Brownian dynamics simulation of stiff dumbbells

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(Received 26 April 1984; accepted 26 September 1984)

The effects of stiffness on the diffusion-limited dynamics of dumbbells in solution is studied numerically. The Langevin equation is used with two different models, the so-called Fraenkel and FENE dumbbells. It is found that the dynamics of rotation and stretching are dictated by the two following trends: (i) the density–density correlation function for these modes decays more slowly for larger values of the equilibrium distance between the two beads L (with the spring force constant K fixed), and (ii) it decays more quickly for increasing stiffness (with L fixed) making the bond stretching relaxation time τ_2 smaller. For sufficiently stiff chains the value of τ_2 becomes less than the delay time of the experimental correlator, resulting in a difference between the true and measurable first cumulants.

I. INTRODUCTION

In this paper a simple two-center molecule (dumbbell) is used to study the effect of stiffness on the dynamic scattering function or its initial slope, the first cumulant. The dumbbell is by no means a realistic model for a polymer molecule, but its simplicity and tractability in most analytical manipulations have made it an interesting subject. The dynamic scattering function $S(q, t)$, i.e., the density–density time correlation function can be evaluated analytically in some limiting cases to be discussed below. Of special importance is its initial time derivative (first cumulant) referred to as either $\Gamma(q)$ or $\Omega(q)$ in the literature.[1] Here the symbol $\Gamma(q)$ will be used. $S(q, t)$ in the limit of flexible dumbbell with a purely Gaussian potential has been known for a long time[2] in the free draining case. If one looks at the dumbbell as the smallest ring polymer, preaveraged hydrodynamic interaction can also be included.[3] The other limit in stiffness corresponds to the rigid dumbbell for which $S(q, t)$ is also known.[4] The main goal of the present work is to investigate $S(q, t)$ in situations of intermediate stiffness (between purely flexible and rigid). This is done by (numerically) simulating the Brownian motion of the dumbbell in solution with appropriate interbead potentials. Both the "Fraenkel" dumbbell[5] potential

$$U_1(r) = k_BT3K(r - L)^2/2 \tag{1}$$

and the "finitely extendable nonlinear elastic" dumbbell[6] potential

$$U_2(r) = -k_BT3K \ln[1 - r^2/R_0^2]/2 \tag{2}$$

are considered. In these expressions, r denotes the intermonomer distance, with equilibrium value L, K plays the role of a spring force constant, and R_0 is a parameter which restricts the extension of the FENE dumbbell to $L - R_0 < r < L + R_0$.

Stiffness can be introduced by increasing the spring force constant K, which tends to constrain the motion of r to a smaller interval around $r = L$. This way of imposing "hard constraints" is physically realistic and allows us, in the limit of infinite K, to start from the equation of motion of a rigid rod. This approach is to be contrasted with imposing "flexible or soft constraints" in which case the equation of motion is solved in the full configuration space and constraints are imposed as the very last step. The results obtained by using these two approaches can be different, as has been pointed out by many authors.[3,7–9]

In the following section, we review the analytical forms of $S(q, t)$ and

$$\Gamma(q) = -\lim_{t\to 0} \frac{d}{dt} \ln S(q, t)$$

in the cases of flexible and rigid dumbbells. We then discuss the Brownian dynamics simulation program that solves the Langevin equation for the internal (intermonomer distance $\mathbf{r}$) motion. The external (center of mass) motion is decoupled (pure diffusion).

II. DYNAMIC SCATTERING FUNCTION AND FIRST CUMULANT

We consider a symmetric dumbbell consisting of two beads of equal friction constants ζ located at $\mathbf{R}_1$ and $\mathbf{R}_2$, respectively. For convenience, the center of mass $\mathbf{R} = (\mathbf{R}_1 + \mathbf{R}_2)/2$ and relative $\mathbf{r} = \mathbf{R}_1 - \mathbf{R}_2$ coordinates are used. Coordinates corresponding to an asymmetric dumbbell with different friction coefficients ($\zeta_1 \neq \zeta_2$) could also be used. In this last case, one would define a center of friction [$R = (\zeta_1 R_1 + \zeta_2 R_2)/(\zeta_1 + \zeta_2)$] instead of the center of mass. Since this little generalization is irrelevant to the problem of stiffness, we will stay with $\zeta_1 = \zeta_2$. The dynamic scattering function $S(q, t) = \langle \rho^*(q)\rho(q, t)\rangle_{\psi(\mathbf{R},\mathbf{r},t)}$ is the time correlation of the bead density $\rho(q) = \exp(i\mathbf{q}\cdot\mathbf{R})\cos(\mathbf{q}\cdot\mathbf{r}/2)$ and the brackets symbolize an ensemble average over all conformations of the dumbbell

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 0021-9606/85/010401-05$02.10

represented by an equilibrium distribution $\psi(\mathbf{R}, \mathbf{r}, t)$. If the separability $\psi(\mathbf{R}, \mathbf{r}, t) = \psi(\mathbf{R}, t)\psi(\mathbf{r}, t)$ is anticipated (i.e., if external and internal motions are decoupled), $S(q, t)$ becomes

$$S(q, t) = \langle \exp\{i\mathbf{q} \cdot [\mathbf{R}(t) - R_0]\} \rangle_{\psi(\mathbf{R},t)} \times \langle \cos(\mathbf{q} \cdot \mathbf{r}_0/2) \cos[\mathbf{q} \cdot \mathbf{r}(t)/2] \rangle_{\psi(\mathbf{r},t)}. \quad (3a)$$

The motion of the center of mass is a pure diffusion with distribution

$$\psi(\mathbf{R}, t|\mathbf{R}_0) = (1/2\pi D_m t)^{3/2} \exp[-(\mathbf{R} - \mathbf{R}_0)^2/2D_m t],$$

(D_m being the diffusion coefficient of each bead). The first ensemble average in $S(q, t)$ [hereafter noted $S^E(q, t)$] can therefore be performed to yield:

$$S^E(q, t) = \langle \exp\{i\mathbf{q} \cdot [\mathbf{R}(t) - \mathbf{R}_0]\} \rangle_{\psi(\mathbf{R},t)} = \exp[-q^2 D_m t/2]. \quad (3b)$$

The effect of preaveraged hydrodynamic interaction is to rescale time as [3] $t \rightarrow (1 + B)t$, where B is the draining parameter. In order to perform the second ensemble average,

$$S^I(q, t) = \langle \cos(\mathbf{q} \cdot \mathbf{r}_0/2) \cos[\mathbf{q} \cdot \mathbf{r}(t)/2] \rangle_{\psi(\mathbf{r},t)}, \quad (3c)$$

the Langevin equation describing the internal $\mathbf{r}$ motion is solved. Actually, we are interested in the fluctuations from the equilibrium value, i.e.,

$$\delta S^I(q, t) = S^I(q, t) - S^I(q, \infty) = \langle \cos(\mathbf{q} \cdot \mathbf{r}_0/2) \cos[\mathbf{q} \cdot \mathbf{r}(t)/2] \rangle - \langle \cos(\mathbf{q} \cdot \mathbf{r}_0/2) \rangle \langle \cos[\mathbf{q} \cdot \mathbf{r}(t)/2] \rangle. \quad (3d)$$

A. Analytical solutions

In this section, we briefly review a few well known analytical results which will be valuable in testing our numerical simulations.

A flexible dumbbell with a Gaussian potential $U_1^0(r) = 3k_B T K r^2/2$ is first considered. The parameter K is usually written as $1/b^2$ where $b^2 = \langle r^2 \rangle$. Each bead obeys a Langevin equation:

$$\zeta d\mathbf{R}_1/dt + \partial U/\partial \mathbf{R}_1 = \mathbf{F}_1,$$
$$\zeta d\mathbf{R}_2/dt + \partial U/\partial \mathbf{R}_2 = \mathbf{F}_2, \quad (4)$$

where inertial effects have been neglected. The relative motion obeys also a Langevin equation,

$$\zeta d\mathbf{r}/dt + 2\partial U/\partial \mathbf{r} = \mathbf{f}. \quad (5)$$

The random force $\mathbf{f} = \mathbf{F}_1 - \mathbf{F}_2$ is assumed to be a Gaussian process that obeys

$$\langle \mathbf{f}(t) \rangle = 0,$$
$$\langle \mathbf{f}(t_1)\mathbf{f}(t_2) \rangle = \mathbf{I} 4 D_m \delta(t_1 - t_2) \zeta^2. \quad (6)$$

A Smoluchovski equation for the conditional distribution $\psi(\mathbf{r}, t|\mathbf{r}_0)$ can therefore be obtained,

$$\partial\psi(\mathbf{r}, t|\mathbf{r}_0)/\partial t = 2D_m[\partial^2/\partial \mathbf{r}^2 + \partial(3K\mathbf{r})/\partial \mathbf{r}]\psi(\mathbf{r}, t|\mathbf{r}_0), \quad (7)$$

whose solution was obtained by Uhlenbeck and Orstein[2] as

$$\psi(\mathbf{r}, t|\mathbf{r}_0) = \left[\frac{3K}{2\pi(1 - e^{-12KD_m t})}\right]^{3/2} \times \exp\left[-\frac{3K}{2}\frac{(\mathbf{r} - \mathbf{r}_0 e^{-6KD_m t})^2}{(1 - e^{-12KD_m t})}\right]. \quad (8)$$

With this solution, and the use of an initial distribution

$$\psi(\mathbf{r}_0) = (3K/2\pi)^{3/2} \exp[-3Kr_0^2/2], \quad (9)$$

the ensemble average involved in $\delta S^I(q, t)$ can be performed and yields

$$\delta S^I(q, t) = \exp[-q^2/12K] \times [\cosh(q^2 e^{-6KD_m t}/12K) - 1], \quad (10)$$

which when normalized to one is denoted

$$\delta S_N^I(q, t) = \delta S^I(q, t)/\delta S^I(q, 0).$$

The effect of preaveraged hydrodynamic interaction can be introduced here also by rescaling time but with the other Zimm eigenvalue,[3] i.e., $t \rightarrow (1 - B)t$ where $B = \zeta/\eta_0 b\pi\sqrt{6\pi}$ and η_0 is the solvent viscosity.

The first cumulant is the sum $\Gamma(q) = \Gamma^E(q) + \Gamma^I(q)$ of a translational part $\Gamma^E = q^2 D_m/2$ and of a part which described relaxation of stretching modes,

$$\Gamma^I(q) = (q^2 D_m/2)\sinh(q^2/12K)/[\cosh(q^2/12K) - 1]. \quad (11)$$

In the case of a rigid dumbbell ($r = L$), $S^I(q, t)$ has been derived by Pecora.[10] In this case besides the overall translational diffusion, there is a rotational diffusion around the center of mass. The distribution function for the rotational motion obeys $\partial\psi(\Omega, t)/\partial t = I^2\theta\psi(\Omega, t)$ where I^2 is the angular momentum operator and $\theta = 2D_m/L^2$ is the rotatory diffusion coefficient. Pecora[10] gives

$$S^I(q, t) = \sum_{l \text{ even}} (2l + 1) e^{-l(l+1)\theta t} j_l^2(qL/2), \quad (12)$$

where j_l is the spherical Bessel functions.

The "internal" part of the first cumulant for a rigid dumbbell follows straightforwardly[10]:

$$\Gamma^I(q) = \sum_{l \text{ even}} (2l + 1) l(l + 1)\theta j_l^2(qL/2)/ \left[\sum_{l \text{ even}} (2l + 1) j_l^2(qL/2) - j_0^2(qL/2)\right], \quad (13)$$

and can be simplified further to read[3]

$$\Gamma^I(q) = q^2 D_m[1/3 - j_1(qL)/qL]/ [1 + j_0(qL) - 2j_0^2(qL/2)]. \quad (14)$$

This result was obtained by Pecora[10] when rigid constraints are imposed on the dumbbell. Another form for the first cumulant (case of flexible constraints) is worth recalling at this point. Akcasu, Benmouna, and Han[3] restricted the freely jointed chain result to a dumbbell to obtain for the internal part of $\Gamma(q)$:

$$\Gamma^I(q) = q^2 D_m[1 - j_0(qL)]/$$
$$[1 + j_0(qL) - 2j_0^2(qL/2)]. \quad (15)$$

The difference between these two results has been discussed elsewhere[3,9] and is presented in Fig. 1. We notice that for both of these cases the limiting values of $\Gamma^I(q)$ are reached at long distances through an oscillatory behavior.

Stockmayer and Burchard[9] have considered a situation of intermediate stiffness near the rod limit. They used the Fraenkel dumbbell potential which allows for small stretching deviations $\xi = r - L$ of root mean square $\sqrt{\langle \xi^2 \rangle} \ll L$. In this case, the angular distribution $\psi(\Omega, t|\Omega_0)$ is the same as in the rigid dumbbell case, the radial distribution is the one-dimensional version of Eq. (8), i.e.,

$$\psi(\xi, t|\xi_0) = [3K/2\pi(1 - e^{-12KD_m t})]^{1/2}$$
$$\times \exp[-3K(\xi - \xi_0 e^{-6KD_m t})^2/2(1 - e^{-12KD_m t})], \quad (16)$$

and the initial distributions are chosen as follows:

$$\psi(\Omega_0) = 1/4\pi,$$
$$\psi(\xi_0) = (3K/2\pi)^{1/2} \exp[-3K\xi_0^2/2]. \quad (17)$$

Using expansions of $\cos(\mathbf{q}\cdot\mathbf{r}/2)$ and $\cos(\mathbf{q}\cdot\mathbf{r}_0/2)$ in terms of spherical harmonics and spherical Bessel functions the following formula can be derived:

$$S^I(q, t) = \sum_{l \text{ even}} (2l + 1)\exp[-l(l + 1)\theta t]$$
$$\times \sum_{S,S'=0}^{\infty} \frac{j_l^{(S)}(qL/2)}{S!} \frac{j_l^{(S')}(qL/2)}{S'!}$$
$$\times \langle (q\xi/2)^S (q\xi_0/2)^{S'} \rangle_{\psi(r,t)}. \quad (18)$$

$j_l^{(S)}(qL/2)$ is used to represent $d^S j_l(\xi)/d\xi^S$ taken at $\xi = qL/2$. This formula was first derived by Stockmayer and Burchard[9] in the limit $b \ll L$.

In this last case, the first cumulant contains both the translational and rotational parts and, as discussed by these authors,[9] it also contains a contribution from stretching if the rigid limit is taken as the very last step.

At this point, we should emphasize that for this model (Fraenkel dumbbell) stretchings should be restricted to $\sqrt{\langle \xi^2 \rangle} \leqslant L$ for Eq. (17) to hold. The FENE potential on the other hand, allows for any degree of stiffness provided the other parameter R_0 is kept smaller than L. Unfortunately, the complexity in the use of this potential prohibits analytical attempts.

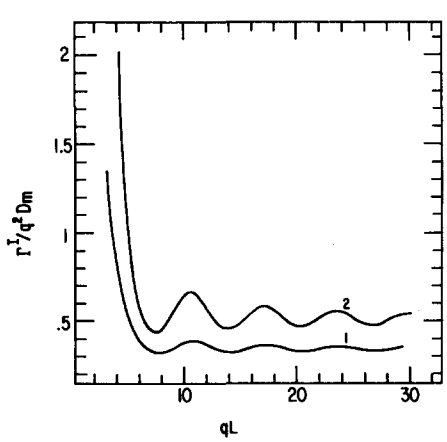

FIG. 1. Represents the behaviors shown (1) by Eq. (14) and (2) by Eq. (15).

B. Numerical simulation

In this section, we describe the Brownian dynamics simulation program used to study stiff dumbbells. Since the diffusion of the center of mass is decoupled:

$$[S^E(q, t) = \exp(-q^2 D_m t/2)],$$

we focus our efforts on the internal motions, i.e., on the behavior of

$$S^I(q, t) = \langle \cos(\mathbf{q}\cdot\mathbf{r}_0/2)\cos[\mathbf{q}\cdot\mathbf{r}(t)/2] \rangle_{\psi(r,t)}.$$

Our aim is to solve the Langevin equation:

$$\zeta d\mathbf{r}/dt + 2\partial U/\partial \mathbf{r} = \mathbf{f},$$

where $\mathbf{f}$ is a Gaussian stochastic process that satisfies Eq. (6). The finite difference equation reads

$$\mathbf{r}(t + \Delta t) = \mathbf{r}(t) - (2/\zeta)\partial U/\partial \mathbf{r}\Delta t + \mathbf{F}(\Delta t)/\zeta, \quad (19a)$$

where a new random process has been defined,

$$\mathbf{F}(\Delta t) = \int_0^{\Delta t} dt \mathbf{f}(t),$$

with the assumption that the potential term $\partial U/\partial \mathbf{r}$ is a slowly varying function of time compared to $\mathbf{f}(t)$. $\mathbf{F}(\Delta t)$ is a Gaussian process itself[11] with a variance of $4D_m\zeta^2\Delta t$. Forms other than Eq. (19a) are also available.[12] It is more convenient to redefine time as $\tilde{t} = D_m t$ so that the finite difference equation becomes

$$\mathbf{r}(\tilde{t} + \Delta\tilde{t}) = \mathbf{r}(\tilde{t}) - (2/k_B T)\partial U/\partial \mathbf{r}\Delta\tilde{t} + \tilde{\mathbf{F}}\sqrt{4\Delta\tilde{t}}, \quad (19b)$$

where $\mathbf{F}$ has been replaced by the rescaled $\tilde{\mathbf{F}} = \mathbf{F}/\sqrt{4\zeta^2\Delta\tilde{t}}$ which has a Gaussian distribution of variance unity. This last equation is the starting point of the simulation program.

A set of random forces $\tilde{\mathbf{F}}$, for each realization, and a set of random initial values $\mathbf{r}_0$ with distribution $\psi(\mathbf{r}_0)$ are needed. Once the different histories $\mathbf{r}(\tilde{t})$ have been generated, an arithmetic average of $\cos(\mathbf{q}\cdot\mathbf{r}_0/2)\cos[\mathbf{q}\cdot\mathbf{r}(\tilde{t})/2]$ over all these realizations yields $S^I(q, \tilde{t})$. A subtraction of the equilibrium part and normalization to one gives $\delta S_N^I(q, \tilde{t})$.

III. DISCUSSIONS

Dynamics of a dumbbell with intermediate stiffness have been studied in order to make some inferences as to the effect of stiffness on the dynamics of macromolecules in solution. In a set of figures we report on the overall "scenario" of the changes in $\delta S_N^I(q, \tilde{t})$ when either the stiffness K or the length L are changed.

Figure 2 represents the analytically soluble case of a Gaussian dumbbell and reproduces the results presented in Eq. (10) for $\delta S_N^I(q, \tilde{t})$ and in Eq. (11) for $\Gamma^I(q)$. An

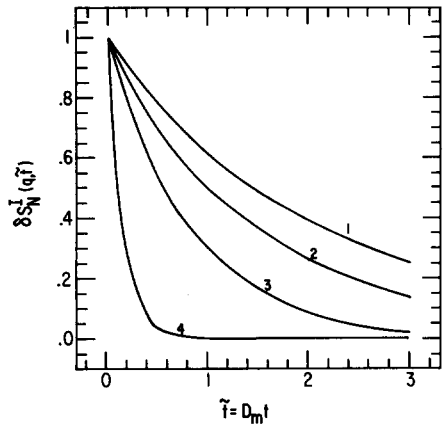

FIG. 2. Case of Fraenkel potential with $q = 1$ and $L = 0$ (Gaussian limit) for increasing values of K: (1) $K = 0.005$, (2) $K = 0.05$, (3) $K = 0.1$, and (4) $K = 0.5$.

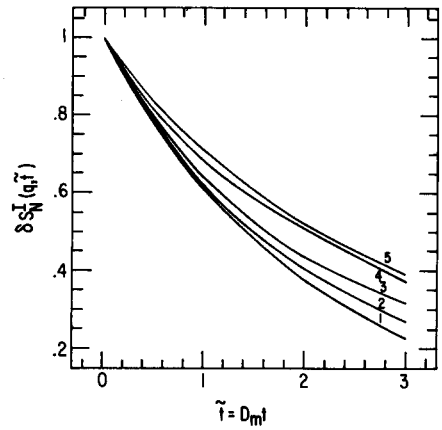

FIG. 5. Case of Fraenkel potential with $q = 1$ and $L = 30$ for (1) $K = 0.005$, (2) $K = 0.05$, (3) $K = 0.1$, (4) $K = 0.5$, and (5) $K = 5$.

increase in stiffness yields a decrease in the stretching relaxation time $\tau_S = 1/\Gamma^I$, bearing in mind that $\Gamma^I \geqslant q^2 D_m/2$. This behavior is expected to hold for flexible macromolecules.

In Fig. 3, we have also reproduced the other analytically soluble case of a rigid dumbbell quite closely with

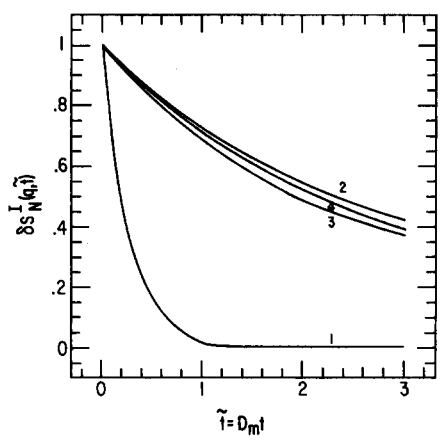

FIG. 3. Case of Fraenkel potential with $q = 1$ and $K = 5$ (practically at the rod limit) for increasing values of L: (1) $L = 2$, (2) $L = 8$, (3) $L = 11$, and (4) $L = 30$.

$K = 5$ which gives us even more confidence in the program itself. An increase in L results in a decrease in $\Gamma^I(q)$ as in Eq. (14) but not monotonously, rather through oscillations [(as shown in Fig. (1)] to reach the asymptotic value of $\Gamma^I(q) = q^2 D_m/3$. This trend also holds for rodlike macromolecules but the asymptotic value[13-15] [$\Gamma^I(q) = q^2 L^2 \theta/12$ for isotropic diffusion] is reached smoothly.

Figures 4 and 5 show situations of intermediate stiffness. Fixing the length L fixes the upper curve for $\delta S_N^I(q, t)$ to which other curves corresponding to increasing degrees of stiffness tend.

To make a better contact with the case of macromolecules, it is more convenient to define a general stiffness parameter, $\sigma = (3/2)[5/3 - \langle r^4\rangle/\langle r^2\rangle^2]$, which varies between zero (Gaussian limit) and one (rigid limit) instead of the simple minded spring force constant K. Two relaxation times, $\tilde{\tau}_1 = \langle r^2\rangle$ and $\tilde{\tau}_2 = 1/K$, can also be introduced. These relaxation times coalesce in the Gaussian limit and are split into a rotational ($\tilde{\tau}_1 = L^2$) and a stretching ($\tilde{\tau}_2 = 0$) relaxation time in the rigid limit. For convenience, we redefine $\bar{\tau}_1 = \tilde{\tau}_1/\langle r^2\rangle$ equal to unity and $\bar{\tau}_2 = \tilde{\tau}_2/\langle r^2\rangle$ varies between zero and one when σ increases as shown in Fig. 6. Note that the curvature of the $\bar{\tau}_2$ behavior could not have been predicted analyt-

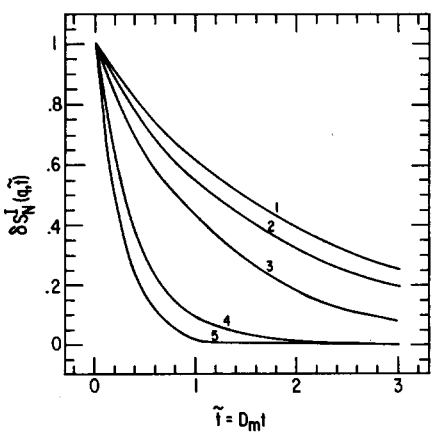

FIG. 4. Case of Fraenkel potential with $q = 1$ and $L = 2$ for (1) $K = 0.005$, (2) $K = 0.05$, (3) $K = 0.1$, (4) $K = 0.5$, and (5) $K = 5$.

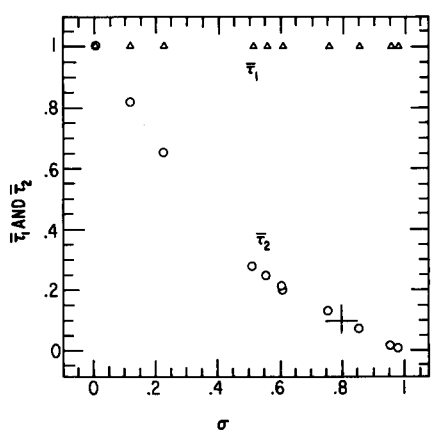

FIG. 6. Relaxation times $\bar{\tau}_1$ and $\bar{\tau}_2$ for increasing stiffness between the Gaussian dumbbell value $\sigma = 0$ and the rigid dumbbell value $\sigma = 1$.

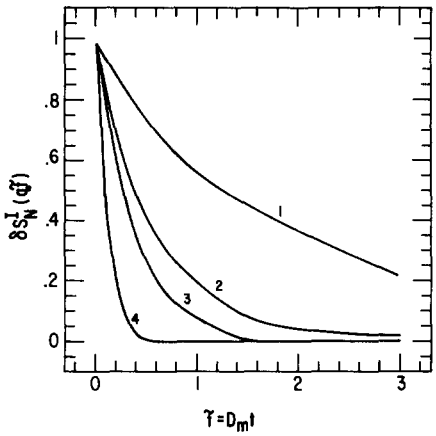

FIG. 7. Case of FENE potential with $q = 1$ and $R_0 = 5$ for (1) $K = 0.005$, (2) $K = 0.05$, (3) $K = 0.1$, and (4) $K = 0.5$.

ically. If we arbitrarily set a delay time for the experimental correlator equal to $0.1\tilde{\tau}_1$, we see from Fig. 6 that for values $\sigma \geqslant 0.8$, what is measured as the initial slope corresponds to $\tilde{\tau}_2 = 0.1$ instead of the real value which may even be zero; in other words the steep initial decay of $\delta S_N^I(q, t)$ has been missed and the measured first cumulant is found to be smaller than the true one. Note also that in situations where $\tilde{\tau}_2$ and $\tilde{\tau}_1$ can be unambiguously extracted from $\delta S_N^I(q, t)$ their ratio yields a value for σ (from Fig. 6) and therefore, an estimate of $\langle r^2 \rangle$ and $\langle r^4 \rangle$.

The FENE potential has been used to plot Fig. 7 which shows that a finite value of the parameter R_0 acts as a kind of stiffness also. Its effect is to move $\delta S_N^I(q, t)$ curves downward in cases where $R_0 \leqslant b$ and has no effect in cases where $R_0 \gg b$. We did not consider an extension of the FENE potential with a finite equilibrium length L as

$$U_2(r) = -k_B T(3KR_0^2/2)\ln[1 - (r - L)^2/R_0^2],$$

since the generation of the initial distribution $\psi(r_0)$ in this case cannot be done directly (it would involve numerical integrations).

The dynamics of semiflexible macromolecules in solution are a lot more complicated than this simplified dumbbell problem where anisotropy in the diffusion, bending modes, hydrodynamic interaction, excluded volume effects, etc. cannot be easily and/or realistically included.

ACKNOWLEDGMENTS

I thank Professor W. H. Stockmayer for suggesting this research idea and for his help in discussing the results. Dr. M. Schmidt's help in programming at the early stages is also appreciated. This work was supported by the National Science Foundation under Grant No. 79-13054, Division of Materials Research, Polymers Program.

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