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Rheology of Suspensions of Rodlike Particles

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Suspensions of rigid rodlike particles in Newtonian suspending fluids are considered. We discuss the dependence of the relative viscosity μ_r upon the volume fraction of particles ϕ, their aspect ratio a_r, and the particle orientation distribution when the particles are sufficiently large that hydrodynamic forces are dominant. Theoretical results are reviewed for a variety of long slender particles. Experimental results obtained using classical rheometrical techniques are discussed. It is shown that when $a_r \leqslant 25$, data from several laboratories agree and they indicate that μ_r depends more strongly upon ϕ than a_r. Previous experimental results using falling ball rheometry are discussed as well as some more recent findings. These are shown to provide insights heretofore unavailable into the macroscopic rheology of suspensions of randomly oriented and oriented rods.

KEY WORDS: Rheology; rods; viscosity; aspect ratio; suspension.

1. INTRODUCTION

This paper focuses on measurements of the rheological or flow properties of suspensions of rigid rodlike particles in Newtonian suspending fluids. We are principally concerned with suspensions having particles sufficiently large that hydrodynamic forces dominate, as specified by the rotary Peclet number $N_{\mathrm{Pe}} = \dot{\gamma}/D_r \gg 1$, where $\dot{\gamma}$ is a characteristic shear rate of the flow and D_r is the rotary Brownian diffusion coefficient. The particle Reynolds number will always be sufficiently small that inertial effects can be neglected, $N_{\mathrm{Re}} = \rho\dot{\gamma}d_p/\mu_s \ll 1$, where ρ is the fluid density, d_p is a characteristic particle dimension, and μ_s is the viscosity of the suspending fluid.

Typical suspensions which fall into these categories consist of short glass or graphite fibers in a high-viscosity silicone oil, or, at the early stages of curing, an epoxy resin. Such suspensions can exhibit strong

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nonlinear behavior. For example, using classical rheometrical techniques for determining the shear viscosity often gives rise to a nonlinear shear stress versus shear rate relationship which can be interpreted in terms of a shear thinning viscosity.[22,39] Rod climbing,[2] associated with normal stresses in viscoelastic fluids, is sometimes observed for suspensions of high-aspect-ratio particles in a Newtonian fluid. The recent work of Lipscomb *et al.*[37] on entry flows also shows that small amounts of high-aspect-ratio particles have a large effect on the flow field.

A primary interest in both theoretical and experimental rheology is the determination of the shear viscosity μ. For suspensions in a Newtonian fluid, the relative viscosity $\mu_r = \mu/\mu_s$ is usually taken as the characteristic material property.[31] A suspension of uniform particles has a relative viscosity which depends upon the detailed geometrical description of the particles,[14] their orientation distribution, as well as the volume fraction of particles ϕ. This reduces to a dependence upon ϕ only in the case of spherical particles.

We shall consider the two most widely studied elongated particles: prolate ellipsoids, having a major axis of length $2b$ and a minor axis of length $2a$; and, rods having length L and diameter d. Each particle is characterized by its aspect ratio, $a_r = b/a$ or L/d. These particles are considered as slender bodies when $\varepsilon = \{\ln 2a_r\}^{-1} \ll 1$, which, if $a_r \approx 11{,}000$, is about 0.1. We restrict our attention to suspensions in which $\dot{\gamma} \gg D_r$, with $D_r = kT/(6\mu_s V_p\, {}^rK_\perp)$, where k is Boltzmann's constant, T is the temperature, V_p is the particle volume, and ${}^rK_\perp$ is a geometrical constant.[14] For blunt-ended (rodlike) bodies[14,28]

$$ {}^rK_\perp = \frac{2}{9}\left\{\frac{a_r^2}{\ln a_r}\left[1 - \frac{0.307}{\ln a_r}\right] + 0.651\right\} $$

while for long, thin, prolate ellipsoids,[14]

$$ {}^rK_\perp = \frac{a_r^2}{3(\ln 2a_r - 0.5)} $$

Section 2 provides a brief review of the theoretical work relevant to the prediction of the relative viscosity of suspensions of elongated particles. When hydrodynamic forces are dominant, theoretical difficulties arise in the calculation of μ_r which make the problem indeterminate and necessitate

[2] Rod climbing refers to an experiment in which a solid cylinder is rotated at a constant angular velocity about its axis of revolution in a suspension. The stresses generated in suspension cause it to climb up the rod, as opposed to being moved away from the cylinder due to centripetal forces.

the introduction of rotary Brownian forces. Although suspensions in which hydrodynamic forces dominate are the principal focus of this work, we include a broader set of results which are necessary to critically evaluate experiments. More complete reviews of the theories may be found elsewhere (e.g., see refs. 2, 8, 14, and 35). We discuss one problem in which when only hydrodynamic forces are present, a determinate form of the extra stresses due to the presence of the particles can be calculated, namely, uniaxial extensional flow. We mention a new theoretical approach which allows momentum transport to be calculated in suspensions of slender fibers even when $N_{\mathrm{PE}} \gg 1$. Not covered in this review, but worthy of note, is the recent use of liquid crystal-type continuum models to describe the flow of fiber suspensions.[3,37]

Section 3 discusses available experimental results and presents some new findings by Ganani[23] and Morrison.[48] Section 3.1 is concerned with the determination of the shear viscosity and the effect of the particle geometry and concentration. We demonstrate that agreement is emerging among various laboratories on the effect of ϕ upon μ_r for low-aspect-ratio particles. We provide a summary of evidence for the relationship between the suspension microstructure and macroscopic stresses, as reflected by the transient stresses observed upon the inception of shearing flow. Section 3.2 briefly deals with experimental results for the extensional (Trouton) viscosity in light of the recent theory of Acrivos and Shaqfeh.[1] Lastly, Section 3.3 summarizes the findings made with my co-workers[25,43,46,53] using falling ball rheometry.[45] We show that this technique can be used to determine the viscosity of both randomly oriented and oriented suspensions.

2. THEORETICAL RESULTS

Investigations of the mechanics of suspensions of elongated particles began with Jeffrey's[30] calculation of the disturbance flow produced by a neutrally buoyant, isolated ellipsoidal particle in an unbounded linear flow. Specializing his results to shearing flow, having Cartesian components $(\dot{\gamma}x_2, 0, 0)$, such a particle is found to rotate periodically in Jeffrey orbits which depend uon the particle's geometry and its initial orientation relative to the flow. For an ellipsoid of revolution (spheroid) the period is given by

$$T_{\mathrm{J}} = \frac{2\pi(a_r + a_r^{-1})}{\dot{\gamma}} \tag{1}$$

Blunt-ended bodies also execute Jeffrey orbits; however, their periods of rotation are not given directly by Eq. (1). Rather, an equivalent aspect ratio

$$a_{re} = \frac{1.24 a_r}{(\ln a_r)^{1/2}} \tag{2}$$

is defined.[16] To calculate the period of rotation, L/d is measured and used in Eq. (2) to calculate a_{re}, which is inserted in Eq. (1).

Jeffrey wished to determine the viscosity increase due to the presence of hydrodynamically isolated nonspherical particles. In the context of suspension rheology, this amounts to determining $[\mu]$, the intrinsic viscosity, which for a dilute suspension ($\phi \to 0$) is related to μ through

$$\mu = \mu_s(1 + [\mu]\phi) \tag{3}$$

However, the rotations of the particles rendered his energy dissipation calculation indeterminate: rather than $[\mu]$ being a constant, it is time dependent, reflecting the instantaneous particle orientation, and dependent upon the initial particle orientation. The minimum $[\mu]$ for some particles can be less than 2.5, the value for spheres.[19] Jeffrey[30] discussed mechanisms by which this indeterminate problem could be made theoretically determinate, including: (1) using an averaging scheme over a population of randomly oriented particles, and, (2) speculating that inertia might cause all particles to drift toward a specific orientation which is stable. In most suspensions, inertia does not operate on a time scale sufficiently small to make its practical observation possible. The former view was taken by Simha,[59] who calculated the excess power dissipation associated with maintaining a suspension randomly oriented while it undergoes shearing flow and thereby obtained $[\mu]$ for prolate and oblate ellipsoids. Simha's intention was to calculate the viscosity of a suspension subject to strong Brownian forces. However, his technique accounts for Brownian forces in an *ad hoc* way, rather than using a conservation law for the orientation distribution function and directly inserting the Brownian diffusion term including the direct Brownian contribution. This was recognized by Kirkwood and co-workers[54] and Saito.[55] Saito[55] and Scheraga[56] developed theories which correctly accounted for rotary Brownian forces in suspensions of spheroidal particles; however, both obtained the same algebraic relationship between $[\mu]$ and a_r as Simha.[59] Haber and Brenner[26] were the first to resolve this paradox by showing that Simha's theory assumes that: (i) the particle angular motions are not determined by Jeffrey's hydrodynamical analysis, but rather, the particles rotate with the local angular velocity of the fluids; and (ii) the direct Brownian contribution to the stress is zero. The contributions to the bulk stress due to each of these factors were shown by Haber and Brenner[26] to be first order. However, they cancel exactly when the particles are bodies of revolution, such as rods or prolate ellipsoids. This cancellation renders Simha's formula fortuitously correct for suspensions of particles subject to strong Brownian motion. It might somewhat more accurately be cast as a formula for a suspension of rods which maintains a random orientation distribution in shearing flow—by whatever means. For large aspect ratios, this theory,[59] as well as the correctly formulated theories for suspensions subject to strong Brownian motion by Saito[55] and Scheraga,[56] yields

$$[\mu] = \frac{a_r^2}{15(\ln 2a_r - 3/2)} + \frac{a_r^2}{5(\ln 2a_r - 1/2)} + \frac{14}{15} \tag{4}$$

The intrinsic viscosity for suspensions of randomly oriented, long, slender, rodlike bodies is

$$[\mu] = \frac{4a_r^2}{15 \ln a_r} \tag{5}$$

which, when blunt ends are added, becomes more complicated and will not be given here.[14] The difference between the predictions for two types of particles can be large, as demonstrated by the following examples:

$a_r = 19.8$[25,43]

prolate ellipsoids: $[\mu] = 44.8$ blunt-ended rods: $[\mu] = 29.2$

$a_r = 48.9$[42]

prolate ellipsoids: $[\mu] = 170$ blunt-ended rods: $[\mu] = 121$

Strong Brownian forces are not necessary to eliminate the indeterminacy in the calculation of $[\mu]$. When either $(a_r^3 + a_r^{-3}) \ll N_{\text{Pe}}$ or when $1 \ll N_{\text{Pe}} \ll (a_r^3 + a_r^{-3})$ and $a_r \to \infty$, Hinch and Leal[27] showed

$$(a_r^3 + a_r^{-3}) \ll N_{\text{Pe}}: \qquad [\mu] = 0.315 \frac{a_r}{\ln a_r} \tag{6a}$$

$$1 \ll N_{\text{Pe}} \ll (a_r + a_r^{-1})^3: \qquad [\mu] = N_{\text{Pe}}^{-1/3} \frac{0.5a_r^2}{\ln a_r} \tag{6b}$$

In the complete absence of Brownian forces, the stress in a suspension of rods is determinate for flows in which the induced macroscopic particle motion does not include a rotational component. In one such flow, uniaxial extensional flow, large elongated particles will, at steady state, align along the extensional axis and thereby produce a constant orientation distribution. The Cartesian components of the undisturbed velocity are $(\dot{\varepsilon}x_1, -\frac{1}{2}\dot{\varepsilon}x_2, -\frac{1}{2}\dot{\varepsilon}x_3)$, where $\dot{\varepsilon}$ is the extensional rate, and x_1 is the extensional axis. The stresses in this flow are characterized by the extensional or Trouton viscosity μ_T, which for a Newtonian fluid is three times the shear viscosity. Using slender-body theory, Batchelor[6,7] first calculated the relative Trouton viscosity μ_{T_r} for a suspension of completely aligned rods. His results are valid for both dilute and concentrated suspensions, as characterized by an average interparticle spacing $h=(nL)^{-1/2}$, where n is the number density of rods. A dilute suspension has $L/2h \ll 1$ [or $\varepsilon n(L/2)^3 \ll 1$] and

$$\mu_{T_r} = 1 + \frac{2\phi\varepsilon a_r^2}{9}\left(\frac{1+0.64\varepsilon}{1-1.5\varepsilon} + 1.659\varepsilon^2\right) \tag{7a}$$

whereas, in a concentrated suspension $d \ll h \ll L$, and

$$\mu_{T_r} = 1 + \frac{4\phi a_r^2}{9\ln(\pi/\phi)} \tag{7b}$$

The effective medium theory of Acrivos and Shaqfeh[1] has recently been used to calculate μ_{T_r}. Their theory holds for particles having $a_r^{-1} \ll 1$ and over the concentration range $\phi \ll a_r^{-2}$ (dilute) to $1 \gg \phi \gg a_r^{-2}$ (concentrated), and hence has broader applicability than the cell model used by Batchelor.[7] For concentrated suspensions they obtain a formula identical to Eq. (7b), except that the factor of π/ϕ is replaced by $6/\phi$. A highly promising approach to the study of suspensions of fibers has been pursued by Shaqfeh and Fredrickson,[58] who have examined heat,[57] mass,[20] and momentum transport.[58] In this last case, they calculated the relative viscosity in aligned and randomly oriented suspensions through the semidilute range [as defined by $n(L/2)^3 \gg 1$ and $nd(L/2)^2 < 1$]. For dilute suspensions, their results correspond with Batchelor's.[7] To first order, semidilute suspensions are found to behave similarly, regardless of whether the particles are randomly oriented or completely aligned. To $O(1/\ln^2(1/\phi))$, these results are summarized as follows:

Slender Cylindrical Fibers

$$\mu_r - 1 = \frac{\pi n L^3}{3\ln(1/\phi)}\left\{1 - \frac{\ln\ln(1/\phi)}{\ln(1/\phi)} + \frac{0.6634}{\ln(1/\phi)}\right\} \quad \text{(random)} \tag{8a}$$

$$\mu_r - 1 = \frac{\pi n L^3}{3[\ln(1/\phi) + \ln\ln(1/\phi) + 0.1585]} \quad \text{(aligned)} \tag{8b}$$

Slender Ellipsoids

$$\mu_r - 1 = \frac{\pi n L^3}{3 \ln(1/\phi)} \left\{ 1 - \frac{\ln \ln(1/\phi)}{\ln(1/\phi)} - \frac{0.6170}{\ln(1/\phi)} \right\} \qquad \text{(random)} \qquad (9a)$$

$$\mu_r - 1 = \frac{\pi n L^3}{3[\ln(1/\phi) + \ln \ln(1/\phi) + 1.4389]} \qquad \text{(aligned)} \qquad (9b)$$

3. EXPERIMENTAL RESULTS

3.1. Shearing Flows

There has been considerable effort to obtain unambiguous measurements of the shear viscosity of suspensions of rodlike particles in order to provide the same level of understanding that exists for suspensions of spherical particles, at least at low to moderate volume fractions.[3] In an early review(39) large scatter in the data from laboratory to laboratory caused any correlation attempt to fail. A later effort(22) apparently succeeded in this regard, although Ganani and Powell(23) subsequently noted this was likely fortuitous. There are no quantitative measurements which clearly delineate the effect of aspect ratio and volume fraction on the relative shear viscosity of suspensions of rods in a Newtonian fluid, that is, $\mu_r(a_r, \phi)$. In this section, we discuss some of the more recent results for measurements in shearing flows.

Recent experimental results(9,23,28,29) have shown that fiber suspensions in Newtonian fluids cannot be characterized solely by their steady-state shearing response. The transient shearing response, that is, the development of the stresses in the fluid after the imposition of shearing flow, must also be considered. In a dilute suspension, this response is well-defined. Rods which are initially aligned will, upon imposition of shearing, rotate in their Jeffrey orbits, causing periodic stresses.(28,29) Figure 1 demonstrates such behavior. Here μ_{sp}/ϕ versus $t\dot{\gamma}(a_r + a_r^{-1})^{-1}$ is plotted for various values of the volume concentration. The time axis is nondimensionalized by the time scale associated with a single-particle Jeffrey orbit. In all cases, the time-dependent viscosities (or transient shear stresses) are periodic with a decaying amplitude. This decay can result from several sources. Okagawa *et al.*(51) showed theoretically that slight aspect ratio variations can result in a decay time scale of $\tau_\sigma = a_r^\sigma f_1(\bar{a}_r)\dot{\gamma}^{-1}$, where a_r^σ is the

[3] Jeffrey and Acrivos(31) provide an excellent review of the rheology of suspensions of spherical particles, although, since their review, simulation studies(13) and the elucidation of effects associated with shear-induced migration(36) have led to reinterpretation of many of the earlier results.

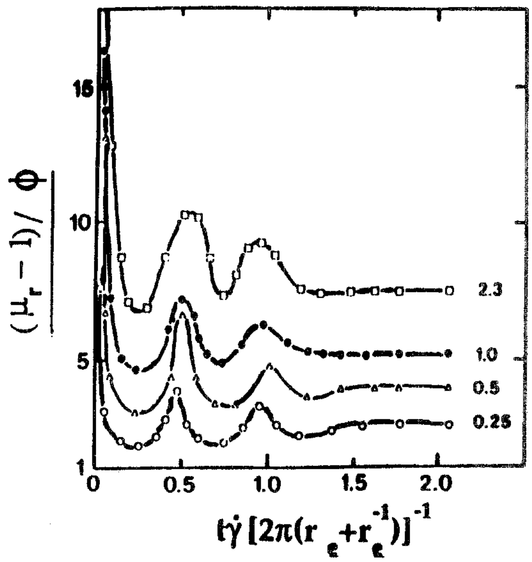

Fig. 1. The time-dependent specific viscosity (μ_{sp}/ϕ) for suspensions of rods ($\bar{a}_r = 5.2$, $a_r^\sigma = 0.9$, $\dot\gamma = 2.51$ sec^{-1}) of various volume percents. The rods are initially aligned and shearing is initiated at $t/T_J = 0$. (Reprinted from Ivanov *et al.*[28] Copyright 1982 *J. Rheol.*).

standard deviation in the mean aspect ratio distribution $\bar{a}_r$, and $f_1(\bar{a}_r) = (\bar{a}_r^2 + 1)^2/(\sqrt{2}\,|\bar{a}_r^2 - 1|)$. For $\bar{a}_r = 5.2$ rods, $\tau_\sigma = 0.78 T_J$, where T_J is the mean period of rotation. This provides a reasonable estimate for the decay times indicated by the data in Fig. 1. A second mechanism, two-body interactions with the associated time scale $\tau_\phi = (\dot\gamma^{-1} \ln a_r)/nL^3$,[51] was observed at the higher concentrations. Two other mechanisms could possibly account for the stress decay: weak Brownian motion[27] and particle inertia. However, in the experiments in Fig. 1, decay due to weak Brownian motion, which scales as D_r^{-1}, is negligible. Likewise, Reynolds numbers are very small, and inertial effects can be ignored.

Transient effects at higher volume fractions have been examined by Ganani,[22] Ganani and Powell.[23] They showed that semiconcentrated suspensions of nearly monodispersed short glass fibers ($\bar{a}_r = 24.3$, $a_r^\sigma = 11.3\,\%$ of the mean) exhibit shear stress transients qualitatively different from those found by Ivanov *et al.*[28,29] In the initial transient period (that is, those transient shear stress data taken immediately after loading their rotational viscometer), they observed shear stresses similar to those found for polymeric fluids.[10] Upon inception of shearing, the shear stress grows, reaches a maximum value (*stress overshoot*), and then decays to a final steady state. Depending upon the shearing histories, more complicated

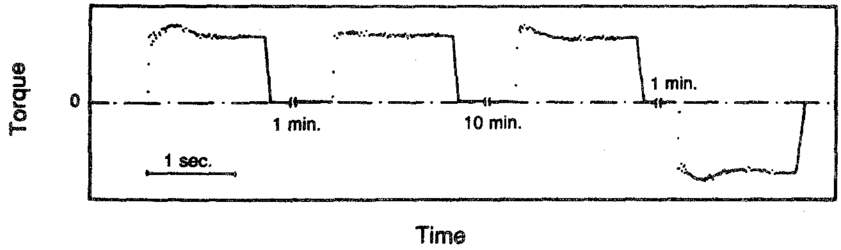

Fig. 2. The effect of intermittent shearing on the torque (shear stress) obtained while shearing ($\dot{\gamma} = 43.7\ \mathrm{sec}^{-1}$) a suspension ($\phi = 0.08$) of fibers ($\bar{a}_r = 24.3$) in a cone and plate viscometer (75 mm diameter, 1° angle). The sample is initially loaded in the viscometer and shearing in the clockwise direction is initiated. Shearing is then stopped and the sample is allowed to rest for 1 min before being resumed in the same direction. Next, shearing is stopped and the sample rests for 10 min. In the final sequence, after allowing the sample to rest for 1 min, shearing is resumed, but in the counterclockwise (reverse) direction.

behavior was also found. In the experiment shown in Fig. 2 the suspension is initially sheared in the clockwise direction, and a stress overshoot observed. Shearing is then stopped and resumed after 1 min, with no overshoot being observed. Indeed, the stress response is instantaneous, reflecting Newtonian fluid behavior. Upon cessation of shearing, waiting for 10 min, and then resuming shearing in the same direction, a shear stress overshoot is again observed similar to that found in the first experiment. It appears that the particles tend to rerandomize during extended periods at rest. Because of the size of the particles used ($D_r = 3 \times 10^{-11}\ \mathrm{sec}^{-1}$), slight sedimentation is the only possible mechanism. The last sequence in Fig. 2 shows the effect of reversing the flow after letting the suspension rest for 1 min. A transient period is observed, including a stress overshoot, prior to reaching steady state. The suspension assumes a new microstructure on a time scale similar to that found in the first and third experiments. This behavior corresponds to that found in highly concentrated suspensions of spherical particles.[(21)] However, while later work[(36)] has shown that shear-induced migration may be responsible for the behavior found by Gadala-Maria and Acrivos,[(21)] it is unlikely that such a mechanism is dominant here. Rather, we expect that network structures, formed upon loading the suspensions or as a result of slight sedimentation during periods of resting, give rise to the observed transients. It would also seem likely that shear-induced diffusion in suspensions of high-aspect-ratio particles would likely act on a time scale different from that found for spherical particles.

From the transient studies we see that for sufficiently long times, an equilibrium orientation distribution is obtained which allows a steady shear viscosity to be measured. If no randomizing influences are present, the equilibrium distribution should be the same in all shear flows, and, in principle, $\mu_r(a_r, \phi)$ can be determined. This appeared feasible using the data available prior to 1985,[23] at least for semiconcentrated suspensions, which were previously defined as having $a_r^{-2} < \phi < a_r^{-1}$. However, most of these data, particularly for aspect ratios of 100 or greater, exhibited shear thinning behavior, implying the existence of a time scale which characterizes the onset of such behavior. The only two time scales which were operative in most suspensions were τ_ϕ and τ_σ, both of which are proportional to $\dot{\gamma}^{-1}$. Using such time scales reduces all of the data for a particular suspension to a single vertical line (on a relative viscosity versus dimensionless shear rate plot) and hence, would not supply the appropriate scaling. Most existing data, particularly those at higher aspect ratios, therefore include some experimental artifacts which make their use in obtaining a master curve for $\mu_r(a_r, \phi)$ questionable. At lower aspect ratios, say $a_r \leqslant 25$, the available data are consistent with the notion that suspensions in Newtonian fluids should, under steady shearing conditions, themselves be Newtonian.[9,23,28,33] There appear to be particle boundary interaction effects at the higher aspect ratios (despite claims that such effects should not be significant when the ratio of the characteristic viscometer gap to particle length is greater than 1.2,[9] or persistent transient effects. It is unlikely that slight shear thinning in the suspending fluid causes shear thinning in the suspensions.[40] At high shear rates, suspensions of spheres in Newtonian[15] and slightly viscoelastic[21] fluids can show very slight shear thinning behavior, but not the dramatic effects found in suspensions of rods.

Figure 3 shows a comparison of some of the more recent data for μ_r obtained by three different groups[9,23,28] for low-aspect-ratio particles. The data might best be considered in two sets: particles having $a_r = 17$ and 24.3, and particles having $a_r = 5.2$ and 6. The data for particles having the higher aspect ratios nearly coincide. However, the lower-aspect-ratio data are dramatically different. In fact, the $a_r = 6$ data of Bibbo *et al.*[9] are generally larger than any of the other data. Ivanov *et al.*'s[28] data[4] roughly coincide with the data for the higher aspect ratios, although the highest volume fractions used by that group was only 0.023. It appears that for small-aspect-ratio particles in the dilute to semiconcentrated regime, the volume fraction primarily influences the relative viscosity, with the effect of aspect ratio being secondary. As discussed below, the relative viscosity of suspensions of randomly oriented rods shows a strong dependence on the aspect ratio as well as the volume fraction. When the rods are aligned, for example, by shearing flow, the effect of aspect ratio diminishes. Such a result is corroborated by the recent experiments of Keville.[33] Using particles

[4] To obtain the actual values, we have used $[\mu] \cong 5$.

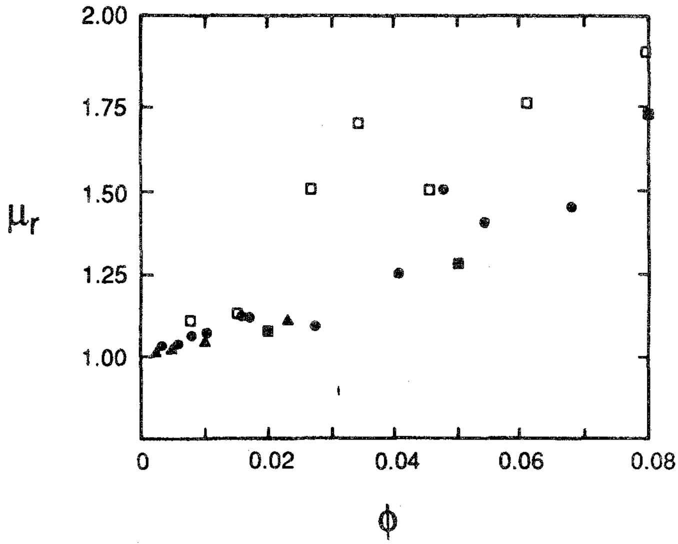

Fig. 3. Relative shear viscosity versus volume fraction for suspensions of rods as measured using rotational rheometers. (▲) $a_r = 5.2$,[28] (□) $a_r = 6$ and (●) $a_r = 17$,[9] (■) $a_r = 24.3$.[23]

having $1 < a_r < 7$ at volume fractions up to 0.12, he found little difference between μ_r for their suspensions and the values which would be expected if the particles were spherical.

3.2. Extensional Flows

The best agreement between rigorous theories[1,7,57,58] and experimental results[34,41,52,63] has been obtained in the case of uniaxial extensional flows. It is assumed that complete fiber alignment can be obtained experimentally. However, recent work of Pittman and Bayram[52] appears to show that such alignment cannot be experimentally realized at high concentrations, where hindered rotation of particles does not allow parallel fiber alignment to be achieved. As predicted, the measured extensional viscosity is independent of the extensional rate, and is considerably higher than the viscosity of the suspending fluid. The measurements of Mewis and Metzner[41] and Pittman and Bayram[52] cover the widest range of aspect ratios and concentrations. Their data and the theories of Batchelor,[7] Acrivos and Shaqfeh,[1] and Shaqfeh and Fredricksen[58] are compared in Table I in terms of α, where $\alpha = (\mu_T - 1)/3\mu_s$. In the latter case, we use Shaqfeh and Fredricksen's[58] results for aligned rods. All three theories match the data of Mewis and Metzner[41] reasonably well. Batchelor's[7]

Table I. Comparison between Extensional Flow Data[41,52] and the Theories of Batchelor,[7] Acrivos and Shaqfeh,[1] and Shaqfeh and Fredricksen[58]

				α (Theoretical)		
Reference	a_r	ϕ	α (Measured)	ref. 7	ref. 1	ref.58
Mewis and Metzner[41]	282	0.00930	51	56.5	50.8	51.5
	586	0.00099	17.5	18.7	17.3	16.8
	586	0.00287	74	62.6	57.3	56.3
	586	0.00890	260	231	208	211
	1259	0.00096	59	83.6	77.3	74.8
Pittman and Bayram[52]	54	0.0014	0.35	0.314	0.29	0.28
	54	0.003	0.50	0.746	0.68	0.66
	54	0.009	2.36	2.66	2.40	2.39
	300	0.0004	1.48	1.80	1.68	1.60
	300	0.0005	1.84	2.30	2.14	2.06

theory predicts the data for the $a_r = 586$ suspensions at the highest two volume fractions slightly better than the other two theories. Shaqfeh and Fredricksen's[58] theory is slightly better in the other three cases, and it is almost always better for the data of Pittman and Bayram.[52] This last point is particularly significant, since the theory of Shaqfeh and Fredricksen[58] can be applied to smaller values of a_r^{-1}, such as the $a_r = 54$ found in Pittman and Bayram,[52] than either the theory of Batchelor[7] or Acrivos and Shaqfeh.[1] These very positive comparisons between recent theoretical and experimental studies indicate that our understanding of the extensional flow of fiber suspensions is poised for further advances, with more data being necessary to provide adequate verification of theories.

3.3. Measurements of the Viscosities of Suspensions of Rods Using Falling Ball Rheometry—The Milliken Problem[5]

3.3.1. Viscosity Measurements of Randomly Oriented Suspensions. The measurements and theories described in previous sections assume that suspension properties can be observed on a scale which is large relative to a typical length scale in the suspension. This characteristic length might be related to particle dimensions or interparticle spacing. Suspensions of rods there can possess different interparticle spacings if the rods are aligned[7] or randomly oriented.[17]

[5] As first applied by Prof. Sangtae Kim.

While theories for suspensions of rods are explicit in their use of a particular, e.g., volume, averaging scheme and careful in their definition of the appropriate averaging lengths, the same accuracy of definition cannot usually be found in experiments. The macroscopic shear viscosity must be independent of viscometer geometry, which must be ascertained empirically. An entirely different avenue consists of conducting an experimental program using *ensemble* rather than volume averaging.[7] The ensemble would consist of many realizations of the same macroscopic experiment. In each realization, the suspension experiences the same macroscopic conditions, but the exact locations and orientations of the particles are different.

Recently, my co-workers and I have used the ensemble average approach to determine the macroscopic viscosity of suspensions of rods.[25,42,43,48,53] A *realization* consists in moving a sphere under a constant force through a homogeneous suspension of neutrally buoyant, randomly oriented rods. The terminal velocity is measured and used to calculate the suspension viscosity, over which the ensemble average is taken.

In these experiments, large, macroscopic rods are suspended in a density-matched Newtonian fluid. The suspension is characterized by the aspect ratio of the suspended particles and their volume fraction, and it is stirred prior to each experiment to achieve a new realization. A brass ball bearing sufficiently small so as to only slightly disturb the microstructure is dropped along the centerline of the column. Measurements are made according to the criteria of Sonshine *et al.*[60] to eliminate effects due to the upper liquid free surface and the bottom bounding surface of the glass column. The viscosity is calculated using Stokes' law for the velocity of a sphere moving at zero Reynolds number through a Newtonian fluid under a constant force coupled with the correction for wall effects,

$$\mu = \frac{g\, d_{\text{ball}}^2(\rho_b - \rho)}{18v}\left\{1 - 2.104\,\frac{d_{\text{ball}}}{D_{\text{col}}} + 2.09\left[\frac{d_{\text{ball}}}{D_{\text{col}}}\right]^3 - 0.95\left[\frac{d_{\text{ball}}}{D_{\text{col}}}\right]^5\right\} \tag{10}$$

where ρ_b is the density of the failing ball, d_{ball} is its diameter, and D_{col} is the diameter of the column containing the suspension. Equation (10) is correct to $O(d_{\text{ball}}/D_{\text{col}})^5$ and assumes that the suspension behaves as a Newtonian fluid. It has been verified for suspensions of rods[43,53] and spheres.[45]

For a particular (nominal) size of the test sphere, the viscosities calculated using Eq. (10), μ_i, are ensemble-averaged to obtain the average macroscopic viscosity, that is,

$$\mu_{\text{avg}} = \frac{1}{N}\sum_{i=1}^{N} \mu_i \tag{11}$$

Usually, at least ten realizations must be used before an ensemble is achieved which is independent of the sample size, as measured using a t-test with a 95% confidence interval.

The principal results of the experiments of Milliken *et al.*,[43] presented in terms of $\mu_{sp} = \mu_r - 1$ versus ϕ, are shown in Fig. 4. These were obtained using suspensions of rods having an average aspect ratio of 19.8 and are typical of all results to date.[48] Each symbol in Fig. 4 represents the average of four ensembles (test sphere diameters), each of which was made over about 20 realizations (individual experiments). There are three features of Fig. 4 to note, each of which is consistent with our more recent findings.[48] First, if, on a logarithmic basis, the data for the four lowest volume fractions are fit to a straight line, we find that $\mu_{sp} \propto \phi$. This implies that the suspension is dilute and its viscosity is given by Eq. (3). Second, if the data beyond this dilute regime are again fit to a straight line (using the data for the three highest concentrations) we find that $\mu_{sp} \propto \phi^3$. Lastly, the transition between these two regimes occurs at $\phi = 0.12$. In the remainder of this section, we discuss the implications of each of these findings. Additionally, we shall mention some new results[48] on the effect of the viscometer boundaries.

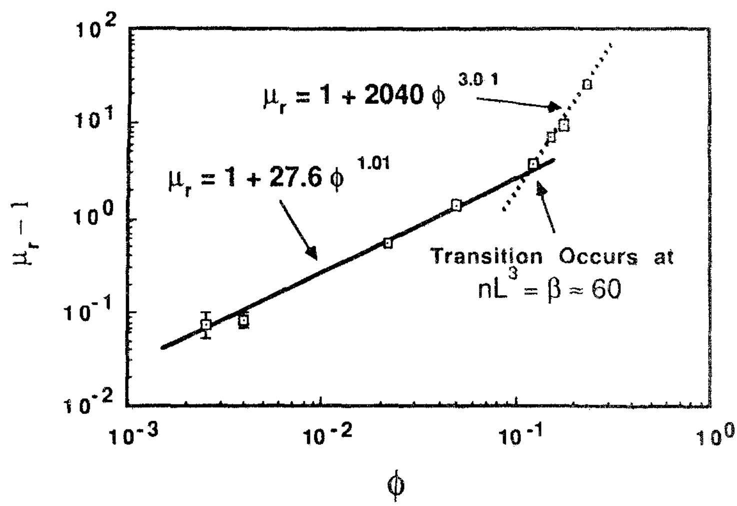

Fig. 4. Specific viscosity versus volume fraction for suspensions of randomly oriented rods ($\bar{a}_r = 19.8$, $a_r^\sigma = 0.73$) as obtained using falling ball rheometry.[44] Each data point represents the results of approximately 80 individual experiments. The error bar is the 95% confidence limit; on each of the other data points, the 95% confidence limit falls within the data point. The solid line is the best fit through the four points having the lowest volume fraction ($\mu_{sp} = 28.5\phi^{1.01}$, $\phi < 0.125$). The dashed line is the best fit through the three points having the highest volume fraction ($\mu_{sp} = 2040\phi^{3.01}$, $\phi > 0.125$).

At first glance, the physical characteristics of these suspensions and the unique nature of the measuring instrument do not allow for comparisons between our results and existing theories. Our suspensions consist of *randomly oriented rods in which Brownian forces are absent.* As discussed previously, when measuring the shear viscosity in a viscometric shearing flow, such rods tend to align along the planes of shear. Ideally, we wish to compare our findings with calculations of the shear viscosity of randomly oriented suspensions, as measured, say, in shearing flow, with the *caveat* that the randomness is not induced by strong Brownian forces. Rather, the randomness must be imposed artificially; which, in essence, is the approach of Simha.[59] By correctly identifying the range of validity of his theory (to bodies of revolution), Haber and Brenner[26] have justified comparing the theoretical value of the shear viscosity for a suspension of rods subject to strong Brownian forces[14] with the results from our experiments, in which the test sphere experiences a suspension of randomly oriented rods dominated only by hydrodynamic forces. The value of $[\mu]$ obtained by Milliken *et al.*[43] is 27.6, while Brenner's theory[14] for blunt-ended rods yields a value of 29.2, a difference of about 5.5%, well within the confidence limits of our data. Subsequent measurements by Powell *et al.*[53] further demonstrated the usefulness of Brenner's theory for predicting the results of falling ball rheometry, although for the $a_r = 10$ rods used in that study, the agreement was only to within about 30%. This might be attributed to the use of slender body theory in obtaining Brenner's results, which should only apply in the limit of large aspect ratio. Recent results of Morrison[48] further support this finding. To carry these arguments one step further and compare the results of the falling ball experiments with viscosities of suspensions of rods subject to strong Brownian motion obtained using conventional rotational viscometers is difficult. The most significant effort to perform such measurements has been that of Keville[33]; however, his particles were of such low aspect ratio ($a_r \leqslant 7$) that the intrinsic viscosity could essentially not be distinguished from the value expected for a spherical particle.

Our findings concerning the form of the μ_{sp} versus ϕ curve at high concentrations and the transition point between dilute and (semi) concentrated behavior do not enjoy the same theoretical justification as the findings in the dilute regime. The $\mu_{sp} \propto \phi^3$ behavior[43,48] is consistent with the theory of Doi and Edwards[17] for solutions of rodlike macromolecules. The relationship for viscosity is obtained using

$$\mu = \mu_s + \frac{nkT}{D_r} \tag{12}$$

where n is the number density of rods, k is Boltzmann's constant, T is temperature, and D_r is the rotary diffusion coefficient. For (semi) concentrated solutions

$$D_r = \frac{\beta D_{ro}}{(nL^3)^2} \tag{13}$$

where β is a constant of order unity[17] and $D_{ro} = (kT \ln a_r)/(3\pi\mu_s L^3)$ is the rotary diffusion coefficient for an isolated rod of high aspect ratio. Combining Eqs. (12) and (13) leads to $\mu_{sp} \propto \phi^3$. Hence, the dependence found by Milliken *et al.*[43] and Morrison,[48] while consistent with the Doi–Edwards formulation, cannot be mechanistically described by it. Rotary diffusion is explicitly required. Furthermore, most experimental verifications of their theory[47,50,64] have come from measurements of the rotary diffusion coefficient rather than viscosity.

The falling ball results are also consistent with the predicted transition concentration between dilute and (semi) concentrated solutions of rodlike macromolecules. This transition is defined in terms of the parameter β, which is the critical value of nL^3 where rods become locked into cages wherein they can only diffuse along their lengths. In the original Doi–Edwards[17] theory, β is a constant of order unity. Subsequent molecular simulations[11,32,38] yield $\beta \approx 50$–70 which is consistent with the falling ball results,[43,48] where $60 \leqslant \beta \leqslant 75$. This apparently shows that the dilute to semiconcentrated behavior results primarily from steric effects rather than hydrodynamic effects.

3.3.2. Viscosity Measurements of Oriented Suspensions. The macroscopic flows of conventional rheometric techniques, based upon viscometry and elongational rheometry, orient the rods in suspension. The falling ball rheometer only disturbs the microstructure slightly, and so provides a measure of the resistance to flow of the microstructure which is induced prior to an experiment. In a recent paper[46] we have determined the viscosities of *oriented suspensions* by falling ball rheometry using rods of a single aspect ratio ($a_r \approx 20$) at two volume fractions, 0.02 and 0.05. The viscosities agreed quite well with the shear viscosity measurements of Ganani and Powell,[23] who conducted shear flow experiments using suspensions of nearly monodispersed glass fibers having nominal aspect ratios of 25. They were also substantially lower than the viscosities of randomly oriented suspensions. At $\phi = 0.02$ the relative viscosity of the randomly oriented suspension was 30% larger than that of the aligned suspension, whereas for the $\phi = 0.05$ suspension, it was nearly 60% larger. Both differences were well above the uncertainties in the measurements and they provide conclusive evidence of the effect of the mean orientation distribution on the net resistance to flow. These results also show the possibility of using falling ball rheometry to determine a wide spectrum of properties in suspensions, including a viscosity tensor for anisotropic suspensions. They appear to contradict the results of Shaqfeh and Fredricksen,[58] who predicted the same viscosity for dilute suspensions of randomly oriented and aligned rods. It is plausible that the falling ball technique, while being a sensitive probe of microstructure, may not yield theoretically well-defined measures of the suspension viscosity of aligned systems. On the other hand, previous theoretical studies have demonstrated that the intrinsic viscosity of suspensions of prolate ellipsoids is significantly lower when weak Brownian forces are present ("aligned") than when the Brownian forces are dominant ("randomly oriented"). This raises the possibility that the results of Shaqfeh and Fredricksen[58] cannot be simply compared with either earlier theoretical or experimental studies.

3.4. Effects of Viscometer Boundaries

As a material property, viscosity must be independent of the rheometer used for its measurement. For suspensions of rods, particularly critical is the ratio of the characteristic length associated with the viscometer to the length of the rod. Ideally, any measurement would be made in a sufficiently large device (e.g., a sufficiently large-diameter capillary, a sufficiently large-gap Couette viscometer) that there is no effect of the bounding surfaces. In a dilute suspension, individual rods could execute their Jeffrey orbits[30] with a period that is unaffected by the boundaries. Mason and his co-workers at McGill University conducted an extensive program aimed at testing the direct applicability of the Jeffrey equations to systems which can be realized in the laboratory. Care was taken to ensure that the typical viscometer gap was at least ten times the particle length.[4,5,24,62] The effect of narrowing the viscometer gap, to determine the range of applicability of Jeffrey's predictions was not explicitly tested, although, in the case of the flow of suspensions through tubes, Goldsmith and Mason[24] observed that when a rod is about one particle length from the wall, the Jeffrey orbit is affected. The only theoretical study to date is that of Ingber,[27] who used the boundary element technique to calculate the period of rotation of a single rod in a simple shearing flow between parallel planes. His preliminary results indicate that Jeffrey orbits can only be roughly maintained when the distance between the planes is more than four times the particle length. At this stage of his work, this appears to be a lower bound, and it is possible that an even larger distance is necessary.

It is more difficult to assess the effect of rheometer boundaries on measurements of shear viscosity. A gap-to-particle length ratio of at least three is usually maintained,[12,23,49] although rheometers have been used with characteristic measuring lengths equal to or less than the particle length.[9] In the former case, it is likely that some effect of boundaries is present, but that it is well within the measurement error. In the latter case, it is possible that the effects of viscometer boundaries are severe. For suspensions of randomly oriented rods, results from recent falling ball rheometry experiments provide the basis for such an assessment. Wall effects[6] can be measured by either maintaining a fixed particle size and varying the diameter of the suspension container D_{col},[44] or by maintaining fixed container dimensions and particle aspect ratio while varying the dimensions of the particles.[48] For particles having nominal aspect ratios of 20, Milliken *et al.*[44] found that if $D_{col}/L \geqslant 3.2$, the measured viscosity was unaffected by the bounding surfaces of the container. When the D_{col}/L was 1.6, a statistically significant decrease of about 24% was observed, which was likely due to orientation of the rods along the axis of the cylinder.

Morrison's results[48] using particles having aspect ratios of 30.7 and 48 corroborate the earlier studies. For $a_r = 30.7$, when $D_{col}/L = 4.7$, $[\mu] = 58.9$, or nearly 30% greater than the value of $[\mu] = 40.8$ when $D_{col}/L = 3.0$. At the higher aspect ratio the measured differences in the intrinsic viscosities is nearly a factor of two. When $D_{col}/L = 3.0$, $[\mu] = 84.0$, while when $D_{col}/L = 4.0$, $[\mu] = 155$. As with Milliken *et al.*[44] for both aspect ratios, viscosities are observed when D_{col}/L is sufficiently small, suggesting that there is boundary-induced orientation.[46]

These results bring into question whether the notion of a macroscopic viscosity can be considered when the characteristic viscometer length is less than three to four times the particle length. In shear viscosity measurements, the induced orientation of the rods results in a different characteristic particle dimension becoming relevant, namely, the particle diameter. Since most experiments are conducted using suspensions of small fibers,[23] these measurements are made with viscometer gaps that are much larger than fiber diameters. The shear viscosity is therefore that of a substantially aligned suspension, which is consistent with the findings of Mondy *et al.*[46] On the other hand, all systematic experiments to date using suspensions that are known to be randomly oriented clearly demonstrate that the small gap in the parallel plate apparatus used by Bibbo *et al.*[9] in their shear inception experiments must result in experimental artifacts. Using gaps, as they did, which are approximately the same size as the particle length cannot result in measurements with randomly oriented suspensions that truly reflect material properties.

[6] By "wall effects" we mean effects due to the hindered particle rotations or induced orientation due to the presence of the container boundaries, not the extra drag experienced by the falling ball due the presence of the container walls, which is always adequately described[25,44,53] by Eq. (10).

4. CONCLUDING REMARKS

Except for some isolated instances, suspensions of rodlike particles have proven to be particularly difficult systems both from the theoretical and experimental standpoints. Recently, experiental results using falling ball rheometry have provided new insights into the macroscopic rheology, elucidating the effects of aspect ratio, volume fraction, and orientation distribution. From the theoretical side, the recent study of Shaqfeh and Fredrickson[58] is the basis for a new line of investigation. It now appears possible to systematically calculate viscosities over a wide range of concentrations for suspensions in which only hydrodynamic forces are present. Other theoretical advancements on the horizon concern the use of "numerical experiments" to stimulate the falling ball studies and applying Stokesian dynamics to suspensions of nonspherical particles.

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