Dynamics of Polymers in Solution: The Role of Time-Dependent Hydrodynamic Interactions

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ABSTRACT: The role of time-dependent hydrodynamic interactions in the dynamics of polymer solutions is analyzed. We obtain the equation of motion for the chain and derive the mobility kernel and the fluctuation–dissipation theorem in a nonstationary situation. The influence of fluid motion on the dynamics of the chains is then studied through time-dependent correlation functions.

1. Introduction

In the theory of polymer dynamics several models have been proposed to describe the motion of the macromolecules in solution. The first one was introduced by Rouse[1] by assuming that the segments of the chain experience a friction force given by Stokes law. Zimm[2] extended the Rouse model by incorporating the presence of hydrodynamic interactions between segments. This approach then takes into account the coupling between the dynamics of both, fluid and macromolecules, through the Oseen tensor, which corresponds to the propagator of the perturbations in the stationary case. A further generalization was carried out by Edwards and Freed[3] by allowing nonstationary situations. However, on the one hand, the variational principle they use is difficult to handle, while, on the other hand, the model for polymers with an internal viscosity makes the analysis of the role of the dynamics of the fluid more complex.

In this paper we propose an alternative procedure to study the dynamics of polymers. We start simply from the equations of motion of the segments and the Navier–Stokes equation, which may incorporate random sources to account for fluctuations. The coupling between these equations then leads us to reformulate the problem in terms of induced forces.[4] The method enables us to arrive in a clear and systematic way at the equation of motion of the macromolecule in solution where the mobility kernels and the fluctuation–dissipation theorem are explicitly derived. The resulting equation allows us to analyze the influence of fluid motion on the dynamics of polymers.

The paper is organized as follows. Section 2 is devoted to obtaining the time-dependent mobility kernel for a system of N interacting particles. To this purpose, we use the Navier–Stokes–Langevin equation with appropriate induced forces accounting for the presence of the particles in the fluid. We also derive the fluctuation–dissipation theorem for the segments starting from fluctuating hydrodynamics. In section 3 we obtain the equation of motion for the polymer chain in θ-conditions. We then show that the velocity of each segment has two contributions: a systematic term, which involves the mobility kernel, and a random term, arising from the presence of fluctuations in the fluid. Our expression is general since in its derivation we have not specified the type of direct interactions between monomers. Therefore, it may be applied when external fields, electrostatic interactions, or excluded-volume effects are present. Moreover, the dynamics of the fluid is contained in the mobility kernel, which may also incorporate the effect of velocity gradients.[5] In section 4 we analyze the motion of the polymer by introducing normal modes for the position vectors of the segments. We study the effect of the fluid relaxation time on the correlation functions of the normal coordinates and the normal velocities for ideal chains. In the last section we discuss our main results and we indicate how to describe more general models. In particular, we briefly comment on the incorporation of excluded-volume effects.

2. Mobility Kernel for a System of Interacting Particles

We will consider a single flexible chain suspended in an incompressible Newtonian fluid of density ρ and viscosity η at constant temperature. We will model the polymer by a chain of N spherical particles with radius a (referred to as beads). For low Reynolds numbers the dynamics of the fluid is described by the linearized Navier–Stokes equation

$$\rho\frac{\partial\vec{v}(\vec{r},t)}{\partial t} = -\nabla\cdot\vec{\vec{P}}(\vec{r},t) \tag{2.1}$$

together with the incompressibility condition

$$\nabla\cdot\vec{v} = 0 \tag{2.2}$$

Here $\vec{v}(\vec{r},t)$ is the velocity of the fluid and $\vec{\vec{P}}$ is the pressure tensor given by

$$P_{\alpha\beta} = p\delta_{\alpha\beta} - \eta\left(\frac{\partial v_\beta}{\partial r_\alpha} + \frac{\partial v_\alpha}{\partial r_\beta}\right) + \Pi^R_{\alpha\beta} \equiv P^S_{\alpha\beta} + \Pi^R_{\alpha\beta} \tag{2.3}$$

where p is the hydrostatic pressure and $\Pi^R_{\alpha\beta}$ is the fluctuating contribution to the pressure tensor. This fluctuating contribution is Gaussian and white, and its correlations are given by

$$\langle\vec{\vec{\Pi}}^R(\vec{r},t)\rangle = 0 \tag{2.4}$$

$$\langle\Pi^R_{\alpha\beta}(\vec{r},t)\,\Pi^R_{\gamma\mu}(\vec{r}',t')\rangle = 2k_BT\eta\Delta_{\alpha\beta\gamma\mu}\delta(\vec{r}-\vec{r}')\,\delta(t-t') \tag{2.5}$$

with

$$\Delta_{\alpha\beta\gamma\mu} = \delta_{\alpha\gamma}\delta_{\beta\mu} + \delta_{\alpha\mu}\delta_{\beta\gamma} - \frac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\mu} \tag{2.6}$$

It is clear that the above expressions are valid in the fluid,

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that is, outside the beads.

In the analysis of the dynamics of the system composed by the fluid and the beads, it is convenient to extend the above equations and, in particular, also eqs 2.4 and 2.5, to be valid also inside the beads by introducing an induced force density.[4] When eq 2.3 is used, the Navier–Stokes equation then becomes

$$\rho\frac{\partial\vec{v}(\vec{r},t)}{\partial t} = -\nabla p(\vec{r},t) + \eta\nabla^2\vec{v}(\vec{r},t) + \sum_i \vec{F}_i(\vec{r},t) - \nabla\cdot\vec{\vec{\Pi}}^R(\vec{r},t) \tag{2.7}$$

where $\vec{F}_i$ is the induced force density inside and on the surface of the ith bead. By construction the induced force density on the ith bead is zero outside this bead. Inside the beads this induced force density is chosen such that

$$p(\vec{r},t) = 0; \quad |\vec{r} - \vec{R}_i| < a \tag{2.8}$$

$$\vec{v}(\vec{r},t) = \vec{u}_i(t); \quad |\vec{r} - \vec{R}_i| \le a \tag{2.9}$$

We will not consider a possible rotational velocity of the beads as it does not couple with the translation of the beads in the approximation we will be using. On the surface of the beads we use stick boundary conditions so that the extended velocity field is continuous on the surface of the beads. It follows from these expressions together with eq 2.7 and the boundary conditions that the induced force density is given by

$$\vec{F}_i(\vec{r},t) = \hat{n}(\vec{r},t)\cdot\vec{\vec{P}}^s(\vec{r},t)\,\delta(|\vec{r} - \vec{R}_i(t)| - a) + \left[\rho\frac{d\vec{u}_i}{dt} - \nabla\cdot\vec{\vec{\Pi}}^R(\vec{r},t)\right]\theta(a - |\vec{r} - \vec{R}_i(t)|) \tag{2.10}$$

where $\hat{n}(\vec{r},t) = (\vec{r} - \vec{R}_i)/|\vec{r} - \vec{R}_i|$.

In order to explicitly solve the linearized Navier–Stokes equation, it is convenient to introduce the Fourier transform of the various fields with respect to the position. For instance, one has for the velocity field

$$\vec{v}(\vec{k},t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\vec{v}(\vec{r},t) \tag{2.11}$$

where $\vec{k}$ is the wavevector. In this representation, the linearized Navier–Stokes equation becomes

$$\rho\frac{\partial\vec{v}(\vec{k},t)}{\partial t} = -i\vec{k}p(\vec{k},t) - \eta k^2\vec{v}(\vec{k},t) + \sum_i \vec{F}_i(\vec{k},t) - i\vec{k}\cdot\vec{\vec{\Pi}}^R(\vec{k},t) \tag{2.12}$$

while the incompressibility condition reads

$$\vec{k}\cdot\vec{v}(\vec{k},t) = 0 \tag{2.13}$$

Using the transverse nature of the velocity field, one may formally solve eq 2.12 and one obtains for the velocity field due to the induced forces and the random pressure tensor

$$\rho\vec{v}(\vec{k},t) = \int_{-\infty}^{t} dt'\, e^{-\nu k^2(t-t')}(\vec{\vec{1}} - \hat{k}\hat{k})\cdot\left[\sum_i \vec{F}_i(\vec{k},t') - i\vec{k}\cdot\vec{\vec{\Pi}}^R(\vec{k},t')\right] \tag{2.14}$$

where $\nu = \eta/\rho$ is the kinematic viscosity, $\vec{\vec{1}}$, the unit matrix and $\hat{k} = \vec{k}/k$.

If one studies the behavior of correlations of time differences much larger than a^2/ν, one may neglect the volume-induced force density and use the following approximation

$$\vec{F}_i(\vec{k},t) \simeq e^{-i\vec{k}\cdot\vec{R}_i(t)}\left(\frac{\sin ka}{ka}\right)\vec{F}_i(\vec{k}=0,t) \tag{2.15}$$

This approximation takes the total force of the ith bead on the fluid $\vec{F}_i(\vec{k}=0,t)$ and locates it as a constant force distribution on the surface of this bead. The total drag force exerted by the fluid on the ith particle is then $\vec{F}_i^H(t) \equiv -\vec{F}_i(\vec{k}=0,t)$. Substitution of this approximation into the solution given in eq 2.14 gives

$$\rho\vec{v}(\vec{k},t) = -\int_{-\infty}^{t} dt'\, e^{-\nu k^2(t-t')}(\vec{\vec{1}} - \hat{k}\hat{k})\cdot\left[\sum_i e^{-i\vec{k}\cdot\vec{R}_i(t')}\left(\frac{\sin ka}{ka}\right)\vec{F}_i^H(t') + i\vec{k}\cdot\vec{\vec{\Pi}}^R(\vec{k},t')\right] \tag{2.16}$$

Equation 2.16 gives us the velocity field as a function of the drag forces exerted by the fluid on the particles. One may now obtain a relationship between the drag forces and the velocities of all the particles by calculating the averages of the velocity field over the surfaces of the spheres and by using the stick boundary conditions given by eq 2.9. This leads us to

$$\vec{u}_i(t) = \frac{1}{4\pi a^2}\int d\vec{r}\,\vec{v}(\vec{r},t)\,\delta(|\vec{r} - \vec{R}_i(t)| - a) = \frac{1}{(2\pi)^3}\int d\vec{k}\, e^{i\vec{k}\cdot\vec{R}_i(t)}\left(\frac{\sin ka}{ka}\right)\vec{v}(\vec{k},t) \tag{2.17}$$

which, when we use eqs 2.16, reads

$$\vec{u}_i(t) = -\int_{-\infty}^{t} dt' \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2(t-t')}\left(\frac{\sin ka}{ka}\right)e^{i\vec{k}\cdot\vec{R}_i(t)}\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho}\cdot\left[\sum_j e^{-i\vec{k}\cdot\vec{R}_j(t')}\left(\frac{\sin ka}{ka}\right)\vec{F}_j^H(t') + i\vec{k}\cdot\vec{\vec{\Pi}}^R(\vec{k},t')\right] \tag{2.18}$$

This expression may now be written as the sum of two contributions. One is due to the random pressure tensor and is given by

$$\vec{u}_i^R(t) = -\int_{-\infty}^{t} dt' \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2(t-t')}\left(\frac{\sin ka}{ka}\right)e^{i\vec{k}\cdot\vec{R}_i(t)}\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho}\cdot[i\vec{k}\cdot\vec{\vec{\Pi}}^R(\vec{k},t')] \tag{2.19}$$

and the other is due to the induced force density

$$\vec{u}_i^s(t) = -\sum_j \int_{-\infty}^{t} dt' \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2(t-t')}\left(\frac{\sin ka}{ka}\right)\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho}\cdot e^{-i\vec{k}\cdot(\vec{R}_i(t) - \vec{R}_j(t'))}\left(\frac{\sin ka}{ka}\right)\vec{F}_j^H(t') \equiv -\sum_j \int_{-\infty}^{t} dt'\, \vec{\vec{\mu}}_{ij}(t-t';\vec{R}_i(t) - \vec{R}_j(t'))\cdot\vec{F}_j^H(t') \tag{2.20}$$

where the time-dependent mobility kernels are defined as

$$\vec{\vec{\mu}}_{ij}(\tau;\vec{R}_{ij}) \equiv \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2\tau} e^{i\vec{k}\cdot\vec{R}_{ij}}\left(\frac{\sin ka}{ka}\right)^2\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho} \tag{2.21}$$

with $\tau = t - t'$ and $\vec{R}_{ij} = \vec{R}_i(t) - \vec{R}_j(t)$. It should be noted that the velocity $\vec{u}_i$ depends on the past history of the whole system through $\exp[-i\vec{k}\cdot(\vec{R}_i(t) - \vec{R}_j(t'))]$. However, in our case one may replace $\vec{R}_i(t) - \vec{R}_j(t')$ by $\vec{R}_i(t) - \vec{R}_j(t)$ in view of the linearization of the Navier–Stokes equation in the velocity (cf. appendix A).

For $i = j$ we can perform the integral in eq 2.21 and obtain for $\tau \gg a^2/\nu$

$$\vec{\vec{\mu}}_{ii}(\tau) = 1/12\rho(\pi\nu\tau)^{3/2} \tag{2.22}$$

This is the usual long-time behavior of the single-particle mobility. One may also Fourier transform the single-particle mobility as given in eq 2.21 in order to get the frequency dependence. This gives the following expression

to linear order in αa

$$\vec{\vec{\mu}}_{ii}(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}\vec{\vec{\mu}}_{ii}(\tau) = \frac{1}{6\pi\eta a}[1 - \alpha a] \quad (2.23)$$

where

$$\alpha \equiv (-i\omega/\nu)^{1/2} \qquad \mathrm{Re}\,(\alpha) > 0 \quad (2.24)$$

This expression for the frequency-dependent single-particle mobility is correct up to order (αa), that is, as long as $|\omega| \ll \nu/a^2$. For this domain it agrees with the result first given by Stokes. If one considers the contribution proportional to $(\alpha a)^2$, one finds a sresult that differs from the corresponding term given by Stokes. The origin of this difference is the small-k approximation (eq 2.15) used in our analysis. As is clear from our result, this approximation gives the asymptotic behavior for small ω and large time correctly.

In the expression for the two-particle mobility we may easily evaluate the integral over $\vec{k}$ in eq 2.21 with $i \neq j$, if $|\vec{R}_{ij}| \gg a$. One may then take $ka = 0$ (point particle approximation) in eq 2.21 as a good approximation, and one finds

$$\vec{\vec{\mu}}_{ij}(\tau;\vec{R}_{ij}) \equiv \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2\tau} e^{i\vec{k}\cdot\vec{R}_{ij}} \frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho} \quad (2.25)$$

After integration we arrive at

$$\vec{\vec{\mu}}_{ij}(\tau;\vec{R}_{ij}) = \frac{e^{-R_{ij}^2/4\nu\tau}}{\rho(4\pi\nu\tau)^{3/2}}\vec{\vec{1}} + \frac{1}{4\pi\rho}\nabla_{\vec{R}_{ij}}\nabla_{\vec{R}_{ij}}\frac{1}{R_{ij}}\Phi\left(\frac{R_{ij}}{(4\nu\tau)^{1/2}}\right) \quad (2.26)$$

$\Phi(x)$ being the error function defined as

$$\Phi(x) \equiv \frac{2}{\sqrt{\pi}}\int_0^x d\xi\, e^{-\xi^2} \quad (2.27)$$

We find that the time-dependent hydrodynamic interaction kernel for point particles is given by the time-dependent Green function for the velocity field. Notice that $\vec{\vec{\mu}}_{ij}(\tau\to\infty;\vec{R}_{ij}) \sim \tau^{-3/2}$, the usual long-time hydrodynamic behavior. Moreover, we can Fourier transform eq 2.26 and obtain

$$(8\pi\eta R_{ij})\vec{\vec{\mu}}_{ij}(\omega;\vec{R}_{ij}) = e^{-\alpha R_{ij}}(\vec{\vec{1}} + \hat{R}_{ij}\hat{R}_{ij}) + \left[\frac{2}{\alpha^2 R_{ij}^2} - e^{-\alpha R_{ij}}\left(\frac{2}{\alpha^2 R_{ij}^2} + \frac{2}{\alpha R_{ij}} + 1\right)\right](3\hat{R}_{ij}\hat{R}_{ij} - \vec{\vec{1}}) \quad (2.28)$$

One may compare this result with the expression found by van Saarloos and Mazur[6] using a more general scheme. It then follows that corrections to eq 2.28 appear, which are of the order $(\alpha a)^2$ and $(a/R_{ij})^2$. Equation 2.28 is therefore valid up to order αa but also up to order a/R_{ij}. If we take the limit $\omega \to 0$ in eq 2.28, we will recover the steady-state two-particle mobility tensor (in the point particle approximation)

$$\vec{\vec{\mu}}_{ij}^{st}(\vec{R}_{ij}) = \vec{\vec{\mu}}_{ij}(\omega=0,\vec{R}_{ij}) = \frac{1}{8\pi\eta R_{ij}}(\vec{\vec{1}} + \hat{R}_{ij}\hat{R}_{ij}) \quad (2.29)$$

which is the usual Oseen tensor. If one adds the corrections to second order in (a/R_{ij}), one finds the Rotne–Prager tensor. This may be verified by replacing $[(\sin/ka)/ka]^2$ in eq 2.21 by $1 - (1/3)k^2a^2$ rather than 1 as we did above. The time-dependent analogue of the Rotne–Prager tensor for $t \gg a^2/\nu$ can also be obtained from eq 2.21 in this manner.

To conclude our analysis of the contributions to eq 2.18, we will discuss the random part of the velocity given in eq 2.19. The properties of the stochastic pressure tensor, shown in eqs 2.4, 2.5, and 2.19, fully determine the properties of $\tilde{u}_i^R$. The calculation is straightforward (cf. appendix B) and leads to

$$\langle \tilde{u}_i^R(t) \rangle = 0 \quad (2.30)$$

$$\langle \tilde{u}_i^R(t)\, \tilde{u}_j^R(t') \rangle = k_B T \vec{\vec{\mu}}_{ij}(t-t';\vec{R}_{ij}) \quad (2.31)$$

where $\vec{\vec{\mu}}_{ij}$ is given by eq 2.21, which reduces to eq 2.26 in the case $i \neq j$ as well as to eq 2.22 if $i = j$, in the approximations we are considering. In fact, eq 2.31 is closely related to the fluctuation–dissipation theorem, as we will show in appendix C. As is clear from the result, the average is calculated by freezing the positions of the beads.

3. Equation of Motion for the Chain

Our purpose in this section is to obtain the equation governing the motion of a polymer in solution. For the sake of simplicity, we will consider θ conditions under which the chain can be taken as ideal, i.e., where it follows Gaussian statistics. Under this condition, it is well-known that the radius of gyration, R_G, is given by

$$R_G = N^{1/2}b/\sqrt{6} \quad (3.1)$$

where b is the effective bond length.

The equation of motion of the ith particle of the chain is given by

$$M\frac{d\tilde{u}_i(t)}{dt} = \vec{F}_i^H(t) + \vec{F}_i^{ext}(t) \quad (3.2)$$

where $\vec{F}_i^H$ is the fluctuating hydrodynamic drag also appearing in eq 2.18 and $\vec{F}_i^{ext}$ includes all the other forces. In the absence of external fields, $\vec{F}_i^{ext}$ only contains forces between segments. According to the Rouse–Zimm model, these are given by

$$\vec{F}_i^{ext} = -H(2\vec{R}_i - \vec{R}_{i+1} - \vec{R}_{i-1}) \quad (3.3)$$

for the internal beads and

$$\vec{F}_1^{ext} = -H(\vec{R}_1 - \vec{R}_2)$$

$$\vec{F}_N^{ext} = -H(\vec{R}_N - \vec{R}_{N-1}) \quad (3.4)$$

for the beads at the ends of the chain. The constant H is

$$H = 3k_BT/b^2 \quad (3.5)$$

We will take the continuous chain limit. In this case, the elastic force (eq 3.3) is

$$\vec{F}_n^{ext} = H\frac{\partial^2\vec{R}_n}{\partial n^2} \quad (3.6)$$

with eq 3.4 given by

$$(\partial\vec{R}_n/\partial n)_{n=0} = (\partial\vec{R}_n/\partial n)_{n=N} = 0 \quad (3.7)$$

where the discrete index i has been substituted by the continuous index n. Equation 2.18 can be written by changing the sum to an integral over n. Combining eq 3.2 with eq 2.18 and taking the continuous limit, we get

$$\tilde{u}_n(t) = \int_{-\infty}^{t} dt' \int_0^N dm\, \vec{\vec{\mu}}_{nm}(t-t';\vec{R}_{nm}) \cdot \left[\vec{F}_m^{ext}(t') - M\frac{d\tilde{u}_m}{dt'}\right] + \tilde{u}_m^R(t) \quad (3.8)$$

Here, the mobility kernel is given by eq 2.26 for $|\vec{R}_{nm}| \gg a$. If $|\vec{R}_{nm}|$ becomes comparable to a, we will use eq 2.26 for $|R_{nm}| > a$ and 0 for $|\vec{R}_{nm}| < a$. This cutoff is necessary

in order to avoid the divergences that originate from the use of a continuous chain. The use of the mobility kernel given by eq 2.26 make the global motions of the chain have a characteristic time proportional to R_G rather than to the bead size.

In appendix C we will show that eq 3.8 can be written in the form of a generalized Langevin equation. However, for our purposes it is convenient to keep it in its actual form. We want to stress that eq 3.8 is an equation for polymer motion containing all the information we need about the dynamics of the fluid and its fluctuations. These fluid fluctuations are, in fact, responsible for the Brownian motion performed by the macromolecule.

Equation 3.8 is a nonlinear equation because the mobility kernel $\vec{\vec{\mu}}_{nm}(\tau;\vec{R}_{nm})$ explicitly depends on the vector $\vec{R}_{nm}$. This problem is the same as the one that arises when dealing with the hydrodynamic interaction described by the Oseen tensor. We will eliminate this nonlinearity in the usual way, by replacing the mobility by its equilibrium average (preaveraging approximation). This approximation gives reasonably good results in the steady-state case, but in our case it should be understood as a conjecture. However, as a matter of consistency, dynamical quantities could be alternatively computed by making the stationary limit of eq 2.26 and, after, the preaveraging approximation or by performing first the approximation in the nonstationary case and, afterward, taking the stationary limit.

The equilibrium average of the mobility kernel (eq 2.26) is calculated in appendix D and is found to be equal to

$$\langle \vec{\vec{\mu}}_{nm}(\tau;\vec{R}_{nm})\rangle_{eq} = \frac{2}{3\rho(4\pi\nu)^{3/2}} \frac{\vec{\vec{1}}}{(b^2|n-m|/6\nu+\tau)^{3/2}} \equiv \mu_{nm}(\tau)\vec{\vec{1}} \tag{3.9}$$

Notice that the averaging procedure leads to convergent expressions for the averaged mobility kernel (referred to simply as the mobility kernel), which is independent of the cutoff a. One can also notice that the averaged mobility kernel $\mu_{nm}(\tau)$ exhibits the long-time tail $\tau^{-3/2}$. After integration in time, eq 3.9 gives the steady-state mobility

$$\mu_{nm}^{st}\int_0^\infty d\tau\, \mu_{nm}(\tau) = \frac{1}{\eta\pi b(6\pi|n-m|)^{1/2}} \tag{3.10}$$

in agreement with the result obtained after averaging the Oseen tensor.[8]

Equation 3.8 can then be written in its final form

$$\frac{\partial \vec{R}_n}{\partial t} = \int_{-\infty}^t dt' \int_0^N dm\, \mu_{nm}(t-t')\left[H\frac{\partial^2 \vec{R}_m}{\partial m^2} - M\frac{\partial^2 \vec{R}_m}{\partial t'^2}\right] + \tilde{u}_n^R \tag{3.11}$$

where use has been made of eq 3.6 and $\partial\vec{R}_n/\partial t \equiv \tilde{u}_n$. Equation 3.11 with the preaveraged kernel is the time-dependent version of the Zimm model. We will show that the results obtained with the Zimm model are recovered in the long-time limit.

The average and the correlations of $\tilde{u}_n^R$ are obtained from eqs 2.30 and 2.31 by also averaging over the equilibrium distribution of the bead position, which gives

$$\langle \tilde{u}_i^R(t)\rangle = 0 \tag{3.12}$$

$$\langle \tilde{u}_i^R(t)\, \tilde{u}_j^R(t')\rangle = k_B T \mu_{ij}(t-t') \tag{3.13}$$

Notice that the average indicated by $\langle ... \rangle$ now also includes the average over the equilibrium distribution of the beads, which was not the case in eqs 2.30 and 2.31.

4. Analysis in Terms of Normal Modes

Our purpose in this section is to study collective motions of the chain. To this end, we will introduce the normal modes defined in the usual way[8]

$$\varphi_p(n) = \cos(p\pi n/N) \tag{4.1}$$

which satisfy the orthogonality condition

$$\int_0^N \frac{dn}{N}\varphi_p(n)\,\varphi_q(u) = \frac{1}{2}\delta_{pq}(1+\delta_{p0}) \tag{4.2}$$

Then, we can write

$$\vec{R}_n = \vec{X}_0 + 2\sum_{p=1}^N \vec{X}_p(t)\,\varphi_p(n) \tag{4.3}$$

where

$$\vec{X}_p(t) = \int_0^N \frac{dn}{N}\vec{R}_n(t)\varphi_p(n) \tag{4.4}$$

According to eqs 4.1–4.4, it is possible to obtain from eq 3.11 the equation of motion for the normal coordinates

$$\frac{\partial \vec{X}_p}{\partial t} = \sum_q \int_{-\infty}^t dt'\, \mu_{pq}(t-t')\left[K_q\vec{X}_q - NM\frac{\partial^2 \vec{X}_q}{\partial t'^2}\right] + \tilde{w}_q^R \tag{4.5}$$

where we have introduced the definitions

$$K_p = \frac{Hp^2\pi^2}{N} = \frac{6k_B T_p^{\,2}\pi^2}{Nb^2} \tag{4.6}$$

$$\mu_{pq}(\tau) = \frac{1}{N^2}\int_0^N dn\, dm\, \mu_{nm}(\tau)\,\varphi_p(n)\,\varphi_q(m) \tag{4.7}$$

$$\tilde{w}_p^R(t) = \frac{1}{N}\int_0^N dn\, \tilde{u}_n^R(t)\,\varphi_p(n) \tag{4.8}$$

Here K_p is an effective elastic constant corresponding to the p-mode, μ_{pq} accounts for the coupling between modes p and q, and the random term $\tilde{w}_p^R$ satisfies the stochastic properties

$$\langle \tilde{w}_p^R(t)\rangle = 0$$

$$\langle \tilde{w}_p^R(t)\, \tilde{w}_q^R(t')\rangle = k_B T \mu_{pq}(t-t')\vec{\vec{1}} \tag{4.9}$$

Our next step is to calculate the explicit values of the mobility kernel μ_{pq}. Substituting the mobility given in eq 3.9 and using eq 4.1, one obtains

$$\mu_{pq}(\tau) = \frac{2}{3(4\pi\nu)^{3/2}N^2}\left(\frac{6\nu}{b^2}\right)^{3/2}\int_0^N dn\Bigg[\cos\left(\frac{p\pi n}{N}\right)\times \cos\left(\frac{q\pi m}{N}\right)\int_{-n}^{N-n} dm\, \frac{1}{(|m|+6\nu\tau/b^2)^{3/2}}\cos\left(\frac{q\pi m}{N}\right) - \cos\left(\frac{p\pi n}{N}\right)\sin\left(\frac{q\pi m}{N}\right)\int_{-n}^{N-n} dm\, \frac{1}{(|m|+6\nu\tau/b^2)^{3/2}}\times \sin\left(\frac{q\pi m}{N}\right)\Bigg] \tag{4.10}$$

Following ref 8, the integral over m will converge quickly if q is large. Then we can approximate it by extending the lower limit $-\infty$ and the upper to ∞. The final result for $p \neq 0$ and $q \neq 0$ is

$$\mu_{pq}(t_p) \equiv \mu_p(t_p)\,\delta_{pq} = \delta_{pq}\frac{1}{\tau_p\xi_p}\phi_p(t_p) \tag{4.11}$$

where use has been made of the definitions

$$\tau_p = R_G^2/\nu\pi p \tag{4.12}$$

$$t_p = t/\tau_p \tag{4.13}$$

$$\xi_p = (12\pi^3)^{1/2}\eta p^{1/2}N^{1/2}b \tag{4.14}$$

$$\phi_p(t_p) = \cos t_p(1 - 2S(\sqrt{t_p})) - \sin t_p(1 - 2C(\sqrt{t_p})) - (2/\pi t_p)^{1/2} \tag{4.15}$$

Here τ_p is the relaxation time of the perturbation caused by the motion of a blob of radius $R_G/(\pi p)^{1/2}$, t_p is a dimensionless time, and ξ_p is the effective friction coefficient for the p-mode. The functions $C(x)$ and $S(x)$ are the Fresnel integrals given by

$$C(x) = \frac{2}{(2\pi)^{1/2}}\int_0^x \cos y^2\, dy$$

$$S(x) = \frac{2}{(2\pi)^{1/2}}\int_0^x \sin y^2\, dy \tag{4.16}$$

The approximation used to find the value of μ_{pq} is not valid for $p = q = 0$. However, μ_{00} can easily be obtained from eq 4.7 by substituting the corresponding values of p and q. We then obtain

$$\mu_{00}(\tau) = \frac{1}{N^2}\int_0^N dn\, dm\, \mu_{nm}(\tau) = \frac{3}{4\xi_0\tau_0}\phi_0(t_0) \tag{4.17}$$

where we have introduced the quantities

$$\tau_0 = R_G^2/\nu \tag{4.18}$$

$$t_0 = t/\tau_0 \tag{4.19}$$

$$\xi_0 = 3(6\pi^3)^{1/2}\eta N^{1/2}b/8 \tag{4.20}$$

$$\phi_0(t_0) = t_0^{-1/2} - 2[(1 + t_0)^{1/2} - t_0^{1/2}] \tag{4.21}$$

which are analogous to their corresponding quantities defined in eqs 4.12–4.14 and 4.15.

Using the dimensionless quantities, we can finally rewrite eq 4.5 in the more suitable form

$$\frac{\partial \vec{X}_0}{\partial t_0} = -\int_{-\infty}^{t_0} dt_0' \frac{3NM}{4\xi_0\tau_0}\phi_0(t_0 - t_0')\frac{\partial^2 \vec{X}_0}{\partial t_0'^2} + \tau_0 \vec{w}_0^R \tag{4.22}$$

for the zeroth-order mode and

$$\frac{\partial \vec{X}_p}{\partial t_p} = \int_{-\infty}^{t_p} dt_p' \frac{\tau_p}{\xi_p}\phi_p(t_p - t_p')\left[K_p \vec{X}_p - \frac{NM}{\tau_p^2}\frac{\partial^2 \vec{X}_q}{\partial t_p^2}\right] + \tau_p \vec{w}_q^R \tag{4.23}$$

for the higher order modes.

To get an idea about the relative importance of the different relaxation times appearing in eq 4.23, it is convenient to introduce ratios between them. For the zeroth-order mode, which gives the motion of the center of mass of the polymer, there is no contribution of any elastic force. We can define the parameter γ_0 by comparing the time associated with the relaxation of the acceleration, NM/ξ_0,[9] with the time related to the relaxation of the fluid disturbances, τ_0, defined in eq 4.18

$$\gamma_0 = 3NM/4\xi_0\tau_0 \tag{4.24}$$

In the case of higher order modes, there appear three time scales instead of two, due to the presence of the effective elastic force, which has an associated relaxation time given by ξ_p/K_p. In such a case, we can define two parameters

$$\gamma_p = NM/\tau_p \tag{4.25}$$

$$\alpha_p = \tau_p K_p/\xi_p \tag{4.26}$$

which will be used in forthcoming subsections to analyze the corresponding dynamic processes.

4.1. Motion of the Zeroth-Order Mode. In this subsection we will solve eq 4.22. Before proceeding, we will discuss the order of magnitude of the coefficient γ_0. According to eqs 4.18, 4.20, and 4.24, we have

$$\gamma_0 = \frac{3NM}{4\xi_0\tau_0} \sim \frac{\rho^*}{\rho}\frac{a^3}{b^3}\frac{1}{N^{1/2}} \ll 1 \tag{4.27}$$

where ρ^* is the polymer density, which is of the same order of magnitude as ρ. Notice that this situation is completely different from the one of a rigid sphere of radius R_G suspended in a fluid. In fact, if the density of the particle is $\tilde{\rho}$, this coefficient scales as the Lorentz parameter, $\tilde{\rho}/\rho$, and is on the order of 1. Then, for a suspended particle the relaxation time of the acceleration is of the same order of magnitude as the one related to the fluid disturbances. In the case of a polymer coil, the inertia of its mass is negligible compared to the inertia of the fluid moving with it. This feature is especially important in the case of dilute solutions, where there is no screening of the hydrodynamic interactions.

Our starting point will be the study of the velocity correlation function $\langle \dot{\vec{X}}_0(t_0)\, \dot{\vec{X}}_0(0)\rangle$. In order to solve the stochastic differential equation (eq 4.22), we will use the fact that the stochastic process is stationary, the system is assumed to be in equilibrium at $t = 0$, and the random noise $\vec{w}_0^R(t_0)$ is not correlated with the initial $\dot{\vec{X}}_0(0)$.[9] Then, multiplying both sides of eq 4.22 by $\dot{\vec{X}}_0(0)$ and averaging, we obtain an equation for the correlation

$$\langle \dot{\vec{X}}_0(t_0)\, \dot{\vec{X}}_0(0)\rangle = -\gamma_0\int_0^{t_0} dt_0\, \mu\, \phi_0(t_0 - t_0')\frac{d}{dt_0'}\langle \dot{\vec{X}}_0(t_0')\, \dot{\vec{X}}_0(0)\rangle \tag{4.28}$$

with the initial condition being the equilibrium correlation given by the law of equipartition of energy

$$\langle \dot{\vec{X}}_0(0)\, \dot{\vec{X}}_0(0)\rangle = \frac{k_B T}{NM}\vec{\vec{1}} \tag{4.29}$$

To compute the velocity autocorrelation function, we will introduce the Laplace transform, which, for an unspecified function $A(t)$, is defined as

$$A(s) \int_0^\infty dt\, e^{-st}A(t) \tag{4.30}$$

with the inverse transformation

$$A(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} e^{st}A(s) \tag{4.31}$$

Transforming eq 4.28 and solving for the correlation, we get

$$\langle \dot{\vec{X}}_0(s_0)\, \dot{\vec{X}}_0(0)\rangle = \frac{\gamma_0\phi_0(s_0)}{1 + \gamma_0 s_0\phi_0(s_0)}\langle \dot{\vec{X}}_0(0)\, \dot{\vec{X}}_0(0)\rangle \tag{4.32}$$

where $s_0 \equiv s\tau_0$ and

$$\phi_0(s_0) = \frac{\Gamma(1/2)}{s_0^{1/2}} - \frac{2}{s_0^{3/2}}[e^{s_0}\Gamma(3/2, s_0) - \Gamma(3/2)] \tag{4.33}$$

is the Laplace transform of $\phi_0(t_0)$ with $\Gamma(x)$ and $\Gamma(x,y)$ the gamma function and the incomplete gamma function, respectively.

In the time range under consideration ($t_0 \sim 1$), $\langle \dot{\hat{X}}_0(t_0)\, \dot{\hat{X}}_0(0)\rangle$ can be obtained from eq 4.32 simply by neglecting the term proportional to $\gamma_0 s_0$ in the denominator. This approximation will be valid for $t_0 \gg \gamma_0$ and yields

$$\langle \dot{\hat{X}}_0(t_0)\, \dot{\hat{X}}_0(0)\rangle \simeq \gamma_0 \phi_0(t_0) \langle \dot{\hat{X}}_0 \dot{\hat{X}}_0\rangle \qquad (4.34)$$

where use has been made of the shorthand notation $\langle \dot{\hat{X}}_0 \dot{\hat{X}}_0\rangle \equiv \langle \dot{\hat{X}}_0(0)\, \dot{\hat{X}}_0(0)\rangle$. The approximation introduced here is precisely the elimination of acceleration as is usually done in classical Brownian motion. We will discuss eq 4.34 later on. However, one should wonder in what time regime the effect of the neglected term can be important and what its consequences are. The time derivative will be important for times $t_0 \sim \gamma_0$, which are extremely short according to eq 4.27. This situation corresponds to the limit $s_0 \to \infty$ in eqs 4.32 and 4.33, which leads to

$$\langle \dot{\hat{X}}_0(s_0)\, \dot{\hat{X}}_0(0)\rangle \simeq \frac{\gamma_0(\sqrt{\pi}/s_0^{1/2})}{1 + \gamma s_0 \sqrt{\pi}/s_0^{1/2}} \langle \dot{\hat{X}}_0 \dot{\hat{X}}_0\rangle \qquad (4.35)$$

that is

$$\langle \dot{\hat{X}}_0(t_0)\, \dot{\hat{X}}_0(0)\rangle \simeq e^{\beta^2 t_0}(1 + \Phi(\beta t_0^{1/2}))\langle \dot{\hat{X}}_0 \dot{\hat{X}}_0\rangle \qquad (4.36)$$

with $\beta = (\sqrt{\pi}\,\gamma_0)^{-1}$. Notice that the equilibrium value of the correlation function is recovered from eq 4.36 for $t \to 0$, while in eq 4.34 the same limit diverges as $t^{-1/2}$. The inclusion of the finite relaxation time for the acceleration gives corrections in the diffusion coefficient on the order of γ_0 compared to 1, which are completely negligible. From now on, we will use the result given in eq 4.34. As we said before, for short times the velocity correlation function has a nonexponential decay $t_0^{-1/2}$. On the other hand, taking the limit $t_0 \to \infty$ in eq 4.34, we obtain

$$\langle \dot{\hat{X}}_0(t_0 \to \infty)\, \dot{\hat{X}}_0(0)\rangle \to \gamma_0 \phi_0(t_0 \to \infty)\, \langle \dot{\hat{X}}_0 \dot{\hat{X}}_0\rangle = \frac{2}{3}\frac{k_B T}{\rho(4\pi\nu t)^{3/2}}\bar{\bar{1}} \qquad (4.37)$$

where the substitution $t = t_0\tau_0$ has been made. This result shows the hydrodynamic long-time tail $t^{-3/2}$ and exactly coincides with the long-time limit for the velocity correlation function of a single Brownian particle.[10] Notice that no reference to characteristic lengths of the polymer coil (or the Brownian particle) remains. One can then expect that the velocity correlation function of a single polymer will be universal in that limit.

As we will see later on, the velocity correlation function for modes $p \neq 0$ decays much faster than that for $p = 0$. For this reason the internal degrees of freedom do not affect the long-time behavior of the center of mass velocity correlation function. However, taking into consideration coupling between modes, i.e., assuming that μ_{pq} may have nondiagonal contributions (cf. eq 4.10), should, in fact, modify the short-time behavior $t^{-1/2}$ we have found.[12]

To calculate the diffusion coefficient, we will use the Green–Kubo formula[9]

$$D_G = \frac{1}{3}\int_0^\infty dt\, \langle \dot{\hat{X}}_0(t)\cdot\dot{\hat{X}}_0(0)\rangle = \frac{k_B T}{\xi_0} = \frac{8}{3}\frac{k_B T}{(6\pi^3)^{1/2}\eta b N^{1/2}} \qquad (4.38)$$

where use has been made of eqs 4.21, 4.29, and 4.34. Then, the result given in ref 8 for the continuous Zimm model is recovered.

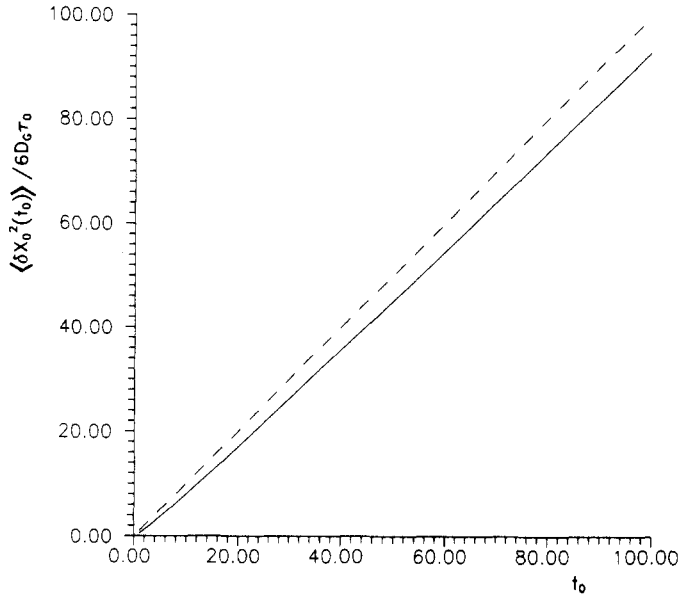

Figure 1. Mean-square displacement for the center of mass motion. Dashed line: Zimm model. Solid line: time-dependent hydrodynamic interactions.

It is also possible to arrive at the frequency-dependent diffusion coefficient defined as

$$D_G(\omega) = \frac{1}{3}\int_0^\infty dt\, e^{i\omega t}\langle \dot{\hat{X}}_0(t)\cdot\dot{\hat{X}}_0(0)\rangle \qquad (4.39)$$

which, for $\omega\tau_0 \ll 1/\gamma_0$, gives

$$D_G(\omega) = \frac{3k_B T}{4\xi_0}\int_0^\infty dt_0\, e^{i\omega\tau_0 t_0}\phi_0(t_0) \qquad (4.40)$$

This result can be obtained from eq 4.33 by replacing s_0 by $-i\omega\tau_0$, yielding

$$D_G(\omega) = \frac{3}{4}\frac{k_B T}{\xi_0}\left[\frac{\Gamma(1/2)}{(-i\omega\tau_0)^{1/2}} - \frac{2}{(i\omega\tau_0)^{3/2}} \times [e^{-i\omega\tau_0}\Gamma(3/2,-i\omega\tau_0) - \Gamma(3/2)]\right] \qquad (4.41)$$

The limit $D_G(\omega \to 0)$ gives the result eq 4.38 again.

We can also compute the mean-square displacement defined as

$$\delta\hat{X}_0(t) \equiv \hat{X}_0(t) - \hat{X}_0(0) = \int_0^t dt'\, \dot{\hat{X}}_0 \qquad (4.42)$$

One has[11]

$$\langle \delta X_0^2(t)\rangle = 2\int_0^t dt'\, (t - t')\langle \dot{\hat{X}}_0(t')\cdot\dot{\hat{X}}_0(0)\rangle \qquad (4.43)$$

Making use of eq 4.34, one finally arrives at

$$\langle \delta X_0^2(t)\rangle = 6\frac{k_B T}{\xi_0}\tau_0\left\{t_0 + t_0^{3/2} - \frac{2}{5}[(1 + t_0)^{5/2} - t_0^{5/2} - 1]\right\} \qquad (4.44)$$

This result has been plotted in Figure 1. The long-time limit of eq 4.44 leads us again to the well-known result

$$\langle \delta X_0^2(t \to \infty)\rangle \to 6\frac{k_B T}{\xi_0}\tau_0 t_0 = 6D_G t \qquad (4.45)$$

where use has been made of $t = t_0\tau_0$. From eq 4.44 and Figure 1 one can see that the behavior of the mean-square displacement very slowly tends to the diffusive behavior shown in eq 4.45, as $t_0^{-1/2} \to 0$. The result given by Zimm's model for this quantity still differs 10% from our result for times $t \sim 60\tau_0$.

4.2. Motion of the Internal Degrees of Freedom. For $p \neq 0$ the situation is completely different from the one discussed in eq 4.1. Here, the longest relaxation time is the one associated with the elastic constant K_p, which dominates the configurational changes. From eqs 4.6, 4.12, 4.14, and 4.26, we can see that

$$\alpha_p = \frac{\tau_p K_p}{\xi_p} \sim \frac{k_B T p^{1/2}}{\rho \eta^2 b N^{1/2}} \ll 1 \tag{4.46}$$

In this expression, the restriction $1 \leq p \leq N$, arising from the fact that b is the smallest length scale of the system, should be implicitly considered. In the same way as in section 4.1, we will also adiabatically eliminate the acceleration. After that, we introduce the Laplace transform of eq 4.23, multiply both sides by $\dot{\vec{X}}_p(0)$, and solve for the velocity correlation function, yielding

$$\langle \dot{\vec{X}}_p(s_p)\cdot\dot{\vec{X}}_p(0)\rangle = -\frac{\gamma_p s_p \phi_p(s_p)}{s_p - \alpha_p \phi_p(s_p)}\langle \dot{\vec{X}}_p\cdot\dot{\vec{X}}_p\rangle \simeq -\gamma_p \phi_p(s_p)\langle \dot{\vec{X}}_p\cdot\dot{\vec{X}}_p\rangle \tag{4.47}$$

Here, $s_p \equiv s\tau_p$ and $\phi_p(s_p)$ follows from the Laplace transform of $\phi_p(t_p)$

$$\phi_p(s_p) = \frac{s_p}{s_p + 1}(s_p - (2s_p)^{1/2} + 1) - 1 \tag{4.48}$$

Moreover, according to the energy equipartition theorem, one has

$$\langle \dot{\vec{X}}_p\cdot\dot{\vec{X}}_p\rangle = 3k_B T/NM \tag{4.49}$$

Transforming back in time, eq 4.47 gives

$$\langle \dot{\vec{X}}_p(t_p)\cdot\dot{\vec{X}}_p(0)\rangle \simeq -\frac{3k_B T}{\xi_p \tau_p}\phi_p(t_p) \tag{4.50}$$

In the limit $t_p \ll 1$ this equation gives rise to the nonexponential decay $t^{-1/2}$ and, in the case $t_p \gg 1$, to $t^{-5/2}$. This last limit coincides with the long-time tail for the rotational motion of a spherical particle.

Another important quantity is the correlation function $\langle \vec{X}_p(t_p)\cdot\vec{X}_p(0)\rangle$. This can also be obtained from eq 4.23 using the fact that $\dot{\vec{X}}_p(s_p) = s_p\vec{X}_p(s_p) - \vec{X}_p(0)$ and $\langle \vec{w}_p(t)\cdot\vec{X}_p(0)\rangle = 0$. One then arrives at

$$\langle \vec{X}_p(s_p)\cdot\vec{X}_p(0)\rangle = \frac{1}{s_p - \alpha_p \phi_p(s_p)}\langle \vec{X}_p(0)\cdot\vec{X}_p(0)\rangle \tag{4.51}$$

in which the equilibrium correlation function also satisfies the energy equipartition theorem

$$\langle \vec{X}_p(0)\cdot\vec{X}_p(0)\rangle \equiv \langle X_p^2\rangle = k_B T/K_p \tag{4.52}$$

The usual result for this correlation function is easily recovered after elimination of the time dependence of the fluid motion by substituting $\phi_p(s_p)$ for $\phi_p(s_p{=}0) = -1$ in eq 4.51. In time, it is given by[8]

$$\langle \vec{X}_p(t)\cdot\vec{X}_p(0)\rangle = e^{-\alpha_p t_p}\langle X_p^2\rangle = \frac{k_B T}{K_p}e^{-(K_p/\xi_p)} \tag{4.53}$$

The correction introduced by the fluid motion in the long-time behavior of this correlation function is on the order of α_p and therefore can be neglected. Consequently, the fluid motion does not introduce any correction over the long-time behavior of any quantity depending on configurational changes.

On the other hand, the study of the short-time behavior of $\langle \vec{X}_p(t)\cdot\vec{X}_p(0)\rangle$ can be obtained from eq 4.51 for $s_p \gg \alpha_p$, which leads to

$$\langle \vec{X}_p(s_p)\cdot\vec{X}_p(0)\rangle \simeq \frac{\langle X_p^2\rangle}{s_p}\left[1 - \frac{\alpha_p}{s_p}(1 - s_p\tilde{\phi}(s))\right] \tag{4.54}$$

Here $\tilde{\phi}(s_p)$ is defined from the relation $\phi(s_p) = s_p\tilde{\phi}(s_p) - \tilde{\phi}(0)$ where

$$\tilde{\phi}_p(s_p) = \frac{1}{s_p + 1}(s_p - (2s_p)^{1/2} + 1); \quad \tilde{\phi}_p(0) = 1 \tag{4.55}$$

Notice that $\tilde{\phi}_p(t_p)$ is then

$$\tilde{\phi}_p(t_p) = \cos t_p(1 - 2C(\sqrt{t_p})) + \sin t_p(1 - 2S(\sqrt{t_p})) \tag{4.56}$$

The inverse Laplace transform of eq 4.54 will give us the temporal dependence

$$\langle \vec{X}_p(t_p)\cdot\vec{X}_p(0)\rangle \simeq \frac{k_B T}{K_p}[1 - \alpha_p(t_p + \int_0^{t_p}\tilde{\phi}_p(t_p')\,dt_p')] \tag{4.57}$$

The integration can be easily computed from eq 4.56, obtaining

$$\int_0^{t_p} dt_p\,\tilde{\phi}_p(t_p) = 1 + \sin t_p(1 - 2C(\sqrt{t_p})) - \cos t_p(1 - 2S(\sqrt{t_p})) \tag{4.58}$$

This integral tends to 0 for $t_p \to 0$ and to 1 for $t_p \gg 1$. This means that, for $t_p \sim 1$, the effect due to the elastic force, $\alpha_p t_p$, is already comparable to the one due to the fluid relaxation. Thus, due to the fact that $t_p = \pi p t_0$, when $t_0 \sim 1$, the effect of the elastic force in eq 4.57 is the most important for all modes.

5. Conclusions

In this paper we have derived a theory for polymer motion, which provides a suitable framework to describe the coupled dynamics between the fluid and the polymer. Our treatment can be extended to more concentrated solutions as well as to a wide variety of models for the polymers because in the derivation of eq 2.18 no explicit reference to the particular dynamics of the segments, due to interactions with other segments or external fields, has been made. Thus, excluded-volume interactions as well as the influence of external fields can be taken into account through the equation of motion of the segments.

To introduce this more general description, let us suppose that the forces between segments are given by

$$\vec{F}_n^{\text{ext}} = -\delta\mathcal{H}/\delta\vec{R}_n \tag{5.1}$$

where $\mathcal{H}$ is the interaction potential given by

$$\mathcal{H} = \int_0^N dn\left\{\frac{H}{2}\left(\frac{\partial\vec{R}_n}{\partial n}\right)^2 + \int_0^N dm\; U_{\text{int}}(\vec{R}_n - \vec{R}_m)\right\} \tag{5.2}$$

where H is given by eq 3.5 and U_{int} is an interaction energy between segments. If we take

$$U_{\text{int}}(\vec{R}_n - \vec{R}_m) = \frac{\beta_0}{2}\delta(\vec{R}_n - \vec{R}_m) \tag{5.3}$$

we have the usual model for the excluded-volume interaction,[8] where β_0 is the excluded-volume parameter. Substituting eq 5.1 with eqs 5.2 and 5.3 into eq 3.8, we get

$$\tilde{u}_n(t) = \int_{-\infty}^{t} dt' \int_0^N dm\, \vec{\vec{\mu}}_{nm}(t-t';\vec{R}_n-\vec{R}_m)\cdot\left[H\frac{\partial^2 \vec{R}_m}{\partial m^2} - \frac{\beta_0}{2}\frac{\partial}{\partial \vec{R}_m}\int_0^N dm'\, \delta(\vec{R}_m - \vec{R}_{m'}) - M\frac{\partial^2 \vec{R}_m}{\partial t'^2}\right] + \tilde{u}_n^{\,R} \quad (5.4)$$

If we compare this equation with eq 3.11, we see that a contribution due to the excluded-volume interaction is now included.

A rigorous calculation of the time-dependent correlation functions would be difficult in the case of a chain with long-range interactions. However, we can extract some information about the decay of the center of mass velocity correlation function simply by using the asymptotic form of the static structure factor

$$g(\vec{k}) = \frac{1}{N}\int_0^N dn \int_0^N dm \langle e^{i\vec{k}\cdot\vec{R}_{nm}}\rangle \quad (5.5)$$

For $kR_G \gg 1$, scaling arguments give $g(\vec{k}) \sim k^{-5/3}$ in the case of the chain with excluded volume, while $g(\vec{k}) \sim k^{-2}$ for the ideal chain. We already know that, in the regime $kR_G \ll 1$, $g(k)$ has to be independent of details of the configuration. Therefore, we have that $g(\vec{k}) \sim$ constant for the ideal chain and the excluded-volume chain, as well.

The relationship between the center of mass velocity correlation function and the static structure factor can be visualized as follows. The motion of the center of mass is independent of the internal dynamics of the system in our approximation. Then, we can rewrite (cf. eq 4.34)

$$\langle \dot{\tilde{X}}_0(t)\, \dot{\tilde{X}}_0(0)\rangle \simeq \gamma_0 \phi_0^{(\beta)}(t) \langle \dot{\tilde{X}}_0 \dot{\tilde{X}}_0\rangle \quad (5.6)$$

where the superscript β denotes the fact that the excluded-volume interactions come into the motion of the center of mass through the average of the mobility kernel, that is, through $\phi_0^{(\beta)}(t)$. Thus

$$\langle \dot{\tilde{X}}_0(t)\, \dot{\tilde{X}}_0(0)\rangle \sim \mu_{00}^{(\beta)}(t)\vec{\vec{1}} \quad (5.7)$$

Taking into account eqs 2.25 and 4.17, averaging with the distribution function for the excluded-volume chain and interchanging the order of integration, we obtain

$$\mu_{00}^{(\beta)}(t)\vec{\vec{1}} = \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2 t}\left[\int_0^N \frac{dn\, dm}{N^2}\langle e^{i\vec{k}\cdot\vec{R}_{nm}}\rangle^{(\beta)}\right]\frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho} \quad (5.8)$$

where the term between square brackets is precisely $g(\vec{k})/N$. Due to the isotropy of the system, the structure factor will only be a function of $|\vec{k}|$. Then, we have

$$\mu_{00}^{(\beta)}(t) \sim \int_0^\infty dk\, k^2 e^{-\nu k^2 t} g(k) \quad (5.9)$$

If we now use the asymptotic values for $g(k)$, we find that the center of mass velocity correlation function behaves as $t^{-2/3}$ for $t \ll R_G^2/\nu$ instead of the decay $t^{-1/2}$ obtained for the Gaussian chain. This means that as the polymer swells due to excluded-volume interactions, fluid can flow better through a less dense coil, reducing the inertia and leading to a faster decay. In general, if $R_G \sim bN^\nu$ (here ν stands for the Flory exponent), the short-time decay will be $t^{-(3\nu-1)/2\nu}$, as follows from eq 5.9 using the scaling law $g(\vec{k}) \sim k^{-1/\nu}$. The limit $t \gg R_G^2/\nu$ gives a decay $t^{-3/2}$ as we expected. Notice that the asymptotic behaviors found ensure the existence of the diffusion coefficient because the integral of the velocity correlation function exists.

In section 4 we have used the results of preceding sections to study the effect of fluid motion on polymer dynamics. We have calculated velocity correlation functions which show hydrodynamic behavior. At short times we observe a nonexponential $t^{-1/2}$ decay whereas at long times, the decay is $t^{-3/2}$ for the center of mass motion and $t^{-5/2}$ for the internal motions. These behaviors are the same as the long-time tails of a single Brownian particle undergoing translational ($t^{-3/2}$) and rotational ($t^{-5/2}$) motions. This last result, then, confirms that deformations and rotations have the same long-time behavior.[12] Moreover, the diffusion coefficient is calculated from the center of mass velocity correlation function by using the corresponding Green–Kubo formula. Velocity correlation functions cannot directly be measured,[11] but they can be obtained from molecular dynamics.

Light and neutron scattering experiments give information about those correlation functions involving configurational changes (overall motions as well as internal rearrangements). We have found that the mean-square displacement very slowly tends toward its asymptotic diffusive regime due to the long-time hydrodynamic behavior. This introduces differences of about 10% in a range of time $t \sim 60\tau_0$ below Zimm's model predictions for the same quantity. For solutions of large polymers (with $R_G \sim 10^{-5}$ cm and $\nu \sim 10^{-2}$ cm^2/s), this implies $t \sim 10^{-6}$ s, which are accessible from the experimental point of view. At this point is is interesting to remark the still unclear discrepancy between the experimental and calculated values for the diffusion coefficient[13,14] although the experiments seem to indicate that the behavior is simply diffusive.[15,16]

We have also shown that the fluid finite relaxation time gives irrelevant corrections in internal rearrangements which are mainly governed by the effective elastic force. In a scattering experiment in which the target is, for example, a labeled segment of the chain, we obtain the corresponding dynamic structure factor defined as

$$S_n(\vec{k},t) = \langle e^{i\vec{k}\cdot(\vec{R}_n(t)-\vec{R}_n(0))}\rangle \quad (5.10)$$

This quantity reflects, in fact, the dynamics of the labeled segment in which (cf. eq 4.3) all the normal modes are involved. Consequently, when computing $S_n(\vec{k},t) - S_n(\vec{k},0)$ for $t \sim \tau_0$, only a small difference with respect to the classical results is obtained when taking into account with finite fluid relaxation time. Structural rearrangements constitute the main contribution to the relaxation of the structure factor, even at short times, and the effect of the fluid inertia cannot be observed by means of this experiment.

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Appendix A. Approximation of Low Reynolds Number

Our aim in this appendix is to discuss the validity of the approximation $\vec{R}_i(t) - \vec{R}_j(t') \simeq \vec{R}_i(t) - \vec{R}_j(t)$ in the framework of low Reynolds number hydrodynamics. This approximation in eq 2.21 has to be made in order to be consistent with the linearization of the Navier–Stokes equation. This can be visualized first considering $i = j$. The time dependence on the position of the ith particle in eq 2.18 would be important if $|\vec{R}_i(t) - \vec{R}_i(t')| \simeq a$ in a time interval $t - t' \simeq a^2/\nu$. Taking $\vec{R}_i(t) - \vec{R}_j(t') \simeq \tilde{u}_i(t - t')$, we would finally arrive at the condition $u_i(a^2/\nu) \simeq a$; that is, $R = u_i a/\nu \simeq 1$, where R is the Reynolds number. Then, according to our initial assumption $u_i a/\nu \ll 1$, we can neglect this time dependence.[6,10] Moreover, in the case $i \neq j$, a similar argument leads us to the conclusion that the Reynolds number associated to the whole polymer also has to be small, as is the case. Therefore, the use of

$\vec{R}_i(t) - \vec{R}_j(t')$ instead of $\vec{R}_i(t) - \vec{R}_j(t)$, as in ref 3, in the mobility kernel is inconsistent with the linearization of the Navier–Stokes equation.

Appendix B. Fluctuation–Dissipation Theorem

To obtain relations 2.30 and 2.31, we need to introduce the Fourier transform of eqs 2.4 and 2.5. One arrives at

$$\langle \vec{\vec{\Pi}}^R(\vec{k},t)\rangle = 0$$

$$\langle \Pi^R_{\alpha\beta}(\vec{k},t)\ \Pi^R_{\gamma\mu}(\vec{k}'',t')\rangle = 2(2\pi)^3 k_B T\eta \Delta_{\alpha\beta\gamma\mu}\delta(\vec{k}+\vec{k}'')\ \delta(t-t') \tag{B.1}$$

where $\Delta_{\alpha\beta\gamma\mu}$ is given by eq 2.6. If we average eq 2.19, we obtain

$$\rho\langle \vec{u}_i^R(t)\rangle = \int_{-\infty}^{t} dt' \int \frac{d\vec{k}}{(2\pi)^3} \times e^{-\nu k^2(t-t')} \frac{\sin ka}{ka} e^{i\vec{k}\cdot\vec{R}_i(t)} (\vec{\vec{1}} - \hat{k}\hat{k})\cdot[-i\vec{k}\cdot\langle \vec{\vec{\Pi}}^R(\vec{k},t')\rangle] = 0 \tag{B.2}$$

which corresponds to eq 2.30. To obtain eq 2.31, we must use eq 2.19 and average keeping in mind that $t \geq t'$; that is

$$\langle \vec{u}_i^R(t)\ \vec{u}_j^R(t')\rangle = \int \frac{d\vec{k}}{(2\pi)^3} \frac{d\vec{k}'}{(2\pi)^3} \int_{-\infty}^{t} dt'' \int_{-\infty}^{t'} dt''' \, e^{-\nu k^2(t-t'')} \times e^{-\nu k'^2(t'-t''')} e^{i\vec{k}\cdot\vec{R}_i} e^{i\vec{k}'\cdot\vec{R}_j} \frac{1}{\rho^2} \frac{\sin ka}{ka} \frac{\sin k'a}{k'a} (\vec{\vec{1}} - \hat{k}\hat{k})\cdot \langle (\vec{\vec{\Pi}}^R(\vec{k},t'')\cdot(-i\vec{k}))(-i\vec{k}'\cdot\vec{\vec{\Pi}}^R(\vec{k}',t'''))\rangle \cdot (\vec{\vec{1}} - \hat{k}'\hat{k}') \tag{B.3}$$

Making use of eq B.1, we can perform the integration over $\vec{k}'$ and t''', arriving at

$$\langle \vec{u}_i^R(t)\ \vec{u}_j^R(t')\rangle = 2k_B T\eta \int_{-\infty}^{t'} dt'' \int \frac{d\vec{k}}{(2\pi)^3} \times e^{-\nu k^2(t+t'-2t'')} e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \frac{k^2}{\rho^2} \left(\frac{\sin ka}{ka}\right)^2 (\vec{\vec{1}} - \hat{k}\hat{k}) \tag{B.4}$$

Now, integrating over t'', we get

$$\langle \vec{u}_i^R(t)\ \vec{u}_j^R(t')\rangle = k_B T \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2(t-t')} e^{i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)} \times \left(\frac{\sin ka}{ka}\right)^2 \frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho} = k_B T \vec{\vec{\mu}}_{ij}(t-t';\vec{R}_i-\vec{R}_j) \tag{B.5}$$

in agreement with eq 2.21.

Appendix C. Friction Kernel

We can formally define the friction kernel $\vec{\vec{\xi}}_{nm}(t-t';\vec{R}_{nm})$ as the generalized inverse of the mobility kernel $\vec{\vec{\mu}}_{nm}(t-t';\vec{R}_{nm})$

$$\int_{-\infty}^{\infty} dt' \int_0^N dm\ \vec{\vec{\xi}}_{nm}(t-t';\vec{R}_{nm})\cdot\vec{\vec{\mu}}_{mn'}(t'-t'';\vec{R}_{mn'}) = \int_{-\infty}^{\infty} dt' \int_0^N dm\ \vec{\vec{\mu}}_{nm}(t-t';\vec{R}_{nm})\cdot\vec{\vec{\xi}}_{mn'}(t'-t'';\vec{R}_{mn'}) = \vec{\vec{1}}\delta(t-t'')\ \delta(n-n') \tag{C.1}$$

Multiplying both sides of eq 3.8 by $\vec{\vec{\xi}}_{nm}$, integrating over t and m, and using eq C.1, we obtain

$$M\frac{d\vec{u}_n}{dt} = -\int_{-\infty}^{\infty} dt' \int_0^N dm\ \vec{\vec{\xi}}_{nm}(t-t';\vec{R}_{nm})\cdot\vec{u}_m(t') + \vec{F}_n^{ext}(t) + \vec{F}_n^R(t) \tag{C.2}$$

where

$$\vec{F}_n^R(t) = \int_{-\infty}^{\infty} dt' \int_0^N dm\ \vec{\vec{\xi}}_{nm}(t-t';\vec{R}_{nm})\cdot\vec{u}_m^R(t') \tag{C.3}$$

Equation C.2 is the generalized Langevin equation written in the usual form.[9] The random force defined in eq C.3 satisfies the fluctuation–dissipation theorem

$$\langle \vec{F}_n^R(t)\rangle = 0$$

$$\langle \vec{F}_n^R(t)\ \vec{F}_m^R(t')\rangle = k_B T \vec{\vec{\xi}}_{nm}(t-t';\vec{R}_{nm}) \tag{C.4}$$

as can be easily seen from eqs 2.30, 2.31, and C.1.

Appendix D. Averaged Mobility Kernel

The mobility kernel given in eq 3.9 is obtained by averaging the mobility kernel shown in eq 2.21, using the equilibrium distribution function for the vector $\vec{R}_{nm}$. For an ideal chain this distribution function is Gaussian and reads[8]

$$\Phi(\vec{R}_{nm}) = \left[\frac{3}{2\pi b^2|n-m|}\right]^{3/2} \exp\left\{\frac{3(\vec{R}_n - \vec{R}_m)^2}{2|n-m|b^2}\right\} \tag{D.1}$$

We can then write

$$\langle \vec{\vec{\mu}}_{nm}(\tau,\vec{R}_{nm})\rangle_{eq} = \int \frac{d\vec{k}}{(2\pi)^3} e^{-\nu k^2\tau} \langle e^{i\vec{k}\cdot\vec{R}_{nm}}\rangle_{eq} \frac{(\vec{\vec{1}} - \hat{k}\hat{k})}{\rho} \tag{D.2}$$

In the case in which $\vec{R}_{nm}$ is a Gaussian variable, the average contained in eq D.2 only involves the second moment of the distribution function, that is

$$\langle e^{i\vec{k}\cdot\vec{R}_{nm}}\rangle_{eq} = e^{-[(k^2/6)\langle(\vec{R}_{nm})^2\rangle]} = e^{-[(k^2/6)|n-m|b^2]} \tag{D.3}$$

Substituting eq D.3 into eq D.2 and integrating over the solid angle, we get

$$\langle \vec{\vec{\mu}}_{nm}(\tau,\vec{R}_{nm})\rangle_{eq} = \frac{1}{3\pi^2\rho} \int_0^{\infty} dk\ k^2 e^{-k^2[\nu\tau+|n-m|b^2/6]} \vec{\vec{1}} \tag{D.4}$$

which, after integration, leads us to the result given in eq 3.9.

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