Sphere sedimentation in wormlike micelles: Effect of micellar relaxation spectrum and gradients in micellar extensions

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Abstract

We report experiments on the flow of wormlike micellar solutions based on cetylpyridinium chloride/sodium salicylate past a falling sphere via a combination of particle tracking velocimetry, particle image velocimetry, rheology, and flow induced birefringence (FIB). Recent studies have shown that beyond a critical extensional Deborah number, a falling sphere in wormlike micelles never reaches a constant terminal velocity; instead, it settles with an unsteady velocity. This behavior is linked to the wormlike micellar chain scission in the wake of the sphere. Similar instabilities in viscoelastic polymer solutions, where polymer chain scission is highly unlikely, are thought to be the results of a single-mode relaxation spectrum of the polymer chains or the asymmetry in the polymer chain extensions on the flanks of the falling sphere. In this paper, we examine the effect of micellar relaxation spectrum and gradients in micellar extensions on sphere instability in wormlike micelles over a wide range of sphere. In addition, Mohammadigoushki and Muller have recently carried out a systematic sphere sedimentation experiment in a falling sphere and the sphere diameter). These experiments were performed at vanishingly small Reynolds numbers (Re << 1). Reynolds number is defined as Re = ρsVmax/aη, where ρs and η are density of the sphere and the shear rate-dependent viscosity of the solution, respectively. Jayaraman and Belmonte conjectured that the sphere instability could be the result of the shear banding phenomenon [5]. Chen and Rothstein also reported similar instabilities for spheres moving in shear banding wormlike micelles based on CTAB/NaSal (50 mM/50 mM), for De ≥ 4 [4]. Rothstein and co-workers showed that for conditions that give rise to sphere instability, FIB indicates that micellar extensions on sphere sideways are perfectly symmetric. © 2018 The Society of Rheology. https://doi.org/10.1122/1.5031899

I. INTRODUCTION AND BACKGROUND

Multiphase flow of particles in wormlike micelles is a critical aspect in technological applications such as well drilling, hydraulic fracturing, and consumer products. A fundamental knowledge of the settling velocity of a single particle in wormlike micelles provides the first step toward better understanding of the dynamics of these complex multiphase systems. Wormlike micelles are made by dissolving surfactants and salts in water. Beyond a critical micelle concentration, the addition of salt transforms spherical micelles to wormlike micelles that, at sufficiently high concentrations, entangle and induce a shear-thinning viscoelastic response [1–3]. Wormlike micelles can break and reform under shear. Thus, these viscoelastic solutions sometimes are referred to as “living polymers.”

Recent studies demonstrated very interesting features for a falling sphere in wormlike micelles [4–8]. Jayaraman and Belmonte studied sedimentation of a sphere in shear banding wormlike micelles based on cetyltrimethylammonium bromide and sodium salicylate (CTAB/NaSal) (9 mM/9 mM) and showed that beyond a critical Deborah number De = λA ≈ 45, the falling sphere shows a fluctuating pattern with sudden accelerations and decelerations in sphere velocity [5]. De is defined as De = λA, where A and λ are the characteristic shear rate and the relaxation time of the wormlike micelles, respectively. Shear rate is defined as \( \dot{\gamma} = V_{\text{max}}/a \) (a and V are the average terminal velocity of the falling sphere and the sphere diameter). These experiments were performed at vanishingly small Reynolds numbers (Re << 1). Reynolds number is defined as Re = ρsV/aη, where ρs and η are density of the sphere and the shear rate-dependent viscosity of the solution, respectively. Jayaraman and Belmonte conjectured that the sphere instability could be the result of the shear banding phenomenon [5]. Chen and Rothstein also reported similar instabilities for spheres moving in shear banding wormlike micelles based on CTAB/NaSal (50 mM/50 mM), for De ≥ 4 [4]. Rothstein and co-workers showed that for conditions that give rise to sphere instability, the wormlike micellar filament exhibits a sudden rupture in the filament stretching extensional rheometer [4,9]. In addition, Mohammadigoushki and Muller have recently carried out a systematic sphere sedimentation experiment in a range of wormlike micelles within a wide range of conditions (1 < De < 10) and (10^{-6} < Re < 10) and showed that the Deborah number (De) defined based on the shear rate seems to be insufficient in explaining the threshold of instability and a Deborah number based on the extensional properties of the wormlike micelles, DDe, gives a clear criterion for distinguishing fluctuating sphere motion from steady sphere motion. DDe was defined as DDe = λEεmax, where εmax is the maximum extensional rate in the wake of the sphere \( \varepsilon = (\partial V_x/\partial x) \), where Vx is the velocity of the fluid in the wake of the falling sphere, parallel to the direction of the sphere motion, x. Therefore, the falling sphere instability in the wormlike micelles is linked to the scission of the
wormlike chains in the rear of the falling sphere, where a strong extensional flow is present. Moreover, sphere instabilities are produced in nonshear banding wormlike micelles based on CTAB/NaSal (9 mM/9 mM) at 40 °C (cf. Fig. 2(a) in [6]), which indicates that this instability is not related to the shear banding phenomenon.

However, similar instabilities have been reported for flow of viscoelastic polymer solutions past a falling sphere [10–12]. Bisgaard reported oscillations in the axial velocity, in the flow behind a falling sphere in viscoelastic polymer solutions based on 1% polyacrylamide in glycerol at high Deborah number (De = λ/τ = 30), and negligible inertia (Re << 1) [10]. In addition, similar unsteady settling behavior has been reported in experiments by Mollinger et al. in a viscoelastic polymer solution based on guar gum [12]. We note that the breakage of the polymer chains is highly unlikely in these studies in the limit of low inertia as polymer chains are connected via strong covalent bonds.

Theoretical studies may provide potential explanations for the above subtleties in polymeric solutions. For example, Binous and Phillips reported similar instabilities in flow of viscoelastic finite extensible non-linear elastic (FENE) dumbbell solutions past a falling sphere for De ≥ 6 [11]. Binous and Phillips illustrated that for unsteady settling spheres, dumbbells are extended differently around the flanks of the falling sphere, orthogonal to the direction of the sphere motion. According to these authors, the gradients in the dumbbell extension on sphere sideways (orthogonal to the direction of the sphere motion) push the sphere from regions of highly extended dumbbells to regions where dumbbells are less extended, and this causes fluctuations in the settling velocities [11]. In a relevant work, Graessley and Milner studied startup shear flows of viscoelastic polymer solutions in a parallel plate geometry in the presence of inertia, and calculated the transient evolution of fluid velocity in the middle of the two plates using Lodge model [13]. For calculations with a single-mode relaxation time, a fluctuating velocity profile was reported for long times (typically t > 30λ, where λ is the relaxation time of polymer chains). However, for the model with a broad spectrum of relaxation times, velocity oscillations disappeared in a short period of time (t ≈ 3λ) [13]. Therefore, they concluded that the unsteady response of viscoelastic polymer solutions in shear flows could be controlled by the relaxation spectrum of the polymer chains [13].

Semidilute wormlike micellar solutions display strong analogies with the behavior of polymer solutions and follow similar scaling laws [14]. Considering the similarities between these two viscoelastic systems, it is conceivable that these mechanisms (e.g., gradients in the micellar extensions, orthogonal to the direction of the sphere motion, or a single-mode chain relaxation) can be involved in the time dependent motion of the falling spheres in wormlike micelles. As Graessley and Milner pointed out, wormlike micellar solutions, including those studied in prior sphere studies, exhibit one relaxation time in their linear viscoelastic rheology [4–7,15]. Thus, whether the sphere instability in flow of wormlike micellar solutions arises from micellar chain scission in the wake of the sphere, from the formation of asymmetric gradients in dumbbell extension, or due to the single relaxation time of these solutions remains an open question. Hence, the main objectives of this paper are (1) to examine the potential role of the relaxation mechanism of the wormlike micelles (multiple-mode vs single-mode Maxwell model) on sphere instability and (2) to probe the existence of any gradients in micellar extensions on the flanks of the falling sphere when sphere experiences instabilities. For this purpose, we formulate three wormlike micelles that are best described by multiple-mode and single-mode Maxwell models. Detailed particle image velocimetry (PIV), particle tracking velocimetry, and flow induced birefringence (FIB) allow us to shed more light on the nature of sphere instabilities in wormlike micelles.

II. MATERIALS AND METHODS

In this work, the wormlike micellar solution is composed of cetylpyridinium chloride (CPCI) and NaSal in de-ionized water. CPCI and NaSal are purchased from Sigma-Aldrich and used as received. This wormlike micellar solution has been extensively studied and characterized in the past [16]. The rheological properties of these solutions, including steady flow curve and shear relaxation time, are measured in a commercial Anton-Paar rheometer (model MCR 302) using a Couette co-axial cylinders geometry with Ri = 13.35 mm and Ro = 14.53 mm. R1 and R2 denote the radii of the inner and the outer cylinders. We have also measured the extensional relaxation time and the transient extensional viscosity of the wormlike micellar solutions via a custom made capillary extensional rheometer (CaBER) and a dripping on a substrate (DoS) technique. More details on the CaBER experiments can be found in our recent work [17]. In addition, DoS experiments were carried out in a custom-built setup following the design of Dinic et al. [18]. In these experiments, a wormlike micellar solution is pumped gradually (with a flow rate of 0.01 μl/h) through a vertical needle via a syringe pump (model Fisherbrand Single Syringe Pump, purchased from Fischer Scientific), and touches a solid substrate that is positioned 3 mm below the tip of the needle. The needle has a blunt opening with a diameter of 1.7 mm. As soon as the droplet touches the solid substrate, the flow rate is stopped. This generates a fluid filament between the solid substrate and the needle, which eventually experiences a filament thinning process akin to CaBER experiments. Therefore, the extensional rheological properties of wormlike micelles can be obtained via the DoS device in a similar fashion to the CaBER experiments (see details in Sec. III). Sphere sedimentation experiments are performed in a vertical cylindrical tube (with diameter D = 8.5 cm and length L = 100 cm), positioned inside a temperature-controlled water bath. A wide range of spheres with different densities (Nylon, Delrin, Teflon, Ceramic, and Aluminum) and sizes (a = 1/8th–5/16th) are used for this study. All surfactant solutions are seeded with a small amount of tracing particles (~0.008 wt. %, model 110PB provided by Potters Industries LLC), and a laser (model Genesis MX532-5000 from Coherent Inc.) is used to illuminate the flow field around the falling sphere. Sphere motion is recorded via a CCD camera (model STC-MBS241U3V) equipped with...
different lenses (AF-S DX Micro NIKKOR and AF-S DX NIKKOR 35 mm from Nikon). Fluid motion is quantified with PIV analysis via an open source MATLAB code [19]. To measure the velocity of the sphere center of mass, we performed particle tracking velocimetry via an open source IMAGEJ PLUGIN software developed by MOSAIC Group [20].

In addition, we have performed FIB measurements. For these measurements, the falling sphere in the column is placed between two crossed polarizers, and a white light passes through these crossed polarizers. The crossed polarizers are oriented in $45^\circ/135^\circ$ angle such that the extensional or compressional flows around the falling sphere are highlighted. The main purpose of the FIB measurements is to evaluate the wormlike micellar orientations on the flanks of the falling spheres, orthogonal to the direction of motion as the sphere undergoes the instability.

### III. FLUID CHARACTERIZATION

To study the role of wormlike micellar relaxation on sphere instability, three wormlike micellar systems are studied. In these solutions, CPCl concentration is kept fixed at 25 mM, and the ratio of the salt to surfactant concentration, $R = [\text{NaSal}]/[\text{CPCl}]$, is varied as $R = 0.74$, $R = 0.75$, and $R = 0.82$. Figure 1(a) shows the shear stress as a function of shear rate for these three solutions. The inset of Fig. 1(a) also shows the variation of zero-shear-rate viscosity as a function of salt concentration. All wormlike micellar solutions exhibit strong shear-thinning viscoelastic behavior. The shear-thinning viscosity is fitted to the Carreau model (see Fig. S1 in the supplementary material [30]), and the resulting shear-thinning indices are listed in Table I. It is clear that the solutions of $R = 0.75$ and $R = 0.82$ exhibit shear banding, while the solution with $R = 0.74$ does not show the shear banding behavior.

Figure 1(b) also shows the results of small amplitude oscillatory shear experiments. For the solutions with $R = 0.74$ and $R = 0.75$, linear viscoelastic results are best described by a multimode (7th and 4th mode, respectively) Maxwell model, and as salt concentration increases to $R = 0.82$, the linear rheology is best described by a single-mode Maxwell model. The m-mode generalized Maxwell model can be expressed as follows:

$$G'_{\omega} = \sum_{i=1}^{m} G_i \lambda_i \omega^2, \quad G''_{\omega} = \sum_{i=1}^{m} G_i \lambda_i \omega^2. \quad (1)$$

As noted before, wormlike micelles experience a strong extensional flow in the wake of the falling sphere. Therefore, we have characterized the extensional properties of these solutions with two methods; (1) CaBER and (2) DoS techniques. Figure 2(a) shows the filament diameter as a function of time obtained by CaBER technique for these three solutions along with an exponential fit $D(t) \propto \exp (-t/\lambda_E)$ to the experimental data. Figure 2(b) shows the variation of filament diameter as a function of time obtained via the DoS technique for these solutions. Finally, Table I shows the rheological properties of the wormlike micellar solutions used in this study.

### IV. RESULTS AND DISCUSSION

#### A. Particle tracking velocimetry

Following fluid characterization, we have carried out sphere sedimentation experiments in the wormlike micellar solutions, and the average falling velocity of the sphere center of mass is measured. Sample velocity profiles are provided in the supplementary material [Fig. S2(a)] [30]. To evaluate the deviations from Stokes’ solution, a dimensionless wall correction factor $K$ is defined as

$$K = V_{\text{Stokes}}/V_{\text{max}} = (\rho_s - \rho_i) a^2/18 \eta_0 V_{\text{max}}, \quad (2)$$

where $\rho_s$, $\rho_i$, $a$, and $\eta_0$ are the density of the sphere, density of the fluid, sphere radius, and the zero-shear-rate viscosity

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**TABLE I. Rheological properties of the wormlike micellar solutions.**

<table>
<thead>
<tr>
<th>Solution [CPCI] (nM)</th>
<th>Maxwell modes</th>
<th>$\lambda$</th>
<th>$\eta_0$ (Pa s)</th>
<th>$\eta_{\text{flow}}$ (Pa s)</th>
<th>$\lambda_E$</th>
<th>$\lambda_i$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.74</td>
<td>7</td>
<td>16.5</td>
<td>5.92</td>
<td>9.7 x 10^3</td>
<td>2.5</td>
<td>11.3</td>
</tr>
<tr>
<td>25</td>
<td>0.75</td>
<td>4</td>
<td>20.5</td>
<td>15.5</td>
<td>1.2 x 10^4</td>
<td>4.9</td>
<td>13.3</td>
</tr>
<tr>
<td>25</td>
<td>0.82</td>
<td>1</td>
<td>24.5</td>
<td>54.9</td>
<td>1.3 x 10^4</td>
<td>5.7</td>
<td>20.1</td>
</tr>
</tbody>
</table>

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**FIG. 1.** (a) Shear stress versus shear rate for the three CPCl/NaSal systems. Inset shows the zero-shear-rate viscosity as a function of salt to surfactant concentration. (b) Elastic modulus (filled symbols) and loss modulus (empty symbols) versus angular frequency the three CPCl/NaSal solutions. Inset shows the relaxation time as a function of salt to surfactant concentration. Black curves indicate predictions of the Maxwell models.
of the wormlike micellar solutions, respectively. Figure 3(a) shows the wall correction factor $K$, as a function of $De$ for all spheres tested in the wormlike micellar solutions. Empty symbols denote spheres that fall with steady velocity, while filled symbols indicate the fluctuating spheres. At low Deborah numbers, the wall correction factor is constant around $\sim 1.3$. As the strength of the shear flow ($De$) increases, the wall correction factor decreases, which is consistent with previous results reported for wormlike micelles [4,6]. More importantly, none of the falling spheres in the wormlike micellar solution with $R = 0.74$ and $R = 0.75$ experience the instability for Deborah numbers as high as $De = 255$. However, spheres in the wormlike micellar solution with $R = 0.82$ exhibit unsteady behavior for $De \geq 29.9$. In addition, Fig. 3(b) shows the Deborah number as a function of Reynolds number over a wide range of parameters. It turns out that the steady and unsteady sphere sedimentation regimes cannot be distinguished using this criterion. This is not unusual because the sphere instability in the wormlike micellar solutions has been linked to the wormlike chain scission in the wake of the falling sphere, where the extensional flow is dominant [4,6]. We also explored the relation between shear banding behavior and the sphere instability phenomenon in this work. As noted before [see Fig. 1(a)], both wormlike micellar solutions with $R = 0.75$ and $R = 0.82$ clearly exhibit shear banding in the steady shear experiments. However, spheres fall unsteadily only in solution of $R = 0.82$. This indicates that the shear banding phenomenon is not related to the sphere instability in wormlike micelles studied in this work which is consistent with prior works [6,15].

B. Particle image velocimetry

To elucidate the nature of differences between these three systems, we have characterized the extensional flow in the wake of the falling spheres via a detailed PIV technique. In the following, we first examine the steady flow behavior in these wormlike micellar solutions in detail, and then describe the unsteady results.

Figures 4(a) and 4(b) show the normalized steady state velocity profile of the wormlike micellar solutions on the axis parallel to the direction of the sphere motion. At low Deborah numbers ($De \leq 1.06$ for $R = 0.74$, $De \leq 1.17$ for $R = 0.75$ (results not shown), and $De \leq 1.98$ for $R = 0.84$), the steady velocity profile shows for-aft symmetry, and as the Deborah number increases, a transition to a negative wake behind the falling sphere is observed at $De \geq 1.85$ for $R = 0.74$, $De \geq 2.78$ for $R = 0.75$, and $De \geq 7.37$ for $R = 0.82$, respectively. As the Deborah number increases beyond these critical values, the magnitude of the negative wake $(|V_{\min}|/V_{\max})$ increases. However, the location of the stagnation point remains relatively fixed at $x/a \sim -4 \pm 0.1$ for solution with $R = 0.74$, $x/a \sim -4.6 \pm 0.3$ for solution with $R = 0.75$ (data not shown here) and at about $x/a \sim -4.7 \pm 0.7$ for the wormlike micelles with $R = 0.82$. 

![FIG. 2. Mid-filament diameter as a function of time for the three CPCl/NaSal systems via (a) CaBER method and (b) DoS technique. Black curves are the best fits to the exponential function $D(t) \approx \exp \left( -t/3\lambda_0 \right)$.](image1)

![FIG. 3. (a) Wall correction factor versus Deborah number and (b) Deborah number versus Reynolds number for sphere experiments performed in CPCl/NaSal solutions. Filled and empty symbols correspond to unsteady and steady sphere sedimentation behavior, respectively.](image2)
We note that formation of a negative wake behind a falling sphere in shear-thinning viscoelastic polymer solutions has been predicted theoretically and reported experimentally [21–23]. According to Bush, a negative wake is formed in the rear of a falling sphere, if the ratio of the Deborah number (De) divided by the Trouton ratio (Tr) is beyond a critical value. Bush defined the Trouton ratio as the ratio of the extensional viscosity (γE) to the shear rate-dependent viscosity [γ(γ)] of the viscoelastic fluid. Arigo and McKinley reported formation of a negative wake behind a falling sphere in aqueous viscoelastic solutions based on polyacrylamide for De/Tr = 0.05–0.289. Although formation of the negative wake behind a falling sphere is reported in wormlike micelles [4,6], the transition from no-negative wake to a negative wake structure has not been investigated in view of the Bush criterion. Using the experimental data of Fig. 2 and Table I (i.e., γE∞), we can evaluate this criterion for wormlike micelles in detail. For the wormlike micellar solutions studied in this work, the transition to a negative wake occurs for De/Tr ≥ 0.76–1×10⁻³. For values below this critical threshold, we report a for-aft symmetry in all wormlike micellar solutions tested in this work. We note that the negative wake forms at much lower critical De/Tr ratios in wormlike micelles than in polymer solutions.

We also performed PIV on spheres that fall with unsteady velocities. For such cases, we always report formation of a strong negative wake behind the falling spheres. Figure 5(a) shows a series of velocity profiles parallel to the direction of the sphere motion for a ceramic sphere that falls unsteadily in wormlike micelles with R = 0.82. Figure 5(b) shows the velocity of the center of mass of this sphere as a function of time for the time frame considered in Fig. 5(a). At t = 0.856 s, a negative wake is evident in the rear of the falling sphere with the stagnation point approximately at x/a ≈ −4.5. As the sphere starts accelerating (t = 1.017 s), the stagnation point shifts further downstream of the sphere center of mass to x/a ≈ −7.8. This indicates that a large portion of the wormlike micelles is swept away from the sphere. Finally, at t = 1.098 s, the velocity of the sphere center of mass reaches a maximum, and following that, the sphere decelerates to a smaller velocity (t = 1.218 s).

Figure 5(b) also shows the temporal evolution of the maximum strain rate in the wake of the sphere over the time window presented in Fig. 5(a). It is clear that the sphere instability in this wormlike micellar solution is linked to the extensional flow in its wake.

To quantify the strength of the extensional flow in the wake of the falling spheres, we use the extensional Deborah number defined as DeE = λEγE∞. For this purpose, we have used the extensional relaxation time measured by the CaBER technique. However, using the extensional relaxation time obtained by the DoS technique in defining the extensional Deborah number generates a similar conclusion. For spheres that fall with a constant terminal velocity, the maximum strain rate ̇εmax is constant over time (see Fig. S2(b) in the supplementary material [30]). However, for spheres that fall
unsteadily, $\bar{v}_\text{max}$ shows a maximum when the sphere reaches its maximum velocity (see Fig. S2(b) in the supplementary material [30]). Figure 6(a) shows the wall correction factor as a function of extensional Deborah number for all sphere sedimentation experiments performed in these three wormlike micellar solutions. Here again, the filled symbols indicate the time dependent sphere sedimentation cases, while empty symbols denote the steady sphere sedimentation behavior. For the system with $R = 0.82$, the transition from steady to unsteady behavior clearly occurs for $D_E \geq 2.6$. More interestingly, we do not report any instabilities in the micellar solutions with $R = 0.74$ and $R = 0.75$ despite reaching an extensional Deborah number of $D_E \approx 40.7$.

We note that the strength of the extensional flow ($D_E$) in the wake of the sphere may not be the only factor that controls the transition from steady to unsteady flow in these experiments. Recent experiments by Mohammadigoushki and Muller showed that such transitions could be affected by the presence of inertia [6]. Figure 6(b) shows the extensional Deborah number as a function of inertia for all experiments. For the wormlike micellar solution that follows a single-mode Maxwell model ($R = 0.82$), a transition from steady to unsteady flow is observed. However, when the results for solution with $R = 0.74$ and $R = 0.75$ are added, the steady and unsteady results do not form separate regions over a wide range of flow conditions. In some cases, $D_E$ and Re numbers for steady and unsteady experiments overlap. This result seems to be at odds with recent sphere sedimentation experiments reported in the wormlike micellar solutions based on CTAB/NaSal (9 mM/9 mM), CTAB/NaSal (25 mM/25 mM), CTAT/NaCl (22 mM/50 mM), and CPCl/NaSal (10 mM/12 mM) that a phase diagram based on DeE and Re numbers for steady and unsteady experiments overlap. This analysis produces a $\lambda \approx 1304$ s for $R = 0.82$. For the solution of $R = 0.75$, we use the following relation: $\lambda = (\lambda_{\text{rep}} - \lambda_{\text{br}})^{0.5}$ to estimate the reptation time [24]. This analysis produces a $\lambda_{\text{rep}} \sim 20.5$ s for $R = 0.82$. On the other hand, for the solution of $R = 0.75$, if we consider $\lambda \approx \lambda_{\text{rep}} \sim 20.5$ s (see Table I), we can readily observe that $\lambda_{\text{br}} < \lambda_{\text{rep}}$. Hence, we expect that for both solutions with $R = 0.75$ and $R = 0.82$ micellar breakage to be significant in sphere sedimentation experiments.

The main difference between the wormlike micellar solutions with $R = 0.74$, $R = 0.75$, and other wormlike micellar solutions used in prior studies is that these systems are best described by a 7th mode and a 4th mode Maxwell model (i.e., have a broad distribution of relaxation modes), while the rest of solutions are best described by a single-mode Maxwell model [6,15,4]. Generally, the linear viscoelastic rheology of wormlike micelles is described by two time scales; reptation time ($\lambda_{\text{rep}}$) and the breakage time ($\lambda_{\text{br}}$). For wormlike micelles that are best described by a single-mode Maxwell model, the breakage time is much shorter than the reptation time ($\lambda_{\text{br}} < \lambda_{\text{rep}}$), and therefore, micellar breakage is the dominant relaxation mechanism [24]. However, for wormlike micelles that follow a multimode Maxwell model, the reptation mechanism may be the dominant relaxation mechanism ($\lambda_{\text{rep}} < \lambda_{\text{br}}$). Therefore, it is important to evaluate the relative importance of reptation and micellar breakage for all wormlike micellar solutions studied in this work.

Based on Cates’ theory, if the reptation is the dominant relaxation mechanism, the reptation time scale is almost equal to the longest relaxation time estimated from linear rheology $\lambda \approx \lambda_{\text{rep}}$ (Eq. (13) in [24]). However, in the fast-breaking limit (when $\lambda_{\text{br}}/\lambda_{\text{rep}} \ll 1$), these time scales are related as $\lambda \approx (\lambda_{\text{rep}} \times \lambda_{\text{br}})^{0.5}$ [24]. The breakage time of the wormlike micelles can be estimated from linear viscoelastic data. According to Yesilata et al. [25] and Miller and Rothstein [26], the critical frequency at which the loss modulus shows a “dip” can be used to determine the breakage time of the micelles. For wormlike micelles with $R = 0.74$, we cannot identify a dip in the loss modulus data [see Fig. 1(b)]. However, for solution with $R = 0.75$, the breakage time can be estimated and is about $\lambda_{\text{br}} = 0.25$ s. Similar analysis yields a $\lambda_{\text{br}} = 0.46$ s for solution with $R = 0.82$. For the solution of $R = 0.82$, we use the following relation: $\lambda = (\lambda_{\text{br}} - \lambda_{\text{rep}})^{0.5}$ to estimate the reptation time [24]. This analysis produces a $\lambda_{\text{rep}} \sim 1304$ s for $R = 0.82$. On the other hand, for the solution of $R = 0.75$, if we consider $\lambda \approx \lambda_{\text{rep}} \sim 1304$ s (see Table I), we can readily observe that $\lambda_{\text{br}} < \lambda_{\text{rep}}$. Hence, we expect that for both solutions with $R = 0.75$ and $R = 0.82$ micellar breakage to be significant in sphere sedimentation experiments.

An alternative way to evaluate the possibility of the micellar breakage in the above systems is through extensional measurements performed via CaBER and DoS techniques. This is particularly useful for solution of $R = 0.74$, where a breakage time cannot be determined from linear viscoelastic rheology data. Capillary breakup extensional experiments [shown in Fig. 2(a)] indicate that the extensional relaxation times for all wormlike micellar solutions are generally smaller than the shear relaxation times. Note that for Boger fluids (polymers), the ratio of the extensional relaxation time to the shear relaxation time is around unity [27]. Therefore, even the wormlike
micellar solution of $R = 0.74$ does not behave like polymers in the extensional flow. A time ratio ($\lambda_{G}/\lambda$) smaller than unity implies that the equilibrium structure of the wormlike micelles may have been modified in experiments with CaBER. Wormlike micelles with shorter chain length should produce shorter relaxation times. Therefore, it is possible that wormlike micelles may have experienced flow induced micellar breakage in experiments with CaBER. This may not be surprising because in CaBER experiments the wormlike micellar solution is subject to a strong and sudden step-strain at the beginning of the experiments, and this step-strain together with the strong extensional field may cause wormlike micelles to break. To confirm this hypothesis, we performed extensional experiments on all three wormlike micellar solutions using the DoS technique [see Fig. 2(b)]. As described above, in DoS experiments, the fluid filament undergoes a thinning process similar to the CaBER experiments. However, wormlike micelles do not experience a strong initial step-strain in DoS experiments. Thus, if there exists any micellar breakage in measurements with CaBER, it should be less significant in experiments with the DoS device. Less micellar breakage in extensional flow should yield an extensional relaxation time closer to the shear relaxation time. In fact, data in Table I indicate that the extensional relaxation time measured in DoS experiments is generally larger than the counterparts measured by CaBER. Therefore, this result confirms our hypothesis that even wormlike micelles that follow a multimode Maxwell model ($R = 0.74$) are prone to exhibit micellar breakage in extensional flows. Thus, in the wake of a falling sphere, where the extensional flow is strong, the micellar breakage likely occurs in all solutions tested in this study.

We also note that the above comparison between DoS and CaBER techniques is consistent with the previous results obtained by Miller et al. [28]. Miller et al. showed that the magnitude of the step-strain in CaBER experiments can dramatically lower the extensional relaxation time of the wormlike micelles, while it has no effects on properties of the polymer solution. This implies that micellar chain scission may have occurred in their experiments. This is consistent with our observations that DoS should produce a larger extensional relaxation time than experiments with the CaBER device.

Although based on the above analysis, the micellar breakage should occur in the solutions with multimode Maxwell relaxations, we do not report sphere instability in these solutions. The lack of sphere instability in these systems indicates that in addition to micellar chain scission, the relaxation spectrum of the micelles may have affected the sphere sedimentation dynamics in wormlike micelles. In the following, we will invoke a criterion based on the ratio of stored elastic energy ($G'(\omega)$) to the dissipated energy ($G''(\omega)$) as [13,29]

$$Q = \frac{G'(\omega)}{2G''(\omega)}.$$  

Graessley and Milner showed that the oscillation time scale ($\tau$) for a viscoelastic liquid after imposing a step shear is directly related to the quality factor $\tau \approx Q$. They showed that the quality factor is very high [$\sim O(10^3)$] for systems that follow a single-mode Maxwell model. However, for polymeric systems with a broad distribution of relaxation times, the quality factor is close to unity $O(1)$.

Fluctuations in sphere sedimentation velocity in wormlike micelles could also be linked to the quality factor [i.e., the ratio of $G'(\omega)$ and $G''(\omega)$]. To test this hypothesis, we have plotted the quality factor for all wormlike micellar solutions tested here, and the ones used before in sphere sedimentation experiments. Figure 7 shows the quality factor ($Q$) as a function of dimensionless frequency for wormlike micellar solutions used in sphere sedimentation experiments [4,6,15]. At low frequencies, the loss modulus is larger than the storage modulus; therefore, the quality factor is smaller than unity. As angular frequency increases, the quality factor increases until it reaches a maximum value. It is interesting to note that the quality factor for the wormlike micellar solutions based on CPCl/NaSal ($R = 0.74$ and $R = 0.75$) is smaller than that for all other wormlike micellar solutions that follow a single-mode Maxwell model. If we define a maximum quality factor for all wormlike micelles as $Q_{\text{max}}$, a clear transition from steady to unsteady sphere sedimentation behavior can be identified for $Q_{\text{max}} \geq 2$.

![FIG. 7. Quality factor as a function of dimensionless frequency for a library of wormlike micellar solutions used in sphere sedimentation experiments. The empty symbols show the wormlike micellar systems that experience no sphere instability. The gray dashed line shows the transition from steady to unsteady sphere sedimentation behavior.](image-url)
Although fluctuations in sphere velocity (or the velocity of the wormlike micelles around the sphere) are random [see Fig. S2(a)], a small quality factor (i.e., dissipated energy > stored elastic energy) means that any potential fluctuations in velocity of the wormlike micelles around the sphere are quickly damped out for the CPCl/NaSal system with R = 0.74 and R = 0.75. However, for other wormlike micelles that have larger quality factors (or equivalently a single-mode relaxation spectrum), one fluctuation cycle in wormlike micellar velocity may not subside quickly, and may even trigger more fluctuations as the sphere falls in the wormlike micelles. This approximate analysis provides a criterion that relates the micellar relaxation spectrum to the dynamics of the sphere sedimentation in wormlike micelles. Therefore, in studies that involve motion of a sphere in wormlike micelles, in addition to micellar chain scission, one should consider the effect of micellar relaxation spectrum.

**C. Flow induced birefringence**

As noted before, Binous and Phillips have also recovered a time-periodic sphere sedimentation behavior in a model viscoelastic fluid using a FENE dumbbell model at high Deborah numbers (De ≈ 6). According to Binous and Phillips, the sphere instability is related to the formation of gradients in dumbbell extensions on sphere sideways. It is possible that a similar phenomenon could exist in the flow of the wormlike micellar fluids past a falling sphere. To evaluate the degree of orientation of the wormlike micelles around the falling spheres, we employed FIB technique with a 45°/135° arrangement for the crossed polarizers. With this arrangement, the extensional and/or compressional flows around the sphere are highlighted. Figure 8(a) shows the intensity of the white light source passing through the crossed polarizers as the sphere falls with an unsteady velocity at De = 42.8 in the wormlike micellar solution with R = 0.82. Different snapshots correspond to different instances in time (i: before acceleration, ii: when sphere reaches its maximum falling velocity, and iii: during the decelerating stage). The extensional flow is clearly dominant in the wake of the sphere, and on sphere sideways (here left and right sides of the sphere) a clear zone with a strong extensional flow can be identified.

![Birefringence pattern for a falling sphere in the CPCl/NaSal solution with R = 0.82 during the instability. (b) Light intensity along the red line for three different instances in sphere sedimentation shown in part (a). The intensities at (ii) and (iii) are shifted 60 and 120 units for visual clarity.](image)

**Wormlike micelles tend to orient themselves in the direction of the flow and therefore, for regions that are highlighted as bright, we expect highly oriented wormlike micelles in the direction of the sphere motion. Hence, any potential gradients in the micellar velocity may not subside quickly, and may even trigger more fluctuations as the sphere falls in the wormlike micelles.**

**V. CONCLUSIONS**

Harking back to the motivation of this study, we studied dynamics of a falling sphere in three wormlike micellar solutions that are best described by a single-mode, 7th mode and 4th mode Maxwell models. Our results indicate that in the wormlike micelles with a single-mode relaxation time, spheres exhibit instabilities for DeE ≥ 2.6. However, for equally high or stronger extensional flows (2.5 ≤ DeE ≤ 40.7), spheres in wormlike micelles that follow a 7th or a 4th mode Maxwell models. Our results indicate that in the wormlike micelles with a single-mode relaxation time, spheres exhibit instabilities for DeE ≥ 2.6. However, for equally high or stronger extensional flows (2.5 ≤ DeE ≤ 40.7), spheres in wormlike micelles that follow a 7th or a 4th mode Maxwell model do not show any signs of instabilities. In addition, a phase diagram based on extensional Deborah number and Reynolds number does not allow us to distinguish the steady and unsteady results in these three solutions for a wide range of flow parameters. Although all these wormlike micellar solutions are likely to experience micellar chain breakage in extensional flows, we did not report sphere instability in solutions that follow multiple-mode Maxwell models. Therefore, in addition to micellar breakage, micellar
relaxation spectrum will affect the sphere sedimentation dynamics in wormlike micelles.

The effect of micellar relaxation spectrum can be described by invoking a criterion based on the maximum quality factor (i.e., the ratio of stored elastic energy to the dissipated energy). For wormlike micelles that follow a single-mode Maxwell relaxation, the maximum quality factor is generally larger than a critical threshold ($Q_{\text{max}} \geq 2$). However, for the systems with a broad distribution of relaxation times (i.e., $R = 0.74$ and $R = 0.75$), the maximum quality factor is below this critical threshold. This indicates that in addition to the micellar chain scission, the micellar relaxation spectrum can affect the sphere sedimentation dynamics in wormlike micelles.

Finally, we examined the role of gradients in micellar extensions on sideways of the spheres for conditions that give rise to unsteady sedimentation, and found no evidence of asymmetry in the light intensity (therefore, micellar extensions) on the flanks of the sphere orthogonal to the direction of sphere motion. We hope that this study helps stimulate future theoretical analysis on sphere sedimentation dynamics in wormlike micelles where the role of inertia, elasticity, micellar breakage, and relaxation spectrum can be investigated.

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References

[30] See supplementary material at https://doi.org/10.1122/1.5031899 for calculation of shear thinning index and the particle tracking velocime-try results for sample experiments.