The Rheological Properties of Suspensions of Rigid Particles

Experimental and theoretical work on the rheological properties of suspensions are reviewed. Attention is focused on systems consisting of rigid, neutrally buoyant particles suspended in Newtonian fluids; no restrictions, however, are placed on the concentration of the particles or on the forces acting in the suspension. The assumption that an effective viscosity depending solely on the volume fraction of the particles suffices to describe the rheology of suspensions is examined and shown to be inadequate. Indeed, the experimental evidence strongly supports the view that suspensions behave macroscopically as non-Newtonian fluids whose rheological properties are influenced by a large number of factors; these factors are listed. The various theories that have been put forward to explain the flow of suspensions are discussed, with particular emphasis being placed on the nature of the approximations made, so that purely empirical formulas can be clearly separated from those having a theoretical basis. Suggestions for future work, both theoretical and experimental, are provided.

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SCOPE

A well-known and long-standing problem in fluid mechanics has been the calculation of the effective viscosity of a suspension. In recent years it has become clear that many of the complex phenomena associated with a flowing suspension cannot be explained by using a classical Newtonian description of a fluid with an effective viscosity. Thus, suspensions have to be treated as non-Newtonian fluids whose rheological (flow) properties are influenced by a large number of variables. This review presents some of the reasons why such non-Newtonian behavior occurs and describes the variables that must be included in any proposed theory for such behavior. The discussion is restricted to suspensions of rigid, neutrally buoyant particles in Newtonian fluids and thereby excludes emulsions, reinforced plastics, etc., but otherwise no restrictions are placed on the scope of the review.

CONCLUSIONS AND SIGNIFICANCE

The volume fraction of the particles in a suspension (volume occupied by particles per unit volume of suspension) has often been assumed to be the only variable that influences the observed rheological properties of the suspension. Experimental evidence is presented to show that this is incorrect and that other factors, such as the shape and size distribution of the particles, the presence of electrical charges, and the type of flow being experienced must be considered. It readily follows then that no formula can exist that will give the effective viscosity or other flow properties solely as a function of the volume fraction of the particles. Of the many expressions that have been advanced for predicting the dependence of the flow properties on the factors referred to above, some are empirical while others rest on sound theoretical foundations. Successful empirical formulas generally contain one or more adjustable parameters which must be determined by experiment, and until these parameters can themselves be predicted for any suspension, such formulas will be more useful for correlating data than for predicting them. On the other hand, exact theoretical calculations starting from basic principles have, so far, been successfully completed only for dilute suspensions. They have, however, provided valuable qualitative insight into the mechanisms that determine the rheology of suspensions, and their importance lies in this fact rather than in their ability to make quantitative predictions.

One of the main points we wish to make in this review is that older models used for the calculation of suspension properties are at present being (slowly) displaced by more exact methods which take into account the many factors that determine suspension rheology. Further progress requires experiments that are more careful and complete than those that have been performed to date, as well as the development of more powerful theoretical tools for describing and predicting the flow of suspensions, especially highly concentrated ones in which the non-Newtonian effects are most pronounced.

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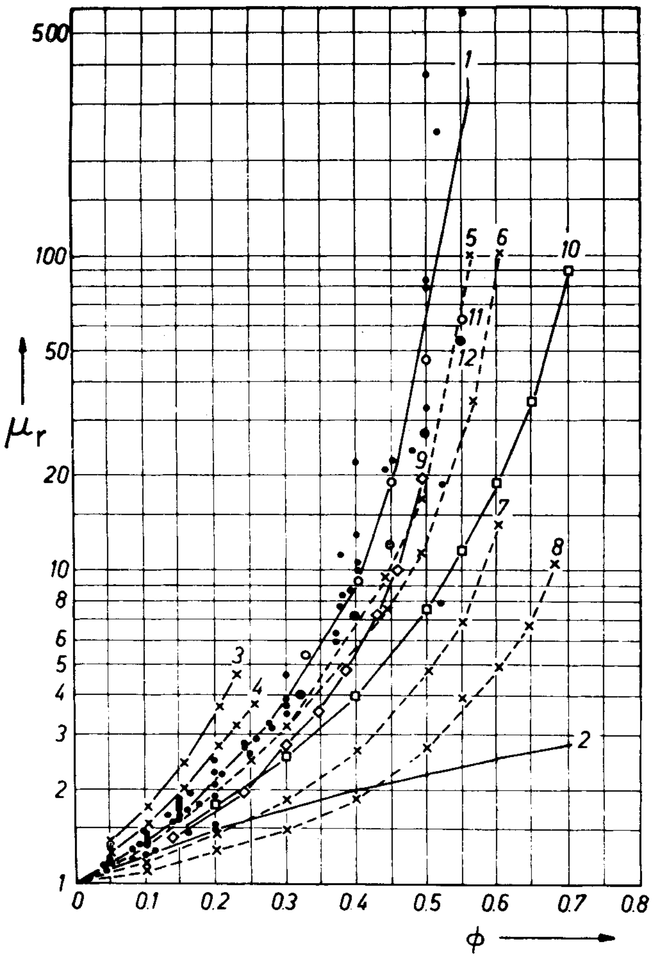

Fig. 1. Data for relative viscosity collected by Rutgers (1962*a*) and plotted against volume fraction. The curve 1 is Rutgers's average curve. The explanation of the numbering of the other curves can be found in the original paper.

When we deal with suspensions, it is not always necessary to acknowledge that they are mixtures of particles and fluid; instead, it is often possible to regard them as homogeneous fluids and to ascribe to them certain effective fluid properties. This is possible when the length scales describing the motion of the suspension as a whole are much larger than the average size or average separation of the particles. The smallness of the particles usually ensures that this condition is satisfied; the particles in a slurry, for example, have a diameter typically in the range 100 to 1 000 μ, and colloidal particles are about 1 μ in diameter. Thus, since the suspension can be treated as homogeneous, the problem becomes one of finding its appropriate effective fluid properties. This can be achieved either by experimental measurements or by theoretical consideration based on the known structure of the suspension. Both methods are considered here.

In view of the fact that several reviews on the flow properties of suspensions have recently appeared (Batchelor, 1974; Brenner, 1972; Jinescu, 1974), it is worthwhile pointing out at the outset one difference between the aim of this review and the aims of the others. Work on suspensions can be divided into two categories: the first contains those studies that have attempted to develop simple empirical equations for the purpose of correlating experimental data taken over the whole range of particle concentration, while the second contains theories having a restricted range of applicability but which, in principle, can be used to perform rigorous calculations. The existing reviews have reflected this separation, the first two mentioned above being concerned with the exact theory and the last with the more qualitative approach. Part of the aim of this review is to set the results of the two points of view in perspective against each other, and, to this end, the early sections discuss the experimental results and general theories and later sections the rigorous theory.

Rheology is the study of the deformation and flow of matter in general (the name was coined by the Society of Rheology), and it provides an appropriate framework for investigating systems, such as suspensions, that show strong departures from the simple Newtonian laws of fluid flow. This framework will be used here to describe the rheological properties of suspensions of rigid, neutrally buoyant particles in Newtonian fluids. The particles need not be spherical, although for reasons of simplicity such particles have been commonly used, nor need they be identical. The first calculation of the effective flow properties of a suspension in terms of the properties of its constituents is usually taken to be Einstein's (see Einstein, 1956), and since this work is still regularly quoted, it makes a convenient starting point for a description of the other early studies of suspensions.

1. EARLY EXPERIMENTS WITH SPHERICAL PARTICLES

Einstein considered a suspension of spherical particles under the condition that the volume fraction of the particles, defined by

$$\phi = \frac{\text{Volume occupied by particles}}{\text{Total volume of suspension}}$$

satisfied $\phi << 1$. The suspension could then be assigned an effective viscosity $\mu^\star$ given by

$$\mu^\star = \mu_0 \left(1 + \frac{5}{2} \phi \right) \qquad (1)$$

where μ_0 is the viscosity of the suspending fluid. The assumptions made in the derivation of this equation (section 12 provides some of the details) are that the particles are far enough apart to be treated independently of each other and that the flow around each particle is described by the hydrodynamic equations of motion with inertia neglected (the Stokes equations). Taking their lead from the form of Equation (1), many experimenters set out to find a formula for the effective viscosity of the form

$$\frac{\mu^\star}{\mu_0} = \mu_r(\phi) \qquad (2)$$

with μ_r, called the relative viscosity, reducing to (1) as $\phi \to 0$. Measurements were also made to test the value of 5/2 for the coefficient of ϕ in (1). Conventional viscometers were used (rheometry will be described in section 3), and values for the coefficient were reported ranging from 1.5 to 5.

There is no need to list these results separately here because they were summarized by Rutgers (1962*a*) in a plot reproduced in Figure 1. A similar attempt to correlate the data of many experimenters was made by Thomas (1965), and his plot is reproduced in Figure 2. The scatter in the data is the most striking feature of these plots, especially at the higher values of ϕ where order-of-magnitude discrepancies are clearly evident. Rutgers and Thomas attempted, therefore, to extract "average" curves that could be used for $\mu_r(\phi)$. Rutgers seems to have assumed that the scatter

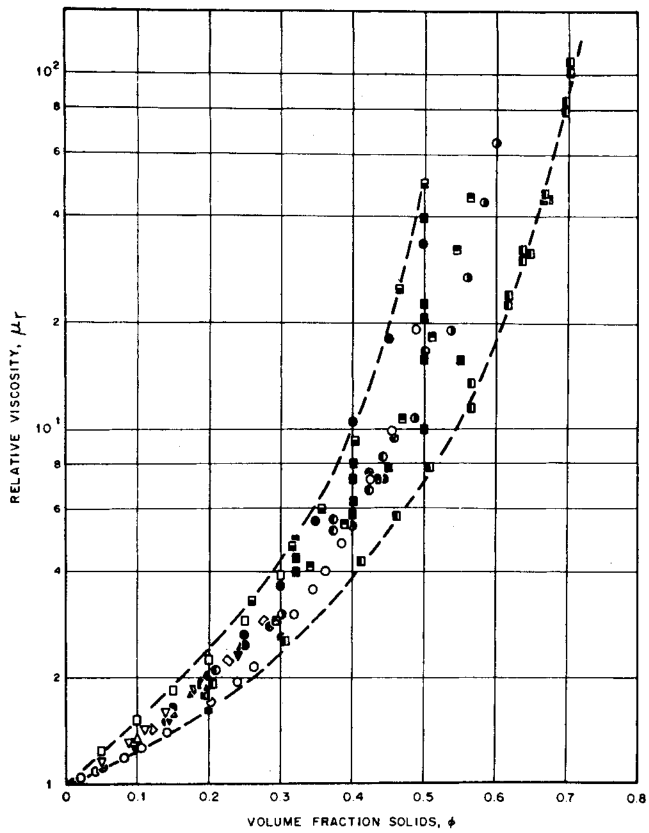

Fig. 2. Data for relative viscosity collected by Thomas (1965) and plotted against volume fraction. The explanation of the symbols can be found in the original paper.

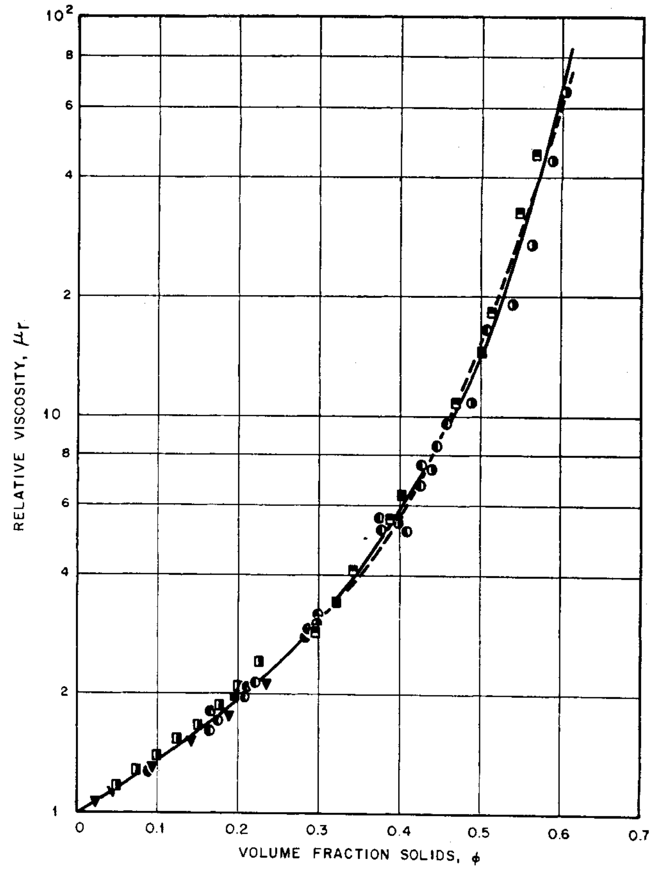

Fig. 3. The data of Figure 2 after being subjected to various extrapolation procedures by Thomas (1965).

was largely due to experimental error and drew a curve, labeled 1 in the figure, with which he hoped to cancel out these errors. Thomas saw more clearly that factors other than ϕ influenced $\mu^\star$ and tried to compensate for them by various extrapolation procedures. His reduced data are shown in Figure 3. In both cases, however, the final curves were largely arbitrary and, not surprisingly, did not agree with each other. Rather than cover up the scatter with average curves, one should therefore examine the other factors influencing suspensions, properties, and this is what will be done in the next section.

2. FACTORS INFLUENCING THE PROPERTIES OF SUSPENSIONS

When the assumptions invoked by Einstein to derive Equation (1) no longer apply, the possibility of using an equation of the form of (2) is also lost. Consider the hydrodynamic assumption first. It has been known to colloid chemists for some time that nonhydrodynamic forces act on particles in suspension. These forces are listed in what is now called the Deryagin-Landau-Verwey-Overbeek theory of colloid stability (Eagland, 1973; Verwey and Overbeek, 1948) and consist of thermal (Brownian) forces, electrical forces arising from charges on the particles and London-van der Waals forces. The DLVO theory is not yet completely free of controversy (for instance, with regard to the status of the Stern layer described below), but the following outline can be given. Brownian forces result from the random jostling of particles by the molecules of the suspending fluid because of thermal agitation and fluctuate on a very short time scale. This allows one to take a time average and replace the forces by a diffusion process on a longer time scale, a process which is described by a diffusion constant $D = kT/R_w$, where k is the Boltzmann constant, T the absolute temperature,

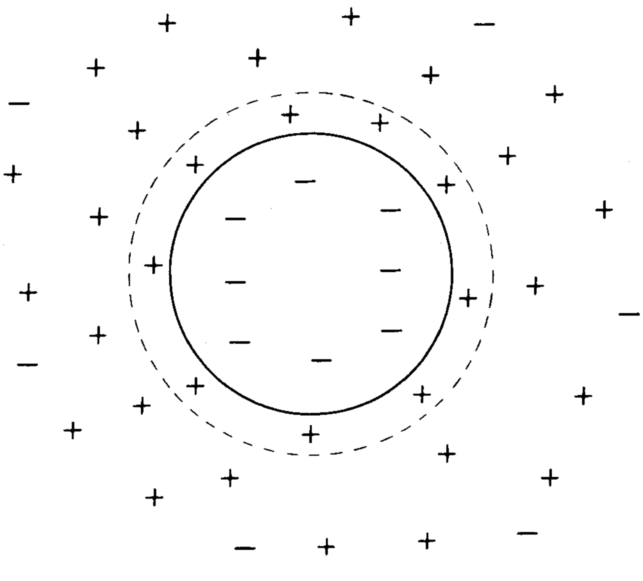

Fig. 4. A charged particle in suspension. The charge on the particle, shown as negative, attracts positive ions from the fluid which form a Stern layer adjacent to the surface of the particle (depicted as the positive charges inside the broken circle) and a Gouy layer outside the Stern layer.

and R_w a resistance coefficient relating a particle's motion (translation or rotation) to the net force acting on it. The resistance coefficient increases as the particle becomes larger, that is, D decreases, and so large particles are less affected by Brownian forces than small ones. Turning now to electroviscous effects, we depict in Figure 4 a charged particle in suspension surrounded by a

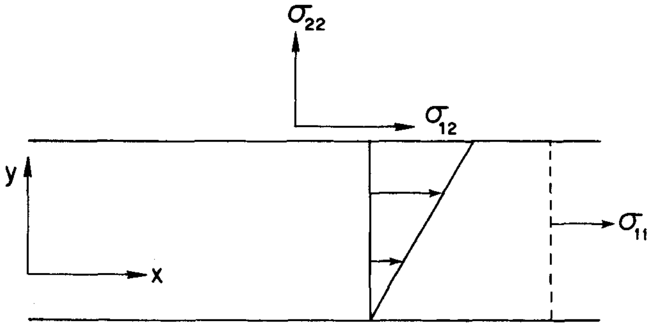

Fig. 5. Shear flow between two plates. The velocity field is $(\gamma y, o, o)$; the normal stresses σ_{11} and σ_{22} are shown, but σ_{33} which acts in the direction normal to the plane of the page is not.

cloud of ions whose charges are predominately of the sign opposite to that of the charge on the particle. The cloud has two layers: an inner (Stern) layer which is immobile and a diffuse outer (Gouy or Debye-Hückel) layer. The charges on the particle and the opposite charges in the cloud make up a double layer* of charge which can store energy the same way a capacitor does; also, the charge cloud screens the charge on the particle and thus reduces the repulsive forces between particles. The parameters associated with electroviscous effects are κ^{-1}, the Debye length which measures the thickness of the cloud, and either the potential or the charge density on the surface of the particle. The values of these parameters are determined from standard electrophoretic measurements. Electroviscous effects are divided into a first effect, coming from the resistance of the cloud to deformation, and a second, coming from repulsion between the particles. As with Brownian effects, they decrease in importance as the size of the particles increases. Finally, London-van der Waals forces are the well-known weak attractive forces that act between all particles. Because of their short range, they are usually only invoked in theories of suspensions to explain the agglomeration of particles. [They have been given a more important role in work by Hoffman (1974) described in section 16] Nonhydrodynamic forces are one group of factors causing non-Newtonian behavior in suspensions because there is a competition between them and hydrodynamic forces resulting in a viscosity which, instead of being constant, depends on the strength of the flow. Experimental support for this point of view is presented in section 4; here we proceed to discuss some of the effects that arise when Einstein's other assumption no longer holds, that is, when particles do interact with each other.

A suspension in which the particles have formed pairs, say, can be considered to be a suspension of single particles of a new shape and as such must be expected to have properties different from a suspension in which the particles remain separated, however small ϕ is. Many of the early failures to verify Einstein's calculation, which obviously applies only to separated spheres, can probably be ascribed to the formation of aggregates, whose presence would lead to a value of the Einstein coefficient larger than 5/2. If the particles are separated but ϕ is too large for the effects of neighboring particles on each other to be ignored, it is important to know whether the particles are all the same size (monodisperse) or mixtures of sizes (polydisperse). It is found experimentally (see Figure 12) that a polydisperse suspension of spheres has a lower viscosity than a similar monodisperse suspension with the same total volume fraction. Thus, a simple volume fraction ϕ is insufficient to describe a polydisperse suspension, and, instead, a distribution function $\Phi(a)$ is required. This is defined so that $\Phi(a)da$ is the volume fraction of particles whose radii fall in the interval $(a, a + da)$, and it satisfies the normalization condition

$$\int_0^\infty \Phi(a)da = \phi$$

ϕ being the volume fraction of all the particles. If the suspension consists of a finite number of species having radii a_i, $(i = 1, 2 \ldots)$, then the volume fractions ϕ_i of the species can be used instead of $\Phi(a)$; the normalization is then $\Sigma\phi_i = \phi$. An alternative distribution function, used by Batchelor and Green (1972), is defined by $g(a) = \Phi(a)/\phi$ and has the convenient normalization of 1.

The type of flow imposed on the suspension can also affect its rheological properties, because there is no reason to expect that particles in suspension, even spherical ones, will be distributed isotropically, and indeed it is found that anisotropic distributions do occur in many flows. Most proposed models for calculating effective viscosities have assumed isotropic conditions, and this is one reason why they have failed to account for non-Newtonian behavior. In addition to producing anisotropy, flow can either promote or inhibit the formation of structures by the particles. An example of the formation of structures will be given in section 4 (Hoffman, 1972); here we shall discuss their breakdown. Clays are suspensions in which, when there is no flow, the particles flocculate and form continuous structures; consequently, they exhibit thixotropy and a yield stress. Thixotropy is a change in the properties of a suspension with time as a result of deformation [Jones and Brodkey (1970); Roscoe (1953) also discusses the similar concept of rheopexy; Fredrickson (1964)]. In the case of clays, this is caused by the breaking down of the structures as the suspension deforms, with the result that the viscosity appears to decrease with time (it will reach a steady state value which will depend on the magnitude of the rate-of-strain). If the structures become large enough, they can give the clay a yield stress, which refers to the critical value of the shear stress that must be exceeded before motion can set in.

3. NON-NEWTONIAN FLOW

The last section has pointed out that Newtonian models are insufficient to describe suspensions, and so some of the fundamentals of the rheology of non-Newtonian flows will be sketched here in order to facilitate the discussion that follows. We first note that the rheological description of a fluid is through a constitutive equation which relates the stress tensor σ_{ij} to the tensors that measure the rate of deformation, of which $e_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, the rate-of-strain tensor, is the simplest. Since it is not possible to deduce the constitutive relation directly from experiment, it is important to know at least what kind of information is needed to characterize completely the behavior of a fluid in any particular flow. One flow for which this is known is shear flow, the basic flow for all viscometric measurements (Coleman, Markovitz, and Noll, 1966; Truesdell, 1974). Steady shear flow between two plates is shown in Figure 5. Here the velocity field is given by $(\gamma y, 0, 0)$, where γ is the shear rate, and the force per unit area on the upper plate has two components: the shear stress σ_{12} or τ and the normal stress σ_{22}. The σ_{11} stress acts over a surface perpendicular to the plate, and σ_{33} acts in the direction out of the page and is not shown. Since the normal stresses include the pressure (which, of course, is $-\sigma_{ii}/3$), it is usual to consider the normal stress dif-

* The term double layer seems to be used by some authors to mean the charge cloud alone (Stern and Gouy layers) and by others to mean, as here, the system of charges on the particle and in the fluid.

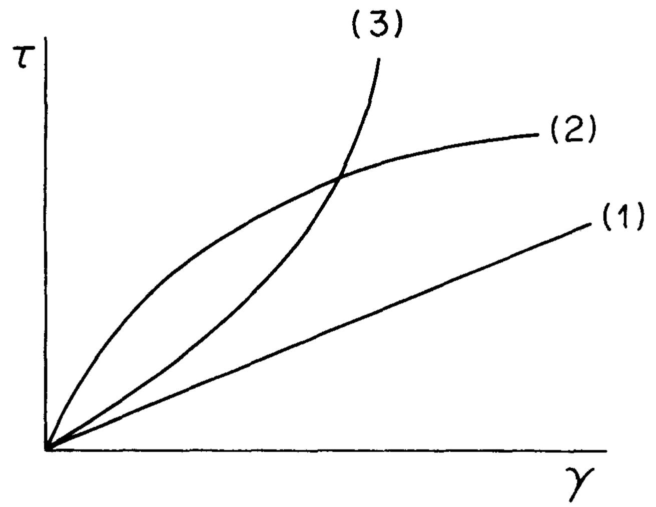

Fig. 6. A schematic representation of the variation of shear stress τ with shear rate γ for the main types of rheological behavior: (1) Newtonian, (2) shear thinning, (3) shear thickening.

ferences $\sigma_{11} - \sigma_{33}$ and $\sigma_{22} - \sigma_{33}$, so that the pressure is eliminated. The shear viscosity is defined by $\mu = \tau/\gamma$, and the three quantities μ, $\sigma_{11} - \sigma_{33}$, and $\sigma_{22} - \sigma_{33}$ are called the viscometric functions (some authors substitute σ_{12} for μ). For Newtonian fluids, μ is independent of γ, and the normal stress differences are zero. For non-Newtonian fluids, however, the three quantities vary with γ, and, in particular, the dependence of τ (or μ) on γ is used to classify fluids as shear thinning (pseudoplastic) or shear thickening. Schematic graphs are given in Figure 6 to show how τ varies with γ for the various cases. It should be noted that μ and the normal stresses are even functions of γ, and, because of this, in the limit $\gamma \to 0$ all fluids will appear to be Newtonian (Walters, 1975). Apart from their importance for viscometry, the viscometric functions are sufficient to predict the details of the laminar flow of a fluid through a pipe which, of course, finds many applications.

Not all steady flows can be predicted by using the viscometric functions: extensional flow is an important example of one that cannot. Figure 7 shows a uniaxial extensional flow in which the velocity field is $(e_{11}x, e_{22}y, e_{33}z)$, with $e_{11} + e_{22} + e_{33} = 0$, $e_{11} > 0$ and $e_{22} = e_{33} < 0$. As its name suggests, this type of flow occurs when fluid is drawn out into threads, and this is in fact how it arises in applications. The characterization of extensional flow (also called pure straining motion) can be studied by using the methods developed for steady shear flow (Coleman and Noll, 1962), and it is found that two new functions are needed. No agreement has been reached as yet regarding the definition (or measurement) of the two functions required to describe non-Newtonian behavior in extensional flow (Stevenson, Chung and Jenkins, 1975), although one widely used function is the extensional or Trouton viscosity

$$\lambda = \frac{\sigma_{11} - \frac{1}{2}(\sigma_{22} + \sigma_{33})}{e_{11}}$$

which is essentially the ratio of the tension in the fluid thread being extended to the rate of extension. For a Newtonian fluid, the Trouton viscosity is three times the shear viscosity, but in general no relation between them can be predicted a priori. It is much more difficult to measure extensional viscosities than viscometric functions, and there are still some problems in interpreting the experimental data. Nevertheless, the experiments that are de-

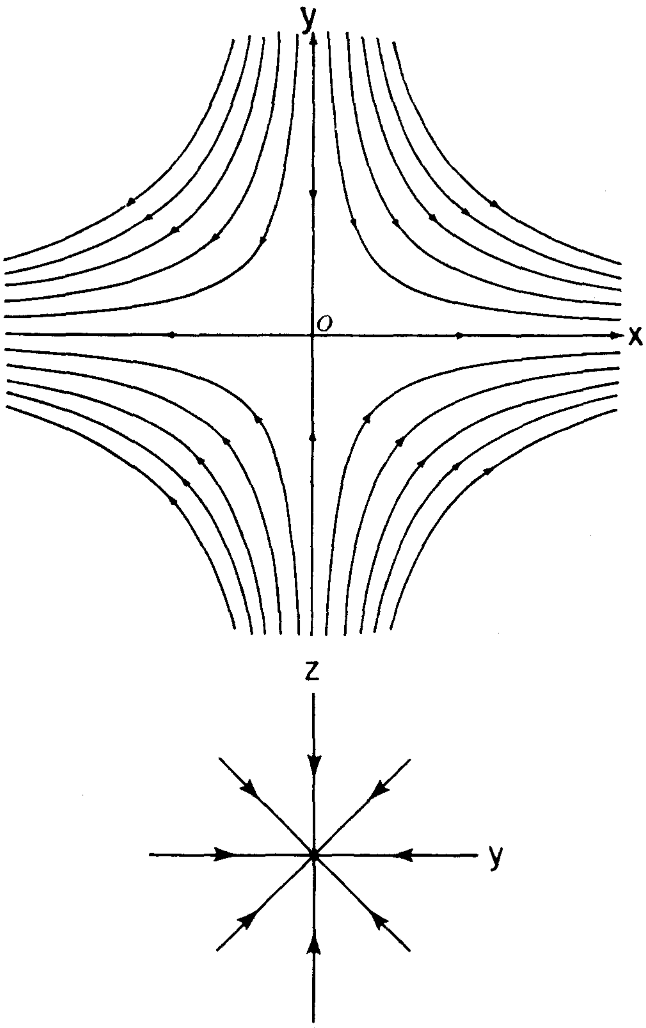

Fig. 7. Uniaxial extensional flow in the XY and YZ planes.

scribed in section 6 show dramatically that measurements on extensional flow, as well as shear flow, are needed if a more complete understanding of the rheological behavior of non-Newtonian fluids is to be gained.

It is important, both for completeness and later discussion, to finish this section with a few words about unsteady flows, even though no experimental data have yet been published for suspensions subjected to such flows. In unsteady flows, non-Newtonian fluids can exhibit viscoelastic properties, which should not be confused with other time-dependent effects such as thixotropy (Fredrickson, 1964). To be specific, let us consider sinusoidal shear flow (such as would result from oscillating the top plate in Figure 5 sinusoidally). The shear stress τ will vary with the same frequency as the shear rate but not in phase with it, the phase angle between τ and γ being equal to $\pi/2$ for a Newtonian fluid (Lodge, 1964). Because the normal stress differences are even functions of the shear rate, they will vary at twice the applied frequency; they will also suffer different phase shifts. Measuring the amplitudes of the stresses and their phase shifts with respect to γ is a standard way of studying viscoelastic effects in non-Newtonian fluids (Walters, 1975). These measurements will not change with time unless the fluid exhibits thixotropy as well.

4. RECENT EXPERIMENTS WITH SPHERICAL PARTICLES

We shall open our discussion of recent experiments by returning to the subject of suspensions of spherical parti-

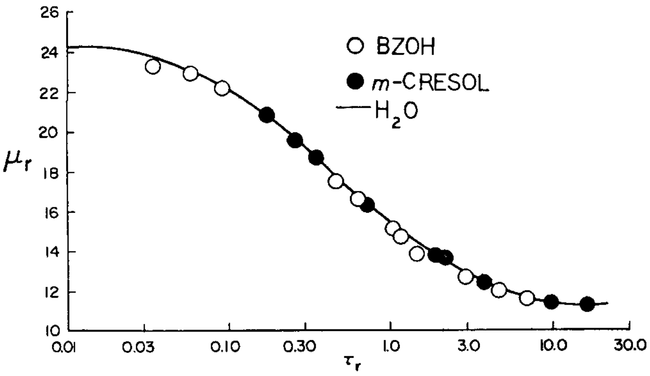

Fig. 8. A graph of the relative viscosities of suspensions of spherical particles ($\sim 1 \mu m$) plotted against shear rate for fixed volume fraction ($\phi = .5$) (Krieger, 1972). The graph combines data for different suspending fluids and shows shear thinning behavior.

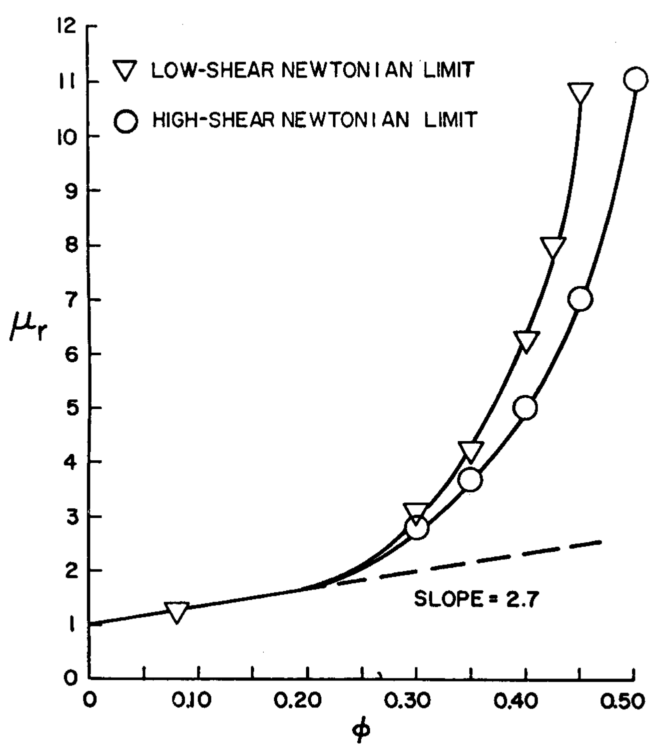

Fig. 9. Graphs taken from Krieger (1972) of the high shear (μ_1) and low shear (μ_2) limits of the relative viscosities plotted in Figure 8. A separate graph similar to Figure 8 was plotted for each volume fraction and μ_1 and μ_2 extracted as functions of ϕ.

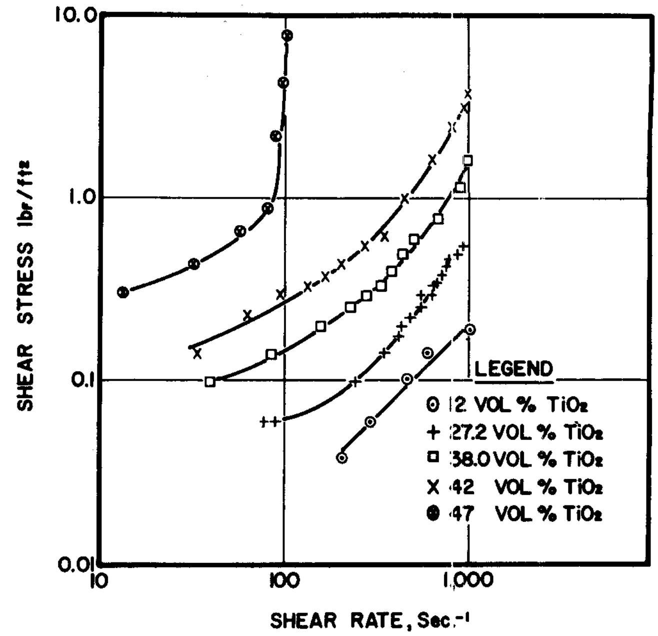

Fig. 10. Shear thickening found by Metzner and Whitlock (1958) as displayed in the variation of shear stress against shear rate. The different curves are for suspensions of different volume fractions.

cles in shear flow. The discussion so far has shown that rather than simply seeking an effective viscosity for such suspensions, one should determine the manner in which the viscometric functions vary with the shear rate and the constitution of the suspension. Experiments following this program have produced valuable data, although so far only for the viscosity and in most cases only for particles in the smallest size range (colloidal particles). Krieger (1972) has described experiments which are notable for their careful specification of the state of the suspension with respect to the variables given in section 2. His particles were monodisperse, and there were no electroviscous effects; therefore the viscosity could only be a function of the shear rate γ, a Brownian diffusion constant D, and the volume fraction ϕ.

Considering first the dependence on γ and D at fixed ϕ, we note that γ and D can be combined into a nondimensional group called a Péclet number, denoted Pe, which measures the relative importance of the flow and diffusion and which takes different forms depending on whether the diffusion is translational or rotational. Specifically, if D_t and Pe_t are the translational quantities and D_r and Pe_r the rotational ones, then $Pe_t = a^2\gamma/D_t$ and $Pe_r = \gamma/D_r$, where a is the radius of a sphere. Krieger and Dougherty (1959) and Brenner (1972) argued, by considering dilute systems, that the translational mode was the most important one and used the expression for D_t that was derived by Einstein (1956) for a single particle in an infinite fluid, $D_t = kT/6\pi\mu_0 a$, to predict that $Pe_t \propto a^3\mu_0\gamma/kT$ would be the important nondimensional parameter. However, the expression for D_r corresponding to that just given for D_t is $D_r = kT/8\pi\mu_0 a^3$, and hence Pe_r is also proportional to $a^3\mu_0\gamma/kT$. Further, in the presence of interactions between particles, the rotation of one particle will affect the motion of its neighbors, and so rotational diffusion cannot be neglected in concentrated suspensions the way it can be in dilute ones. Thus, the nondimensional group $a^3\mu_0\gamma/kT$ cannot distinguish between translational and rotational diffusion. Krieger's measurements of the relative viscosity of many suspensions, all having the same ϕ, are shown in Figure 8 plotted against the nondimensional variable $\tau_r = \tau a^3/kT$, where τ is the shear stress, which serves the purpose of a Péclet number, τ taking the place of $\mu_0\gamma$. The pleasing superposition of results for different suspensions confirms the selection of the variables that govern μ_r under these conditions but does not allow one to distinguish between translation and rotation as the possible mechanisms by which Brownian motion affects the viscosity of concentrated suspensions.

Having demonstrated by means of the graph of μ_r against τ_r the existence of shear thinning in his suspensions, Krieger turned to the problem of determining the functional dependence of μ_r on ϕ. Using Figure 8 as a basis, he argued that μ_r has well-defined limits as $\tau_r \to \infty$ and $\tau_r \to 0$, denoted by μ_1 and μ_2, respectively, and that these limits depend only upon ϕ. Graphs of $\mu_1(\phi)$ and $\mu_2(\phi)$ can thus be drawn, and these are shown in Figure 9. Although the fact that μ_1 exists might be interpreted to mean that the suspension is Newtonian in the limit of high shear, this is, of course, not necessarily the case because Newtonian behavior also requires that the normal stress differences be zero and that viscoelastic effects be absent.

Not all experiments have found suspensions to be shear thinning; Metzner and Whitlock (1958), for example, demonstrated shear thickening using TiO_2 spheres of 1 μ diameter. Typical rheograms for their suspensions are shown in Figure 10, the different curves being for suspensions of different volume fractions. The suspensions used by Metzner and Whitlock were less carefully characterized than Krieger's, and it has not been possible as yet to explain the observed behavior in terms of the forces acting in the suspension (this should not be taken to imply that Krieger's results have been explained quantitatively; what has been established for them is that further calculations should be based on a balance between Brownian diffusion and flow strength). Similar shear thickening has been reported in the Russian literature by Krasheninnikov, Malakhov and Fiöshina (1967). Metzner and Whitlock state that their suspensions changed from shear thinning to shear thickening in different ranges of γ, and further experimental evidence of this type of behavior has been provided by Hoffman (1972).

The results of Hoffman (1972) are probably the most remarkable that have been published to date. His data for 1 μ PVC monodisperse spheres are presented in Figure 11 and clearly show that, for volume fractions above 0.5, there is a discontinuity in the viscosity as a function of γ. Even for volume fractions below 0.5, Hoffman's results are of interest because they support Metzner and Whitlock's contention that both thinning and thickening behavior can be observed at different shear rates. To explain the discontinuities, Hoffman carried out diffraction studies on the suspensions. Below the critical shear rate he found patterns which he interpreted as being caused by the particles forming, and moving in, layers, while above the critical shear rate he observed that the pattern was replaced by a more diffuse one, suggesting that the particles were now moving in a disordered way. It seems then that there are two types of flow and that the layered flow pattern becomes unstable at the critical shear rate. These results show dramatically the need to know something about the structure of the suspension before attempting to understand its rheology. A theory for this flow (Hoffman, 1974) will be described later. It is worth remarking here, however, that the discontinuity is a result of the special kinematics of shear flow in which planes of fluid (and particles) slide over one another, and that such a discontinuity would not occur in a more general flow. This illustrates again the point made earlier that shear flow is rheologically very special. All of the experiments quoted so far have used colloidal particles, and, since nonhydrodynamic forces have less influence on larger particles, suspensions of larger particles should show the effects described above to a lesser degree.

The effect of polydispersity on the viscosity of a suspension was demonstrated by Chong, Christiansen, and Baer (1971) using suspensions with spherical particles of just two sizes. Figure 12 shows how the viscosity of such suspensions varies as the relative proportions of the two species are altered while the total volume fraction is kept fixed. A qualitative explanation of this effect can be given. If we consider a suspension of two species of spheres of very different sizes having volume fractions ϕ_1 and ϕ_2, then qualitatively the large spheres can be viewed as being suspended in a fluid with a certain viscosity. Now, if we suppose for a moment that a function $\mu_r(\phi)$ exists (and it must be emphasized that this is assumed here only for qualitative purposes), then the viscosity of the suspension will be $\mu\mu_r(\phi_1)$, where μ is the viscosity of the fluid of small particles which in turn equals $\mu_0\mu_r(\phi_2)$. Thus the

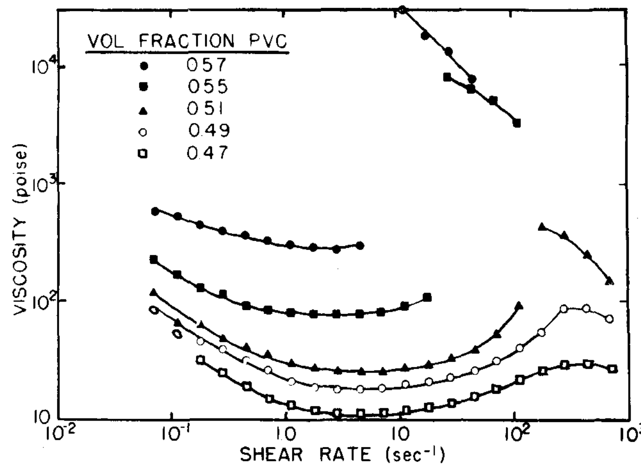

Fig. 11. The discontinuous dependence of viscosity on shear rate found by Hoffman (1972). The size of the discontinuity varies with the volume fraction of the particles.

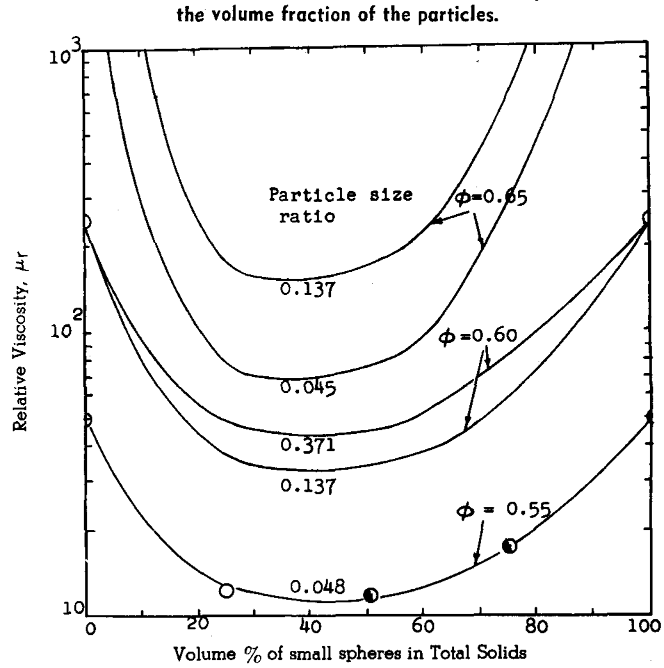

Fig. 12. Data taken from Chong, Christiansen, and Baer (1971) for suspensions consisting of spheres of two sizes. The total volume fraction was held constant and the viscosity plotted against the proportion of spheres of one species in the total sample.

effective viscosity is $\mu_0\mu_r(\phi_1)\mu_r(\phi_2)$. On the other hand, if the particles are all the same size and the volume fraction is $\phi_1 + \phi_2$, then the viscosity will be $\mu_0\mu_r(\phi_1 + \phi_2)$. Now, experimentally, $\mu_r(\phi)$ rises faster than exponentially for $\phi \gtrsim 0.5$ (again the warning must be made that data such as those of Figure 1 are taken only for qualitative purposes), and so $\mu_r(\phi_1 + \phi_2) > \mu_r(\phi_1)\mu_r(\phi_2)$.

5. ELECTROVISCOUS EFFECTS

The origins of electroviscous effects were discussed in section 2; here we shall summarize some experimental findings. The results of Fryling (1963), reproduced in Figure 13, clearly show the enormous differences in viscosity that can be achieved as a result of electroviscous effects. The changes in viscosity are produced by altering the concentration of ions in the suspending fluid which in turn alters the thickness of the charge cloud (κ^{-1}). Although both shear thinning and shear thickening can be seen in the data, the variation of the effective viscosity with shear rate is too weak to call for an explanation. It is of interest, of course, to ask whether such electroviscous effects can

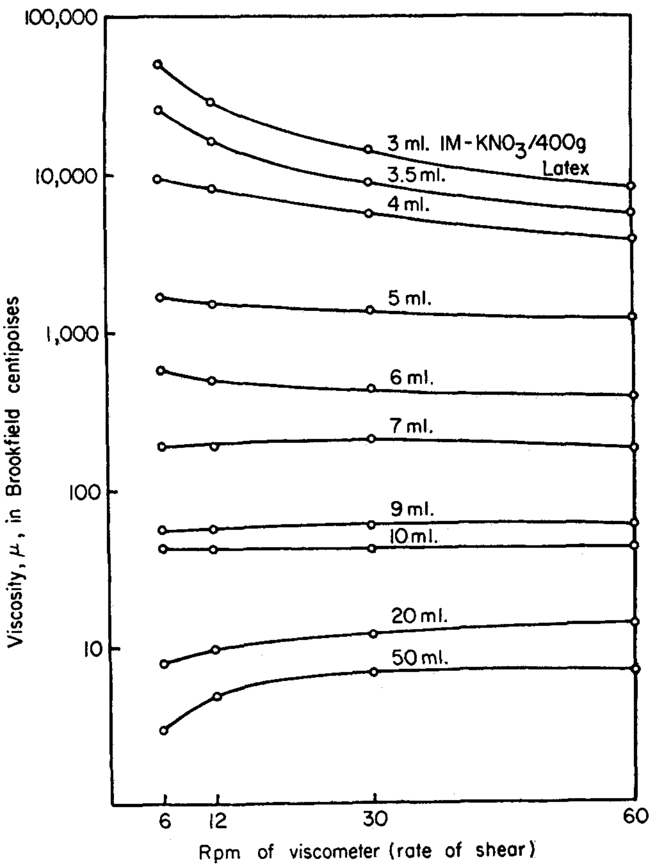

Fig. 13. The results of experiments by Fryling (1963) in which the concentration of electrolyte in the suspending fluid was altered. The different curves are for different electrolyte concentrations with ϕ constant (≈28).

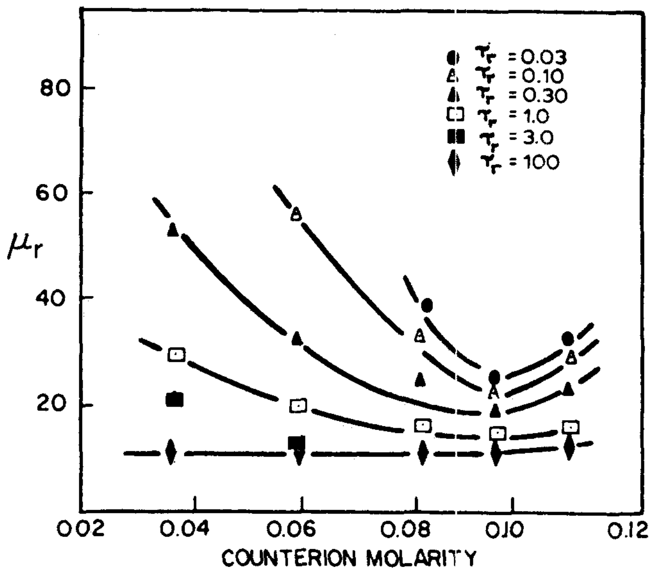

Fig. 14. The plot used by Krieger to find the concentration of electrolyte for which the viscosity (and hence electroviscous effect) was a minimum.

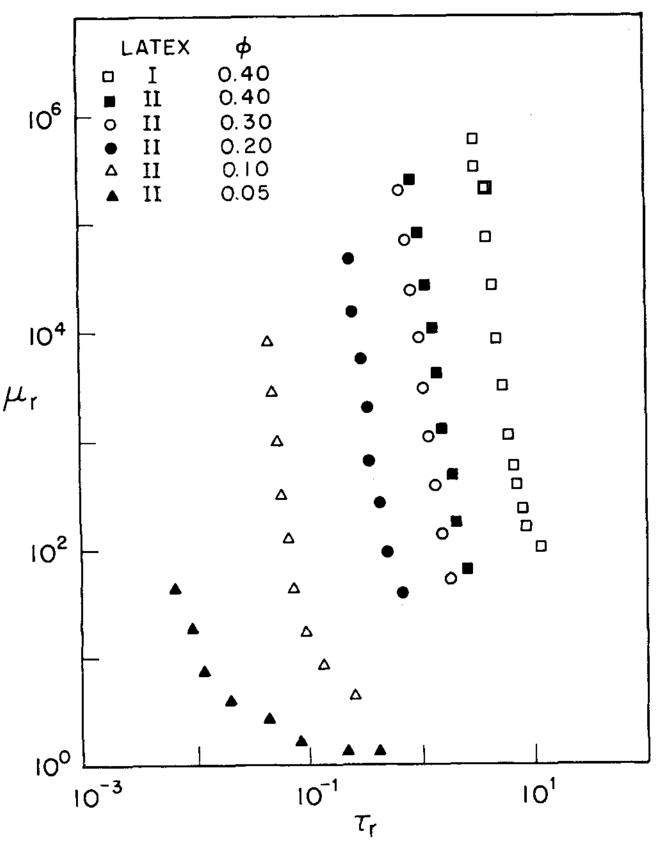

Fig. 15. The relative viscosity of suspensions strongly influenced by electroviscous effects (Krieger and Eguiluz, 1976). The suspensions show a yield stress and shear thinning.

be suppressed, particularly with regard to the discussion of Krieger's experiments, whose interpretation was based on the assumption that electroviscous effects were negligible. Krieger interpreted his data using plots such as those shown in Figure 14. The curves show that there is a concentration of electrolyte for which the viscosity is a minimum, and Krieger conducted all his experiments at this concentration, taking it to be the one for which there would be no electroviscous effects. Of course, plots such as Figure 14 give the level at which electroviscous effects are a minimum, but whether they are completely absent is not settled. Further justification for the assumption must be based on the consistency of the results. The Einstein coefficient, for example, was found to be 2.65, which agrees well with 5/2 and provides strong additional evidence for the absence of electroviscous effects under the stated conditions.

Krieger and Eguiluz (1976) have taken the above observations further and found that in the extreme case when electroviscous effects are at their maximum, the suspension has a yield stress. In such a case the shear stress τ tends to a finite value as the shear rate γ tends to zero, and since viscosity is τ/γ, it must become infinite as $\gamma \rightarrow 0$. This behavior is clearly seen in Figure 15, taken from Krieger and Eguiluz (1976). Of particular interest is the low value of ϕ for which a yield stress seems to exist, since it might be possible to apply the exact theory, which is given below, directly to these results. The other interesting point about the results is that the usual explanation of yield stress requires particles to come together and form continuous structures, but the particles in the suspensions of Krieger and Eguiluz must be presumed to repel each other strongly. Hence, no convincing reason for the observed yield stress can be given at present.

6. EXPERIMENTS WITH RODLIKE PARTICLES IN EXTENSIONAL FLOW

So far we have considered experiments on suspensions of spherical particles in shear flow. Interesting results have also been obtained, however, in an extensional flow which, as remarked earlier, cannot be described by using the conventional viscometric functions. One experiment that has brought out the non-Newtonian character of suspensions in extensional flow was performed by three groups: Weinberger and Goddard (1974), Mewis and Metzner (1974), and Kizior and Seyer (1974), who measured the Trouton viscosity of a suspension of rodlike particles so as to test a theoretical prediction made by Batchelor (1971).

The motion of a rodlike particle in extensional flow is quite different from that in shear flow. In a shear flow an isolated rod tumbles over and over as it is carried along by the mainstream (Jeffery, 1922; Cox and Mason, 1971), but in extensional flow such a rod rotates until its long axis coincides with the principal axis of extension and then stays there (Takserman-Krozer and Ziabicki, 1963). Further, in shear flow a rod spends most of its time approximately parallel to the streamlines, in which position it has least effect on the flow; in contrast, in extensional flow a rod is permanently in the position in which it has maximum effect on the flow. Weinberger and Goddard measured both the shear viscosity and the Trouton viscosity for their suspensions and obtained the results presented in Table 1. Analogous measurements of the extensional viscosity were performed by Mewis and Metzner and by Kizior and Seyer who arrived at results such as those shown in Figure 16, the roman numerals indicating results for particles of different aspect ratios r (= length/breadth). The large differences between the two types of viscosities shown in Table 1 clearly illustrate the non-Newtonian aspect of the suspensions used, while all experiments show that even small concentrations of slender rodlike particles can produce large increases in the stress levels in such systems. A comparison of these results with theory will be made later.

7. THE APPROACH TO THEORY

The experimental results described above will now be used to examine existing theories in accordance with the aim stated in the introduction. We can ask the following questions: What conditions must be fulfilled before a suspension can be treated as though it were a homogeneous fluid? Which factors, and hence which parameters, are important in determining the rheology of a suspension? What are the constitutive relations (or at least the viscometric functions) describing the rheology? The first question came to the attention of experimenters when it was found that capillary viscometers whose bores were not large compared with the size of the particles in the suspension gave effective viscosities that depended upon the bores (the Fâhraeus-Lindqvist effect). The problem arises more frequently in laboratory work than in applications because most commercial viscometers endeavor to use as small a sample as possible. No satisfactory theoretical treatment of the problem has yet been worked out, although several experimental studies have been conducted (Jastrzebski, 1967; Seshadri and Sutera, 1968) which can be used to estimate when the dimensions of the apparatus will interfere with the measurements. Further, Segré and Silberberg (1962) showed that it is possible for inhomogeneous distributions of particles to arise as a result of small inertial forces acting in the flow. Care is thus needed to ensure that the suspension remains homogeneous during measurements.

The second question has mostly been answered already in the earlier sections of this review, where the experimental evidence was presented. Here, a summary of the present state of our knowledge is given. A particle in suspension is subject to hydrodynamic, thermal, electrical, and van der Waals forces, and with these forces are associated the following parameters.

1. Flow strength γ. If the bulk motion of the suspension is described by a rate-of-strain tensor e_{ij}, then $\gamma^2 = 2e_{ij}e_{ij}$. For simple shear flow, γ equals the shear rate.

2. Brownian diffusion coefficient D. The definition is $D = kT/R_w$, where k is Boltzmann's constant, T the absolute temperature, and R_w an appropriate resistance coefficient for translational or rotational motion of the particle.

TABLE 1. COMPARISON OF THE SHEAR VISCOSITY μ AND TROUTON VISCOSITY λ (MEASURED IN POISE) FOR NEWTONIAN FLUIDS WITHOUT AND WITH ELONGATED PARTICLES SUSPENDED IN THEM. (WEINBERGER AND GODDARD, 1974)

Suspending fluid	Without particles		With particles ($r = 57$)	
	μ (poise)	λ (poise)	μ (poise)	λ (poise)
Silicone	1 000	3 000	1 130	29 000
Indopol	205	615	235	5 400

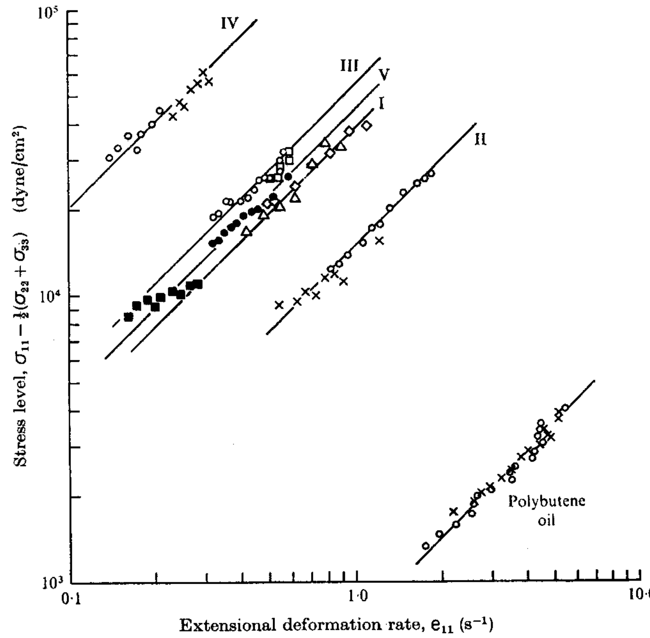

Fig. 16. The stress generated by rodlike particles in an extensional flow as found by Mewis and Metzner (1974). The roman numerals refer to suspensions of particles of different aspect ratios (length/breadth).

3. Surface potential ψ_0 (or surface change density) and Debye length κ^{-1}. The strength of the electrical charge on the surface of a particle is measured by ψ_0 and the thickness of the ion cloud around the particle by κ^{-1}.

4. Hamaker's constant A. The constant appears in the law for the van der Waals force between particles and is fixed for a given suspension. Nondimensional groups formed from these parameters, such as the Péclet number, can be used to measure the relative importance of the various forces, and several such nondimensional groups will be given in later sections. Other important variables that can be added to this list are:

5. Particle size a and aspect ratio r. The size of the particle has an important influence on the relative importance of hydrodynamic and nonhydrodynamic forces in the suspension. The importance of the aspect ratio (= length/breadth) was shown in Figure 16.

6. Thickness of surfactant layer δ. During the emulsion polymerization process, surfactants are used to stabilize the particles, and the thickness of the layer left on the particle will be important when the volume fraction of small particles are calculated or when the volume fraction approaches its maximum value.

7. Volume fraction ϕ and distribution functions $\Phi(a)$ or $g(a)$. Previous sections discussed the importance of the distribution functions when the particles are not all the same size (see Figure 12).

8. Particle Reynolds number R. The Reynolds number

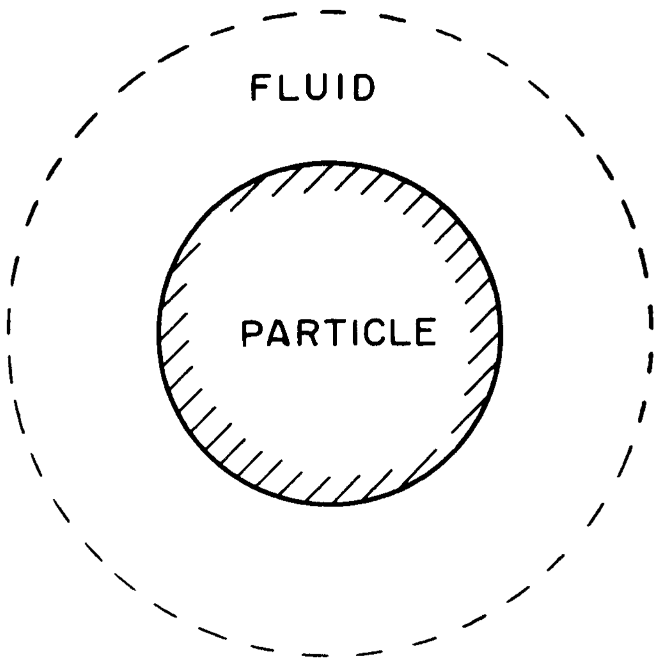

Fig. 17. The situation envisaged for the cell model and self-consistent scheme. For the cell model, the boundary conditions are applied at the dashed outer boundary which has a radius $a\phi^{-1/3}$. For self-consistent schemes, a second fluid having the unknown effective properties surrounds the cell. The usual continuity conditions at an interface between two fluids are applied at the dashed boundary which has been given different radii by different authors.

for the flow around particles will usually be much less than unity; however, inertial effects can influence the motion of larger particles (Segré and Silberberg, 1962; Ho and Leal, 1974) and the rheology of the suspension.

9. Type of flow. No parameter is used to label this, but it is an important consideration.

This completes the discussion of the second question. The third question, on constitutive equations, has been the object of a number of theoretical studies and has been tackled from many different approaches. They are discussed in the following sections with regard to their empirical and theoretical content and the light they shed on the experimental results.

8. CURVE FITTING

In a companion paper to his collection of experimental data, Rutgers (1962*b*) tabulated the many formulas that had been proposed for $\mu_r(\phi)$ up to 1962 and then tested them against his average curve. Recently, Jinescu (1974) did likewise and included in his review suggested functions for the variation of μ_r with shear rate. Of the formulas proposed for $\mu_r(\phi)$, two, both of which contain adjustable parameters, have become widely used. That adjustable parameters are contained in the formulas is not surprising, because it has been shown that no single function $\mu_r(\phi)$ can exist, and so any proposed function that can fit data for more than one suspension must contain adjustable parameters. The formulas are those of Mooney, and Krieger and Dougherty, respectively:

$$\mu_r = \exp\left(\frac{B\phi}{1 - K\phi}\right) \tag{3}$$

$$\mu_r = (1 - K\phi)^{-B/K} \tag{4}$$

In the limit $\phi \to 0$, both of the above reduce to $1 + B\phi$. Thus, B can be interpreted as an Einstein coefficient and should, for spherical particles, lie between 2.5 and about 5 (the lower bound is discussed in section 10, and the upper bound is experimental), depending on the degree of aggregation of the particles and the size of the electroviscous effect. As $\phi \to 1/K$, $\mu_r \to \infty$ in both cases; therefore, K^{-1} refers to the maximum possible value of ϕ, that is, the value for which the suspension loses mobility. Consequently, for a monodisperse suspension of spherical particles, its value is bounded by the volume fractions for touching spheres in cubic and hexagonal packing (0.52 and 0.74) and will be close to the volume fraction for random packing (0.62). The curves in Figure 9 are calculated from Equation (4), with $B = 2.65$ and $1/K = 0.57$ (low shear curve), 0.68 (high shear curve).

Expressions for the variation of μ_r with γ have also been proposed. The one used to fit the data in Figure 8 is

$$\mu_r = \mu_1 + \frac{\mu_2 - \mu_1}{1 + |\tau|/\tau_m} \tag{5}$$

where μ_1 and μ_2 are the high and low shear limit viscosities of the suspension, and τ_m is an adjustable parameter. There seems to be some disagreement about the name of this equation. Krieger calls it a Williamson equation, but Jinescu gives the Williamson equation as

$$\mu_r = \mu_1 + \frac{(\mu_2 - \mu_1)}{1 + (\gamma/C)^2}. \tag{6}$$

At any rate, (5) implies that $d\mu_r/d\tau$ is nonzero at $\tau = 0$. This, of course, is an undesirable feature of the equation because suspensions will become Newtonian as $\tau \to 0$, and this requires $d\mu_r/d\tau$ to equal zero at $\tau = 0$. For suspensions showing a yield stress, the Casson equation is commonly used to fit the data:

$$\tau^{1/2} = \tau_0^{1/2} + \mu_1^{1/2}\,\gamma^{1/2}$$

where τ_0 is the yield stress, and μ_1 is the high shear limiting viscosity. This equation is mostly applied to clays and other strongly electroviscous suspensions; it was used by Krieger and Equiluz (1976) to fit the data shown in Figure 15.

The main drawback common to all of these equations is that the parameters have to be determined from experiments. This vitiates their predictive power because, after the experiments have been performed, the role of such formulas is reduced to one of interpolation. Thus, a more refined theory is clearly needed if the rheology of suspensions is to be predicted with greater accuracy.

9. MODELS FOR SUSPENSIONS

Of the many models that have been proposed for calculating the rheology of suspensions, the cell models have been the most widely used. A full description of their features was given by Happel and Brenner (1965), and although further elaborations have appeared since then, they have generally been concerned with matters of detail only. A cell consists of a particle surrounded by fluid as shown in Figure 17. Its shape is taken as spherical, and the radius of the cell is chosen so that the ratio of particle-to-cell volume equals ϕ; that is, the radius is $a\phi^{-1/3}$. On the outer boundary of the cell, conditions are applied which are chosen to model the average effect of the rest of the suspension. The Stokes equations for creeping flow

$$\mu_0 \nabla^2 \mathbf{u} = \nabla p, \quad \nabla \cdot \mathbf{u} = 0$$

are solved inside the fluid shell subject to the no slip condition on the particle surface and to the chosen conditions at the outer boundary. Several solutions, based on different outer conditions, are given in Happel and Brenner (1965). The choice of a spherical outer boundary at

$a\phi^{-1/3}$ is mathematically convenient but hard to justify otherwise, except that since the cell represents an average situation, an isotropic suspension should be modeled by using an isotropic cell (it will be pointed out in section 14 that suspensions are rarely isotropic). Since the results derived from this model will depend strongly on the somewhat arbitrary choices for the shape of the cell and the boundary conditions, their quantitative significance is clearly open to doubt. Another weakness of the models is that the outer boundary is placed at $a\phi^{-1/3}$, which implies that all particles are as far from each other as possible, and so it fails to take account of the close approach of particles. It is not surprising, therefore, that the formulas given by the cell models have been unsuccessful in explaining the experimental data, particularly at high concentrations (Rutgers, 1962*b*), and have even disagreed at times with well-established results such as Einstein's (see Happel and Brenner, 1965, Equation 9-2.17). Thus, we are forced to conclude that, in spite of the appeal cell models continue to have for many theoreticians, they can contribute little to further advances in the theory of suspensions except, perhaps, in a qualitative sense.

Another approach has used so-called self-consistent schemes which are similar to cell models and which were developed independently in several fields for calculating the properties of two-phase materials (polycrystals, composite materials). The idea behind self-consistent schemes is to immerse the cell of Figure 17 in a second fluid whose properties are the unknown effective properties that are to be calculated. The flow of these two fluids is now solved with the usual conditions at their interface and with the known applied flow at infinity. An implicit expression is obtained for the viscosity. Self-consistent schemes suffer the same drawbacks as cell models and in particular produce expressions for the effective properties which are most accurate at small values of ϕ, just the range of ϕ for which exact solutions are now available. Recent users of this approach have been Buevich and Markov (1973) and Neale and Nader (1974).

A calculation of the effective viscosity of a suspension has been published by Allen and Kline (1968) using equations taken from the theory of micropolar fluids. This approach, however, runs counter to the logical connection between the theory of micropolar fluids and suspension mechanics in that calculations of the rheology of suspensions from basic principles should be the basis for building a theory of micropolar fluids rather than vice versa. This is because the study of suspensions offers the builders of continuum models the advantage that the assumptions of the model can be justified in terms of the known structure of the suspension, and thus there appears to be little point in using models when more fundamental calculations are possible.

10. VARIATIONAL METHODS

Variational methods have been used in other fields where two-phase materials occur, and it is of interest to see whether they can be applied to suspensions because they offer the advantage that they can be used to derive bounds on quantities such as the viscosity which are completely general. Thus, using the well-known analogy between solid mechanics and fluid mechanics, one can transcribe the Hashin-Shtrikman bounds for the elastic moduli of a composite material (Hashin and Shtrikman, 1963) to obtain bounds on the effective viscosity of a fluid suspension (this, of course, means adopting once again the Newtonian approach to suspensions). A lower bound can be derived in this way, but no upper bound can. For small volume fractions, the lower bound for a suspension of spheres coincides with Einstein's formula. The presence of rigid particles in the system is the cause of the failure to find an upper bound, and at present there seems to be no way of improving the Hashin-Shtrikman bounds while retaining the generality spoken of earlier. Keller, Rubenfeld, and Molyneux (1967) have given an upper bound for the effective viscosity, but it was obtained using a model, in which the suspension was treated as a regular array, to evaluate the necessary integrals. Thus, their result does not have the generality spoken of earlier.

11. EXACT RESULTS FOR DILUTE SUSPENSIONS

The lead given by Einstein in studying dilute suspensions has been followed by numerous investigators, and a large number of results are available. The importance of the study of dilute suspensions to the subject as a whole is that all the results are exact, in the sense that once the assumptions about the state of the suspension have been made (what forces are acting, type of particles, etc.), all further work is rigorous and thus devoid of unknown errors. It should be kept in mind though that the value of calculations for dilute systems lies in the insight they give to the mechanisms acting in suspensions rather than in any quantitative predictions, because these would be hard to measure experimentally and would be of small practical value. Thus, for example, the results of dilute theory have been used as test cases for proposed general rheological equations. Although it is not intended to discuss this application of suspension mechanics in detail, the work of Barthés-Biesel and Acrivos (1973) can be quoted as an example of how dilute-suspension results can be applied in a wider context. These authors examined several constitutive relations that were proposed on general rheological principles by Hand, Erickson, and others to see how they compared with the special case provided by suspensions. This work is now being extended by Hinch and Leal (1975), and the review by Bird (1976) contains a section on similar work.

Two different methods for calculating the effective properties of a suspension have been employed in the past. The first, which was used by Einstein, equates the energy dissipated in the suspension to the energy dissipated in a fluid having the effective viscosity $\mu^\star$. It is evident, though, that this approach suffers the disadvantage of yielding only the effective viscosity of the suspension and not the full constitutive relation. The second method, to be described presently, is preferable because it leads to an expression relating the average stress tensor in the suspension to the average rate-of-strain tensor. The basic definitions of the second method have been carefully laid out by Batchelor (1970) who also shows that the first method is subsumed by the second in that the energy dissipated in the suspension is derivable from the average stress and rate-of-strain tensors.

It is possible to define the average stress by either an ensemble average or a volume average (Batchelor, 1970), but for the systems considered here, the definitions are equivalent and so the simpler volume average will be used. The average is taken over a sample volume V which is chosen large enough to contain many particles and yet small enough for the rate of strain to be statistically homogeneous throughout it. The motion of a suspension conforms then to the given average of the rate-of-strain tensor $<e_{ij}>$ defined by

$$<e_{ij}> = \frac{1}{V} \int e_{ij}\, dV \qquad (7)$$

where the integration is over the volume V, and it is desired to calculate the average stress $<\sigma_{ij}>$ given by

$$<\sigma_{ij}> \equiv \frac{1}{V} \int \sigma_{ij}\, dV \qquad (8)$$

It should be noted that this last equation contains an implicit assumption that the effects of inertia in the suspension are negligible; a more general definition will be given later. This is a standard assumption in the study of suspensions, although one calculation of the first effects of inertia will be mentioned in section 13. The average in Equation (8) is to be obtained from the constitutive equation linking σ_{ij} and e_{ij} at each point in the fluid, but before proceeding with this we shall consider the equations of motion for the suspending fluid. Since we wish to include electroviscous effects, the suspending fluid will be characterized at each point by a fluid velocity $\mathbf{u}$, an electric potential ψ, and a charge density ρ. The equation of motion for the fluid now contains a term $\rho\nabla\psi$ from the electric field (Booth, 1950) as well as the usual terms in the Stokes equations:

$$\nabla p + \rho\nabla\psi = \mu_0\nabla^2\mathbf{u} \qquad (9a)$$

$$\nabla \cdot \mathbf{u} = 0 \qquad (9b)$$

Next, Poisson's equation is needed to calculate ψ from the charge density ρ

$$\nabla^2\psi = -\rho/\epsilon \qquad (9c)$$

and finally an equation for the mobility of the ions is required to close the circle and link ρ and $\mathbf{u}$:

$$\mathbf{V}_i = \mathbf{u} - \omega_i\left(\frac{kT}{m_i}\nabla m_i + q_i\nabla\psi\right) \qquad (9d)$$

$\mathbf{V}_i$ is the velocity of the ions of type i, and ω_i, m_i, and q_i are their mobilities, concentration, and charge, respectively.

Just as the electric field enters the equations of motion, so it enters the expression for the stress σ_{ij} in the fluid, and the constitutive equation can be written (Russel, 1976*a*) as

$$\sigma_{ij} = -p\delta_{ij} + 2\mu_0 e_{ij} + M_{ij} + B_{ij} \qquad (10)$$

where

$$M_{ij} = \epsilon\left(\frac{\partial\psi}{\partial x_i}\frac{\partial\psi}{\partial x_j} - \frac{1}{2}\frac{\partial\psi}{\partial x_k}\frac{\partial\psi}{\partial x_k}\delta_{ij}\right)$$

is the Maxwell stress, and B_{ij} represents Brownian stresses. (Russel uses σ_{ij} for the hydrodynamic part of the stress only.) B_{ij} is not a quantity about which a great deal is known; it has been included here for completeness.

The expression for σ_{ij} must now be substituted into Equation (8). The general analysis is complicated (see Russel, 1976*a*), and we shall restrict our discussion to the case when M_{ij} and B_{ij} are negligible. The integral is first broken up into integrals over the volume occupied by the fluid V_1 and by the solid V_2 to yield

$$<\sigma_{ij}> = \frac{1}{V}\int_{V_1}\sigma_{ij}dV + \frac{1}{V}\int_{V_2}\sigma_{ij}dV$$

$$= \frac{1}{V}\int_{V_1}\{-p\delta_{ij} + 2\mu_0 e_{ij}\}dV + \frac{1}{V}\int_{V_2}\sigma_{ij}dV$$

The integral in Equation (7) can be similarly decomposed and the integral over V_1 eliminated from the expression for $<\sigma_{ij}>$:

$$<\sigma_{ij}> = -P\delta_{ij} + 2\mu_0<e_{ij}>$$

$$+ \frac{1}{V}\int_{V_2}\{\sigma_{ij} + p\delta_{ij} - 2\mu_0 e_{ij}\}dV$$

Now in an incompressible medium, the pressure $(-\sigma_{ii}/3)$ is locally indeterminate, being determined by overall constraints on the flow. The trace of $<\sigma_{ij}>$ is thus not of further interest and will simply be denoted by $-P$ and not considered separately. With this simplification, the remaining volume integral can be transformed into an integral over the surfaces of the particles:

$$<\sigma_{ij}> = -P\delta_{ij} + 2\mu_0<e_{ij}>$$

$$+ \frac{1}{V}\int\left\{\sigma_{ik}n_k x_j - \frac{1}{3}\sigma_{lk}x_l n_k\delta_{ij} - \mu_0(u_i n_j + u_j n_i)\right\}dA$$

If, finally, the value of the above surface integral for just one particle is denoted by S_{ij}, then the total surface integral equals the sum of the S_{ij} calculated for each particle in turn, and the equation for $<\sigma_{ij}>$ becomes

$$<\sigma_{ij}> = -P\delta_{ij} + 2\mu_0<e_{ij}> + \frac{1}{V}\Sigma S_{ij} \qquad (11)$$

where the summation is over the particles within the sample volume V. Thus, the preceding analysis has used the fact that the suspension consists of particles and fluid to reduce the volume average in Equation (7), and hence the computation problem, to a consideration of the value of S_{ij} for each particle.

12. EINSTEIN'S SOLUTION

Einstein's calculation of the effective viscosity formula quoted as Equation (1) used the energy dissipation approach. The energy dissipated in the suspension is (when we remember that $e_{ij} = 0$ within a rigid particle)

$$\Phi = 2\mu_0 \int e_{ij}e_{ij}dV$$

which, on setting $e_{ij} = <e_{ij}> + e_{ij}'$, becomes

$$\Phi = 2\mu_0(1-\phi)V<e_{ij}><e_{ij}>$$

$$+ 4\mu_0<e_{ij}>\int e_{ij}'\,dV + 2\mu_0\int e_{ij}'\,e_{ij}'\,dV$$

Einstein supposed that the integral of e_{ij}' could be evaluated as though each particle contributed independently to it (Einstein actually dealt with surface integrals, but the result is the same). If one makes this assumption, though, it turns out that at large distances r from a particle, e_{ij}' falls off as r^{-3}, and so the integral is not absolutely convergent. Einstein circumvented this problem by choosing a spherical volume, for which the integrals take finite values. As a result, however, the average rate of strain in the suspension no longer equaled $<e_{ij}>$ because its calculation required the evaluation of a second nonconvergent integral. However, when Φ was found for the new rate of strain, the contributions from the nonconvergent integrals canceled. It is of interest to note that Einstein did not mention these convergence difficulties in his paper.

Actually, Einstein's formula can be obtained directly from Equation (11) by calculating S_{ij} for each particle as though it were alone in the fluid. If this value is denoted $S_{ij}^{(0)}$, and n is used for the number density of particles in the suspension, we obtain (Batchelor, 1970; Landau and Lifshitz, 1959)

$$<\sigma_{ij}> = -P\delta_{ij} + 2\mu_0<e_{ij}> + nS_{ij}^{(0)} =$$

$$-P\delta_{ij} + 2\mu_0\left(1 + \frac{5}{2}\phi\right)<e_{ij}>$$

The last equation follows from the value of $S_{ij}^{(0)}$ for a sphere freely suspended in a flow whose rate of strain far from the particle is $<e_{ij}>$. This equation is superior to (1) because it proves that the suspension is Newtonian under Einstein's assumptions, in addition to giving the value of $\mu^\star$.

13. OTHER $O(\phi)$ SOLUTIONS

If the assumptions about the shape of the particles and the forces acting on them are eased but the assumption of diluteness is retained, so that we still have $S_{ij} \approx S_{ij}^{(0)}$ for each particle, then it is possible to calculate explicitly the non-Newtonian behavior that the suspension now displays. Three types of calculation will be discussed here: those assuming nonspherical particles acted on by Brownian forces, for which the non-Newtonian behavior comes from the competition between the couples acting on the particles; those assuming spherical particles and electroviscous effects where, to $O(\phi)$, only the first electroviscous effect need be considered; and those allowing inertial effects to be important. Most attention in these calculations has been paid to the Einstein coefficient (also often called the intrinsic viscosity and denoted $[\mu]$, although objections to this practice have been raised). It is the coefficient B in the equation

$$\mu_r = 1 + B\phi + O(\phi^2)$$

and, as explained in earlier sections, is not generally a constant but a function of the flow variables. The many solutions for the first of the types of problems mentioned above have been summarized in the paper-cum-monograph by Brenner (1974), and only a general discussion is attempted here. The way Brownian effects are included in calculations based on Equation (11) has been the subject of some confusion over the years. Some authors argued that the only effect of Brownian motion would be to change the distribution of particle orientations in space and so first calculated $S_{ij}^{(0)}$ for a given orientation of the particle from the appropriate solution of the Stokes equations and then averaged over the (Brownian affected) distribution of orientations to obtain the final expression for the average stress. It is realized now, however, that the Brownian couples, as well as contributing to the average of $S_{ij}^{(0)}$, make a direct contribution to the value of $S_{ij}^{(0)}$. This direct contribution comes about because the rate of rotation of a particle as calculated from the Stokes equations, call it $\mathbf{\Omega}^s$, is not the actual rotation rate, there being a contribution from Brownian couples as well. To compensate for this, recent authors have calculated $S_{ij}^{(0)}$ using an effective rotation rate $\mathbf{\Omega}^s + \mathbf{\Omega}^{Br}$, where $\mathbf{\Omega}^{Br}$ has a known form (Brenner, 1974), Equation [4.9-10]). The justification for the form of $\mathbf{\Omega}^{Br}$ is not yet complete, although there is general agreement that the presently used one is correct. Of the available results, only one need be quoted here to display the non-Newtonian behavior mentioned above. Hinch and Leal (1972) found simple algebraic expressions for the viscometric functions for a suspension of nearly spherical particles, using the small parameter ε to measure departures from sphericity:

$$\mu_r = 1 + 2.5\phi + \varepsilon^2 \{k_1 + k_2 (1 + [\gamma/6D_r]^2)^{-1}\}\phi + O(\phi\varepsilon^3)$$

$$\sigma_{11} - \sigma_{33} = \phi\mu_0\varepsilon^2 D_r k_3 (1 + [6D_r/\gamma]^2)^{-1} + O(\phi\varepsilon^3)$$

$$\sigma_{22} - \sigma_{33} = -6(\sigma_{11} - \sigma_{33}) + O(\phi\varepsilon^3)$$

where k_1, k_2, and k_3 are known constants, and $D_r = kT/8\pi\mu_0 a^3$ is the rotational Brownian diffusion constant for a dilute suspension of spheres. Of course, for $\varepsilon = 0$, that is, for perfectly spherical particles, the non-Newtonian effects disappear.

Booth (1950) calculated the Einstein coefficient for a suspension of spheres in which the first electroviscous effect (distortion of the charge cloud) was important. He took the suspension to be electrostatically dilute; that is, he assumed that the charge clouds do not overlap, the condition for which is $2a\kappa >> \phi^{1/3}$, and that the flow was weak compared with the other forces and found that the Einstein coefficient was simply increased in value by a factor β. There are no non-Newtonian effects to this level of approximation. Thus

$$\mu_r = 1 + 2.5\beta\phi + O(\phi^2)$$

$$\beta = 1 + \sum_{r=1}^{\infty} A_r \left(\frac{q}{e}\right)^r$$

where q is the charge on a particle, e is the electronic charge, and the A_r are coefficients that can be calculated and depend upon the Debye length κ^{-1}.

Non-Newtonian effects can be produced when the inertia in the suspension is included in the calculation (Lin, Peery, and Schowalter, 1970). To calculate the effect of the inertia, the definition of the bulk stress has to be modified to include a momentum transport term. Thus, if Σ_{ij} is the bulk stress and $<\sigma_{ij}>$ is the average of the hydrodynamic stress, we have

$$\Sigma_{ij} = <\sigma_{ij}> - <\rho u_i' u_j'>$$

Combining this with a matched asymptotic expansion analysis, Lin, Peery, and Schowalter found the following expressions for the viscometric functions:

$$\mu_r = 1 + \phi\left(\frac{5}{2} + 1.34R^{3/2}\right)$$

$$\sigma_{11} - \sigma_{33} = \mu_0\gamma\phi R\left(-\frac{2}{3} + 0.35R^{1/2}\right)$$

and

$$\sigma_{22} - \sigma_{33} = \mu_0\gamma\phi R\left(\frac{2}{3} - 0.25R^{1/2}\right)$$

where $R \equiv \gamma a^2/\nu$ is the particle shear Reynolds number.

It is interesting to note that this calculation shows that the suspension is shear thickening.

14. SOLUTIONS TO $O(\phi^2)$

To extend the analysis just described to $O(\phi^2)$, one must take into account interactions between particles. The correct way to do this has only recently been settled (Batchelor and Green, 1972), and consequently only a few calculations have yet been completed. The results quoted here are all for spherical particles. Specifically, if one chooses a test particle and makes it the origin of a set of coordinates, then the state of the suspension is described by a function $P(\mathbf{r}|\mathbf{o})$ which gives the probability density for a second sphere being found with its center at $\mathbf{r}$. This function has to be calculated from the motion of the suspension and is not generally isotropic, implying that the suspension will be non-Newtonian and showing the inadequacy of the cell model and similar approaches. Thus, if one considers the natural extension of Einstein's problem, with spheres interacting purely hydrodynamically (Batchelor and Green, 1972), it is found that in shear flow the function $P(\mathbf{r}|\mathbf{o})$ is indeterminate, and so the inclusion of Brownian motion or electroviscous effects is unavoidable. The latter have been included by Russel (1976*a*, *b*) who, following Booth (1950), assumed an electrostatically dilute suspension. Russel found that three nondimensional numbers were needed to balance the various forces: $a\kappa$, which compares the thickness of the charge

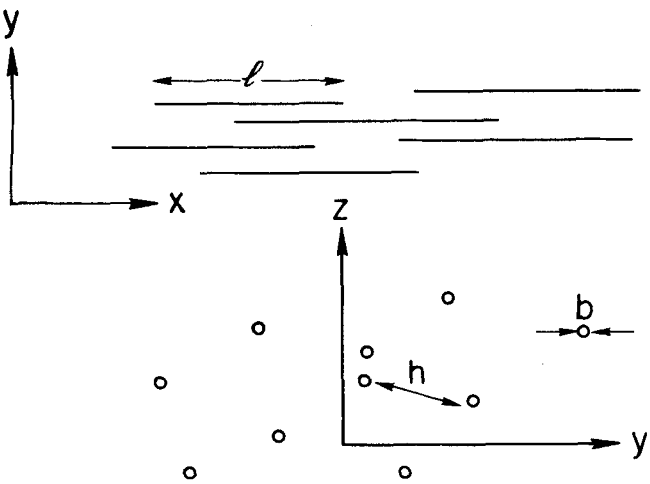

Fig. 18. Two views of a suspension of parallel rodlike particles of length *l* and breadth *b*. Although not dilute when viewed in the xy plane, the suspension obeys a modified diluteness condition in the yz plane.

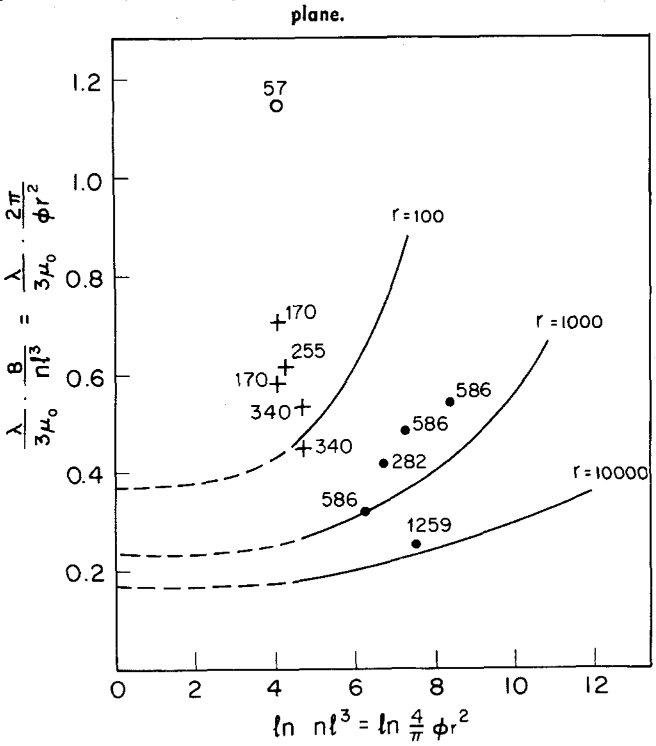

Fig. 19. The data of Weinberger and Goddard (1974) (open circle), Mewis and Metzner (1974) (solid circles), and Kizior and Seyer (1974) (crosses) plotted on a graph taken from Batchelor (1971). Next to each point is written the aspect ratio of the particles that were used to obtain that point.

cloud with the particle radius; α, which measures the ratio of electrostatic force to Brownian diffusion (its algebraic form is too complicated to be quoted here); and Γ, which serves as a Péclet number and measures the importance of convection to diffusion. Russel took $\alpha >> 1$, so that electrostatic repulsion between the particles kept the suspension stable, and then examined separately the cases $a\kappa >> 1$ (thin charge cloud) or $a\kappa << 1$, and $\Gamma << 1$ (limit of low shear). The latter is the simplest to describe because the suspension is Newtonian in this limit, the relative viscosity being

$$\mu_r = 1 + 2.5\beta\phi + 2.5\beta^2\phi^2 + B' \frac{\phi^2}{(a\kappa)^5}$$

where B' depends on α, and β is the factor found by Booth. For general values of Γ, the situation becomes very complicated because of the interplay between the various nondimensional groups. We note, however, that $B'/(a\kappa)^5$ can dominate the hydrodynamic contribution $2.5\beta^2$, and that the suspensions are shear thinning with increasing Γ (or γ).

15. RODLIKE PARTICLES IN EXTENSIONAL FLOW

The experimental results for a system of rodlike particles undergoing uniaxial extensional flow were presented in section 6; here we shall describe the theoretical treatment of Batchelor (1971). The interesting feature of this analysis is that although the volume fraction of the rods is small, the suspension cannot be treated as dilute in the sense used above, that is, with the particles independent of each other. However, one can manipulate the problem so that a new diluteness postulate is possible. The suspension is illustrated in Figure 18 and consists of rods of length l, diameter b, and average separation h (note that l and b are defined slightly differently from Batchelor, 1971). The extensional flow has lined up all the particles so that they are parallel to each other, and it is obvious that the particles cannot be considered independently. What Batchelor realized was that under the conditions $b << h << l$, the velocity $\mathbf{u} - <\mathbf{u}>$ (the local velocity less the average velocity) will be entirely along x and only slowly varying in that direction. Thus, the problem reduces to one in the yz plane, where the particles (or at least their cross sections) are dilute in a noninteracting sense. The two-dimensional problem can be solved and an effective Trouton viscosity λ found for the suspension

$$\frac{\lambda}{\mu_0} = 3 + \frac{4}{3} \frac{\phi r^2}{\ln(\pi/\phi)}$$

where $r = l/b$ is the aspect ratio of the particles. This formula suggests that even though ϕ is small, the factor r^2 can produce substantial increases in λ/μ_0 over the Newtonian value of 3. The experimental studies which tested this prediction were described previously, and a comparison between the measured and predicted values of λ can be seen in Figure 19. The number density of the particles n used in the figure is related to ϕ, b, and l by the equation $\phi = \frac{1}{4}\pi b^2 l n$. The agreement is very satisfactory and becomes better for the particles having the higher aspect ratios for which the assumptions introduced in the theory are most accurate.

16. CONCENTRATED SUSPENSIONS

Although no exact theory comparable with that presented above exists for concentrated suspensions, some asymptotic methods used in recent calculations hold out considerable hope for further development. The first is due to Frankel and Acrivos (1967) who considered the viscosity of a concentrated suspension of spherical particles and used lubrication theory to calculate the energy dissipated in the neighborhood of the small gaps between the particles [independently, Murray (1965) suggested a similar approach]. The key idea is that in a very concentrated suspension the energy dissipation will be dominated by the contribution from the small gaps between the particles, and the need to calculate the entire flow field around the particles can be circumvented. The calculation of $<\sigma_{ij}>$ instead of the energy dissipation would improve this method, as would a more detailed study of the ways in which it is possible for a concentrated suspension to deform.

Finally, an analysis by Hoffman (1974) makes similar use of asymptotic relations for very close spheres to explain the discontinuity in the viscosity he found earlier (Hoffman, 1972, see section 4). Having determined experimentally that the discontinuity was a stability problem involving layers of particles sliding over one another, Hoffman set out to find the balance between stabilizing and destabilizing forces on a layer of particles. One interesting aspect of the work was the inclusion of van der Waals forces acting between the layers of particles, such forces not having been used in dilute theory. To calculate these van der Waals forces, Hoffman had to approximate each layer of particles by a solid plane, and this assumption must be looked on as a weak point of the theory; nevertheless, the result for the stability of the layer showed quite good agreement with experiment.

17. DIRECTIONS FOR FUTURE WORK

The theory of suspensions shows great potential at present for further development. On the theoretical side, there is every indication that the existing results for very dilute suspensions [the $O(\phi)$ results] will be extended soon to provide a corresponding set of results for less dilute systems [$O(\phi^2)$], and this will further improve our understanding of the mechanisms at work in suspensions. At the other end of the concentration scale, the asymptotic method of Frankel and Acrivos (1967) shows promise for being developed into a useful way of studying very concentrated suspensions. At the present time, though, there seems little hope that a general theory will be forthcoming which would be valid for all concentrations.

On the experimental front there are similar opportunities for progress. Krieger has set a good example here by always being careful to describe the state of the suspension before starting to take viscosity measurements. His lead in searching for nondimensional representations for his results is also worth following, and at the very least experimenters should present results for relative viscosity rather than absolute viscosity. In view of the non-Newtonian nature of suspensions, measurements of all the viscometric functions are needed; the measurement of normal forces is standard practice for polymers and should become so for suspensions. Equally interesting from the non-Newtonian point of view would be measurements in unsteady flows (viscoelastic effects) and nonviscometric flows (such as extensional flow). A systematic study of the rheology of suspensions as a function of the factors itemized by the recent advances in the theory together with the development of more powerful tools for theoretical predictions should result in significant progress in our knowledge of this branch of fluid mechanics.

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NOTATION

A = Hamaker's constant
a = radius of sphere
B = Einstein coefficient
B_{ij} = Brownian stress
C = parameter
D = Brownian diffusion constant
e_{ij} = rate of strain
g = distribution function
h = average lateral spacing of particles
k = Boltzmann constant
K = parameter
l = length of particle
m_i = mobility of ion
M_{ij} = Maxwell stress
n = number density of particles
p, P = pressure
P = probability density
Pe = Péclet number
q_i = charge on ion
R = Reynolds number
R_w = Resistance coefficient
r = aspect ratio
S_{ij} = stresslet defined in (11)
T = absolute temperature
$\mathbf{u}$ = velocity of suspending fluid
$\mathbf{V}_i$ = ion velocity
V = volume element

Greek Letters

β = factor in Booth's equation for electroviscous effect
γ = shear rate
δ = thickness of surfactant layer
ϵ = permittivity
κ^{-1} = Debye length
λ = extensional viscosity
$\mu^\star$ = effective viscosity
μ_0 = viscosity of suspending fluid
μ_r = $\mu^\star/\mu_0$
μ_1 = high shear limit of μ_r
μ_2 = low shear limit of μ_r
ρ = charge density
σ_{ij} = stress
τ = shear stress
τ_r = $a^3\tau/kT$
τ_0 = yield stress
τ_m = parameter
ϕ = volume fraction
Φ = distribution of volume fractions
ψ = electric potential
ω_i = mobility

Symbols

$< >$ = average

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