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Brownian motion in a single relaxation time Maxwell fluid

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A simple model of Brownian motion in a single relaxation time Maxwell fluid is described and compared to diffusing wave spectroscopy measurements of colloidal motion in representative viscoelastic fluids, namely, CTAB/KBr wormlike micelle solutions. The experimentally measured Brownian motion conforms to the model predictions at long times (low frequencies) and is an additional confirmation of the essentially Maxwellian stress relaxation behavior of wormlike micelle solutions at low frequencies. Surprisingly, the Maxwell model predicts a plateau onset time which, while capable of reducing the measured mean-square displacements to a master curve, also grossly underestimates the actual plateau onset time. The predicted rescaling is shown to be essentially that also predicted by the Doi-Edwards tube model for polymer solutions under good solvent (excluded volume) conditions where a more proper accounting of the short-time dynamics is made. This indicates that the success of the predicted Maxwell model plateau onset time rescaling is purely fortuitous.

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I. INTRODUCTION

Recently there has been strong interest in determining the local and bulk viscoelasticity of soft materials by monitoring the thermal fluctuations of dispersed spherical probe particles with various optical techniques [1–5]. The so-called local viscoelasticity should be representative of small-scale structure and dynamics as sampled by small spherical probes, while a technique that allows for the determination of bulk rheological properties from small samples would prove to be invaluable to the biomedical community where sample quantities can be exceedingly minute. In addition, these optical techniques can access much higher frequencies than conventional mechanical rheometry [1–5], are noninvasive in that they probe quiescent or unperturbed dynamics in theory, and provide a potential means for testing theoretical models over large frequency ranges.

Brownian motion in simple viscous liquids is well understood and the connection between this thermal motion and hydrodynamic response is readily apparent [7]. In a similar manner, bulk mechanical properties should be recoverable if the thermal motion of spherical probes dispersed within a viscoelastic medium can be measured. Since viscoelastic fluids store energy, a certain ''memory'' of the particle's past motion must exist. For this reason, a memory function is oftentimes utilized to account for the frictional resistance experienced by a diffusing particle in a Langevin description of Brownian motion in such systems. This frictional resistance is nonlocal in time and the frictional force experienced by a diffusing particle at time t is influenced by its velocity at some earlier time t' [7–9]. One of the first descriptions of the connection between correlation functions and memory kernels was that of Zwanzig [10]. Berne and co-workers derived similar results and applied them to molecular velocity autocorrelation functions where they proposed a two-parameter exponentially decaying function as a memory kernel ansatz [11]. Later, Zwanzig and Bixon established the connection between a frequency-dependent friction coefficient in the Stokes-Einstein formalism and the memory function in a Langevin description of Brownian motion via the hydrodynamic theory [12]. A Langevin description of Brownian motion in more complicated media would entail a proper model and development of an appropriate memory kernel pertinent to the suspending medium which, for example, has recently been done for the case of concentrated colloidal dispersions where interparticle interactions are present [13].

Several groups have investigated the connection between a colloidal particle's Brownian motion and the bulk rheological properties of the medium in which the particle is suspended. There have been two different, yet related approaches [1–6]. In the first approach elasticity is built into a framework that is exact for a purely viscous fluid [1–4]. The foundation of this approach is the assumption that the no-slip Stokes-Einstein relationship can be generalized to all frequencies. Here a mean-field assumption is made wherein macroscopic stress relaxations are directly connected to microscopic stress relaxations or, more simply put, there is no delineation between local and bulk viscoelasticity. This assumption establishes a direct relationship between the suspending medium's shear modulus and the mean-square displacement of a Brownian particle. The second approach makes a more direct accounting of the elastic component of the suspending medium. The equation of elastic equilibrium is solved exactly for a rigid spherical surface exhibiting the no-slip boundary conditions to yield an effective compliance for sphere displacement [5,6]. At sufficiently high frequencies this effective compliance is directly proportional to the inverse of the shear modulus when it is assumed that the suspending medium is incompressible owing to viscous coupling between the solvent and the matrix material [6]. However, at lower frequencies this coupling does not exist and the suspending medium's osmotic compressibility may also influence the Brownian motion of any suspended

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*Author to whom correspondence should be addressed. Email address: john_vz@ncsu.edu probes. Therefore, both the suspending medium's longitudinal and transverse moduli may influence a probe's Brownian motion below some critical frequency. It should be noted that there has been an extensive amount of previous work concerning long-time probe diffusion in polymer solutions, especially by Phillies and co-workers [14]. This work has focused on the validity of the Stokes-Einstein relationship for long-time probe diffusion in polymer solutions and the connection between long-time probe diffusion and polymer solution dynamics.

II. BROWNIAN MOTION IN A SINGLE RELAXATION-TIME MAXWELL FLUID

The standard Langevin description of a neutrally buoyant particle of mass m undergoing Brownian motion can be easily modified to include memory, or viscoelastic, effects [7–12]

$$m\frac{d\mathbf{v}(t)}{dt}=-\int_0^t \zeta(t-t')\mathbf{v}(t')dt'+\mathbf{f}_R(t). \tag{1}$$

Here $\mathbf{v}(t)$ is the particle velocity and $\mathbf{f}_R(t)$ denotes the random Brownian or thermal forces acting on the particle. $\zeta(t)$ is a time-dependent memory function for an isotropic, incompressible viscoelastic fluid allowing for both energy loss and storage and is related to the instantaneous friction coefficient. The integral term accounts for the viscous damping of the fluid and reflects the viscoelastic nature of the suspending complex fluid. As noted before, owing to its viscoelastic nature the suspending medium can store energy upon deformation, thus motivating the use of the memory function form of the Langevin equation. This ability to store energy profoundly changes the temporal correlations of the stochastic forces acting upon the particle at thermal equilibrium since the suspending medium must satisfy the fluctuation-dissipation theorem, $\langle \mathbf{f}_R(0)\cdot\mathbf{f}_R(t)\rangle = kT\zeta(t)$ [15]. Therefore, in principle, the measurement and analysis of particle motions should allow the determination of the memory function $\zeta(t)$.

The single relaxation-time Maxwell fluid is the simplest model of a viscoelastic material. As such, it is an appropriate place to start when considering Brownian motion in viscoelastic media. The memory function for the single relaxation-time Maxwell fluid can be found by solving the creeping flow sphere problem under the condition that the symmetric, traceless part of the stress tensor obeys Maxwell's constitutive equation [16,17]. The resulting memory function can be incorporated into the viscoelastic Langevin equation for Brownian motion to yield

$$m\frac{d\mathbf{v}(t)}{dt}=-\frac{\zeta}{\tau}\int_0^t e^{-(t-t')/\tau}\mathbf{v}(t')dt'+\mathbf{f}_{\mathbf{R}}(t), \tag{2}$$

where ζ is the particle friction coefficient and τ is the terminal relaxation time. The particle friction coefficient is given by $\zeta=6\pi\eta R$ where η is the suspending medium's zero shear viscosity and R is the particle radius. This equation can be recast in the form of a differential equation describing the temporal evolution of the particle's velocity autocorrelation function [18]

$$\tau\tau_B\frac{d^2}{dt^2}\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle+\tau_B\frac{d}{dt}\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle+\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle=0, \tag{3}$$

where τ_B denotes the Brownian time m/ζ. The nature of the particle's velocity autocorrelation function is strongly dependent on the values of τ_B and τ. For typically encountered viscoelastic materials $\tau/\tau_B \gg 1/4$ and, therefore the particle velocity autocorrelation, as well as the particle mean-square displacement, will exhibit oscillations. The velocity autocorrelation function (when $\tau/\tau_B > 1/4$) is

$$\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle=\frac{3kT}{m}e^{-t/2\tau}\left(\cos\frac{\sqrt{4(\tau/\tau_B)-1}}{2\tau}t + \frac{1}{\sqrt{4(\tau/\tau_B)-1}}\sin\frac{\sqrt{4(\tau/\tau_B)-1}}{2\tau}t\right). \tag{4}$$

This is essentially the same result calculated for the ansatz of Berne and co-workers [8,11]. The particle's mean-square displacement can be calculated from the velocity autocorrelation function in the usual manner [7–9]. The mean-square displacement of a Brownian particle undergoing thermal motion in a single relaxation-time Maxwell fluid is

$$\begin{aligned}\langle \Delta r^2(t)\rangle=\frac{6kT}{m}\Bigg(&\tau_B t+\tau_B(\tau_B-\tau)\\ &\times\left[e^{-t/2\tau}\cos\frac{\sqrt{4(\tau/\tau_B)-1}}{2\tau}t-1\right]\\ &+\frac{\tau_B^2}{4}e^{-t/2\tau}\sin\frac{\sqrt{4(\tau/\tau_B)-1}}{2\tau}t\\ &\times\left[\frac{1}{\sqrt{4(\tau/\tau_B)-1}}-3\sqrt{4(\tau/\tau_B)-1}\right]\Bigg).\end{aligned} \tag{5}$$

The expected particle motion is recovered in the short-time and long-time limits, ballistic $[\lim_{t\to 0}\langle\Delta r^2(t)\rangle = (3kT/m)t^2]$ and diffusive behavior $[\lim_{t\to\infty}\langle\Delta r^2(t)\rangle \sim (6kT/\zeta)t]$, respectively. At times shorter than the terminal relaxation time ($t \leqslant \tau$) the mean-square displacement is very similar to that found for an underdamped, harmonically bound Brownian particle [19] in that it exhibits oscillations, while at much longer times ($t \gg \tau$) the mean-square displacement is that of a free Brownian particle [7–10,19]. This observation owes to the fact that the suspending medium's viscoelastic response is dominated by its elastic component (i.e., the storage modulus) at high frequencies, while its viscous component (i.e., the loss modulus) dominates at low frequencies. The plateau region oscillations are bounded above by the suspending medium's elastic response and below by its viscous component. That is, the particle oscillates in an elastic cage while undergoing very slow viscous dissipation. The plateau region upper bound is actually twice the value expected for an overdamped, harmonically bound Brownian particle [19], but this overshoot is simply a result of insufficient viscous dampening at short times and eventually decays to the result expected from equipartition when viscous dampening becomes appreciable (i.e., at $t \gg \tau$). This lack of viscous dampening at early times also significantly extends the duration of the ballistic regime in comparison to that expected for purely viscous fluids. The ballistic motion persists until $t \cong (\tau\tau_B)^{1/2}$ for the single relaxation-time Maxwell fluid in contrast to the case of purely viscous fluids where ballistic motion is essentially extinguished when $t \cong \tau_B$. This extended ballistic motion regime is simply a result of the single relaxation-time Maxwell fluid model used in this calculation. A more realistic model incorporating multiple relaxation times would allow for viscous dissipation over a wide frequency range and subsequently an earlier attenuation of the ballistic motion regime.

The plateau region reflects the existence of the elastic response and as such can be used to estimate the plateau modulus G_0 or terminal relaxation time τ from experimental data. While the time of the plateau onset can be shown to scale as $t \sim (\tau\tau_B)^{1/2}$, and the onset of diffusive motion scales as $t \sim \tau$, the magnitude of the plateau can also be used to estimate the relaxation time. This is especially true for systems in which the mean-square displacement does not completely saturate, but actually exhibits a slow monotonic increase in an apparent plateau region or for cases wherein the terminal relaxation time is very long. For the single relaxation-time Maxwell fluid the mean-square displacement saturates at

$$\langle \Delta r^2(t) \rangle_{\text{plateau max}} = \frac{12\tau\tau_B kT}{m} = \frac{12\tau kT}{\zeta} = \frac{2\tau kT}{\pi\eta R} = \frac{2kT}{\pi R G_0}, \tag{6}$$

where $G_0 = \eta/\tau$. Other than the numerical factor, the last relation in Eq. (6) can also be derived from scaling arguments [2]. It is apparent that the zero shear viscosity is required to calculate the relaxation time τ from the mean-square displacement plateau. While the single relaxation-time Maxwell fluid is a very simple viscoelastic system, it does provide some insight into more complicated systems. As most real systems typically exhibit a spectrum of relaxation times occurring over a large temporal range, this plateau region will not be truly flat or exhibit distinct oscillations in reality. However, the dominant relaxation time can still be estimated from the mean-square displacement plateau value if the zero shear viscosity is known. Of course, the best estimate of this so-called terminal time is the time at which the longtime diffusion behavior commences. It should be noted that for the case of extremely long terminal times this plateau method could be the only experimentally realistic approach. Also, from the previous discussion it is obvious that there would have to be a significant separation of relaxation times in order to observe two distinct plateaus in the mean-square displacement.

At very late times ($t \gg \tau$) inertial effects completely diminish (i.e., the oscillations are completely damped) and the mean-square displacement becomes

$$\langle \Delta r^2(t) \rangle = \frac{6kT}{\zeta}(t + \tau - \tau_B) \equiv \frac{6kT}{\zeta}(t + \tau). \tag{7}$$

This is simply the result expected for free diffusion. The latter relationship can also be derived via the approach of Mason and Weitz [1–3] if the single relaxation-time Maxwell fluid kernel is used in their calculational scheme, which is not surprising as their method neglects inertial effects (see Appendix A). Interestingly this expression qualitatively captures the behavior of the mean-square displacement beyond the ballistic regime and should prove capable of estimating the terminal relaxation time from mean-square displacement measurements of probe motion for $(\tau\tau_B)^{1/2} \leqslant t \leqslant \tau$.

III. WORMLIKE MICELLES AS A REPRESENTATIVE MAXWELL FLUID

Several complex fluid systems are known to exhibit near Maxwellian behavior, at least in the frequency range typically probed by mechanical rheometry [20]. For instance, several aqueous surfactant solutions are known to contain very long, flexible self-assembled wormlike micelles. These wormlike micelles are similar to polymers in that they are quite flexible (typical persistence lengths of ~20 nm versus diameters of ~5 nm) and they exhibit contour lengths on the order of microns [21]. These so-called living polymers are different from classical polymers in that they are constantly breaking and recombining and, therefore, do not exhibit a quenched distribution of lengths. This ability to break and recombine profoundly affects the dynamical behavior of these systems [22]. Stress relaxation in entangled classical polymer solutions is well described via a reptation mechanism in which the polymer chains diffuse along their contour path or tube until they escape, at which point the imposed stress is completely relaxed [23]. While living polymers or wormlike micelles can also relax stress via curvilinear diffusion or reptation, their ability to break and recombine provides another route for stress relaxation. The so-called reptation time is the time a polymer chain requires to diffuse along its contour length thereby escaping from the stressed initial tube. When the wormlike micelle breaking/recombination time is much longer than the wormlike micelle reptation time, stress relaxation is dominated by the reptation process and the stress relaxation behavior of living polymers should be essentially the same as for classical polymers. However, when the wormlike micelle breaking/recombination time is much shorter than the reptation time, the breaking/recombination kinetics dominate the stress relaxation process leading to monoexponential or Maxwellian stress relaxation behavior [22].

Aqueous solutions of cetyltrimethylammonium bromide (CTAB) and potassium bromide (KBr) are known to form wormlike micelles at various temperatures [24–28]. This well-known wormlike micelle system has been thoroughly characterized via mechanical rheometry and dynamic light scattering [22,24–28]. The thermal motion of 0.966 μm diam polystyrene latex spheres in a 0.1 g/cm^3 (0.27 M) CTAB-2.5 M KBr solution at various temperatures is shown in Fig. 1. The mean-square displacement was measured by diffusing wave spectroscopy and as such is an average over thousands of particles [1–3]. The time evolution of the tracer mean-square displacement contains a wealth of information as to the state of the suspending medium. At first glance it may appear that the system is behaving as a purely viscous solution at 30.2 °C, however the mean-square displacement is actually subdiffusive, $\langle \Delta r^2(t) \rangle \propto t^{0.8}$. This may be an indication that this system behaves as a solution of semiflexible

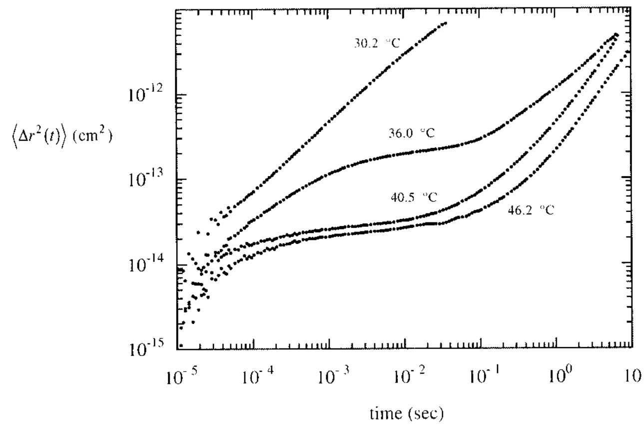

FIG. 1. Diffusion of 0.966 μm diam polystyrene latex spheres in a CTAB-KBr solution with $[\mathrm{CTAB}]=0.1$ g/cc and $[\mathrm{KBr}]=2.5$ M. The CTAB-KBr system has been shown to form wormlike micelles and exhibit single exponential stress relaxation behavior at low frequencies under certain conditions.

polymers at these frequencies as $\langle \Delta r^2(t) \rangle \propto t^{3/4}$ for the predicted semiflexible polymer solution shear modulus [29,30] (see Appendix B). The lack of a plateau for this particular composition may owe to the fact that the experimental configuration utilized here can only measure mean-square displacements below a threshold value somewhat less than $10^{-11}\,\mathrm{cm}^2$. A plateau, albeit somewhat brief, is finally observed at 36.0 °C. However, there is no distinct power-law scaling at either short or long times in this case. The lack of long-time diffusion is simply a result of the limited experimentally accessible mean-square displacement range, as given enough time, colloidal thermal motion in any viscoelastic system should eventually exhibit diffusive scaling. Distinctly Maxwellian behavior, a nearly flat plateau that is followed by purely diffusive motion at long times, is readily apparent at both 40.5 and 46.2 °C.

A representative mean-square displacement time trace for a Maxwellian 0.1 g/cm^3 (0.27 M) CTAB-2.0 M KBr solution at 36.0 °C is shown in Fig. 2. It is apparent that the inertialess Maxwell model for Brownian motion, Eq. (7), provides an excellent description of the experimentally observed thermal motion at long times, $t \geqslant 10^{-3}$ s. The fitted curve corresponds to a single relaxation time Maxwell fluid with a zero shear viscosity of 8800 p and a terminal relaxation time τ of 1.05 s, both of which are of the same magnitude as mechanical rheology measurements of similar systems (see Table I) [24–28]. Deviations from the predicted Maxwellian behavior are apparent at short times and are most likely a result of Rouse and breathing modes [23], as the influence of inertial effects can be entirely discounted for the systems under consideration here (see Appendix B). That is, the downturn from the plateau takes place at times much removed from the ballistic path prediction. All of the strongly Maxwellian systems display the same behavior as that shown in Fig. 2. In all cases of Maxwellian behavior there is no distinct, multidecade power-law scaling for the mean-square displacement at the shortest times accessible to the experimental measurements.

The mean-square displacement of 0.966 μ polystyrene spheres in a whole host of Maxwellian CTAB-KBr solutions is shown in Fig. 3. A wide range of terminal relaxation times

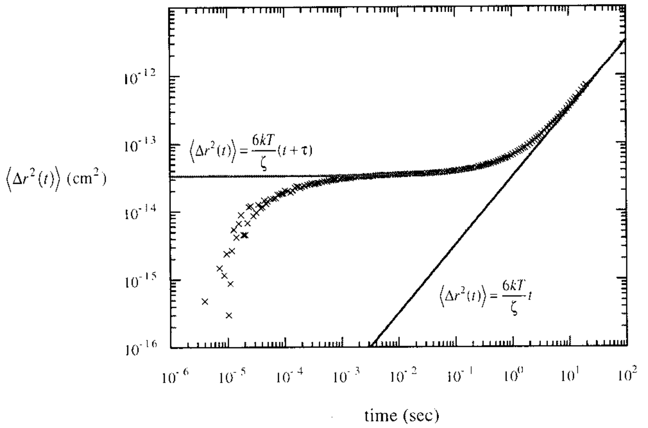

FIG. 2. Viscoelastic CTAB-KBr systems exhibit single relaxation-time Maxwell fluid behavior at long times. The mean-square displacement 0.966 μm polystyrene latex spheres dispersed in a solution with $[\mathrm{CTAB}]=0.1$ g/cc, $[\mathrm{KBr}]=2.0$ M and $T=36.0\,^\circ\mathrm{C}$ is shown. The fitted curve corresponds to the predicted late time probe mean-square displacement in a single relaxation-time Maxwell fluid with a zero shear viscosity of 8800 P and a terminal relaxation time τ of 1.05 s both of which correspond very well with mechanical measurements on a similar system.

($0.03\ \mathrm{s} \leqslant \tau \leqslant 1.10$ s) and zero shear viscosities ($10^2\ \mathrm{p} \leqslant \eta \leqslant 10^4$ p) are represented. The applicability of the Maxwell model to late time diffusion in these systems is readily apparent from the late time rescaling representation, $m\langle \Delta r^2(t) \rangle / 6kT\tau\tau_B$ vs t/τ, shown in Fig. 4. The measured mean-square displacement data are collapsed onto a master curve for $t/\tau \geqslant 10^{-2}$, which demonstrates that the CTAB-KBr solutions considered here exhibit essentially Maxwellian dynamics at long times or low frequencies. The viscosi-

TABLE I. Rheological properties of CTAB/KBr solutions.

CTAB (M)	KBr (M)	T (°C)	η (P)	τ (s)	G_0 (dyn/cm^2)
Mean-square displacement measurements: This paper					
0.27	0.50	30.2	3500	0.83	4200
0.27	0.50	36.0	710	0.16	4400
0.27	0.50	40.5	130	0.03	3800
0.27	2.0	36.0	8800	1.05	8400
0.27	2.0	40.5	2000	0.30	6600
0.27	2.0	46.2	750	0.12	6300
0.27	2.5	40.5	1500	0.12	1300
0.27	2.5	46.2	670	0.06	1200
Mechanical rheometry measurements[a]					
0.25	1.50	35.0	850	0.45	1880
0.30	1.50	35.0	1560	0.60	2600
0.35	0.40	31.0	520	0.14	3700
0.35	1.00	31.0	2000	0.69	2900
0.35	1.50	31.0	4100	1.37	3000
0.35	2.00	31.0	4000	1.36	2950
0.35	0.40	35.0	300	0.05	5600
0.35	1.00	35.0	1400	0.33	4300
0.35	1.50	35.0	2200	0.69	3200
0.35	2.00	35.0	2000	0.56	3600

[a] Reference [26].

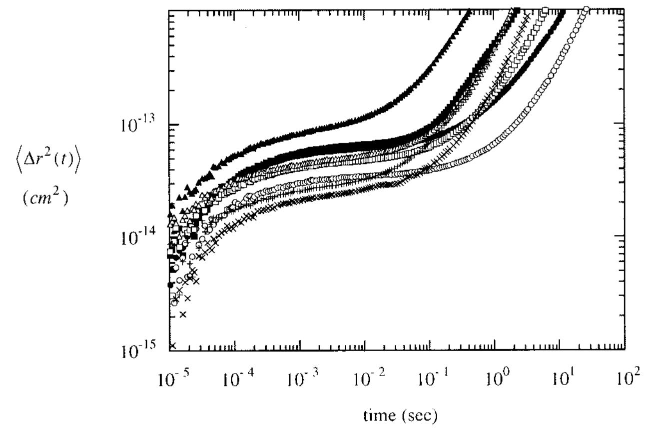

FIG. 3. Probe diffusion in several viscoelastic CTAB-KBr solutions: [CTAB] = 0.1 g/cc, [KBr] = 0.5 M, and $T = 30.2$ (●), 36.0 (■), and 40.5 °C (▲); [CTAB] = 0.1 g/cc, [KBr] = 2.0 M, and $T = 36.0$ (○), 40.5 (□), and 46.2 °C (△); [CTAB] = 0.1 g/cc, [KBr] = 2.5 M, and $T = 40.5$ (×) and 46.2 °C (+). The probe particles are 0.966 μm diam polystyrene latex spheres.

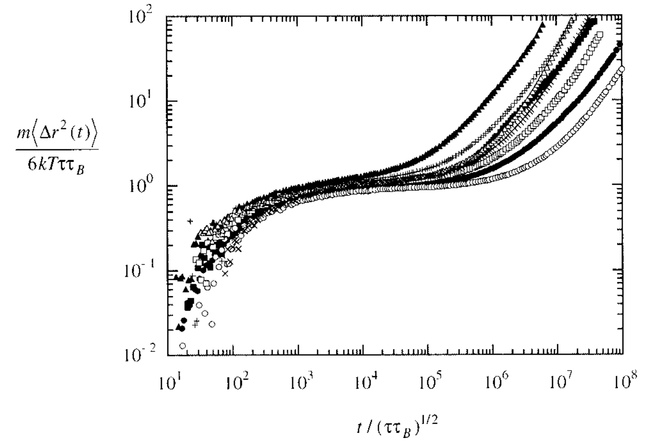

FIG. 5. Probe diffusion rescaled with respect to the plateau onset time predicted for a single relaxation-time Maxwell fluid. $t \sim \sqrt{\tau\tau_B}$, and the plateau mean-square displacement. Symbols are the same as in Fig. 3.

ties, terminal relaxation times, and plateau moduli estimated from mean-square displacement measurements are of the same order of magnitude as mechanical rheometry measurements made by other investigators (see Table I) [24–28].

In principle, the short-time rescaling $m\langle \Delta r^2(t) \rangle/6kT\tau\tau_B$ vs $t/(\tau\tau_B)^{1/2}$, should not be applicable since Rouse and breathing modes should dominate at short times or high frequencies [23]. However, at first glance, the short-time rescaling appears to describe the data very well (see Fig. 5) as they collapse quite neatly. However, the plateau onset occurs at a $t/(\tau\tau_B)^{1/2}$ value of $\approx 10^2 - 10^3$, not unity, indicating that this result may be somewhat fortuitous with respect to the Maxwellian dynamics. Also, the plateau onset time in the Maxwell model is the time at which the particle's ballistic motion ceases [i.e., $\langle \Delta r^2(t) \rangle \propto t^2$]. This is not the case for the experimental data where the mean-square displacement is obviously subdiffusive before the plateau onset time and not ballistic. If the plateau onset time τ_e, predicted by the Doi-Edwards tube model, is considered, a model that also predicts subdiffusive particle motion within the Mason-Weitz approximation at early times (see Appendix B), the following estimate can be made for the plateau onset time τ_e:

$$\tau_e \cong \frac{\zeta_s \phi a^2}{G_0 b^3} \sim \frac{\phi}{G_0},$$

where ϕ is the polymer volume fraction (concentration), ζ_s is the polymer segment friction coefficient within the Rouse model, b is the effective bond length, and a is the primitive chain step size, which is closely related to the tube diameter. Since wormlike micelle solutions should behave as classical polymer solutions for times much less than the average micelle breaking time, it is expected that the Doi-Edwards estimate of the plateau onset time should be reasonably applicable here. The plateau onset time is readily shown to exhibit the following scaling. When excluded volume effects are important it is expected that in the excluded volume case $\tau_e \sim \phi G_0^{-1} \sim G_0^{-0.57}$ (good solvent) and in the mean-field case $\tau_e \sim G_0^{-1/3}$ (theta solution). As these two estimates bound the observed scaling, it is apparent that the Doi-Edwards tube model can account for the observed early time scaling and that the Maxwell fluid plateau onset time prediction was purely fortuitous.

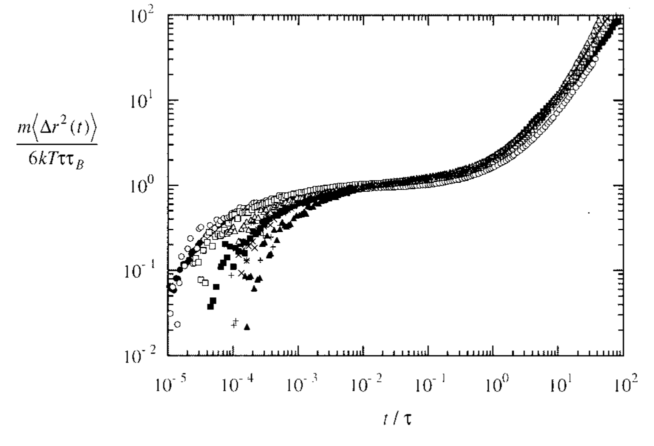

FIG. 4. Probe diffusion rescaled with respect to the terminal relaxation-time and plateau mean-square displacement confirming the near Maxwellian behavior of these CTAB-KBr wormlike micelle solutions at long times. Symbols are the same as in Fig. 3.

IV. CONCLUSIONS

A simple model of Brownian motion in a single relaxation-time Maxwell fluid was developed and compared to diffusing wave spectroscopy measurements of colloidal motion in CTAB/KBr wormlike micelle solutions. The experimentally measured Brownian motion was observed to conform to the model predictions at long times and thereby provided an additional confirmation of the essentially Maxwellian mechanical behavior of wormlike micelle solutions at low frequencies. In addition, the plateau moduli and terminal times determined from the Brownian motion measurements were of the same order of magnitude as those found by other investigators via conventional mechanical rheometry. Surprisingly in light of its neglect of short-time dynamical processes, the Maxwell model predicted a plateau onset time with which the measured mean-square displacements could be reduced to a master curve. However, the prediction grossly underestimated the actual plateau onset time. The predicted rescaling was shown to be essentially that also predicted by the Doi-Edwards tube model for polymer solutions under good solvent conditions where a more proper accounting of the short-time dynamics was made. This indicated that the success of the predicted Maxwell model plateau onset time scaling was purely fortuitous.

APPENDIX A

An alternate approach to solving the generalized Langevin equation for arbitrary memory function has been utilized by Mason and co-workers [1–3]. The exact relationship between a particle's mean-square displacement and the suspending medium's memory function in the frequency domain is

$$\tilde{\zeta}(s)=\frac{6kT}{s^2\langle\Delta\tilde{r}^2(s)\rangle}-ms \tag{A1a}$$

or, neglecting the inertial term,

$$\tilde{\zeta}(s)\cong\frac{6kT}{s^2\langle\Delta\tilde{r}^2(s)\rangle}, \tag{A1b}$$

where $\tilde{f}(s)=\int_0^\infty e^{-st}f(t)dt$ denotes a Laplace transformed quantity. Utilizing our single relaxation-time Maxwell fluid memory function, $\zeta(t)=(\zeta/\tau)e^{-t/\tau}$ with $\zeta=6\pi\eta R$, the mean-square displacement in the frequency domain (neglecting inertia) is

$$\langle\Delta\tilde{r}^2(s)\rangle\cong\frac{6kT}{\zeta}\left(\frac{1}{s^2}+\frac{\tau}{s}\right). \tag{A2}$$

Following the Laplace inversion the mean-square displacement in the time domain is found to be

$$\langle\Delta r^2(t)\rangle\cong\frac{6kT}{\zeta}(t+\tau). \tag{A3}$$

This is the same result found in the long-time limit of our more rigorous calculation wherein the inertial terms were retained. However, it should be noted that the mean-square displacement plateau is underestimated by a factor of 2 as shown earlier.

An even more interesting result arises from a further approximation of Mason and co-workers wherein they attempt to establish the connection between a Brownian particle's mean-squared displacement and the suspending medium's shear modulus [1–3]. Here they have assumed that the Stokes-Einstein relationship is valid at all frequencies (i.e., a frequency-dependent viscosity, no-slip boundary condition at the sphere surface, incompressible medium) such that

$$\tilde{\zeta}(s)=6\pi\tilde{\eta}(s)R. \tag{A4}$$

Recall that this relation is exact for a purely viscous fluid with no slip boundary conditions. The suspending medium's shear modulus $G(t)$, can be expressed in the Laplace domain as

$$\tilde{G}(s)=s\tilde{\eta}(s)=\frac{s\tilde{\zeta}(s)}{6\pi R}=\frac{kT}{s\pi R\langle\Delta\tilde{r}^2(s)\rangle}. \tag{A5}$$

Utilizing the expression for a single relaxation-time Maxwell fluid's memory function or, better yet, the inertialess mean-square displacement of a Brownian particle undergoing thermal motion within a single relaxation-time Maxwell fluid, the single relaxation-time Maxwell fluid's shear modulus in the frequency domain within the Mason-Weitz approximation is given by

$$\tilde{G}(s)=\eta\frac{s}{s\tau+1}. \tag{A6}$$

The complex shear modulus, $G^*(\omega)$ (the form familiar from the theory of linear viscoelasticity), can be found using analytic continuation, substituting $i\omega$ for s and then taking the real and imaginary parts to yield the storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, respectively:

$$G^*(\omega)=\eta\frac{i\omega}{i\omega\tau+1} \tag{A7}$$

with

$$G'(\omega)=\frac{\eta\omega^2\tau}{\omega^2\tau^2+1} \tag{A8a}$$

and

$$G''(\omega)=\frac{\eta\omega}{\omega^2\tau^2+1}. \tag{A8b}$$

These are the exact expressions for the viscoelastic moduli of a single relaxation-time Maxwell fluid [31], thereby demonstrating the success of the Mason-Weitz approximation for at least the simple, incompressible, viscoelastic continuum model outlined here.

APPENDIX B

The single relaxation-time Maxwell fluid provides some insight into the validity of ignoring inertial effects in the Langevin representation of Brownian motion in viscoelastic media. In order for this condition to be met, the following inequality must be satisfied within the approximation of Mason and Weitz:

$$ms\ll\tilde{\zeta}(s). \tag{B1}$$

For the case of a single relaxation-time Maxwell fluid this inequality becomes

$$s(s\tau+1)\ll\frac{\zeta}{m}=\tau_B^{-1}=\frac{9\eta}{2R^2\rho_P}, \tag{B2}$$

where ρ_P is the particle density. For the terminal relaxation times typical of viscoelastic materials, $s\tau\gg 1$ will hold near the limiting frequency. Inertial effects become important when the following inequality is no longer satisfied:

$$s\ll(\tau\tau_B)^{-1/2}=\sqrt{\frac{9\eta}{2R^2\rho_P\tau}}=\sqrt{\frac{9G_0}{2R^2\rho_P}}. \tag{B3}$$

This is exactly the plateau onset frequency predicted by the single relaxation-time Maxwell model mean-square displacement as expected. Interestingly, the mean-square displacement oscillations predicted by the single relaxation-time Maxwell fluid model begin at this time and persist until the terminal relaxation time is reached. Therefore in the single relaxation-time Maxwell fluid case, when inertial effects are assumed negligible, as in the Mason-Weitz approximation, not only is the ballistic regime neglected as expected, but other components of the dynamical behavior are also eliminated. This phenomenon is also manifested in the plateau mean-square displacement difference predicted by the exact calculation and the Mason-Weitz approximation.

Polymer solutions and melts exhibit much more complex stress relaxation behavior than a single relaxation-time Maxwell fluid [23]. The short-time stress relaxation modulus found from the Doi-Edwards tube model is

$$G_r(t)=G_{t\leq\tau_e}\left(\frac{\tau_e}{t}\right)^{\alpha} \tag{B4}$$

when $t\leq\tau_e$. Here $G_r(t)$ is the stress relaxation modulus and τ_e denotes the time at which tube constraints become important. The values of $G_{t\leq\tau_e}$ and α depend on the nature of the polymer chains (i.e., flexible, semiflexible, or stiff). In the classic Doi-Edwards model for flexible chains in the melt $G_{t\leq\tau_e}=G_0$ is the plateau modulus and α is 1/2. In order to neglect inertia within the Mason-Weitz approximation the following inequality must be satisfied:

$$ms\ll\tilde{\zeta}(s)=6\pi R\tilde{G}_r(s). \tag{B5}$$

It is a straightforward calculation to show that inertial effects can be neglected only for frequencies satisfying the following inequality:

$$s\ll\left(\frac{9G_{t\leq\tau_e}\tau_e^{\alpha}\Gamma(2-\alpha)}{2(1-\alpha)R^2\rho_P}\right)^{1/(2-\alpha)}, \tag{B6}$$

where $\Gamma(x)$ denotes the gamma function. This leads to a somewhat less restrictive (i.e., higher) frequency limit than the single relaxation-time Maxwell fluid model. That is, the high-frequency Rouse modes provide a means for viscous dissipation at short-time scales and thereby reduce the duration of ballistic motion exhibited by a Brownian particle. If this critical frequency is much larger than $1/\tau_e$, then the mean-square displacement when $t\leq\tau_e$ is simply given by

$$\langle\Delta r^2(t)\rangle\cong\frac{kT(1-\alpha)}{\pi R G_{t\leq\tau_e}\tau_e^{\alpha}\Gamma(1+\alpha)\Gamma(2-\alpha)}t^{\alpha}. \tag{B7}$$

Here we have neglected the small mean-square displacement offset resulting from the initially ballistic motion. The neglected mean-square displacement offset would be of order

$$\langle\Delta r^2\rangle_{\mathrm{offset}}\approx 9^{(4-\alpha)/(2-\alpha)}\frac{kT}{4\pi}\times\left(\frac{2(1-\alpha)\rho_P}{9G_{t\leq\tau_e}\tau_e^{\alpha}\Gamma(2-\alpha)}\right)^{1/(2-\alpha)}R^{(3\alpha-2)/(2-\alpha)}. \tag{B8}$$

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