University, is also gratefully acknowledged.

References and Notes

(1) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1961.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(3) McCrum, N. G.; Read, B. E.; Williams, G. *Unelastic and Dielectric Effects in Polymeric Solids*; Wiley: New York, 1967.
(4) Stockmayer, W. H. *Pure Appl. Chem.* **1967**, *15*, 539.
(5) North, A. M.; Phillips, P. J. *Trans. Faraday Soc.* **1967**, *63*, 1537.
(6) Ngai, K. L.; Mashimo, S.; Fytas, G. *Macromolecules* **1988**, *21*, 3030.
(7) Fytas, G.; Ngai, K. L. *Macromolecules* **1988**, *21*, 804.
(8) Adachi, K.; Kotaka, T. *Macromolecules* **1984**, *17*, 120.
(9) Adachi, K.; Kotaka, T. *Macromolecules* **1985**, *18*, 466.
(10) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7585.
(11) Adachi, K.; Kotaka, T. *Macromolecules* **1988**, *21*, 157.
(12) Rouse, P. E. *J. Chem. Phys.* **1953**, *21*, 1272.
(13) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(14) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(15) Doi, M. *Chem. Phys. Lett.* **1974**, *26*, 269.
(16) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(17) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1971**, *66*, 80.
(18) Kohlrausch, R. *Prog. Ann. Phys.* **1847**, *12*, 393.
(19) Havriliak, S.; Negami, S. *J. Polym. Sci. Part C* **1966**, *No. 14*, 99.
(20) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(21) Zwanzig, R. *Annu. Rev. Phys. Chem.* **1965**, *16*, 67.
(22) Adachi, K.; Fukui, F.; Kotaka, T., to be submitted for publication in *Polym. J.*
(23) Tschoegl, N. W. *Rheol. Acta* **1971**, *10*, 582.
(24) Imanishi, Y.; Adachi, K.; Kotaka, T. *J. Chem. Phys.* **1988**, *89*, 7593.
(25) Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules* **1987**, *20*, 2563, 2569, 2574.
(26) Plazek, D. J. *J. Phys. Chem.* **1965**, *69*, 3480.
(27) Gray, R.; Harrison, G.; Lamb, J. *Proc. R. Soc. London* **1977**, *356*, 77.
(28) Cochrane, J.; Harrison, G.; Lamb, J. *Polymer* **1980**, *21*, 837.
(29) Williams, M. L.; Ferry, J. D. *J. Colloid Sci.* **1954**, *9*, 479.
(30) Yin, T. P.; Ferry, J. D. *J. Colloid Sci.* **1961**, *16*, 166.
(31) Fujino, K.; Senshu, K.; Kawai, H. *J. Colloid Sci.* **1961**, *16*, 262.
(32) Kurath, S. F.; Passaglia, E.; Pariser, R. *J. Appl. Phys.* **1957**, *28*, 499.
(33) Aklonis, J. J.; Tobolsly, A. V. *J. Appl. Phys.* **1965**, *36*, 3483.
(34) Adachi, K.; Kotaka, T. *Macromolecules* **1987**, *20*, 2018.
(35) Nemoto, N.; Odani, H.; Kurata, M. *Macromolecules* **1972**, *5*, 531.
(36) Gotro, J. T.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2767.
(37) Ngai, K. L. *Comments Solid State Phys.* **1979**, *9*, 127.
(38) Ngai, K. L.; Rendell, R. W.; Rajagopal, A. K.; Teitler, S. *Ann. N.Y. Acad. Sci.* **1986**, *484*, 150.
(39) Nagi, K. L.; Rendell, R. W. *Polym. Prepr.* **1989**, *30*, 89.
(40) Boese, D.; Kremer, F.; Fetters, L. J. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 367.
(41) Ngai, K. L.; Plazek, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 2159.
(42) Mckenna, G. B.; Ngai, K. L.; Plazek, D. J. *Polymer* **1985**, *26*, 1651.

Viscoelastic Properties of Simple Flexible and Semirigid Models from Brownian Dynamics Simulation

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ABSTRACT: A Brownian dynamics simulation procedure to obtain the frequency dependence of the complex solution viscosity of macromolecular models is presented. From simulated trajectories, data for the time-autocorrelation function of a component of the momentum-flux tensor are obtained. After the simulated data are fitted to a mono- or multiexponential function, the frequency-dependent viscosity is obtained according to the Green–Kubo formula. The results of this procedure are checked against theoretical prediction for four different models: the quasirigid dumbbell, the Gaussian dumbbell, the semiflexible trumbbell, and Gaussian chains.

Introduction

The complex interplay existing between shape or flexibility, hydrodynamic interactions, and, eventually, solvent flow makes it practically impossible to find analytical solutions for many problems in polymer hydrodynamics.[1,2] A useful alternative, or complement, to analytical theory is the computer simulation of the Brownian dynamics of the polymer. In the field of flexible macromolecules, Brownian dynamics simulation has been used to study fluctuating hydrodynamic interactions,[3-5] internal modes,[6] elongation in flows,[7-9] and shear-dependent rheological properties.[9,10] For semiflexible macromolecules, Brownian dynamics has been used in the study of wormlike chains[11,12] and segmentally flexible macromolecules.[13,14]

The simulation of the intrinsic viscosity and its frequency dependence has not received enough attention. The zero-shear, zero-frequency viscosity can be obtained from shear rate dependent viscosities obtained by simulation.[9,10] This procedure is rather influenced by the

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high statistical errors of the results at low shear rate and is inefficient since it requires the simulation of several trajectories. There is another way based in the autocorrelation function of the momentum flux. To our knowledge, this way has been explored only a few years ago by Fixman,[3,4] who used an elaborated algorithm for flexible chains to obtain the zero-frequency viscosity by integration of the correlation function.

In this paper we consider the obtainment of the frequency-dependent viscosity of some flexible and semiflexible polymer models by Brownian dynamics simulation, using the very simple algorithm of Ermak and McCammon.[14] We study the problems that arise in the calculation of the dependence of viscosity on frequency from the time decay of the simulated correlation function, which is represented by some fitting function. Our conclusions provide practical information that will be useful in future studies of more complex systems.

Theory and Methods

The Green–Kubo formula for the complex, frequency-dependent, intrinsic viscosity $[\eta(\omega)]$ is[15–19]

$$[\eta(\omega)] = \frac{N_A kT}{M\eta_0}\int_0^\infty \exp(-i\omega t)\, C(t)\, \mathrm{d}t \qquad (1)$$

where N_A is Avogadro's number, M is the molecular weight of the polymer, η_0 is the solvent viscosity, kT is the thermal energy, and $C(t)$ is the time-autocorrelation function of the xy-component of the momentum-flux tensor, $J^{(xy)}$, given by

$$C(t) = \langle J^{(xy)}(0)\, J^{(xy)}(t)\rangle \qquad (2)$$

where

$$J^{(xy)} = \sum_{j=1}^{N} y_j'\, F_j^{(x)} \qquad (3)$$

and $\langle ...\rangle$ denotes an ensemble average or, equivalently, an average over choices of the initial instant of the motion of a single particle. y_j' is the y coordinate of the ith polymer element in a reference system of coordinates centered in a hydrodynamic center, C. In a fixed system of coordinates, where the y coordinates of the center and the ith bead are y_C and y_i, respectively, we have

$$y_j' = y_j - y_C \qquad (4)$$

Overlooking the problem of what is the hydrodynamic center for $[\eta]$, we make a practical choice for C: it is the point with coordinate

$$y_C = \sum_{j=1}^{N} \zeta_j y_j \Big/ \sum_{j=1}^{N} \zeta_j \qquad (5)$$

where ζ_j is the frictional coefficient of the jth element. It should be remarked that the hydrodynamic center obtained from eq 5 is not the same as the rigorous center of resistance in the presence of hydrodynamic interaction. In the polymer models studied in this paper the elements are spherical beads of identical sizes with a Stokes law friction coefficient $\zeta = 6\pi\eta_0\sigma$, where σ is the frictional radius of the beads. In this particular case C coincides with the center of mass if uniform density is assumed. In eq 3, $F_j^{(x)}$ is the x component of the total force due to external fields and internal constraints but does not include frictional terms.

It is sometimes convenient to separate the real and the imaginary part of the viscosity, which are denoted as η' and η'', so that

$$[\eta(\omega)] = [\eta'(\omega)] - i[\eta''(\omega)] \qquad (6)$$

It is also useful to work with dimensionless quantities, which are obtained by dividing the physical quantities by the following terms: length, b (which is some characteristic length in the polymer model); time, $\zeta b^2/kT$; frequency, the reciprocal of the latter; forces, kT/b. Using the superscript asterisk for reduced quantities, we have defined the reduced intrinsic viscosity as

$$[\eta(\omega)]^* \equiv (12M\eta_0/N_A b^2\zeta)[\eta(\omega)] \qquad (7)$$

where the factor 12 has been introduced in an ad hoc manner, so that the reduced intrinsic viscosity of a dumbbell without hydrodynamic interaction is the unity, as it will be shown latter (in other papers the intrinsic viscosity has been normalized to $N_A b^2/M$). Then, eq 1 takes the form:

$$[\eta(\omega)]^* = 12\int_0^\infty C^*(t^*) \exp(-i\omega^* t^*)\, \mathrm{d}t^* \qquad (8)$$

$c^*(t)$ and $J^{*(xy)}$ are defined as in eqs 2 and 3 with reduced forces and coordinates.

In some cases of interest, the time correlation function can be expressed as a sum of exponentials with amplitudes a_m and relaxation times τ_m^*:

$$C^*(t^*) = \sum_m a_m e^{-t^*/\tau_m^*} \qquad (9)$$

In such a case, the complex intrinsic viscosity in dimensionless form is, according to eq 7, given by

$$[\eta(\omega)]^* = \sum_m \frac{c_m}{1 + i\omega^*\tau_m^*} \qquad (10)$$

where

$$c_m = 12 a_m \tau_m^* \qquad (11)$$

The real and imaginary parts are

$$[\eta'(\omega)] = \sum_m \frac{c_m}{1 + (\omega^*\tau_m^*)^2} \qquad (12)$$

and

$$[\eta''(\omega)] = \sum_m \frac{c_m \tau_m^* \omega^*}{1 + (\omega^*\tau_m^*)^2} \qquad (13)$$

The zero-frequency intrinsic viscosity is then

$$[\eta(0)]^* = \sum_m c_m \qquad (14)$$

In this work we evaluate the time correlation function, eq 2, from trajectories of the polymer model that are generated by simulation of its Brownian dynamics. The simulation procedure used in this work is based on the algorithm of Ermak and McCammon.[14] If $\mathbf{r}_i^0$ is the position vector of bead i, the position after a time step Δt is given by

$$\mathbf{r}_i = \mathbf{r}_i^0 + \frac{\Delta t}{kT}\sum_j \mathbf{D}_{ij}^0 \mathbf{F}_j + \Delta t \sum_j \left(\frac{\partial \mathbf{D}_{ij}}{\partial \mathbf{r}_j}\right)^0 + \mathbf{R}_i(\Delta t) \qquad (15)$$

where $\mathbf{D}_{ij}^0$ is the ij block of the diffusion tensor, whose value depends on how hydrodynamic interaction is described, and $\mathbf{R}_i$ is a random vector with a Gaussian distribution having a mean and a covariance given by

$$\langle \mathbf{R}_i \rangle = \mathbf{0} \qquad (16)$$

$$\langle \mathbf{R}_i \mathbf{R}_j \rangle = 2\mathbf{D}_{ij}{}^0 \Delta t \tag{17}$$

When dimensionless quantities are used, eq 15 can be rewritten as

$$\mathbf{r}_i^* = \mathbf{r}_i^{0*} + \Delta t^* \sum_j \mathbf{D}_{ij}{}^{0*} \mathbf{F}_j^* + \Delta t^* \sum_j \left(\frac{\partial \mathbf{D}_{ij}^*}{\partial \mathbf{r}_j^*} \right)^0 + \mathbf{R}_i^*(\Delta t^*) \tag{18}$$

From the simulated trajectories the autocorrelation function is evaluated in discrete[12] form as the average of all the possible products $J^{*(xy)}(t^*) J^{*(xy)}(t'^*)$, with $t = l\Delta t^*$, $t'^* = k\Delta t^*$, and $k = t^*/\Delta t^*$. Other details of the simulation and correlation analysis are as described elsewhere.[12,14,20,21]

The number of steps, n, and the time step Δt are specified later for each particular case. In all cases we checked that a further decrease in Δt (with the corresponding increase in n as to maintain fixed the trajectory length, $n\Delta t$) does not change appreciably $[\eta(\omega)]$ at moderate ω. The effect of increasing n with fixed Δt is a decrease in the noise of $C(t)$ at longer times. The level of noise that we obtain is acceptable as confirmed (see later) by comparison of our simulations with available results.

Results and Discussion

Quasirigid Dumbbells. A quasirigid (or Fraenkel[22]) dumbbell consists of two beads joined by a very stiff spring with equilibrium length b. The spring forces on the beads are

$$\mathbf{F}_2 = -\mathbf{F}_1 = [(1 - r)/(\delta^2 r)]\mathbf{r} \tag{19}$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and δ is a flexibility parameter. We take $\delta = 0.1$[14,20] for which $\langle r^2 \rangle = 1.05b^2$, so that $\langle r^2 \rangle^{1/2}$ is only 2.5% larger than the equilibrium distance.

Theoretical results derived by Felderhof et al.[17] are available for this polymer model with Oseen hydrodynamic interaction. For an infinitely stiff dumbbell ($\delta = 0$) with beads having friction coefficients ζ_1 and ζ_2, with $D = kT/\zeta_1 + kT/\zeta_2$, we have

$$[\eta(\omega)] = \frac{N_A kT}{15 M \eta_0} \frac{b^2}{D(1-\alpha)} \left[\frac{3/2}{1 + i\omega\tau} + \frac{1-\alpha}{1-2\alpha} \right] \tag{20}$$

with

$$\tau = \zeta b^2 / 12kT(1 - \alpha) \tag{21}$$

where α is a hydrodynamic interaction parameter so that $\alpha = 0$ if hydrodynamic interaction is absent, or $\alpha = 3\sigma^*/4$, with $\sigma^* = \sigma/b$, for Oseen interaction. If $\alpha = 0$, eq 20 reduces to a well-known result[2,22,23]

$$[\eta(\omega)] = \frac{N_A \zeta b^2}{12 M \eta_0} \left[\frac{2}{5} + \frac{3}{5} \frac{1}{1 + i\tau_0 \omega} \right] \tag{22}$$

where

$$\tau_0 = \zeta b^2 / 12kT \tag{23}$$

Wilemski[18] has evaluated the zero-frequency intrinsic viscosity for the quasirigid dimer without hydrodynamic interaction, obtaining

$$[\eta(0)] = \frac{N_A \zeta b^2}{12 M \eta_0} (1 + 5\delta^2) = \frac{N_A \zeta \langle r^2 \rangle}{12 M \eta_0} \tag{24}$$

Values of $[\eta(0)]$ for zero frequency can be obtained from the above expressions and are found to be in agreement with those estimated using the rigid-body theory.[24,25]

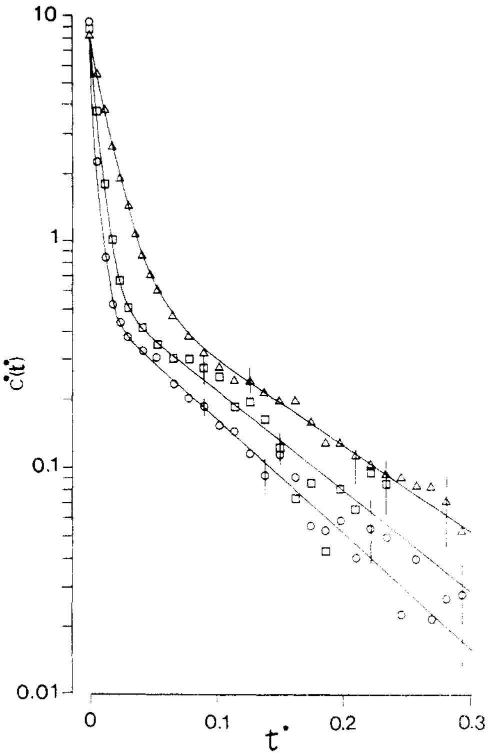

Figure 1. Results of the correlation function $C^*(t^*)$ for quasirigid dumbbells from Brownian dynamics simulation: (○) without hydrodynamic interaction; (□) hydrodynamic interaction by Oseen tensor, with $\sigma^* = 0.256$; (△) the same with $\sigma^* = 0.5$. The continuous lines are biexponential fits.

Table I
Values of the Zero-Frequency Intrinsic Viscosity and the Amplitudes and Relaxation Times of the Autocorrelation Functions, $C^*(t^*)$, for Quasirigid Dumbbells

case	$[\eta(0)]^*$	c_1^*	τ_1^*	c_2^*	τ_2^*
		No HI			
simulation	0.96	0.54	0.085	0.40	0.0037
theoretical	1.00		0.0833		
		HI Oseen, $\sigma^* = 0.256$			
simulation	1.33	0.72	0.098	0.61	0.0064
theoretical	1.39		0.103		
		HI Oseen, $\sigma^* = 0.5$			
simulation	2.29	1.04	0.136	1.25	0.0140
theoretical	2.56		0.133		

In Brownian dynamics simulation, typical values of the number of steps and Δt^* were 10^6 and 0.002, respectively. These values have been shown to be adequate in the simulation of the rotational diffusion.[20] In all the cases simulated, the autocorrelation functions were found to be biexponential, as shown in Figure 1, where we present the $C^*(t^*)$ results without HI, and with Oseen interactions for $\sigma^* = 0.25$ and $\sigma^* = 0.5$ (the latter value corresponds to touching beads at the equilibrium conformation). The resulting values of c_m and τ_m^* are presented in Table I, and the frequency-dependent viscosity is displayed in Figure 2.

The simulation results are generally in good agreement with the theoretical values, particularly when hydrodynamic interaction is absent or moderate. This is seen in Table I for the $\eta(0)$ and τ and in Figure 2 for the frequency dependence. The discrepancy noted at high frequencies is not due to the procedure but to physical differences: the quasirigid dumbbell does not present a limiting viscosity at infinite frequency because of its residual flexibility, to which the second relaxation time τ_2 is associated.

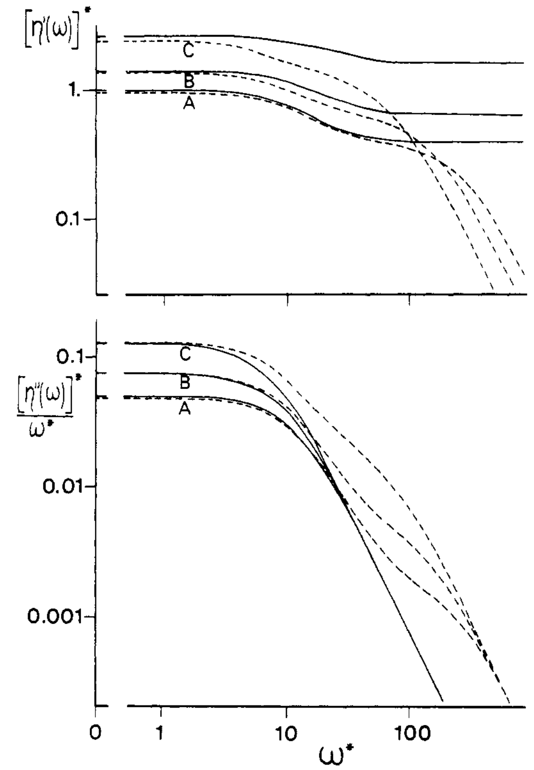

Figure 2. Variation of the real and the imaginary parts of the intrinsic viscosity with frequency for quasirigid dumbbells. (—) Theoretical results. (- - -) Simulation results: (A) without HI; (B) Oseen tensor $\sigma^* = 0.256$; (C) Oseen tensor $\sigma^* = 0.5$.

Gaussian Dumbbells. The Gaussian dumbbell has two beads separated by a flexible connector in such a way that the center-to-center distance, r, follows a Gaussian statistics with $\langle r \rangle = 0$. The characteristic length b is defined as $b \equiv \langle r^2 \rangle^{1/2}$. The forces on the beads are

$$\mathbf{F}_1 = -\mathbf{F}_2 = \frac{3kT}{b^2}\mathbf{r} \tag{25}$$

The theoretical results for Gaussian dumbbells without hydrodynamic interaction are well-known. The relaxation time, τ, is given by the same expression, eq 21, as for the rigid dimer, although the definition of b is different. In dimensionless form, $\tau^* = {}^1/_{12}$, also for the no-interaction case. The intrinsic viscosities are given by

$$[\eta'(\omega)]^* = \frac{1}{1 + (\tau^*\omega^*)^2} \tag{26}$$

$$[\eta''(\omega)]^* = \frac{\tau^*\omega^*}{1 + (\tau^*\omega^*)^2} \tag{27}$$

We recall that intrinsic viscosities are normalized to the value for $\omega = 0$ without hydrodynamic interaction. Equations 26 and 27 correspond to a monoexponential decay of $C(t)$.

We are not aware of complete results for $[\eta(\omega)]$ with hydrodynamic interaction. The value for $\omega = 0$, calculated by Fan, is $[\eta(0)]^* = 1.32$ for $h^* = 0.25$, where h^* is the usual hydrodynamic interaction parameter, corresponding to $\sigma^* = 0.256$.

In Brownian dynamics simulation, trajectories of typically 5×10^5 steps with $\Delta t^* = 0.01$ were generated. The autocorrelation function was calculated and adjusted to a single exponential ($m = 1$ in eqs 9, 10, and 12). Examples of the results are shown in Figure 2. The values of the relaxation times and the resulting intrinsic viscosities at zero frequency (now $[\eta(0) = c = 12a\tau^*)$ are listed in Table II.

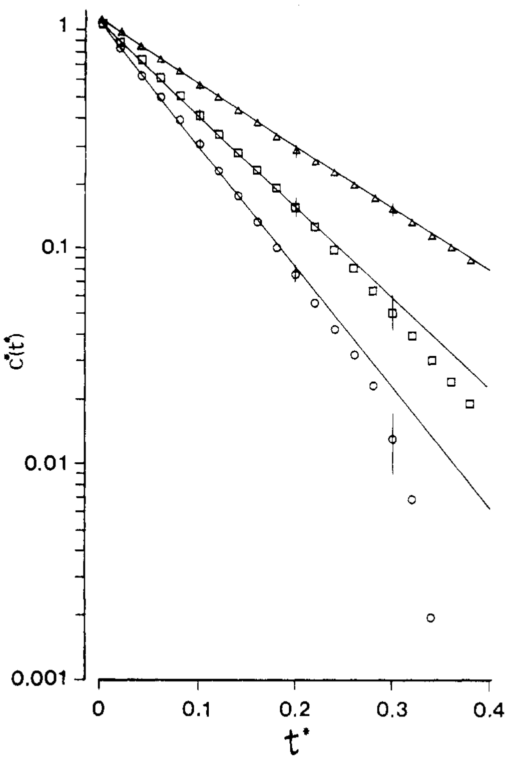

Figure 3. Same as in Figure 1 for Gaussian dumbbells.

Semiflexible Trumbbells. The trumbbell is one of the simplest semiflexible models. It is composed by three beads joined by two quasirigid bonds. A restoring potential $V/kT = Q\alpha^2$ opposes bending of angle α, Q being a stiffness parameter. A previous Brownian dynamics simulation study of these models has been reported by Díaz and García de la Torre in ref 26, where more details about it can be found. The viscoelastic properties of semiflexible trumbbells with rigid bonds have been calculated in the absence of hydrodynamic interaction by Roitman and Zimm,[27] who derived a spectrum of relaxation constants by numerically solving the diffusion equation. Our purpose here is just to illustrate the applicability of the simulation technique to compute viscoelastic properties of semiflexible models of that type, comparing our simulation results without hydrodynamic interaction with those of Roitman and Zimm.

Simulations were run for the following: $Q = 50$, which practically corresponds to a rigid, straight trumbbell; $Q = 0.5$, which is a typical value for a hinged fibrous protein, namely the myosin rod;[28] $Q = 0$, which corresponds to the completely flexible (freely bending) trumbbell. In order to obtain reproducible results, particularly for the highest Q, the trajectories must have several million steps with $\Delta t^* = 2\text{–}4 \times 10^{-4}$.

In Figure 4 we present the $C^*(t^*)$ simulation results. For the purpose of integration we fit the data for each Q to a multiexponential function of the type of eq 9. Two components are sufficient for the highest Q, while for $Q = 0.5$ and 0, a further improvement in the fit was noticed with a triexponential function. Figure 4 also shows the Roitman–Zimm results. We see that the agreement is good except for small t^*. The results for $[\eta'(\omega)]$ and $[\eta''(\omega)]$ are displayed in Figure 5. The agreement with the Roitman–Zimm theory is good for small and intermediate frequencies: the onset of the frequency dependence and its behavior at intermediate frequencies (up to, say, $\omega^* \cong 50$) are very similar. The differences at high ω^* and those noted in $C^*(t^*)$ at small t^* are due to a physical difference between the trumbbell model of Roitman–Zimm and

Table II
Values of the Zero-Frequency Intrinsic Viscosity and the Parameters of the Autocorrelation Function, $C^*(t^*)$, for Gaussian Dumbbells

case	$[\eta(0)]^*$	τ^*	a
	No HI		
simulation	1.00	0.0823	1.00
theoretical	1.00	0.0833 = 1/12	
	HI Oseen, $\sigma^* = 0.256$		
simulation	1.33	0.103	1.08
theoretical	1.32		
	HI Oseen, $\sigma^* = 0.5$		
simulation	1.98	0.147	1.12

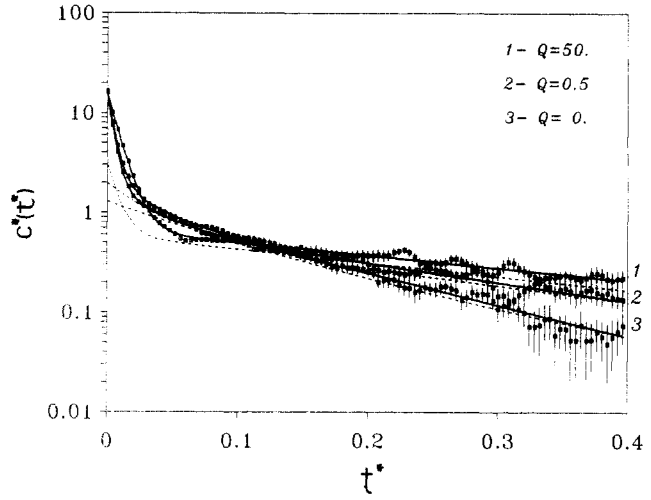

Figure 4. Correlation functions $C^*(t^*)$ for semirigid trumbbells: (□) results from Brownian dynamics simulation; (—) multiexponential fits for these results; (- - -), calculations of Roitman and Zimm.[27]

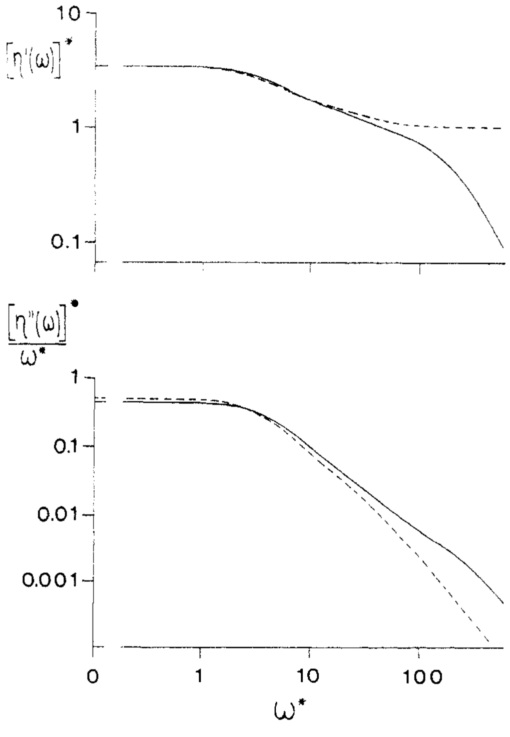

Figure 5. Real and imaginary parts of the intrinsic viscosity from the simulation results (—) and from the work of Roitman and Zimm[27] (- - -).

ours; in the former, the bonds are rigid and $\eta' \rightarrow \infty$, while in the other, the bonds are slightly flexible and therefore the viscosity to zero at infinite frequencies.

Table III
Zero-Shear Intrinsic Viscosity $[\eta(0)]$ (Relative to That of the Dimer) and Longest Relaxation Time, τ_1, of Trumbbells

	rigid-body treatment		Roitman–Zimm		simulation of viscoelasticity (this work)		ref 26[a]
Q	$[\eta(0)]$	τ_1^{-1}	$[\eta(0)]$	τ_1^{-1}	$[\eta(0)]$	τ_1^{-1}	τ_1^{-1}
	Without Hydrodynamic Interaction						
50 ($Q^{-1} \cong 0$)	4.20	2.86	4.18	3.00	4.32	2.92	2.93
0.5	3.45	3.96	3.41	3.67	3.43	4.50	4.30
0	2.84	5.37	2.79	5.44	2.88	6.70	5.71
	With Hydrodynamic Interaction						
50 ($Q^{-1} \cong 0$)	5.70	2.31			5.68	2.63	2.69
0.5	5.42	2.99			5.06	5.40	3.79
0	4.94	3.74			2.44	6.00	5.04

[a] Reference 26: Simulation of rotational diffusion.

In Table III we list numerical results for $[\eta^*(0)]$ and τ_1^* from our simulation along with those obtained by Roitman–Zimm as well as those calculated using the rigid-body treatment.[28,29]

We see that the zero-shear intrinsic viscosity values obtained from simulation agree with the Roitman–Zimm results in the case of no hydrodynamic interaction. This confirms the good performance of our procedure. Both sets of values agree well, in turn, with those from the rigid-body treatment, which give confidence in the use of rigid-body calculations for the intrinsic viscosity of semiflexible models. The agreement between simulation and rigid-body results is also acceptable in the cases with hydrodynamic interaction.

Although the discussion of the relaxation times is influenced by the well-known problems arising from multiexponential fits, we note that our simulation results do not differ very much from those of our previous simulation of rotational Brownian dynamics. We see also that the rigid-body values for the relaxation times in cases with interaction are not as good as those in the absence of interaction. In general, the simulated values of relaxation times are influenced by the well-known difficulties of parameter estimation in multiexponential fits and, in this regard, we recall that we use the multiexponential function (eq 9) merely as an interpolating function for $C(t)$ intended to be used in the Green–Kubo equation.

Gaussian Chains. In order to illustrate the procedure for a typical flexible polymer model, we have performed the simulation of a bead-and-spring chain having $N = 6$ beads without hydrodynamic interaction. The Rouse theory[30] gives the following expression for the coefficients in eq 10

$$\tau_m^* = 1/24 \sin^2 (m\pi/N) \qquad m = 1, ..., N-1 \qquad (28)$$

$$C_m = 12\tau_m^* = 1/2 \sin^2 (m\pi/N) \qquad m = 1, ..., N-1 \qquad (29)$$

We simulated 20 subtrajectories each having 50 000 time steps with $\Delta t^* = 0.01$. The correlation function $C^*(t^*)$ obtained from the trajectory was fit to a biexponential function. The results are given in Table IV. We see that a biexponential approximation to $C^*(t^*)$ is able to yield the $[\eta^*(0)]$ value with excellent accuracy. Of course, owing to their empirical character, the two relaxation times in the biexponential are not comparable to the two first Rouse relaxation times. The important finding is that the simulated $C^*(t^*)$ is well fit within statistical error up to $t^* = 1.5$ (beyond twice the Rouse τ_1). This is illustrated in Figure 6, where we also see that the simulation results follow closely those from the Rouse theory. We plotted the frequency dependence of the real and imaginary intrinsic viscosities as in Figures 2, 3, and 5. The Rouse val-

Table IV
Zero-Shear Intrinsic Viscosity and Coefficients in Equation 10 for a Rouse Chain with $N = 6$. Comparison with Simulation Results

case	$[\eta^*(0)]$	c_1	τ_1	c_2	τ_2	c_3	τ_3	c_4	τ_4	c_5	τ_5
a	11.66	7.46	0.622	1.99	0.166	1.00	0.0833	0.666	0.0555	0.536	0.0447
b	11.80	8.68	0.534	3.12	0.0668						

[a] Rouse theory. [b] Simulation, biexponential fit.

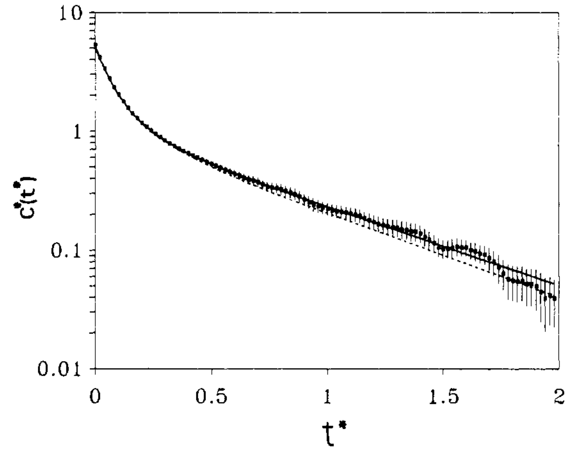

Figure 6. Correlation function $C^*(t^*)$ for a Rouse chain with $N = 3$: (□) results from Brownian dynamics simulation; (—) biexponential fit; (- - -), theoretical function.

ues and the simulation results were in excellent agreement; in fact they were undistinguishable in the plots (not shown) up to ω^*'s of the order of 10^2, including a transition region observed at $0.8 < \omega^* < 20$.

The influence of including rigorously hydrodynamic interaction in the simulation of the viscoelasticity of Gaussian chains is a relevant aspect that we consider in detail in a separate paper.[31]

Conclusions

Brownian dynamics simulation can be used to obtain the autocorrelation function $C(t)$ of a cross-component of the momentum-flux tensor. From the simulated data, the frequency-dependent, complex intrinsic viscosity may be evaluated from the Green–Kubo formula. This requires a function that fits the simulated data. A function containing up to (and possibly less than) three exponential terms suffices for that purpose, even when $C(t)$ is theoretically a sum of many, or infinite, exponentials.

The procedure has been checked for rigid, semiflexible, and flexible models. The zero-shear intrinsic viscosity estimated from simulation is in quantitative agreement with theory in all cases. With the exception, in some cases, for the region of very high frequencies, where our models do not give a limiting η due to a residual flexibility, the simulated frequency dependence agrees well also with theory.

The direct simulation of $C(t)$ for models with constraints or stiff potentials presents problems that have been discussed exhaustively by Fixman.[32] The simplicity of the Ermak–McCammon algorithm used here does not help in that regard. It is remarkable that we had to use 10^6 steps for the quasirigid dumbbell ($N = 2$). For some particular (flexible) situations, Fixman[3,4] obtained $[\eta(0)]$ using a clever procedure in which the nonpreaveraging correction to $C(t)$ is estimated by simulation and then applied to the theoretical $C(t)$ with preaveraged interaction to obtain finally the viscosity via the Green–Kubo formula. Our direct procedure is not based on a previous knowledge of analytical approximations and may therefore be of some utility in the study of semiflexible biomolecular models for which no other procedure is applicable.

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References and Notes

(1) Yamakawa, H. *Modern Theories of Polymer Solutions*; Harper and Row: New York, 1971.
(2) Bird, R. B.; Hassager, O.; Armstrong, R. C.; Curtiss, C. F. *Dynamics of Polymeric Liquids*; Wiley: New York, 1977.
(3) Fixman, M. *Macromolecules* **1981**, *14*, 1710.
(4) Fixman, M. *J. Chem. Phys.* **1983**, *78*, 1594.
(5) Fixman, M. *J. Chem. Phys.* **1986**, *84*, 4085.
(6) Rey, A.; Freire, J. J.; García de la Torre, J. *J. Chem. Phys.* **1989**, *90*, 2053.
(7) Dotson, P. J. *J. Chem. Phys.* **1983**, *79*, 5770.
(8) Saab, H. H.; Dotson, P. J. *J. Chem. Phys.* **1987**, *86*, 3039.
(9) Díaz, F. G.; García de la Torre, J.; Freire, J. J. *Polymer* **1989**, *30*, 259.
(10) Zylka, W.; Öttinger, H. C. *J. Chem. Phys.* **1989**, *90*, 474.
(11) Allison, S. A.; McCammon, J. A. *Biopolymers* **1984**, *23*, 363.
(12) Allison, S. A. *Macromolecules* **1986**, *19*, 118.
(13) Lewis, R. J.; Allison, S. A.; Eden, D.; Pecora, R. *J. Chem. Phys.* **1988**, *89*, 2490.
(14) Ermak, D. L.; McCammon, J. A. *J. Chem. Phys.* **1978**, *69*, 1352.
(15) Stockmayer, W. H.; Gobush, W.; Chikahisa, Y.; Carpenter, D. K. *Faraday Discuss. Chem. Soc.* **1970**, *49*, 182.
(16) Yamakawa, H.; Tanaka, G.; Stockmayer, W. H. *J. Chem. Phys.* **1974**, *61*, 435.
(17) Felderhof, B. H.; Deutch, J. M.; Titulaer, U. M. *J. Chem. Phys.* **1975**, *63*, 740.
(18) Wilemski, G. *J. Chem. Phys.* **1984**, *81*, 6106.
(19) Jagannathan, A.; Oono, Y.; Schaub, B. *J. Chem. Phys.* **1986**, *86*, 2276.
(20) Díaz, F. G.; Iniesta, A.; García de la Torre, J. *J. Chem. Phys.* **1987**, *87*, 6021.
(21) Lee, S.; Karplus, M. *J. Chem. Phys.* **1984**, *81*, 6106.
(22) Fraenkel, J. *Chem. Phys.* **1952**, *20*, 642.
(23) Kirkwood, J. G.; Auer, P. L. *J. Chem. Phys.* **1951**, *191*, 281.
(24) García de la Torre, J.; Bloomfield, V. A. *Biopolymers* **1978**, *17*, 1605.
(25) García de la Torre, J.; Bloomfield, V. A. *Quart. Rev. Biophys.* **1981**, *14*, 81.
(26) Díaz, F. G.; García de la Torre, J. *J. Chem. Phys.* **1988**, *88*, 7698.
(27) Roitman, D. B.; Zimm, B. H. *J. Chem. Phys.* **1984**, *81*, 6333.
(28) Iniesta, A.; Díaz, F. G.; García de la Torre, J. *Biophys. J.* **1988**, *54*, 269.
(29) Hagerman, P.; Zimm, B. H. *Biopolymers* **1982**, *20*, 1481.
(30) Rouse, P. E. *J. Chem. Phys.* **1956**, *21*, 1272.
(31) Rey, A.; Freire, J. J.; García de la Torre, J. *J. Chem. Phys.*, in press.
(32) Fixman, M. *J. Chem. Phys.* **1988**, *89*, 2442.