d L^{-d/2} B_r(\tilde{F}) + \cdots \right), \quad (23)$$

where $$\delta r_z = \langle r^z(0, t) - r^z(L, t) \rangle$$, $$\tilde{F} = \beta F \sqrt{lL/2d}$$ and

$$B_r(\tilde{F}) = \int_0^1 dx_2 \int_0^{x_2} dx_1 \left( \frac{2r_2 - 1}{(x_2 - x_1)^{d/2 - 1}} A(y) \right). \quad (24)$$

The computation of integrals in equation (24) over $$x_1$$ and $$x_2$$ for a small force yields

$$B_r(\tilde{F} \to 0) = \frac{4}{(8 - d)(6 - d)} A(0).$$

The finiteness of the latter at four dimensions means, in the context of the renormalization group method, that the parameters $$F$$, $$L$$, $$l$$ and $$T$$ appearing in the prefactor of equation (23) do not renormalize. The only quantity which renormalizes is the monomer friction coefficient. The hydrodynamic interaction results in decreasing the size of the polymer.

5. Results

Our aim is now to study the behavior of the velocity and the longitudinal size of the polymer chain as a function of the driving force $$F$$ and the chain length $$L$$. 

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5.1. Small elongation

The first-order perturbational correction to the velocity is the starting point to perform the renormalization group (RG) analysis, which enables one to take into account the effect of hydrodynamic interaction beyond first order. The basic observation to apply RG is that the integral in (16) diverges logarithmically in four dimensions (i.e. the critical dimension is four; for \( d > 4 \) the hydrodynamic interactions become irrelevant). This divergence manifests itself in \( d < 4 \) dimensions as a \( 1/(4 - d) \) pole. To regularize the theory these poles in perturbation expansions have to be removed by an appropriate renormalization of the friction coefficient. In the limit of a small pulling force the renormalized friction coefficient is derived from (16) as

\[
    f = f_0 \left(1 - \frac{3}{2 \varepsilon} \xi_0 (L^{e/2} - \lambda^{e/2}) + \cdots\right),
\]

where \( \xi_0 = (f_0/(\eta_s d))(d/(2\pi l))^{d/2} \) is the expansion parameter of perturbation series in powers of the hydrodynamic interactions and \( \varepsilon = 4 - d \). The ultraviolet cutoff \( \lambda \) in (25) is introduced to enable the limit to four dimensions. The cutoff excludes the hydrodynamic interactions between monomers separated along the chain by the contour length less than \( \lambda, |s_1 - s_2| < \lambda \). The renormalization of the friction coefficient (25) obtained from equation (16) coincides with that obtained by studying different problems in polymer dynamics [10]–[12]. Note that, in the absence of the excluded volume interaction, only the friction coefficient renormalizes.

In addition to the renormalization of the friction coefficient one should consider the renormalization of the coupling constant (i.e. expansion parameter) controlling the strength of the hydrodynamic interaction. The inspection of equations (16) or (23) yields the bare dimensionless expansion parameter as

\[
    w_0 = \frac{f_0}{\eta_s d} \left(\frac{d}{2\pi l}\right)^{d/2} L^{e/2}.
\]

It follows from equation (26) that the coupling constant renormalizes in the same way as the friction coefficient.

The renormalization group is based on the observation that the regularization, i.e. the elimination of the \( 1/\varepsilon \) poles from perturbation expansions, can be performed step by step by changing the cutoff \( \lambda \rightarrow \lambda' \rightarrow \lambda'' \rightarrow \cdots \rightarrow \lambda_m \). The renormalization of the friction coefficient and the strength of the hydrodynamic interaction due to an infinitesimal change of the cutoff are given by differential equations. To the one-loop order one obtains

\[
    \lambda' \frac{\partial f}{\partial \lambda'} = \frac{3}{4} w, \quad \lambda' \frac{\partial w}{\partial \lambda'} = \varepsilon w - \frac{3}{4} w^2 + \cdots = \beta(w),
\]

with the dimensionless effective coupling constant \( w = (f/(\eta_s d))(d/(2\pi l))^{d/2} \). The solutions of equations (27) and (28) are

\[
    f = \frac{f_0}{1 + (3/2 \varepsilon) \xi_0 (\lambda_m^{e/2} - \lambda^{e/2})},
\]

where \( \xi_0 = (f_0/(\eta_s d))(d/(2\pi l))^{d/2} \) is the expansion parameter of perturbation series in powers of the hydrodynamic interactions and \( \varepsilon = 4 - d \). The ultraviolet cutoff \( \lambda_m \) in (29) is introduced to enable the limit to four dimensions. The cutoff excludes the hydrodynamic interactions between monomers separated along the chain by the contour length less than \( \lambda_m, |s_1 - s_2| < \lambda_m \). The renormalization of the friction coefficient (29) obtained from equation (16) coincides with that obtained by studying different problems in polymer dynamics [10]–[12]. Note that, in the absence of the excluded volume interaction, only the friction coefficient renormalizes.

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    \lambda' \frac{\partial f}{\partial \lambda'} = \frac{3}{4} w, \quad \lambda' \frac{\partial w}{\partial \lambda'} = \varepsilon w - \frac{3}{4} w^2 + \cdots = \beta(w),
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with the dimensionless effective coupling constant \( w = (f/(\eta_s d))(d/(2\pi l))^{d/2} \). The solutions of equations (27) and (28) are

\[
    f = \frac{f_0}{1 + (3/2 \varepsilon) \xi_0 (\lambda_m^{e/2} - \lambda^{e/2})},
\]
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\[ w = \frac{f}{\eta_s d} \left( \frac{d}{2\pi l} \right)^{d/2} \lambda_m^{\varepsilon/2}. \]  

(30)

It follows from equations (29) and (30) that, at large \( \lambda_m \), \( w \) approaches the fixed-point value \( w^* = 2\varepsilon/3 \), which corresponds to the zeroth point of the Gell-Mann–Low function \( \beta(w) \). At the fixed point the effective friction coefficient depends on \( \lambda_m \) as the power law \( \lambda_m^{-\varepsilon/2} \). At low forces \( \lambda_m \) is equal to \( L \), so that the renormalized (effective) friction coefficient scales as

\[ \frac{w^*}{\eta_s l^{d/2} L^{-\varepsilon/2}}. \]

(31)

The drift velocity behaves consequently as

\[ v^*_c \simeq \frac{F}{fN} \simeq \frac{F}{\eta_s (Ll)^{d/2-1}}, \]

which agrees in \( d = 3 \) with the Stokes formula (3).

The inspection of the first-order correction to the longitudinal size of the polymer yields that it is finite in four dimensions. This is what is expected, because the friction coefficient, which is the only quantity to renormalize, does not appear in the zeroth-order correction to the longitudinal size of the polymer. Thus, the RG prediction for the longitudinal size consists in replacing the bare expansion parameter in equation (23) by the renormalized one. According to equation (30) the first-order correction is of order \( \varepsilon \) and is thus small in the vicinity of four dimensions.

For small forces the velocity and the elongation are given in the renormalized theory by expressions

\[ v^*_c = \frac{F}{fN} \left( 1 + \frac{1}{4} w B_v(\beta F \sqrt{Ll/2d}) + \cdots \right), \]

(32)

\[ \langle r^*(0,t) - r^*(L,t) \rangle = \frac{FLl}{2dk_BT} \left( 1 - \frac{1}{4} w B_r(\beta F \sqrt{Ll/2d}) + \cdots \right). \]

(33)

The function \( B_v(\tilde{F}) \) in (32) is defined by

\[ B_v(\tilde{F}) = \int_0^1 dx_2 \int_0^{x_2} dx_1 (A(y) - A(0))/ (x_2 - x_1)^{d/2-1}. \]

The effective expansion parameter \( w \) is a small number (\( \sim O(\varepsilon) \)), so that the expansions (32) and (33) are reliable. The expansion of the functions \( B_v(z) \) and \( B_r(z) \) for small \( z \) are given by

\[ B_v(z) = -\frac{1136}{14175} z^2 + \frac{19366}{7882875} z^4 + \cdots, \]

(34)

\[ B_r(z) = \frac{64}{45} - \frac{464}{31185} z^2 + \frac{10786}{19144125} z^4 + \cdots. \]

(35)

Expressions (32) and (33) demonstrate that the velocity and the longitudinal polymer size show the nonlinear response, i.e. non-Stokes behavior at moderate pulling forces.

Note that the Zimm result for the velocity (3) can also be obtained in a simple way following the Kirkwood-type approach to the diffusion constant [2]. That consists in neglecting one in the bracket of (16). The friction coefficient then drops, and the dependence on \( N \) is the same as (3).

5.2. Large elongation

We will now study the first-order corrections to the velocity and the longitudinal elongation for large argument \( \beta F \sqrt{Ll/2d} \). To estimate the integrals in (16) and (24)
for large forces we use the asymptotic expression of $A(y)$ given by equation (19). To prevent the divergence in the integral over $t = x_2 - x_1$ from the integration region $t = 0$, we introduce an cutoff $t_0 \approx 6/Ll\beta^2F^2$. The evaluation of the integrals over $t$ and $x_2$ can be performed analytically and gives for $d = 3$

$$v_c^z = \frac{F}{f_0N} \left(1 + c_v\zeta_0 L^{1/2} \ln(\beta F (Ll)^{1/2}) \ln(\beta F (Ll)^{1/2}/3) + \cdots\right), \quad (36)$$

with a numerical constant $c_v$. We would like to stress that the integral in equation (16) computed numerically can be approximately fitted with $(\ln F)^{1.72}/F$ instead of the estimate given by equation (36). The difference is due to the complicated form of the expression for $y$ in equation (18).

For large $F$ and finite $L$ we arrive at the Rouse result. However, for large $L$ and finite $F$ the correction increases logarithmically with $L$, and will become large for large $L$. Unfortunately, there are no analytical means to study the effect of the whole perturbation expansion on $v_c^z$ in this case. The extrapolation of (36) a la Kirkwood, i.e. the disregard of one in the bracket of equation (36), yields

$$v_c^z \approx \frac{k_B T}{\eta_b N l^2} \ln(\beta F (Ll)^{1/2}) \ln \frac{\beta F (Ll)^{1/2}}{3}. \quad (37)$$

Equation (37) shows that in this regime (finite $F$ and large $L$) the hydrodynamic interactions determine the behavior of the polymer. The friction coefficient drops in the expression of the velocity in this regime. We expect that the hydrodynamic interactions remain important due to the thermal fluctuations of the pulled chain. The presence of $k_B T$ in (37) supports this statement. Note that the logarithmic dependencies of $v_c^z$ on the force does not allow us to write equation (37) in the form of equation (1) with some effective friction coefficient. Equation (37) can be formally obtained from equation (1) by simultaneous replacements

$$f_0 \rightarrow f \approx \eta_b/\ln(\beta F (Ll)^{1/2}), \quad F \rightarrow \frac{k_B T}{l} \ln \frac{\beta F (Ll)^{1/2}}{3}. \quad (38)$$

The ‘renormalized’ friction coefficient in equation (38) resembles, to some extent, the friction coefficient, $L\eta_b/\ln(L/l)$, of a slender body (a cylinder of length $L$ and cross-sectional radius $l$, $L \gg l$) in a flow [13, 1] (see also [4]). However, the elongated polymer chain is different from a rod and the comparison is only qualitative.

A similar computation of the first-order correction to the chain size yields

$$\delta r_z = \frac{F L l}{2dk_B T} \left(1 - c_r\zeta_0 L^{1/2} \frac{(\ln(\beta F (Ll)^{1/2}/3) - 2) \ln(\beta F (Ll)^{1/2})}{\beta F (Ll)^{1/2}} + \cdots\right). \quad (39)$$

Note that the integral in equation (24) computed numerically can be approximately fitted with $(\ln F)^{2.48}/F$ instead of the analytical estimate in equation (39). For large $F$ and finite $L$, we arrive at the Rouse result. In contrast, for large $L$ and finite $F$ the first-order correction to the longitudinal size increases logarithmically with $L$. This results in a decrease of the longitudinal size of the polymer. It is difficult, due to the absence of an analytical method, to make predictions on the total effect of the hydrodynamic interaction for polymer elongation. Note that the corrections in equations (16) and (23) at $F \neq 0$ imply the nonlinear response of the polymer on the pulling force.
6. Summary

To summarize, we have studied the drift of an ideal polymer driven by a constant force applied at one polymer end using perturbation expansions in powers of hydrodynamic interactions. For moderate force, where the hydrodynamic interactions are not screened and the polymer elongation is small, the renormalization group method permits us to compute the velocity and the longitudinal elongation of the polymer. These quantities are nonlinear functions of the driving force in this regime. For large elongation we found two regimes. For large force but finite chain length $L$ the hydrodynamic interactions are screened, so that both the velocity and the longitudinal polymer elongation are given by the corresponding results of the Rouse theory. For large $L$ but finite force, the regime which we have studied for $d = 3$, the hydrodynamic interactions are partially screened. The first-order corrections to $v_c^z$ and $\langle r^z(0, t) - r^z(L, t) \rangle$ increase logarithmically with $L$. Following Kirkwood’s treatment of the diffusion constant we make a prediction for the velocity, equation (36), beyond the first order of perturbation theory. It would be of great interest to check experimentally these predictions by pulling a polymer in a solvent using optical tweezers.

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