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The viscosity–volume fraction relation for suspensions of rod-like particles by falling-ball rheometry

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The relative viscosities of suspensions of randomly oriented rods in a Newtonian fluid were measured using falling-ball rheometry. The rods were monodisperse and sufficiently large to render colloidal and Brownian forces negligible. Steel and brass ball bearings were dropped along the centreline of cylindrical columns containing the suspensions. The terminal velocities of the falling balls were measured and used to determine the average viscosities of the suspensions. The suspensions behaved as Newtonian fluids in that they were characterized by a constant viscosity. They exhibited a linear relative viscosity–volume fraction relationship for volume fractions less than 0.125, and, for volume fractions between 0.125 and 0.2315, the specific viscosity increased with the cube of the volume fraction. The relative viscosity was found to be independent of falling-ball size for a ratio of falling ball to fibre length greater than 0.3. It was found to be independent of the diameter of the containing cylindrical column for a ratio of column diameter to fibre length greater than 3.2. The value determined for the intrinsic viscosity is in good agreement with theoretical predictions for suspensions of randomly oriented rods.

1. Introduction

When only hydrodynamic forces are present, the macroscopic rheology of suspensions of rods in Newtonian fluids depends upon the volume fraction, ϕ, the particle aspect ratio, a_r, the rod orientations, and their distribution in space. The constitutive relation for a suspension of rods can be anisotropic, time dependent, and sensitive to the initial particle orientation. In this paper, we restrict our attention to the viscosity of homogeneous isotropic suspensions. By isotropic, we mean that the angular distribution of the orientations of the rods is random. The suspensions are composed of non-Brownian, neutrally buoyant, and monodispersed rods in Newtonian fluids. Herein, we report the effect of volume fraction on the relative shear viscosity, μ_r, for a fixed aspect ratio, $a_r = 19.83$.

Most macrorheological studies of suspensions of rods have sought to determine the relative viscosity as a function of volume fraction and aspect ratio. The results of much of this work were recently summarized by Ganani & Powell (1985). In nearly all of the work reviewed in that paper, the rotary Péclet numbers, $Pe = \dot{\gamma}/D_r$ (where

$\dot{\gamma}$ is the shear rate and D_r is the rotary Brownian diffusion coefficient), were quite large ($Pe > 10^6$). Since the Reynolds numbers based on the particles were small and colloidal effects were absent, the macroscopic shear stress should have been linear in the suspending-fluid viscosity and shear rate. However, much of the available data from several laboratories were observed to show nonlinear constitutive behaviour, such as shear thinning, when $a_r^{-2} < \phi < 2a_r^{-1}$. Consequently, it was not possible to define a unique relationship between relative viscosity, volume fraction, and aspect ratio.

Several of the factors that could account for such nonlinear behaviour include fibre flexibility, flow-induced migration, and fibre breakage. These findings led Ganani & Powell (1986) to conduct a study which sought to minimize these effects. They used suspensions of nearly monodispersed glass rods, ($a_r = 25, Pe \gg 1, Re < 1$) in a Newtonian fluid at volume fractions up to 0.08. Using rotational rheometry, the steady shear stress was found to be linear with shear rate. Hence, under carefully controlled conditions, they showed that, potentially, a unique μ_r– ϕ–a_r surface could be defined. They also observed a shear-stress transient upon inception of shearing. The shear stress did not immediately rise to the steady-state value; it rose to a maximum value, then decayed to the steady state. This transient behaviour was qualitatively different from that found in dilute suspensions. The decaying periodic stresses in a dilute suspension observed by Ivanov, Van de Ven & Mason (1982) correspond directly with the Jeffrey orbits executed by individual rods (Jeffrey 1922; Trevelyan & Mason 1951; Okagawa, Cox & Mason 1973).

In our current study, we use falling-ball rheometry to measure the relative shear viscosity of randomly oriented, homogeneous suspensions of rods in a Newtonian fluid. Experimentalists have thus far been unable to measure the viscosity accurately while maintaining a randomly oriented configuration of rods. Viscometric and extensional flows, the usual tools of rheologists, deform the microstructure of the suspension from its initial configuration. For suspensions of non-Brownian rods in Newtonian fluids these standard techniques induce an alignment of the rods. In contrast, a ball falling through the suspension only slightly perturbs the original microstructure of the suspension. Falling-ball rheometry has been shown to provide an accurate, reproducible method for measuring the viscosity of suspensions of spheres (Mondy, Graham & Jensen 1986*a*) and, in a pilot study, of randomly oriented rods (Graham *et al.* 1987). With this technique the initial orientational distribution of the rods can be controlled and fibre-aligning effects of the flow field are minimal. Therefore, it provides a unique tool for measuring the viscosity of suspensions of randomly oriented rods.

Viscosity measurement using falling-ball rheometry is based on Stokes's law for a sphere falling under the influence of gravity in an infinite, inertialess, Newtonian fluid (Batchelor 1967). If, as in our experiments, the fluid is bounded by a cylindrical container, Stokes's law must be modified to account for the additional drag caused by the container boundaries. This effect was analysed by Faxén (1923) and extended to higher order by Bohlin (1960). They showed that, in the limit of zero Reynolds number (based on the falling ball), the shear viscosity, μ, is given by

$$\mu = \left[1 - 2.104\left(\frac{d}{D}\right) + 2.09\left(\frac{d}{D}\right)^3 - 0.95\left(\frac{d}{D}\right)^5 + O\left(\frac{d}{D}\right)^6\right]\left[\frac{d^2(\rho_s - \rho)g}{18v}\right]. \tag{1}$$

Here, d is the diameter of the falling ball, D is the diameter of the cylinder containing the fluid, ρ_s and ρ are the densities of the falling ball and liquid, respectively, g is the acceleration due to gravity, and v is the terminal velocity of the ball along the centreline of the column. Equation (1) implies that for falling-ball experiments conducted using two Newtonian liquids of identical densities with identical balls and cylinders, the viscosity of one liquid relative to the other is

$$\mu_r = \mu_2/\mu_1 = v_1/v_2. \tag{2}$$

In a previous study using falling-ball rheometry (Mondy *et al.* 1986*a*), it was found that a suspension of spheres behaved, on the average, as an equivalent single-phase fluid characterized by a shear viscosity. Wall effects in these suspensions were described by Faxén's formula (1). Hence, the μ_r in (2) was the usual relative viscosity with the subscripts 1 and 2 referring, respectively, to the suspending fluid and the suspension. We shall show that the results for suspensions of rods are consistent with this assumption. Because suspensions are two-phase systems, their viscosities have meaning only in an averaged sense. Since the velocity of a falling ball varies as it interacts with individual rods, it is the velocity averaged over a large number of rod/ball interactions that is used to calculate an average relative viscosity of the suspension.

In the following section, we describe the experimental technique. Section 3 describes results for the relative viscosity as a function of the volume fraction, the dimensionless ball diameter d/D, and the dimensionless column diameter D/L. Following this, we describe the relationship of our experiments to earlier theoretical and experimental results.

2. Experimental

Thermally controlled, cylindrical columns were filled with suspensions of rods in the volume fraction range 0.0025 to 0.2315. A high-speed, digitizing video system was used to record the trajectory of the ball. The terminal velocities of steel and brass balls were measured for various ball sizes and column diameters; these were used to determine the relative viscosities of the suspensions.

2.1. *Suspensions*

The rods were individually cut to a length, L, of 3.165 cm from a 0.1588 cm diameter (nominal) polymethyl methacrylate rod (Thermo Plastics Inc., Cleveland, OH). The rods were cylindrical and had flat, blunt ends (figure 1). The aspect ratios of 100 rods were measured and the average was 19.83. Because the standard deviation of the aspect ratio was 0.73, the rods were considered to be essentially monodisperse. We note that most of the variations in aspect ratio resulted from variations in the diameter of the rods (average diameter = 0.1596 cm, standard deviation = 0.0059 cm, average length = 3.165 cm, standard deviation = 0.008 cm).

The elastic modulus of polymethyl methacrylate is $2.4–3.4 \times 10^9$ N/m^2 (Weast 1986). The effect of fibre bending can be estimated by substituting this value into Forgacs & Mason's (1959) prediction for the onset of fibre bending in shear flow. Their criterion indicates that fibre bending should occur when the shear rate is greater than about 1250 s^{-1}. The characteristic shear rate in falling-ball experiments is estimated by $2v/d$ (Gottlieb 1979); for our experiments, it is in the range $0.05 < 2v/d < 15$ s^{-1}. Hence, bending is negligible and these rods can be considered rigid. The rotary Brownian diffusion coefficient of the rods is 3.0×10^{-17} s^{-1} (Brenner 1974), and, for the shear rates in these experiments, the rotary Péclet number is greater than 1.6×10^{15}. Therefore, the effect of Brownian forces is clearly negligible.

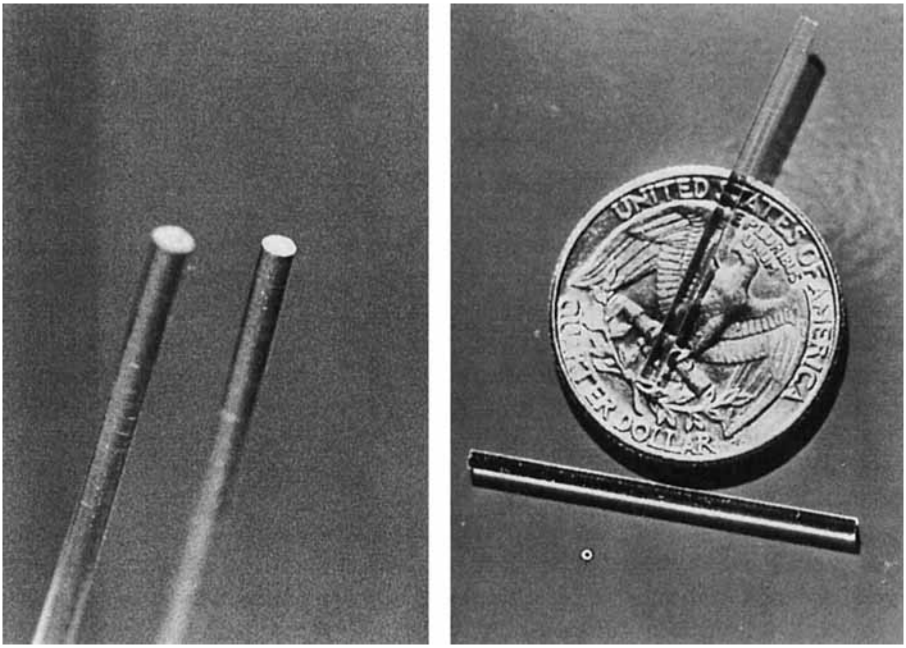

FIGURE 1. Photograph of two polymethyl methacrylate rods. Rods were individually cut to a length of 3.165 cm and had a nominal diameter of 0.1588 cm. The average aspect ratio based upon a sample of 100 rods was 19.83 ± 0.73.

Short rayon fibres (AB Bernhard Steffert, Sweden) were used at a volume fraction of 0.05. They were used at this one volume fraction to examine the effect of d/L when $d/L \gg 1$ and $D/L \gg 1$ and to compare the measured viscosity with that found for the suspension of polymethyl methacrylate rods at the same volume fraction. Electron micrographs of these fibres are shown in figure 2. From these micrographs we measured 23 rods and found an average length of 370 μm, an average diameter of 20 μm, and an average aspect ratio of 18.5, with a standard deviation of 2.3. The length and diameter of some of these fibres could only be estimated because they were twisted and bent and their diameters were not constant. The fibres were more polydispersed than the polymethyl methacrylate rods and they had irregular ends. The rotary Péclet number for the fibres was greater than 1.9×10^9, so the effect of Brownian forces was negligible. The criterion of Forgacs & Mason (1959) indicates that the onset of bending in these fibres occurs at a shear rate of about 500 s^{-1}, which is at least an order of magnitude higher than the characteristic shear rate in these experiments. These fibres were not used for most of the experiments because they were not as regular in shape as the polymethyl methacrylate rods and they were more polydisperse. Hence, they would have added an extra error to the measurements which could not be quantified.

The fluid was a mixture of polyalkylene glycol (UCON-HB-9500 Union Carbide Corporation, Danbury, CT), 1,1,2,2-tetrabromoethane (Eastman Kodak Company, Rochester, NY), and Tinuvin 328 (Ciba-Geigy, Ashley, NY). The quantity of tetrabromoethane in the mixture was adjusted so that the density of the fluid mixture matched that of the rods at 20.00 °C, 1.1818 g/cm^3 for the polymethyl methacrylate rods, and 1.476 g/cm^3 for the rayon fibres. A small quantity ($\leqslant$0.2

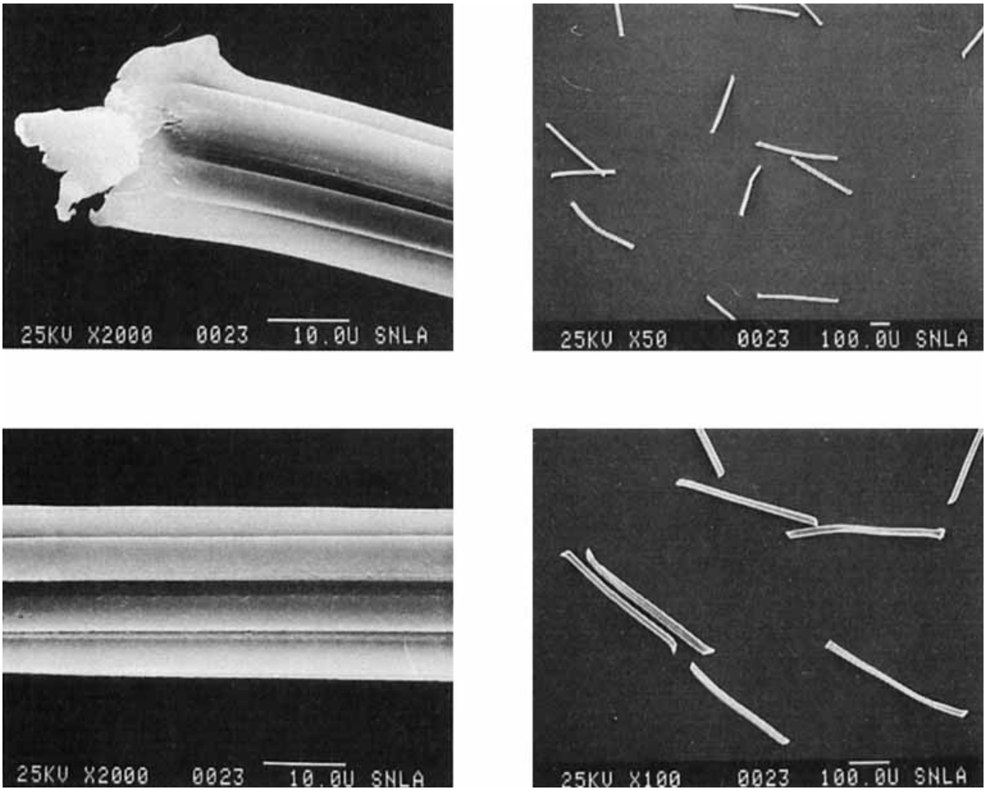

FIGURE 2. Electron micrographs of rayon fibres. The fibres were obtained commercially. The average aspect ratio based upon a sample of 23 rods was 18.7 ± 2.3.

Material	Property	Notation	Value (units)	Standard deviation
Polymethyl methacrylate	Density	ρ	1.1818 (g/cm^3)	—
	Length	L	3.165 (cm)	0.008
	Diameter	d_R	0.1596 (cm)	0.0059
	Aspect ratio	a_r	19.83	0.73
	Rotary Brownian diffusion coefficient	D_r	3.0×10^{-17} (s^{-1})	—
	Elastic modulus	—	$2.4–3.4 \times 10^9$ (N/m^2)†	—
Rayon	Density	ρ	1.476 (g/cm^3)	—
	Length	L	370 (μm)	20
	Diameter	d_r	20 (μm)	2
	Aspect ratio	a_r	18.7	2.3
	Rotary Brownian diffusion coefficient	D_r	2.6×10^{-11} (s^{-1})	—
	Elastic modulus	—	6×10^8 (N/m^2)‡	—

† From Weast (1986).
‡ From Kroschwitz (1987).

TABLE 1. Properties of the rods

Suspended rods	Density (g/cm^3) (20.00 °C)	Viscosity (Pa s) (20.00 °C)
Polymethyl methacrylate	1.1818	11.95
Rayon	1.476	9.43

TABLE 2. Properties of the fluids

wt%) of Tinuvin, an antioxidant, was added to the mixture to prevent the breakdown and discoloration of the tetrabromoethane by ultraviolet light.

The viscosity of both fluids was measured by falling-ball rheometry. The fluid used for the polymethyl methacrylate rods had a viscosity of 11.95 Pa s and that for the rayon fibres had a viscosity of 9.43 Pa s. The viscosity of the fluid used to suspend the polymethyl methacrylate rods was also measured on a Viscoelastic Analyzer (Sangamo-Schlumberger, Bognor Regis, UK) (Lam, Rakesh & Powell 1985). The measurements agreed with the results of the falling-ball experiments and the fluid was found to be Newtonian over the range of shear rates characteristic of these experiments. The fluid used to suspend the rayon fibres was measured on a Rheometrics RDS Mechanical Spectrometer (Rheometrics, Piscataway, NJ) and found to have a dynamic viscosity independent of the frequencies tested (10^{-1}–10^3 s^{-1}).

Before the suspensions were made, the rods were cleaned with soap and water, rinsed with deionized water, and dried. The suspensions were made by weighing out the required quantities of fluid and rods on a Mettler PC8000 balance. The balance was accurate to ± 0.1 g, but was limited to a weight of 8 kg. The suspensions required 16–24 kg of fluid, resulting in an inaccuracy of the added weights of each suspension less than or equal to ± 0.3 g. The uncertainty in the volume fraction was determined to be less than 5×10^{-5} (less than 2% at the lowest volume fraction) and is contained within the symbols representing the data points on all figures in this paper. A summary of the properties of the rods and fluids used in these experiments is given in tables 1 and 2.

2.2. *Apparatus*

The suspensions were contained in cylindrical glass columns 50.1 cm high and 15.3, 10.2, and 5.1 cm in diameter. The tops of the columns had removable covers with guide tubes at the centre to ensure that the falling ball was dropped along the centreline. The guide tubes were fabricated from Teflon rods and had bore diameters slightly greater than the falling balls.

There was a thin slot in the cover from the guide tube to the wall of the column for a stirrer. The stirrer, which was used to randomly orient the suspended particles, was a long brass rod with a handle on the top and eight short prongs on the bottom. We mixed the suspension thoroughly before each ball was dropped by briskly raising, lowering, and twisting the stirrer. A few coloured test rods were placed in one suspension and their orientations were observed after stirring. There was no correlation between the orientations or positions of the test rods in successive stirrings. Although a few rods were broken by the stirring, this did not affect the measured value of the viscosity within the accuracy of our experiments. Care was taken when stirring to avoid the introduction of air bubbles.

The cylindrical columns were placed in an insulated water tank controlled by a constant-temperature circulator (Lauda Company, Brinkman Instruments, Westbury, NY). The columns were thermally equilibrated for at least 24 h before any experiments were performed. The temperature of a suspension was measured with a thermocouple probe to within ±0.01 °C (Instrulab Inc., Dayton, OH). The temperature was measured at the beginning of an experiment and after each set of 10 individual measurements. The probe allowed measurement of the temperature at different points in the suspension to ensure thermal homogeneity. Falling-ball experiments were performed when the measured temperature was within ±0.10 °C of the desired set point (20.00 °C).

The balls used in these experiments were brass and chrome-plated steel ball bearings (Anti-Friction Bearing Manufacturers grade 200, Hoover Universal Company, Ann Arbor, MI). The steel balls were used at the beginning of the experimental programme because they could be recovered from the suspension with a magnet and the same balls could be dropped in each suspension. Brass ball bearings were used in later experiments because they did not oxidize as quickly in tetrabromoethane. The relative viscosity of the suspension of polymethyl methacrylate rods in which both types of balls were used ($\phi = 0.0218$) showed no significant dependence on the type of ball.

Prior to the experiments, the balls were placed in the water bath and thermally equilibrated to the temperature of the suspension. Four different nominal diameters were used: 0.953, 1.27, 1.59, and 1.91 cm. The actual diameter of each ball was measured to ±0.0003 cm, and the weight of each was measured to ±0.0002 g. These values were used with (1) to calculate the viscosity. The characteristic Reynolds number, $Re = \rho v d/\mu$, was in the creeping-flow regime (<0.1) (Batchelor 1967) for all of the ball sizes and suspension concentrations except the largest ball size in the two most dilute suspensions. For these balls, the Reynolds number was less than 0.14, but, to within the uncertainty of the measurements, no change was found in the relative viscosity.

2.3. *Measurement techniques*

The trajectory of each ball was recorded on a video tape. The velocity was measured in the middle third of the column, at least one column diameter from the top and bottom, to ensure that end effects would be negligible (Tanner 1961; Sonshine, Cox & Brenner 1966*a*, *b*). Positions and times were recorded at the top and bottom of the viewing screen, and an average velocity was determined for the falling ball. The average velocity was also determined over the top and the bottom halves of the screen. Throughout the experiments, the averages of the three velocities for each ball size were statistically indistinguishable at the 95% confidence level, indicating that terminal velocity had been reached.

At low concentrations, the balls were filmed optically with a high-speed digitized video system, the SP2000 Motion Analysis System (Spin Physics Division of Eastman Kodak, Rochester, NY). This was done to: (i) minimize systematic errors in spatial and temporal resolution; (ii) allow the same data analysis procedures to be used in both transparent and opaque suspensions; and, (iii) archive data for future review. In the last case, data from several experiments were analysed by more than one experimenter to ascertain whether any biases were being introduced. With this system, any frame could be examined and data for position and time could be taken. The accuracy in position and time was better than ±0.06 cm and ±0.002 s, respectively. The uncertainty in position represents a distance of one pixel. The length of a pixel was determined by hanging a plumb bob of known dimensions in the suspensions and measuring its length in pixels.

The frame rate was chosen so that the ball moved less than half a pixel from one frame to the next. A rate of 200 frames per second was sufficient in most experiments, but a rate of 500 frames per second was needed for the larger balls at the low concentrations ($\phi = 0.0025$, 0.004, 0.0218). The column was illuminated by two strobe lights. During long experiments (greater than 30 s) the lights were turned on only when the ball was at the top, in the middle, and at the bottom of the screen. In this way, the position and time of the ball was recorded, and, at the same time, the heating due to the lights was minimized.

Although the polymethyl methacrylate rods were transparent, they had a different refractive index from that of the fluid. At high concentrations, $\phi \geqslant 0.15$, the refraction of light at the surfaces of the rods made optical filming of the falling balls impossible. For these opaque suspensions, the ball was followed by real-time radiography (Mondy *et al.* 1986*b*). X-Rays were passed through the suspension and into an image intensifier. The output of the image intensifier was recorded by the same high-speed video system. Subsequent data analysis was the same as that used at low concentrations.

3. Results

The measured velocities were used with (1) and (2) to calculate the relative viscosities of the suspensions. The relative viscosities calculated from individual balls of the same nominal diameter could differ by over 100% at the highest volume fractions. This variation in viscosity resulted from variations in the angular and spatial distributions of the rods over the measuring section of the column from one experiment to the next. With the polymethyl methacrylate rods, many experiments were needed to reach a reproducible average viscosity. When a sufficient number of balls was dropped a reproducible average value was always obtained.

The actual numbers of balls used to determine the average viscosity for each ball diameter and volume fraction are given in table 3. Generally, at least ten balls of each diameter were used. In most studies, we dropped balls in sets of five. After each set, the average relative viscosity was calculated. When the values of μ_r were indistinguishable based on a Student *t*-distribution (Walpole & Myers 1972), the average of the combined sets was taken to be the viscosity of the suspension. When μ_r did differ significantly, additional balls were dropped until μ_r reached a constant average value.

The purpose of this work was to determine the effect of volume fraction on the relative viscosity when the suspension behaved as an unbounded continuum, i.e. $d/D \ll 1, d/L \gg 1, D/L \gg 1$. This required first measuring the effect of these three dimensionless parameters.

The effect of d/D was established by varying both column and ball diameters. These results are shown in figure 3 for three volume fractions which are representative of the concentrations studied. The solid lines indicate the average viscosity value at each concentration. There is only a very small degree of variation in viscosity with dimensionless ball size. Although a dependence cannot be supported statistically, the variation may result from larger scale structures or hindered rotations of the rods. In calculating these viscosities (1) and (2) have been applied, i.e. the suspensions were assumed to behave as Newtonian liquids. The results shown in figure 3 are consistent with this assumption. The Faxén (1923) formula (1) correctly accounts for the effect of container boundaries and yields the same value of viscosity for all ball sizes used in these experiments.

The error bars in figure 3 represent the 95% confidence limits in the data based on

ϕ $[nL^3]$	$\frac{d}{D} = 0.13$	$\frac{d}{D} = 0.109$	$\frac{d}{D} = 0.087$	$\frac{d}{D} = 0.065$	Total average
0.0025 [1.25]	1.078 ± 0.039 (6)	1.052 ± 0.051 (5)	1.085 ± 0.87 (8)	1.076 ± 0.023 (10)	1.075 ± 0.023 (29)
0.004 [2.00]	1.101 ± 0.025 (16)	1.117 ± 0.045 (10)	1.069 ± 0.021 (10)	1.065 ± 0.020 (26)	1.083 ± 0.013 (62)
0.0218 [10.9]	1.473 ± 0.076 (24)	1.565 ± 0.078 (17)	1.620 ± 0.118 (20)	1.499 ± 0.118 (26)	1.499 ± 0.043 (87)
0.05 Polymethyl methacrylate rods [25.1]	2.358 ± 0.319 (5)	2.345 ± 0.369 (14)	2.331 ± 0.232 (10)	2.427 ± 0.172 (18)	2.374 ± 0.111 (47)
0.05 Rayon fibres [22.3]	— —	1.957 ± 0.083 (10)	2.004 ± 0.056 (15)	2.029 ± 0.036 (21)	2.004 ± 0.026 (45)
0.125 [62.6]	4.920 ± 0.676 (20)	4.685 ± 0.650 (10)	4.603 ± 0.921 (10)	4.675 ± 0.763 (20)	4.763 ± 0.253 (60)
0.15 [75.2]	8.60 ± 2.21 (10)	7.13 ± 1.22 (26)	8.50 ± 0.949 (24)	8.68 ± 1.32 (20)	8.15 ± 0.61 (80)
0.175 [87.7]	10.58 ± 2.66 (20)	9.03 ± 1.48 (15)	12.11 ± 1.84 (29)	9.93 ± 1.69 (20)	10.66 ± 0.96 (84)
0.2315 [116]	24.1 ± 6.3 (24)	26.9 ± 6.4 (24)	28.3 ± 6.9 (25)	28.3 ± 8.8 (18)	26.7 ± 3.3 (91)

TABLE 3. Relative viscosity values and uncertainties. The numbers in parentheses are the numbers of balls in the average relative viscosity. Except for one suspension made using rayon fibres ($\phi = 0.05$), all suspensions were made using polymethyl methacrylate rods.

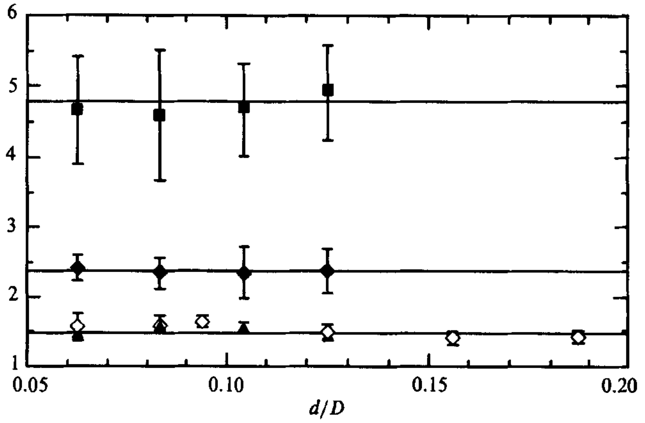

FIGURE 3. Relative viscosity versus dimensionless ball size: $\phi = 0.0218$, $D = 15.3$ cm (▲); $\phi = 0.0218$, $D = 10.2$ cm (◇); $\phi = 0.05$, $D = 15.3$ cm (◆); $\phi = 0.125$, $D = 15.3$ cm (■). The lines through the data points mark the combined average at that volume fraction.

a Student t-distribution. This statistical uncertainty results from the variation in the velocities of individual balls. The uncertainties in the measurements and their contributions to the uncertainty in the measured relative viscosity at $\phi = 0.0218$ for a ball of diameter 0.953 cm are listed in table 4. The total uncertainty in physical measurements in this case is less than 1.0% of the relative viscosity as compared with the statistical uncertainty of 5.1%. At higher volume fractions, the statistical uncertainty increases considerably and that due to the measuring devices becomes negligible relative to it.

Measured quantity	Uncertainty	Percent uncertainty in the measured viscosity
1. Distance travelled (one pixel)	0.06 cm	0.6 %
2. Elapsed time	0.002 s	<0.01 %
3. Radius of falling ball	0.0003 cm	0.2 %
4. Mass of falling ball	0.0002 g	<0.01 %

TABLE 4. The uncertainties in physical measurements and their contributions to the uncertainty in the measured viscosity of a 0.953 cm ball at $\phi = 0.0218$. The statistical uncertainty in the viscosity for the 0.953 cm ball at $\phi = 0.0218$ is 5.1 % of the measured viscosity

ϕ	D/L	μ_r
0.0218	4.8	1.53 ± 0.04
0.0218	3.2	1.51 ± 0.04
0.0218	1.6	1.39 ± 0.06
0.2315	4.8	26.7 ± 3.3
0.2315	3.2	25.8 ± 4.4

TABLE 5. The effect of dimensionless column diameter on the relative viscosity

The second parameter investigated was the effect of the ratio of the column diameter to fibre length (D/L) on the relative viscosity. This effect should not be confused with the additional drag on the falling ball caused by the cylindrical walls of the column. This is accounted for by the use of (1). Here, we are concerned with the effect that the container boundaries have on the viscosity of the suspension caused by the restricted motion and induced alignment of the rods. As seen in table 5, there is no significant difference between the relative viscosity at D/L of 4.8 and 3.2 over the tested concentration region. However, the viscosity measured for D/L of 1.6 at a volume fraction of 0.0218 is lower. This leads us to conclude that D/L of 4.8 is sufficiently large to ensure that wall effects are negligible to within the error of these measurements. Wall effects become significant when $1.6 < D/L < 3.2$. This ratio is in agreement with the results found in shearing flows, where viscometer boundaries do not influence the measurements if the ratio of characteristic viscometer gap to fibre length is greater than 2.6–3.0 (Attanasio *et al.* 1972; Nawab & Mason 1958; Blakney 1966). A somewhat lower value has been reported by Bibbo, Dinh & Armstrong (1985).

Ideally, viscosity measurements should be made in the limit $d/L \gg 1$ when, relative to the falling ball, the suspension approximates a continuum. Although the dimensionless parameter d/L is the product of d/D and D/L, it must be considered separately because it is not necessarily much greater than one when $D/L \gg 1$ and $d/D \ll 1$. We see in figure 3 that the relative viscosity does not depend on d/L for $0.3 \leqslant d/L \leqslant 0.6$. Similar behaviour is observed in the case of the rayon fibres for which $26 \leqslant d/L \leqslant 52$ and $D/L = 400$, as indicated by the constant viscosity value for the different ball sizes in table 3. From this we conclude that the relative viscosity is independent of d/L for $d/L > 0.3$, and that the values of d/L used in these experiments are sufficiently large to measure the viscosity of the suspension. Preliminary measurements indicate that the relative viscosity decreases monotonically with d/L below this value; this will be discussed in a subsequent paper by the present authors.

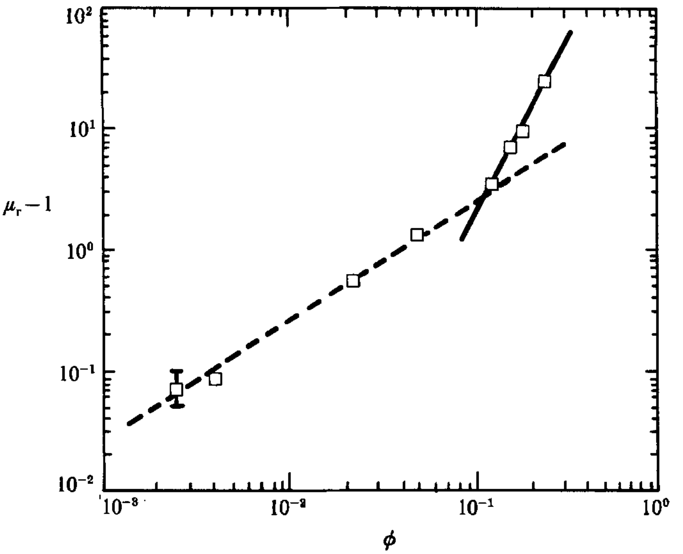

FIGURE 4. Specific viscosity versus volume fraction. The dashed line is (4) and the solid line is (5).

The rayon fibres have an aspect ratio that is slightly less than the polymethyl methacrylate fibres (18.7 compared to 19.8). Suspensions of the two different rods at the same volume fraction would be expected to have comparable relative viscosities. The relative viscosity of the suspension of rayon fibres for $\phi = 0.05$ was determined to be 2.00. This is remarkably close to the relative viscosity measured for the polymethyl methacrylate rods, 2.37, considering that the rayon fibres are not regular cylinders with blunt ends, cf. figures 1 and 2. Also, the difference in the relative viscosity is consistent with that predicted by theory for the difference in aspect ratios: the suspension of lower-aspect-ratio rods has the lower relative viscosity (Brenner 1974). This decrease may result from a weak dependence of μ_r on d/L for $d/L \gg 1$. In this region, the passage of the much larger falling balls may cause some alignment of the fibres. The comparable values of the relative viscosities further supports the conclusion that the d/L-values used in these experiments are sufficiently large to measure the viscosity of the suspension.

The most important result of this work is shown in figure 4, namely the specific viscosity–volume fraction relation, where the specific viscosity is defined as

$$\mu_{sp} = \mu_r - 1. \tag{3}$$

The dashed and solid straight lines in figure 4 are the least-squares fits to the averaged points for the four lowest and three highest volume fractions respectively. Note that these points represent 585 individual experiments. The numerical values corresponding to the data in figure 4 are given in table 3. The intermediate point, occurring at $\phi = 0.125$, was not included in either fit. However, it is almost exactly the point where the two straight lines intersect, namely $\phi = 0.117$. The equations describing the two lines are

$$\mu_{sp} = 28.5\phi^{1.01}, \quad \phi < 0.125, \tag{4}$$

$$\mu_{sp} = 2040\phi^{3.01}, \quad \phi > 0.125. \tag{5}$$

In both cases, the correlation coefficient is greater than 0.99. It is evident from (4) and figure 4 that suspensions that have $\phi < 0.125$ are dilute, i.e. μ_{sp} is linear in ϕ. The actual μ_{sp} at $\phi = 0.125$ deviates from linearity, (4), by only 11 %. In comparison, the specific viscosity–volume fraction relation for suspensions of spherical particles deviates from linearity by 36 % at the same volume fraction (Thomas 1965).

4. Discussion

Based on (4), the relative viscosity varies linearly with volume fraction to within the error of these experiments for $\phi < 0.125$. Assuming that $\mu_{\text{sp}} = [\mu]\,\phi$, where $[\mu]$ is the intrinsic viscosity, and forcing our data to fall upon a straight line, we find $[\mu] = 27.6$. While there are many theories available that predict the intrinsic viscosity of suspensions of spheroids, rods, etc. the particulars of our experiment as they relate to these theories must be considered when making comparisons. Our suspensions of rods have very large Péclet numbers ($Pe > 10^{15}$) and are initially randomly oriented. Ideally, during a measurement, the rods are only slightly perturbed and the average velocity of a ball is determined by an isotropic effective continuum. The relative shear viscosity calculated by (1) and (2) can be compared with theoretical results for shearing flow when the theories mandate that, at steady state, the particles are randomly oriented.

This is the calculation performed by Simha (1940) who expected that such a theory would model spheroids subject to dominant Brownian motion. This latter point aside, Simha's (1940) theory can be compared with our result if, in addition, we calculate the equivalent aspect ratio, a_{re}, as found by Cox (1970). The equivalent aspect ratio of a rod is the aspect ratio of a spheroid that has the same period of rotation in shear flow. We find that $a_{\text{re}} = 14.2$, which leads to $[\mu] = 22.7$ and compares to within 17.8 % of our measurements.

While the agreement with Simha is reasonable, it is possible to directly compare our results with Brenner's (1974) theory for the rheology of dilute suspensions of *blunt-ended rods*. Brenner's theory more closely describes our system, although it considers rods subject to strong Brownian forces. As detailed in the following paragraphs, the effects of processes analysed for particles subject to strong Brownian motion and the effects of the dominate forces in our experiments can be compared.

The justification for this comparison rests in the work of Haber & Brenner (1984). Rotary Brownian motion contributes to the intrinsic viscosity in two ways: through the equilibrium orientation distribution of the spheroids, which depends upon the rotary Brownian diffusion coefficient D_{r}; and through a direct contribution due to the additional energy dissipation resulting from the random velocity of the suspended particles. These independent effects were neglected by Simha (1940), but were correctly considered by Saito (1951), who obtained the same final result as Simha (1940). By calculating the complete expression for the bulk stress tensor for general triaxial ellipsoids, Haber & Brenner (1984) found that they could explain why the correct approach taken by Saito (1951) yielded the same results as Simha (1940). They found that

$$[\mu] = \tfrac{5}{2}W, \tag{6}$$

where

$$W = \tfrac{2}{15}(Q_1+Q_2+Q_3)+\tfrac{2}{5}(q_1+q_2+q_3)-\tfrac{1}{3}\frac{N_T^2}{{}^rK_T}. \tag{7}$$

The terms Q_i, q_i, N_T, and ${}^rK_T$ describe the geometry of the ellipsoid. For triaxial ellipsoids these parameters are tabulated in Appendix A of Haber & Brenner (1984).

Haber & Brenner (1984) show that the distribution of rod orientations is not random, but rather depends linearly on the shear rate. To obtain Simha's (1940) result, the distribution must be set to a constant representing an isotropic suspension, $1/8\pi^2$, and the angular velocity of the particles must be set equal to the vorticity of the fluid. This results in expressions similar to (6) and (7) but without the term $-\frac{1}{3}N_T^2/{}^rK_T$. Alternatively, Haber & Brenner (1984) show that $N_T = 0$ for any body of revolution, establishing the basis by which Simha's (1940) theory yields numerically correct results for the intrinsic viscosity of spheroids in the limit of strong Brownian motion.

For suspensions of blunt-ended rods, which are bodies of revolution, Brenner's (1974) results for $[\mu]$ should be the same as the results one would obtain using Simha's (1940) method. This permits a direct comparison between our results and Brenner's (1974) theory. For rods having an aspect ratio of 19.83, Brenner (1974) predicts that

$$[\mu] = 29.2, \tag{8}$$

which differs from our experimental result, 27.6, by only 5.8%. This difference, while small, may be attributable to the small disturbance of the random orientation of the rods by the falling ball. In figure 5, we plot our data along with three dilute-regime predictions: blunted-ended rods (Brenner 1974), prolate ellipsoids (Simha 1940), and prolate ellipsoids of equivalent aspect ratio to our rods (Cox 1970). We find excellent agreement with Brenner's (1974) result for $\phi \leqslant 0.125$. At $\phi = 0.125$, the deviation of our data from Brenner's prediction is small (2.4%); this is further evidence of the existence of the extended dilute regime.

In figure 4, there is a sharp transition in the μ_{sp}–ϕ relationship at about $\phi = 0.125$. Theoretical studies on rod-like macromolecules have shown that the transition to the semiconcentrated region occurs at about the same concentration (Keep & Pecora 1985; Magda, Davis & Tirrell 1986). In these studies, the semiconcentrated region is defined, following Doi and Edwards (Doi 1975; Doi & Edwards 1978*a*), as the region where the rods, assumed to be infinitely thin, are confined in their Brownian rotation to 'cages' created by the other rods. Initially, Doi & Edwards (1978*a*) predicted the transition to this region to occur at $nL^3 = \beta$, where n is the number density and β is a constant of order unity. Keep & Pecora (1985) have refined this work and found that the transition must occur above $nL^3 = 50$. At this number density, the volume fraction that would be associated with rods that are not infinitely thin is $\phi = (50\pi/4)\,a_r^{-2}$. For our experiments ($a_r = 19.83$) this corresponds to $\phi = 0.10$. Magda *et al.* (1986) using molecular dynamic simulations, have found that the transition occurs around $nL^3 = 70$ (this corresponds to $\phi = 0.14$ for our large rods). These two predicted values bracket the transition point indicated by our data. Recently, Bitsanis, Davis & Tirrell (1988) have used Brownian dynamic simulations to examine solutions of rod-like macromolecules of aspect ratio 50. In that study, which includes the effect of the solvent on the molecules, no transition was observed up to $nL^3 = 50$.

At the high volume fractions, the best-fit line in figure 4 has a slope of 3.01 and a correlation coefficient greater than 0.99. The viscosity of solutions of rod-like macromolecules in the semiconcentrated region has also been found to be proportional to the cube of the concentration in both experiment (Hermans 1962) and theory (Doi 1975; Doi & Edwards 1978*b*; Bird *et al.* 1987).

The good agreement between the theoretical and experimental studies of macromolecules and our experimental results is in many respects surprising. The rods in our experiments have a finite aspect ratio of 19.83; in addition, they are not affected significantly by forces active at a molecular scale. Furthermore, hydrodynamic interactions between rods, ignored in the macromolecular simulations,

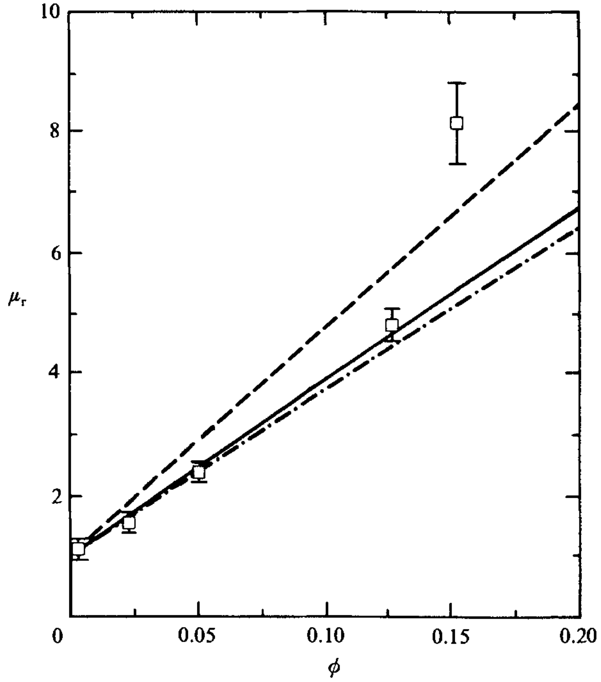

FIGURE 5. Comparison between the relative viscosity measured in these experiments (□) and results for dilute suspensions of randomly oriented rods. Prediction for spheroids of aspect ratio 19.83 (----) (Simha 1940); (——) prediction for blunt-ended rods (Brenner 1974); (-·-·-·) prediction for spheroids of aspect ratio 14.2 which is equivalent to a rod of aspect ratio 19.83 (Cox 1970).

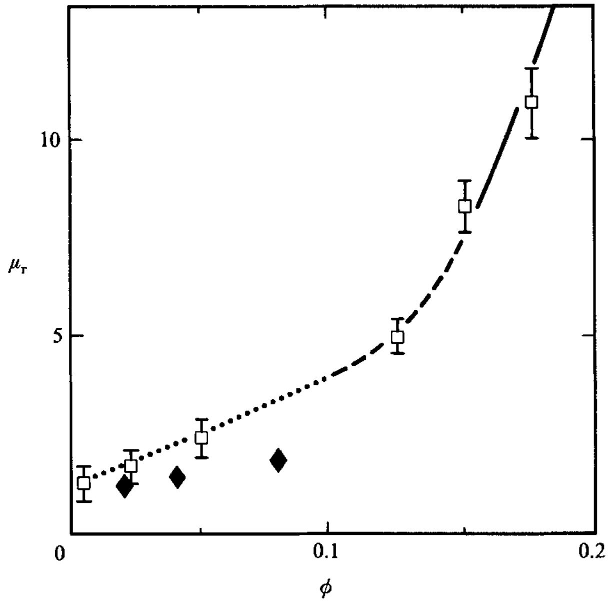

FIGURE 6. Comparison between the relative viscosity measured in these experiments (□) and the results obtained in shear flow (◆) for $a_r = 25$ (Ganani & Powell 1986). The lines are the least-squares fits at the low (.......) and high volume fractions (——), (4) and (5) respectively. The dashed line (----) connects these two best-fit lines.

are important in our experiments because of the high viscosity of the suspending fluid. Recognizing these limitations, it appears that the data from our experiments can provide insight into the physics of the interactions of macromolecules and vice versa. In the non-dilute regime, our experiments, which are dominated by hydrodynamic forces, and studies of macromolecules find a cubic dependence of the viscosity on concentration. This suggests that behaviour in macromolecular systems in which molecular forces dominate can result from hydrodynamic effects similar to those present in our experiments. On the other hand, the transition from the dilute to the semiconcentrated regime predicted by macromolecular simulations agrees with our experimental observations. This suggests that steric effects, present in both, may determine the transition and the cubic concentration dependence.

Our experimental results emphasize the importance of the rod orientation distribution on the macroscopic rheology. The values of μ_r obtained by Ganani & Powell (1986) in shear flow for rods having $a_r = 25$ are considerably lower than those for a randomly oriented suspension as shown in figure 6. Bibbo *et al.* (1985) have measured the 'initial viscosity' of a suspension of randomly oriented rods in a shear-inception experiment. They extrapolate the time-dependent shear stress to measure $\mu_{r(\text{shear inception})}$. Generally, their results lie below those of this study and above those obtained under steady-state shearing (e.g. at $\phi = 0.05$, $\mu_{r(\text{shear inception})} = 2.1$, $a_r = 23$ whereas we find $\mu_r = 2.37$).

5. Conclusions

The following conclusions may be drawn from this study. First, falling-ball rheometry can be used to measure the viscosity of suspensions of randomly oriented rods. Second, the walls of the columns begin to affect the measured viscosity of the suspension when the ratio of column diameter to fibre length has a value between 3.2 and 1.6, which is in agreement with experiments performed in shear flow. Third, the viscosities of the suspensions vary linearly with volume fraction below a volume fraction of about 0.125. This is much higher than previously thought and considerably higher than is found with suspensions of spherical particles. Fourth, the intrinsic viscosity measured by falling-ball rheometry is in good agreement with the theoretical predictions of Brenner (1974). Finally, our data can be represented best by the two separate equations in the two different concentration regions covered by this study: the expected linear dependence in the dilute region and $\mu_{sp} \propto \phi^3$ at higher concentrations.

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