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The rheology of fibre suspensions ☆

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Abstract

We review theoretical work on the rheology of fibre suspensions. We seek to clarify one or two confusions in published work and also give a small improvement to Batchelor's formula for extensional viscosity of suspensions of long fibres between the dilute and semi-dilute régimes. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In theoretical work on suspensions, the approaches which have been adopted use basic hydrodynamics to discover how the motions of the suspending liquid and of the suspended particle influence each other and a statistical approach to model the behaviour of a collection of suspended particles. The three steps in constructing a rheological model are therefore

1. Model the motion of an individual fibre in a homogeneous, possibly time-dependent, flow field. This is discussed in Section 2, below.
2. Model the evolution of the distribution of the orientations of many such fibres. This is discussed in Section 3, below.
3. Calculate the contribution to the bulk stress due to the fibres in terms of the bulk flow. This requires calculation of appropriate averages using the orientation distribution function and is also discussed in Section 3. Results are summarized in Section 4

Almost all theoretical work has been done for dilute suspensions in Newtonian liquids. In Section 5 we discuss non-dilute suspensions, starting from the work of Batchelor. Section 6 covers some aspects of the effect of a non-Newtonian suspending liquid and application to the rheology of polymer-based composites is discussed in Section 7. One important issue, which is relevant for dilute and non-dilute suspensions and for Newtonian and non-Newtonian suspending liquids too, is how to avoid calculating the

☆ Dedicated to Professor David Boger on the occasion of his 60th birthday

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orientation distribution function explicitly. The commonest way of doing this involves a structure tensor (defined as an average of the second moment of the fibre orientation vector) and, to obtain a complete set of equations, a 'closure' approximation. This is discussed below, along with alternative approaches.

In keeping with our title we shall devote our attention primarily to suspensions of long slender particles, although clearly some of what we say will apply to particles of more general shapes. In addition we note that much of the modelling of suspension behaviour can be (and is) used for models of solutions, although the different length scales that are relevant clearly affect the balance between different physical effects. Work on fibre suspensions is particularly relevant to solutions of rigid rodlike polymeric molecules (and vice versa).

Because the field is one where there is much current activity, we include in Section 8 some brief comments on recent papers and also on some in areas which are peripheral to the main topics discussed here. Note that 'peripheral' is not by any means to be equated to 'unimportant'. An idea of the extent of activity may be gained from the fact that at the recent annual meeting of the Polymer Processing Society (PPS15, June 1999) there were over 80 papers on composites and fibre suspensions (out of a total of nearly 300 papers). Of these, probably half dealt in some detail with either the rheology of fibre suspensions or the fibre orientation distribution.

2. Hydrodynamics of a single particle

The basis for all current models for suspensions is the theory of Jeffery [1] for the motion of a single ellipsoid in a Newtonian fluid. The motion is referred to as a Jeffery orbit (Section 2.1 below). The most comprehensive discussion of suspensions of arbitrary rigid, neutrally buoyant, axisymmetric particles is probably that given by Brenner [2]. This deals specifically with particles possessing fore-and-aft symmetry suspended in a Newtonian liquid in a flow with a spatially homogeneous velocity gradient. Both steady and unsteady flows are considered by Brenner and he includes the effect of rotary Brownian diffusion (i.e. the tendency, in the absence of any velocity field, for particles in a suspension to assume a random orientational distribution).

One important prediction concerning the motion of such a particle in a simple shearing flow, in the absence of significant effects of Brownian motion, is the rotation of the particle which is caused by the flow. A rod-like particle moves in what is best described as a tumbling motion; this has been well confirmed experimentally. The result which is important for suspension rheology is that a particle moves in an orbit which is independent of time and the particular orbit is determined by the initial orientation of the particle. This means that, without Brownian motion, the stress in a suspension of many such particles (provided that they did not interact with one another) would vary periodically in a way which was determined by the initial configuration of the particles and would never reach a steady state — such a suspension would not exhibit a 'fading memory'. For suspensions of fibres of length greater than about 3 μ, Brownian motion does not appear to offer an effect of sufficient magnitude, although for long slender fibres the mathematical processes of taking limits of large aspect ratio and of small Brownian motion effect interact subtly (see Hinch and Leal [3] and Section 3 below).

Experimental studies on real suspensions, notably the classic series of papers by Mason and co-workers, are reviewed by Goldsmith and Mason [4] and by Hur [5]. Anczurowski and Mason [6] observe how the loss of memory of phase angle (k in Eq. (4) below) and orbit constant (C in Eq. (5) below) occur on different times scales (the phase angle faster than the orbit constant). More recently, Stover, Koch and Cohen [7] measured an orbit constant correlation function which gives an idea of the rate of loss of memory and Rahnama, Koch and Shaqfeh [8] calculated how hydrodynamic interactions affect this correlation function.

The conclusions are summarized by Zirnsak, Hur and Boger [9] and the principal fact that emerges is that fibre suspensions do rapidly forget any initial configuration and so do, in fact, behave as materials with fading memory. The speed with which an initial configuration is forgotten may be attributable to any one of a number of mechanisms, of which particle–particle interactions, polydispersity (fibres having a range of aspect ratios) and non-uniformity of the flow field (e.g. in Poiseuille flow) are most likely to be important. Hur [5] lists these and also mentions the effect of a non-Newtonian suspending liquid and (obviously) the effect of external forces (which might arise from an electric or magnetic field).

2.1. *Jeffery orbits*

We consider simple shear for a prolate ellipsoid, with

$$v_x = \dot{\gamma} y; \quad v_y = v_z = 0. \tag{1}$$

As we might expect the motion of a particle whose axis of symmetry lies in the *xy*-plane is one of rotation about the *z*-axis. If the axis of symmetry lies parallel to the *z*-axis there is merely rotation of the particle about its axis of symmetry and the rheological effect of any such particle will be equivalent to that of a sphere. These are both effectively two-dimensional situations. For particles which are neither parallel to nor perpendicular to the *z*-axis we find that the ends of the axis of symmetry of the particle trace out a path whose projection onto the *xy*-plane is an ellipse and onto the *xz*-plane is part of a hyperbola (with z taking a maximum value when $y=0$ and a minimum value when $x=0$). There is, in other words, motion of the ends away from the *xy*-plane containing the midpoint of the particle as the particle lines up with the direction of the flow (the *x*-direction) and motion of the ends towards that plane as the particle lines up in the *y*-direction. The elliptical orbit in the *xy*-plane therefore has its major axis along the *y*-axis and its minor axis along the *x*-axis.

The quantitative description of this is given by Jeffery [1] and by Hinch and Leal [3] who discuss several aspects of particle motion thoroughly. We consider the motion of a unit vector $\boldsymbol{u}$ parallel to the axis of symmetry of the particle, which we take to be an ellipsoid of revolution (a spheroid) with aspect ratio r. Following Jeffery, we introduce spherical polar coordinates θ, the angle between $\boldsymbol{u}$ and the *z*-axis, and φ, the angle between the projection of $\boldsymbol{u}$ on the *xy*-plane and the *x*-axis. Almost the same notation is used by Hinch and Leal (θ_1 and φ_1), but note that other authors use different definitions and there is scope for confusion. In our notation, the vector $\boldsymbol{u}$ then has components $u_x=\sin\theta\sin\varphi$, $u_y=\sin\theta\cos\varphi$ and $u_z=\cos\theta$. The orientation of the particle, in the absence of Brownian motion and other effects (e.g. body forces, particle interaction) is governed by the coupled differential equations

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t} = \frac{\dot{\gamma}}{r^2+1}(r^2\cos^2\varphi + \sin^2\varphi), \tag{2}$$

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{\dot{\gamma}}{4}\left(\frac{r^2-1}{r^2+1}\right)\sin 2\theta \sin 2\varphi. \tag{3}$$

These have solutions θ and φ given by

$$\tan\varphi = r\tan\left(\frac{\dot{\gamma}t}{r+r^{-1}} + k\right) \tag{4}$$

and

$$\tan\theta = \frac{Cr}{\sqrt{r^2\cos^2\varphi + \sin^2\varphi}}, \tag{5}$$

where C and k are constants which depend on the initial orientation of the particle. The end of the axis of symmetry of the particle describes a curve given by the intersection of the unit sphere

$$u_x^2 + u_y^2 + u_z^2 = 1 \tag{6}$$

and the hyperboloid

$$r^2u_x^2 + u_y^2 = r^2C^2u_z^2. \tag{7}$$

The constant C can take any non-negative value, with $C=0$ corresponding to the case of the particle being aligned with the z-axis ($\theta=0$ and $\boldsymbol{u}$ not changing) and $C=\infty$ to $\theta=\pi/2$. For a slender particle, $r\gg 1$ and, as Burgers [10] showed, we can simplify things appreciably. We can approximate Eq. (3) by

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \frac{\dot{\gamma}}{4}\sin 2\theta\,\sin 2\varphi, \tag{8}$$

and, provided that $|\varphi|$ is not close to $\pi/2$, Eq. (2) by

$$\frac{\mathrm{d}\varphi}{\mathrm{d}t} = \dot{\gamma}\,\cos^2\varphi. \tag{9}$$

Hinch and Leal [3] discuss this in detail, introducing different polar angles for convenience, and obtain an approximation in the region where $\cos\varphi\to 0$. We note that the times spent in different parts of the orbit are dependent on the particle's aspect ratio and the shear rate. For very long slender particles, most of the time is spent lined up with the flow and the 'flip-over' time (time for rotation through π in the xy-plane) is of the order of r^{-1}.

It is possible to draw parallels between the motion of a single fibre in one of these Jeffery orbits and the motion of liquid-crystalline polymers (LCPs). This is discussed by Chaubal and Leal [11] who point out that the evolution equation for the director $\boldsymbol{n}$ in the Leslie–Ericksen theory is identical to the generalized Jeffery equation, Eq. (20), below. The Leslie–Ericksen theory applies to rigid-rod polymers in the nematic phase (see, for example, Doi and Edwards ([12], Section 10.5)) and is noteworthy for predicting a linear dependence of first normal stress difference on shear rate (see Section 4.2 below). The motion described as 'director tumbling' is like the rotation of a fibre in the xy-plane, $\theta(t)=\pi/2$ for all time, t. When the fibre is perpendicular to the xy-plane, $\theta(t)=0$ for all time, t, we have 'log-rolling'. The term 'kayaking' is used for motions where both $\theta(t)$ and $\varphi(t)$ are periodic functions of time (and not constant). Other motions ('wagging' and 'flow aligning') are discussed by Chaubal and Leal but these have no analogues in the motion of a single fibre in a Jeffery orbit. The discussion by these authors [11] of the effect of Péclet number (see below, Section 3) is useful.

2.2. Non - ellipsoidal particles-effective aspect ratio

The relation between the rate of rotation and the aspect ratio of the ellipsoid can be used to define an effective aspect ratio for non-ellipsoidal particles. This has been justified theoretically by Bretherton [13] who showed that any axisymmetric particle rotates with a period t_{r} given by

$$t_{\mathrm{r}} = \frac{2\pi}{\dot{\gamma}}(r_{\mathrm{e}} + r_{\mathrm{e}}^{-1}), \tag{10}$$

where $\dot{\gamma}$ is the shear rate and r_{e} is the effective aspect ratio of the particle. There have been both theoretical and empirical relations obtained for r_{e} for particular shapes of particle. Burgers [10] obtains the approximate result $r_{\mathrm{e}} = 0.74r$ for infinitely long cylindrical rods, while for long slender bodies Cox [14] obtained $r_{\mathrm{e}}/r = \text{constant}$ for a sharp-ended body and $r_{\mathrm{e}}/r = \text{constant}(\log \mathrm{r})^{-0.5}$ for a blunt-ended body. It appears that Burgers' approximation does not in fact deal with the blunt-ended nature of the cylindrical rods. Measurement of the period of rotation of cylindrical rods enabled Mason et al. [15,16,17] to estimate r_{e} experimentally. They found that r_{e} decreased from $0.7r$ to $0.53r$ as the aspect ratio, r, increased from 20.4 to 115.3 which is acceptably close to the above theoretical results. Brenner's work [2] implicitly includes calculations of r_{e} and is discussed below.

The motion of a particle in simple shear is to be contrasted with its motion in an extensional flow, where there is a tendency for it to line up with the flow. We should make this last statement more precise; to do so requires making a distinction between the long slender particles which are our primary concern here (rods or prolate ellipsoids) and short fat particles (discs or oblate ellipsoids). In uniaxial extension (elongational flow) a rod will tend to line up in the direction of the extension while a disc will line up with its axis of symmetry perpendicular to that direction [18]. Conversely in uniaxial compression (or equibiaxial extension) a disc will line up with its axis of symmetry in the direction of compression while a rod will line up perpendicular to that direction. This gives us two examples of situations where the equilibrium orientation of a particle is indeterminate, and simple shear is a third such example (for any particle). Bretherton has obtained a general result giving the condition under which a particle tends to line up parallel to a specific direction, regardless of its initial orientation [13] (see also [18]). It turns out that the simple flows we prefer to consider (simple shear, axisymmetric extension) are exceptions in this regard.

Brenner [2] shows that for an arbitrary axisymmetric particle (possessing fore-and-aft symmetry) five dimensionless scalars, which depend only on the shape of the particle, suffice to determine completely the hydrodynamic interaction between the particle and the liquid. In Brenner's notation, the scalars are ${}^{r}K_{\perp}$, N, Q_1, Q_2, and Q_3. These five scalars are tabulated [2] for particles of a variety of shapes including ellipsoids of revolution, dumbbells and long slender particles. Hinch and Leal [18] obtain similar scalars which they refer to as shape factors and also [3] tabulate their values for ellipsoids in cases of limiting values of the aspect ratio (very large, very small and close to 1).

Brenner's approach to the effective aspect ratio, discussed above, is to introduce a derived scalar parameter B by

$$B = \frac{5N}{3\,{}^{r}K_{\perp}}, \tag{11}$$

and then define

$$r_{\mathrm{e}} = \sqrt{\frac{(1+B)}{(1-B)}}, \tag{12}$$

when $B < 1$. (For some curiously shaped particles B may exceed unity [2,13] and in such cases r_{e} is not defined.) For an ellipsoid

$$B = \left(\frac{r^2 - 1}{r^2 + 1}\right), \tag{13}$$

and in general it depends only on the effective aspect ratio r_e of the particle. B varies between 0 for a sphere and 1 for an infinitely long slender ellipsoid (or equivalent particle).

One distinction which should be noted is between the hydrodynamic results for sharp-ended and blunt-ended bodies. Brenner [2] points out that any ellipsoid is (as far as this technical usage of the term is concerned) a sharp-ended body. A cylinder (with flat ends) is a blunt-ended body since the cross-sectional area is not a function of distance along the axis of symmetry which tends smoothly to zero at the ends of the particle. Formulae which are asymptotically valid in the limit of large aspect ratio (very long slender particles) are given by Brenner [2] for all the scalar shape factors for both sharp-ended and blunt-ended bodies, although in the case of blunt-ended bodies there is one constant which has not been determined theoretically, but has been estimated empirically.

Some comment is perhaps helpful in addressing the similarities and differences between suspension mechanics and the modelling of polymeric liquids. We have been discussing rigid particles here exclusively; most models of polymeric liquids, though by no means all, involve flexible models of the macromolecules. Further, for models of macromolecules, the phenomenon referred to as hydrodynamic interaction arises (to be modelled or neglected according to the complexity acceptable in the model) [19,20]. In the context of molecular modelling, the term hydrodynamic interaction is normally used to refer to interaction between different parts of the same molecule. This is an intramolecular effect rather than an intermolecular effect and hence it is relevant in dilute solution theory. With flexible macromolecules one typically approximates the hydrodynamic drag on the molecule by considering the drag on each segment of a flexible 'chain' (of beads and springs or beads and rods). Then it is necessary to allow for influence of flow near one part of the chain on other parts. The use of the term hydrodynamic interaction for a rigid macromolecule, e.g. for the so-called *shish-kebab* model of a rod-like molecule [12] describes a simple physical approximation to the hydrodynamics which can be avoided by a more complete analysis [2]. For a rigid fibre, complete solution of the interaction between fibre and liquid incorporates any effect of hydrodynamic interaction between parts of the fibre. One then may use the term hydrodynamic interaction for non-dilute solutions, where it refers to the interaction between different fibres caused by their effect on the flow.

3. Dilute suspension theory

The basic assumptions employed in almost all dilute suspension models are

1. The volume fraction, ϕ, of fibres is so small that hydrodynamic interaction between fibres or between a fibre and a flow boundary may be ignored. In fact $n\ell_p^3$ is really the key magnitude here and for fibres of large aspect ratio this differs considerably from ϕ (see Eq. (58) below). (The fibres have length $2\ell_p$, and number density n.)
2. The fibre length is much smaller than any flow dimension.
3. The aspect ratio, r, (or effective aspect ratio, r_e) of the fibres is uniform.
4. The suspending liquid is incompressible and Newtonian.
5. The effects of inertia and external body forces may be neglected.
6. It is also often the case that the effects of rotary Brownian motion may be neglected.

This last assumption will be discussed carefully here; one of the issues which seems to cause confusion is the question of whether there is in fact a steady state in simple shear, or whether an undamped oscillating shear stress is predicted when a steady shear rate is imposed. The issue of rotary diffusivity also arises in non-dilute suspensions of fibres which are too large for Brownian forces to have an effect. See Section 5 below. In this case the same mathematical term (as the one which describes the effect of rotary Brownian motion) is used to approximate the effect of interactions between fibres.

3.1. The basic flow

We consider a flow with the spatially homogeneous, but possibly time-dependent, velocity field

$$\boldsymbol{v}(\boldsymbol{x}, t) = \boldsymbol{L}(t) \cdot \boldsymbol{x}, \tag{14}$$

in which the velocity gradient tensor $\boldsymbol{L}$ is decomposed into the symmetric rate of strain tensor

$$\boldsymbol{D} = \tfrac{1}{2}(\boldsymbol{L} + \boldsymbol{L}^{\mathrm{T}}), \tag{15}$$

and the anti-symmetric vorticity tensor

$$\boldsymbol{W} = \tfrac{1}{2}(\boldsymbol{L} - \boldsymbol{L}^{\mathrm{T}}). \tag{16}$$

We shall discuss both simple shear, Eq. (1) and extensional flows, in particular uniaxial extension

$$v_x = \dot{\varepsilon} x; \quad v_y = -\tfrac{1}{2}\dot{\varepsilon} y; \quad v_z = -\tfrac{1}{2}\dot{\varepsilon} z. \tag{17}$$

The viscosity, η, (in simple shear) is, as usual, the ratio of shear stress to rate of shear, $\dot{\gamma}$ and the uniaxial extensional viscosity, η_{E} is the ratio of tensile stress to rate of strain, $\dot{\varepsilon}$, with the tensile stress for an incompressible liquid being the difference in normal stresses in the axial and radial directions, $\sigma_{xx} - \sigma_{yy}$. The natural quantities to consider are *specific viscosities* which give the effect of the fibres as a proportional increase over the viscosity of the suspending liquid, η_{s}. In simple shear

$$\eta^{\mathrm{SP}} = \frac{\eta - \eta_{\mathrm{s}}}{\eta_{\mathrm{s}}}. \tag{18}$$

In uniaxial extension

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{\eta_{\mathrm{E}} - 3\eta_{\mathrm{s}}}{3\eta_{\mathrm{s}}}. \tag{19}$$

The generalization of Jeffery's equations, Eqs. (2) and (3), for any linear flow, Eq. (14), is the equation

$$\frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t} = \boldsymbol{W} \cdot \boldsymbol{u} + B(\boldsymbol{D} \cdot \boldsymbol{u} - \boldsymbol{u}(\boldsymbol{u} \cdot \boldsymbol{D} \cdot \boldsymbol{u})), \tag{20}$$

governing the orientation vector of an isolated particle in the absence of effects of Brownian motion [21–24,18] with B defined above.

We consider a collection of suspended particles which, in the simplest situation, are all alike and are sufficiently far apart from each other for hydrodynamic interaction between them to be negligible. For such a dilute suspension, we describe the orientation of the particles by a distribution function $\Psi(\boldsymbol{u}, \boldsymbol{r}, t)$ which gives the probability that a particle located at $\boldsymbol{r}$ at time t has its orientation in a neighbourhood of $\boldsymbol{u}$. Ψ $(\boldsymbol{u}, \boldsymbol{r}, t)$ is normalized, so that the probability of an orientation in the range $0 \leq \theta \leq \pi$, $0 \leq \varphi < 2\pi$ is unity:

$$\int_0^{\pi} \mathrm{d}\varphi \int_0^{2\pi} \mathrm{d}\theta (\sin\theta\, \Psi(\boldsymbol{u}, \boldsymbol{r}, t)) = 1, \tag{21}$$

in which the integration is over all possible values of the orientation vector $\boldsymbol{u}$. In order to trace the evolution with time of the configuration of the suspension, we need to go from an evolution equation for $\boldsymbol{u}$, like Eq. (20), to an evolution equation for Ψ. Such an equation is a convection-diffusion type of equation in general and is variously referred to as a modified Fokker–Planck equation [3] or the Smoluchowski equation. In the absence of Brownian motion it will become a purely convective equation, as Eq. (20) is; the effect of Brownian motion is to 'smooth out' the distribution towards the isotropic distribution, i.e. towards that for a collection of randomly oriented particles.

We obtain a constitutive equation for a suspension by averaging the various contributions to the stress over the collection of suspended particles whose orientation is described by the above distribution function. This was first done by Hand [22] and Giesekus [23,24]; a thorough discussion of the fundamental basis of this averaging is given by Batchelor [25]. Following Doi and Edwards [12] we write the stress as the sum

$$\sigma = \sigma^{(\mathrm{e})} + \sigma^{(\mathrm{v})} + \sigma^{(\mathrm{s})}, \tag{22}$$

where $\sigma^{(\mathrm{s})}$ is the contribution of the suspending liquid, $2\eta_{\mathrm{s}}\boldsymbol{D}$. In the absence of an external field such as gravity (buoyancy effects) or electromagnetic effects, the elastic part of the stress is

$$\sigma^{(e)} = 3nk_{\mathrm{B}}T\boldsymbol{S}, \tag{23}$$

given in terms of the orientational tensor, $\boldsymbol{S}$ and the number of particles per unit volume, n. The orientational tensor is defined by

$$\boldsymbol{S} = \left\langle \boldsymbol{uu} - \frac{\delta}{3} \right\rangle, \tag{24}$$

and $\langle \bullet \rangle$ is an ensemble average, over all possible orientations, $\boldsymbol{u}$, weighted by the distribution function $\Psi(\boldsymbol{u})$, e.g.

$$\langle \boldsymbol{uu} \rangle = \int_0^{\pi} \mathrm{d}\varphi \int_0^{2\pi} \mathrm{d}\theta (\boldsymbol{uu} \sin\theta\, \Psi(\boldsymbol{u}, \boldsymbol{r}, t)). \tag{25}$$

The viscous part of the stress is

$$\sigma^{(\mathrm{v})} = \tfrac{1}{2} n\zeta_{\mathrm{r}} \langle \boldsymbol{uuuu} \rangle : \boldsymbol{L}, \tag{26}$$

where ζ_{r} is the rotational friction constant, $k_{\mathrm{B}}T/D_{\mathrm{r}}$. This takes account of the rigidity of the particle and the consequent hydrodynamic drag of the suspending liquid on the particle (all parts of the particle cannot move affinely with the suspending liquid).

3.2. Brownian motion

The question of whether Brownian motion has a significant effect depends on the magnitude of the Péclet number, which is the dimensionless ratio of a characteristic rate of strain, G, and the rotary diffusivity of the particle, D_{r}:

$$P\acute{e} = \frac{G}{D_{\mathrm{r}}}. \tag{27}$$

Zuzovsky, Priel and Mason [26] discuss the effect of Brownian motion on transients. They name the dimensionless ratio (divided by 2) the rotary Brenner number, an appropriate recognition (which has not been adopted by others) of Brenner's contribution to suspension rheology. At small values of *Pé*, when Brownian motion may dominate, particle orientations are close to random and the suspension is isotropic. The effect of Brownian motion is irreversible and the suspension is non-Newtonian. When *Pé* is large, the effects of Brownian motion are insignificant alongside the effects of the bulk motion of the liquid and the convective terms (tending to align the particles with the flow) dominate. However there are no irreversible effects and (if there is some mechanism damping oscillations associated with Jeffery orbits) Newtonian behaviour is expected.

The rotary diffusivity (or rotational Brownian diffusion coefficient) is obtainable from Brenner's dimensionless scalar ${}^{r}K_{\perp}$ according to the formula

$$D_{\mathrm{r}} = \frac{k_{\mathrm{B}}T}{6V_{\mathrm{p}}\eta_{\mathrm{s}}{}^{r}K_{\perp}}, \tag{28}$$

where k_{B} is Boltzmann's constant, T is the absolute temperature, V_{p} is the particle volume and η_{s} is the viscosity of the suspending liquid. The combination $6V_{\mathrm{p}}\eta_{\mathrm{s}}{}^{r}K_{\perp}$ may be referred to as the rotational friction constant, ζ_{r} [12]. Particle size enters into Eqs. (27) and (28) through the particle volume V_{p}, only, so *Pé* is proportional to V_{p}, and hence to the cube of a typical linear dimension of a fibre.

For long slender particles, with a relatively simple approach to the hydrodynamics of the suspended particles and with Brownian motion, the Smoluchowski equation takes the form [12]

$$\frac{\partial \Psi}{\partial t} = D_{\mathrm{r}}\mathfrak{R}\cdot\mathfrak{R}\Psi - \mathfrak{R}\cdot[\boldsymbol{u}\times\boldsymbol{L}\cdot\boldsymbol{u}\Psi], \tag{29}$$

where $\mathfrak{R}$ denotes the rotational operator ($\mathfrak{R}\bullet = \boldsymbol{u}\times\partial\bullet/\partial\boldsymbol{u}$). Brenner [2] refers to this as the orientational gradient operator, or angular portion of the gradient operator on the unit sphere. It arises from the fact that $\boldsymbol{u}$ is a unit vector, so that the operator, which is often written simply as $\partial\bullet/\partial\boldsymbol{u}$, is really a two-dimensional operator (see, for example, Bird et al. [19], Appendix E6)). D_{r} is the rotary diffusion coefficient (for rotation of the particle about an axis normal to its axis of symmetry) discussed above. The first term on the right-hand side of Eq. (29) is the Brownian diffusion term and the second the convection term; since $\boldsymbol{L}$ is of order G the ratio of magnitudes of the convection term to the diffusion term is given by *Pé*. With more careful consideration of the hydrodynamics of the flow around the suspended particle, Brenner [2] obtains the steady state form of the equation

$$\frac{\partial \Psi}{\partial t} = D_{\mathrm{r}}\mathfrak{R}\cdot\mathfrak{R}\Psi - \mathfrak{R}\cdot[\boldsymbol{W}\cdot\boldsymbol{u}\Psi + B(\boldsymbol{D}\cdot\boldsymbol{u} - \boldsymbol{u}(\boldsymbol{u}\cdot\boldsymbol{D}\cdot\boldsymbol{u}))\Psi] \tag{30}$$

for the distribution function (cf. Eq. (20) for the orientation of a single particle). The geometrical shape factor, B, is unity for long slender particles, in which case this equation reduces to Eq. (29). Physically, we may interpret the parts of the convective term as describing deformation of the fibre's orientation vector, $\boldsymbol{u}$, with the fluid, corrected by subtracting the stretching component of the deformation since $\boldsymbol{u}$ remains constant in length. In the case of unit shape factor, B, this idea can be expressed, after noting the fact that $\boldsymbol{u}\cdot\boldsymbol{W}\cdot\boldsymbol{u}$ is zero because $\boldsymbol{W}$ is antisymmetric, by the equation

$$\frac{\mathrm{D}\boldsymbol{u}}{\mathrm{D}t} = L\cdot\boldsymbol{u} - \boldsymbol{u}(\boldsymbol{u}\cdot\boldsymbol{L}\cdot\boldsymbol{u}), \tag{31}$$

given by Dinh and Armstrong ([27], Eq. (11)).

3.3. Constitutive equations and closure approximations

In order to turn Eq. (22) into an explicit constitutive equation we need to evaluate the ensemble averages in some way. In steady uniaxial extension and steady planar extension there are rigorous solutions of the Smoluchowski equation [2,28]

$$\Psi(\boldsymbol{u}) = K_{\mathrm{E}}^{-1} \exp\left(\frac{3B\dot{\varepsilon}}{4D_{\mathrm{r}}} u_x^2\right) \tag{32}$$

for uniaxial extension, Eq. (17), (in which the velocity gradient tensor is diagonal, with $L_{xx} = \dot{\varepsilon}$, $L_{yy} = L_{zz} = -1/2\dot{\varepsilon}$ and

$$\Psi(\boldsymbol{u}) = K_{\mathrm{p}}^{-1} \exp\left(\frac{B\dot{\varepsilon}}{2D_{\mathrm{r}}} (u_x^2 - u_z^2)\right) \tag{33}$$

for planar extension, with $L_{xx} = \dot{\varepsilon}$,, $L_{yy} = 0$ and $L_{zz} = -1/2\dot{\varepsilon}$. These may be used to evaluate the various averages and hence, in principle, obtain the stress components for these flows. The constants K_{E} and K_{p} are normalization constants, chosen so that $\langle 1 \rangle = 1$. Details of the evaluation of the integrals involved are given by Brenner [2] and asymptotic results for high values of the rate of strain have been discussed elsewhere [29].

In simple shear there is no explicit solution for the distribution function. In such a case, as in the many flow fields where it is not possible to obtain an explicit solution for the distribution function $\Psi(\boldsymbol{u})$, some sort of approximation may be sought. It is possible to obtain an equation for $\langle \boldsymbol{uu} \rangle$ if we multiply the Smoluchowski equation, Eq. (29), by $\boldsymbol{uu} - \delta/3$ and integrate over $\boldsymbol{u}$ to obtain ([12], Eq. (8.127):

$$\frac{\partial \boldsymbol{S}}{\partial t} = -6D_{\mathrm{r}}\boldsymbol{S} + \frac{1}{3}\left(\boldsymbol{L} + \boldsymbol{L}^{\mathrm{T}}\right) + \boldsymbol{L} \cdot \boldsymbol{S} + \boldsymbol{S} \cdot \boldsymbol{L}^{\mathrm{T}} - 2\langle \boldsymbol{uuuu} \rangle : \boldsymbol{L}. \tag{34}$$

This does not contain the distribution function explicitly and is still completely general (as general as Eq. (29) at any rate). It would be solvable for $\boldsymbol{S}$ if we knew $\langle \boldsymbol{uuuu} \rangle$ but that, of course, is the catch—that is the term where the unknown distribution function has been hidden. However hard we try to manipulate algebraically, obtaining higher moments of $\boldsymbol{u}$ for example, we find that in the end an approximation is always necessary [18]. The decoupling approximation [12], or lowest order closure approximation [18],

$$\langle \boldsymbol{uuuu} \rangle^{\mathrm{quadratic}} : \boldsymbol{D} = \langle \boldsymbol{uu} \rangle \langle \boldsymbol{uu} \rangle : \boldsymbol{D}, \tag{35}$$

is one approximation which we may use, together with the definition of $\boldsymbol{S}$, Eq. (24), to replace the awkward term in Eq. (34) by an expression quadratic in $\boldsymbol{S}$. This allows us, in principle, to calculate the orientational tensor, $\boldsymbol{S}$, for a given velocity field, $\boldsymbol{L}$. However it should be noted that this procedure leads to nonlinear differential equations for the elements of $\boldsymbol{S}$ and introduces additional solutions to the mathematical problem which do not correspond to anything in our original suspension model. This has been discussed elsewhere [29,30]. The equation obtainable for particles which are not long and slender (corresponding to Eq. (30)) may be found in Hinch and Leal [18]. They discuss approximations in some detail, considering both weak flows (simple shear) and strong flows (elongation). In addition they present a higher-order approximation designed to improve on Eq. (35). This is ([18], Eq. (17))

$$\langle \boldsymbol{uuuu} \rangle : \boldsymbol{D} = \tfrac{1}{5}[6\langle \boldsymbol{uu} \rangle \cdot \boldsymbol{D} \cdot \langle \boldsymbol{uu} \rangle - \langle \boldsymbol{uu} \rangle \langle \boldsymbol{uu} \rangle : \boldsymbol{D} - 2\boldsymbol{I}\,\langle \boldsymbol{uu} \rangle^2 : \boldsymbol{D} + 2\boldsymbol{I}\,\langle \boldsymbol{uu} \rangle : \boldsymbol{D}]. \tag{36}$$

Frattini and Fuller [31] assess these closure approximations using rheo-optical measurements on the startup of shear.

A closure approximation also allows us to write down an expression for the viscous stress (using, say, Eq. (35) in Eq. (26)) and hence we have set of equations from which we may calculate the stress in a suspension. It is possible to eliminate the orientational tensor (a similar thing is done for the FENE-P dumbbell model of a solution of flexible polymer molecules [19,29]) but it is probably preferable to retain $\boldsymbol{S}$ as a tensor expressing something about the structure of the flowing suspension. The model can then be seen to fall within the class of models discussed by Hand [22,32] in which the microstructure is described by a tensor $\boldsymbol{S}$ (or $\langle \boldsymbol{uu} \rangle$ and Eqs. (34) and (35) provide an evolution equation for this tensor. Useful reviews of the closure problem can be found in the work of Dupret and Verleye [33], Barthés-Biesel and Acrivos [34] and Tucker [35].

We started our discussion with the quadratic closure, Eq. (35), which is exact (and not an approximation) for perfectly aligned fibres. An even simpler closure approximation is the linear one which Hand [32] proposed

$$\langle \boldsymbol{uuuu} \rangle^{\text{linear}} : D = \tfrac{1}{35}[(\boldsymbol{I} : \boldsymbol{D})\boldsymbol{I} + 2\boldsymbol{D}] + \tfrac{1}{7}[(\boldsymbol{I} : \boldsymbol{D})\langle \boldsymbol{uu} \rangle + 2\langle \boldsymbol{uu} \rangle \cdot \boldsymbol{D} + 2\boldsymbol{D} \cdot \langle \boldsymbol{uu} \rangle + (\langle \boldsymbol{uu} \rangle : \boldsymbol{D})\boldsymbol{I}]. \tag{37}$$

This is exact for a random distribution of fibre orientations (an isotropic suspension). The hybrid closure approximation [36] is

$$\langle \boldsymbol{uuuu} \rangle : \boldsymbol{D} = [(1 - f)\langle \boldsymbol{uuuu} \rangle^{\text{linear}} + f\langle \boldsymbol{uuuu} \rangle^{\text{quadratic}}] : \boldsymbol{D} \tag{38}$$

and the scalar f is to be chosen. In some sense it will be a measure of orientation, since $f = 0$ gives an exact closure if the suspension is isotropic while $f = 1$ gives an exact closure if the fibres are fully aligned (as one expects in steady uniaxial extension). The hybrid closure is often used in applications to composites; see, for example, Advani and Tucker [37].

Questions concerning closure approximations continue to arise in the practical application of fibre suspension rheology to composites; see, for example, Cintra and Tucker [38], Chung and Kwon [39] and Han and Im [40]. Among the issues are a trade-off for accuracy against computational cost. In applications, such as injection moulding of fibre-reinforced plastics, a useful approximation is that the out-of-plane components of the orientation tensor are small and constant—the actual values may be assigned empirically. This Quasi-Planar approximation, due to Gupta and Wang, has been developed by VerWeyst et al. [41] into their Optimized Quasi-Planar approximation. It should be noted that the choice of closure approximation is an important feature of the optimal choices made in the approximation.

Lipscomb [42,43] has pointed out a way of avoiding use of a closure approximation (without solving the full Fokker–Planck (Smoluchowski) equation). What is required is the initial orientation distribution function and an 'equivalent strain tensor' which is reminiscent of the tensors introduced in discussion of non-affine convected derivatives. The model still falls with the class of continuum models proposed by Hand and is cast in the form of Ericksen's transversely isotropic fluid (TIF) [21]. The fact that approximate models developed for semi-dilute (or semi-concentrated) fibre suspensions [44,27] are of the same form as the rigorous form obtained by Lipscomb for dilute suspensions is adduced by Lipscomb ([42], p. 305) as evidence supporting the use of the dilute suspension equations beyond the range of concentrations where they can be justified on grounds of diluteness alone.

Szeri [45] has advocated a new approach to the closure problem. He avoids solving the full Fokker–Planck equation for the fibre orientation distribution function and yet avoids the closure problem. He develops an evolution equation for an approximate, simplified deformation of the orientable particles associated with a material point. He then obtains evolution equations for the remaining degrees of freedom in the assumed class of deformations from the Fokker–Planck equation. The resulting equations are as quick to integrate as direct moment tensor evolution equations. It is shown that this model always gives physically sensible results.

With closure approximations there are issues of unphysical behaviour which are analogous to those discussed for FENE models [46,47] where multiple solutions to the equations are found and maybe also analogous to those that Keunings [48] discusses (where the approximate model clearly violates the stated assumptions of the real model). Szeri and Lin [45] investigate whether approximations remain physically acceptable by considering the nonlinear dynamics of models in unsteady, three-dimensional flows. They show that commonly used closure approximations can only be shown to have a unique global attractor when the rotary Brownian diffusivity is large enough (i.e. when the flow is weak enough). They note that a spurious (multiple) attractor was observed by Chaubal, Leal and Fredrickson [50] in uniform shear flow at high Péclet number of a dilute suspension using the closure Eq. (36). The model of Szeri and Lin has a unique global attractor in any steady, three-dimensional flow, provided the rotary Brownian diffusivity is non-zero. This indicates that behaviour is always physically sensible. There is a related discussion by Galdi and Reddy [49] who examine whether the mathematical problem is well-posed and find that a linear closure approximation, Eq. (37), can fail this test while quadratic and hybrid closure approximations, Eqs. (35) and (38), pass.

We note here how Hand [32] introduced many of the ideas discussed in this section, together with some discussed below (Sections 5 and 7). He combines ideas from continuum mechanics on the permissible form of a constitutive equation with ideas motivated by solutions of dumbbells. The use of a structure tensor leads to the need for a closure approximation and a rotary diffusivity (arising from Brownian forces on dumbbells) is also a feature of the equations. These two features recur throughout models developed since then, although the origin of rotary diffusivity for larger (non-Brownian) suspended particles is clearly different. It is commonly used to account for interactions between fibres in non-dilute suspensions and then may depend on the flow (e.g. on the shear rate) and the state of the suspension (i.e. the orientation distribution function for the fibres).

3.4. Steady simple shear

The above development takes Brownian motion into consideration and this is important for the existence of a steady state in simple shear. Where Brownian motion is neglected Hur [5] concludes that

1. The rotation of a particle in a shear flow predicted by Jeffery leads to oscillation in the rheological properties of a fibre suspension. A steady state is never reached in these theories and so in practice some modification is necessary.
2. The bulk properties of the suspension are strongly dependent on the evolution of the particle orientation distribution but are linear in the bulk deformation rate.
3. The dilute suspension theories are formally valid only where $\phi r^2 \ll 1$. Note that this condition is necessary but not sufficient. In simple shear flow at high *Pé*, the theory for the fibre orientation distribution in simple shear requires inclusion of particle interactions (otherwise we have undamped Jeffery orbits) [8].

Hinch and Leal [3] have shown that Brownian motion effects the modification required in (i), even when $Pé \to \infty$. In other words, Brownian motion has a good effect, in the sense that, even when its influence is very weak, the dependence of the orientation of a particle on its initial orientation is much reduced (except in simple shear for particles which are not long and slender [18]). More specifically, for particles whose aspect ratio is not extreme [51], an oscillatory response with frequency proportional to the shear rate $\dot{\gamma}$ is predicted after the start-up of simple shear and this decays with a time constant proportional to the reciprocal of the diffusivity, D_{r}^{-1}. For long slender particles, where the aspect ratio r is large, the frequency of oscillation is reduced proportionally to the reciprocal of r while the characteristic time for decay of this is reduced proportionally to r^{-2} for the most persistent features and proportionally to r^{-4} for some features.

We have already mentioned the experimental evidence that an oscillatory response is rapidly damped out in simple shear (Section 2). This, the above discussion and the other factors mentioned at the end of Section 2 all tend to the same conclusion, that we should not expect the periodic nature of the Jeffery orbits to give rise to a periodic response in a non-periodic flow, except over a relatively short time.

4. Summary of predictions for dilute suspensions

We summarize here predictions for simple shear, both for viscosity and normal stress functions, and for extensional flows. We have already defined *specific viscosities* in simple shear and uniaxial extension. We may also use *intrinsic viscosities* which convey relevant information for very dilute suspensions; in simple shear we have

$$[\eta] = \lim_{\phi \to 0} \frac{\eta^{\mathrm{SP}}}{\phi}, \tag{39}$$

which has the value 2.5 for spheres (the Einstein correction) and 2.0 for prolate ellipsoids according to Jeffery in the case of minimum energy dissipation. In uniaxial extension, we have the intrinsic viscosity

$$[\eta_{\mathrm{E}}] = \lim_{\phi \to 0} \frac{\eta_{\mathrm{E}}^{\mathrm{SP}}}{\phi} = \lim_{\phi \to 0} \frac{\eta_{\mathrm{E}} - 3\eta_{\mathrm{s}}}{3\eta_{\mathrm{s}}\phi}, \tag{40}$$

and we can readily define similar quantities for planar and equibiaxial extension.

The intrinsic viscosity is, in effect, the coefficient of the first (linear) term in a series expansion for specific viscosity as a function of concentration (or volume fraction ϕ) for small values of ϕ. Any further information on dependence on ϕ must involve a non-dilute suspension theory. In general the intrinsic viscosity will be a function of rate of strain or (equivalently) Péclet number as well as of the geometry of the suspended particle.

4.1. Shear viscosity

Predictions of dilute suspension theory for the intrinsic viscosity in simple shear are summarized in Table 1. The ‘min: visc:’ comment refers to the case where each particle is lined up ‘across’ the shear flow (i.e. with its major axis in the z-direction for the flow $v_x = \dot{\gamma} y$) and the ‘max: visc:’ cases are where each particle is perpendicular to the z-axis and is caused by the flow to rotate in the xy-plane. As well as the various formulae, the results of numerical computations have been published, for example

Table 1
Theoretical results for the intrinsic viscosity of suspensions

	Author	Year	Ref.	Shape	$[\eta]$	*Pé*	Comment
1	Einstein	1906	[52]	Spheres	2.5	∞	
2	Jeffery	1922	[1]	Ellipsods	2.0	∞	$r \to \infty$
3	Eisenschitz	1932	[53,54]	Ellipsoids	$0.366r^2/\log 2r$	∞	Isotropic
4a	Guth	1938	[55]	Ellipsoids	2.0	∞	min: visc:
4b	Guth	1938	[55]	Ellipsoids	$2.0(r/(2\log 2r^{-3}))$	∞	max: visc:
5a	Burgers	1938	[10]	Rods	$2r/3\pi(\log 2r - 1.8)$	∞	isotropic
5b	Burgers	1938	[10]	Rods	$r/3(\log 2r - 1.8)$	∞	max: visc:
6a	Simha	1940	[56]	Ellipsoids	$14/15 + (r^2/15(\log 2r - \lambda)) + (r^2/5(\log 2r - \lambda + 1))$	0	$r \gg 1$, $\lambda = 1.5$
6b	Simha	1940	[56]	Rods	$14/15 + (r^2/15(\log 2r - \lambda)) + (r^2/5(\log 2r - \lambda + 1))$	0	$\lambda = 1.8$
7	Kuhn and Kuhn	1945	[57]	Ellipsoids	$1.6 + ((r^2/15(\log 2r - 1.5)) + ((r^2/5(\log 2r - 0.5))$	0	$r > 15$
8a	Leal and Hinch	1971	[58]	Ellipsoids	$2 + (0.312r/(\log 2r - 1.5))$	∞	$r \to \infty$
8b	Leal and Hinch	1971	[58]	Ellipsoids	$3.183 - 1.792r$	∞	$r \to 0$
9	Brenner	1974	[2]	Axisymmetric	$5Q_1 - Q_2 + 2Q_3$	0	See Eqs. (42)–(45)
10	Rosenberg et al.	1990	[59]	Rods	10–12	∞	$r = 20$
11	Phan Thien et al.	1991	[60]	Rods	8.22	∞	$r = 20$

by Scheraga [61] and Stewart and Sørensen [62]. Brenner [2] collected and compared these results and gives an extensive tabulation equivalent to the viscometric functions for dilute suspensions of ellipsoids of various aspect ratios. At vanishingly small shear rate, Brenner obtains the limiting value of the intrinsic viscosity

$$[\eta] = 5Q_1 - Q_2 + 2Q_3 \tag{41}$$

in terms of the geometrical parameters referred to above. This is, in fact, the same for any flow (and we have below the identical first term in the expression for uniaxial extension). Thus, not surprisingly, we have the result that at very small shear rate a suspension is Newtonian, with a modified viscosity whose departure from the value for the suspending liquid is linear in concentration and is affected by particle shape. For an ellipsoid of large aspect ratio r the geometrical parameters are given by the approximations

$$Q_1 = \frac{2}{5} - \frac{6\log 2r}{5r^2}, \tag{42}$$

$$Q_2 = -\frac{r^2}{15(\log 2r - 1.5)} + \frac{2}{5}, \tag{43}$$

$$Q_3 = -\frac{r^2}{10(\log 2r - 0.5)}, \tag{44}$$

and so Eq. (41) gives the same result as Kuhn and Kuhn [57] (Table 1, entry 7). Expressions similar to Eqs. (42)–(44) may be obtained for long slender bodies of arbitrary shape [2].

For slightly less small shear rates, but still in the situation where Brownian motion is dominant ($Pé \ll 1$), Brenner obtains

$$[\eta] = 5Q_1 - Q_2 + 2Q_3 - \tfrac{1}{1260}(12Q_2 + 6Q_3 + 35B^{-1}N)\lambda^2 + \mathrm{O}(\lambda^4), \tag{45}$$

in which $\lambda = BPé$ with B given by Eq. (11) and $Pé = \dot{\gamma}/D_r$. For ellipsoids with $r \gg 1$

$$B = 1 - \frac{2}{r^2}; \quad N = \frac{r^2}{5(\log 2r - 0.5)}. \tag{46}$$

With the values of the parameters given by Eqs. (42)–(44) and Eq. (46) the leading terms (for large r) predict shear thinning behaviour, since

$$12Q_2 + 6Q_3 + 35B^{-1}N \sim \frac{34r^2}{5 \log 2r}, \tag{47}$$

and thus the coefficient of λ^2 is negative.

4.2. Normal stress differences

Predictions for normal stress differences in simple shear are generally that these are small, or even zero, apart from that arising during the start-up period when there are oscillating stresses arising from the tumbling motion of the particles and the non-equilibrium particle orientation distribution. More specifically Hinch and Leal [51] show that steady normal stresses are $O(D_r r^3)$ smaller than the steady shear stress. Calculations [18] for ellipsoids with an aspect ratio of only 5 give a first normal stress difference which is never more than one-third of the shear stress (due to the particles) and a second normal stress difference which is negative and in magnitude less than one-tenth of the first. The dependence of the normal stresses on shear rate is initially quadratic, as for a second-order fluid. Doi and Edwards, considering semi-dilute suspensions, obtain the same result.

Brenner [2] obtains

$$N_1 = \phi\eta_s \frac{D_r N}{3B}\lambda^2 + O(\lambda^4) \tag{48}$$

and

$$N_2 = \phi\eta_s \frac{D_r}{B}\left(-\frac{N}{6} + \frac{Q_3 - Q_2}{7}\right)\lambda^2 + O(\lambda^4). \tag{49}$$

For long slender ellipsoids we may use Eqs. (42)–(44) and Eq. (46) in these and we see that N_2 is negative and to a first approximation $N_2 = -(1/7)N_1$

4.3. Extensional viscosities

The elongational viscosity (in uniaxial extension) is predicted to follow an S-shaped dependence on rate of strain, starting from a value which is, typically, larger than the Trouton value of $3\eta_s$ and rising to a much larger than this, corresponding to an ‘upper Newtonian’ régime in which the fibres are fully aligned and Brownian motion has a negligible influence. The theory of Batchelor [63] which we discuss below (Section 5.2), has nothing to say on the effect of rate of strain; it assumes that the rate of strain and time of straining are large enough for the fibres to be wholly aligned with the flow. These results therefore show the ‘upper Newtonian’ viscosity and its dependence on fibre concentration.

For dilute suspensions, Brenner [2] has derived formulae for uniaxial and planar extension (and from uniaxial extension at negative rates of strain we may obtain results for equibiaxial extension). These can be used to investigate the effect of rate of strain, most easily by considering limiting cases. We have, for example, for long slender particles

$$[\eta_{\mathrm{E}}] = 5Q_1 - Q_2 + 2Q_3 - \frac{\lambda}{7}(Q_2 - Q_3) \tag{50}$$

at small rates of strain and

$$[\eta_{\mathrm{E}}] = 5Q_1 - 5Q_2 + \tfrac{20}{\lambda}(Q_2 + Q_3) \tag{51}$$

at large rates of strain, where $\lambda = B\dot{\varepsilon}/D_{\mathrm{r}}$ and B, given by Eq. (11), is (as we have seen) unity for ellipsoids of very large aspect ratio, in which case $\lambda = P\acute{e}$. For long slender fibres, with $r \gg 1$, we see from Eqs. (42)–(44) that $Q_1 \ll |Q_2|$ and $Q_3 \sim -(3/2)Q_2$ and hence for large aspect ratio

$$[\eta_{\mathrm{E}}] \sim \frac{r^2}{\log r}\left(\frac{4}{15} + \frac{Pe'}{42}\right) \tag{52}$$

at small rates of strain and

$$[\eta_{\mathrm{E}}] \sim \frac{r^2}{\log r}\left(\frac{1}{3} + \frac{2}{3Pe'}\right) \tag{53}$$

at large rates of strain (large Péclet number, negligible influence of Brownian motion).

The ratio of these limits is seen to be 1.25 and this may be compared with the results of Goh et al. [64] who found a ratio 'of the order of 1.5', for uniaxial extension, although their results show that this depends on the aspect ratio of the fibres and, from their Fig. 2 [64], appears closer to 1.33 for the most slender fibres for which they do the calculations. Similarly, they obtain a ratio of 1.1 in planar extension. The limits obtainable from Brenner's results for large and small rates of strain in this case are equal; in each case

$$[\eta_{\mathrm{p}}] = \frac{\lim}{\phi \to 0}\frac{\eta_{\mathrm{p}}^{\mathrm{SP}}}{\phi} = \frac{\lim}{\phi \to 0}\frac{\eta_{\mathrm{p}} - 4\eta_{\mathrm{s}}}{4\eta_{\mathrm{s}}\phi} \sim \frac{4r^2}{15\log r}. \tag{54}$$

It is not clear whether the results of Goh et al. [64] differ significantly from those of Brenner (the limit being for infinite aspect ratio). In a terse note, Brenner [65] draws attention to the omission by Goh of citation of Brenner's work and states that this earlier work [2] evaluates the necessary goniometric integrals analytically rather than numerically.

We conclude with two comments. Firstly, the small increase in extensional viscosity between the limiting value at small rate of strain and the 'upper Newtonian' limiting value reminds us of the comment of Batchelor ([63], p. 820) that 'dilute-suspension theory cannot predict particle stresses which are more than a perturbation of the stress due to the ambient fluid alone.' Secondly, at high rates of strain, the uniaxial and planar extensional viscosities are equal [29]. This contrasts with the zero-strain-rate viscosities which are in the ratio 3 to 4 for uniaxial to planar extensional viscosity.

5. Nondilute suspension theory

It is important to note, as Batchelor ([63], p. 820) does, that the diluteness approximation for a suspension of long slender particles is (formally) very restrictive. With this in mind we should not expect that knowledge of the parameters we have been considering (n, B, D_r, ...) will lead to particularly good a priori predictions of suspension viscosities where the suspended fibres have more than a small effect.

There has not been a great deal of theoretical work on non-dilute suspensions and our first task is to be more precise about the term non-dilute. Doi and Edwards distinguish between three different régimes — dilute, semi-concentrated (or semi-dilute: the terms are used interchangeably) and concentrated or liquid crystalline [12]. We shall not consider this last régime here — it refers to the situation where the fibres interfere with each other so much that they have to line up parallel to each other and move cooperatively. Although not concerned with fibres, but with general suspensions, mention should also be made of the exposition by Phan-Thien [66] who also proposes a constitutive equation.

5.1. Semi-diluteness

We consider a suspension of fibres of length $2\ell_p$ and radius R_p, with fibre aspect ratio

$$r = \frac{\text{fibre length}}{\text{fibre diameter}} = \frac{\ell_p}{R_p}, \tag{55}$$

mean spacing or distance between particles h and number density of fibres n. The mean spacing is flow-dependent, as Doi and Edwards demonstrate for a tube model: if the fibres are randomly oriented they obtain the result [12]

$$h = \frac{1}{4n\ell_p^2}, \tag{56}$$

while if all the fibres are aligned, as might be expected in an extensional flow, they obtain [67]

$$h = \frac{1}{\sqrt{2n\ell_p}}. \tag{57}$$

The volume fraction of fibres is given by $\phi = nV_p$ and $V_p \sim \ell_p R_p^2$ so we replace n by $\phi r^2 \ell_p^{-3}$ (multiplied by a constant of order unity whose precise value depends on the shape of the fibre). For cylindrical fibres $V_p = 2\pi\ell_p R_p^2$ and so

$$\phi = 2\pi n\ell_p R_p^2 = \frac{2\pi n\ell_p^3}{r^2}. \tag{58}$$

The semi-dilute régime is that where

$$R_p \ll h \ll \ell_p, \tag{59}$$

so that the particles are not free to rotate end-over-end, but are sufficiently far apart for the effects of neighbouring particles on the hydrodynamic drag to be approximated in some straightforward way. We may use Eq. (56) or Eq. (57) in Eq. (59) to obtain criteria for diluteness and semi-diluteness, remembering that we are primarily interested in long slender particles for which $R_p \ll \ell_p$ or $r \gg 1$. In either case the dilute régime, where we require $h \gg \ell_p$ is obtained when $\phi \ll r^{-2}$. The semi-dilute régime for randomly oriented fibres is obtained when

$$r^{-2} \ll \phi \ll r^{-1}, \tag{60}$$

while if the particles are aligned we only require

$$r^{-2} \ll \phi \ll 1. \tag{61}$$

The semi-dilute régime has been further described [12] as a régime where the dynamic properties of the liquid are affected by interaction between particles but the static properties (i.e. mechanical properties of the liquid at rest) are not. The excluded volume effect (which means that a particle orientation may not be chosen completely at random because another particle may get in the way) is ignored.

Hur [5] summarized conclusions from the theoretical studies that had been published for non-dilute suspensions prior to 1987.

1. The bulk stress of the suspension is altered little from that of the suspending liquid in shear flow, but may increase by a significant amount in an extensional flow.
2. The rheology is independent of the initial fibre distribution.
3. Wall effects are not important at small strains.

Here we review the main ideas that have been put forward and offer some comments and corrections.

5.2. Aligned fibres; extensional flow

Batchelor [63] treated the semi-dilute régime by assuming a cell model for the flow in the case where the particles are aligned; this will be applicable in extensional flows but not in shearing flows (because of the tumbling motion of fibres). Each particle is taken to be in a cell of diameter h given by Eq. (57) and an expression for the stress is obtained (and hence the extensional viscosity may be estimated). He obtains the estimate

$$\frac{\eta_{\mathrm{E}} - 3\eta_{\mathrm{s}}}{3\eta_{\mathrm{s}}} = \frac{4\phi r^2}{9\,\log(\pi/\phi)} = \frac{4\pi n \ell_{\mathrm{p}}^3}{9\,\log(h/R_{\mathrm{p}})}. \tag{62}$$

In what follows we use the specific extensional viscosity, defined above, Eq. (19) when this is convenient.

Batchelor also suggests an interpolation formula to cover concentrations between dilute and semi-dilute:

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{2\phi r^2}{9(\log 2r - \log(1 + 2r\sqrt{\phi/\pi}) - 1.5}, \tag{63}$$

which reduces to the familiar

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{2\phi r^2}{9(\log 2r - 1.5)} \tag{64}$$

for dilute suspensions when $\phi \to 0$. In fact, Eq. (63) does not agree too well with Eq. (62) for moderate concentrations, and a slightly better interpolation formula turns out to be

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{2\phi r^2}{9(\log 2r - \log(1 + 2r\sqrt{\phi/(\pi e^3)}) - 1.5}. \tag{65}$$

This formula approximates Eq. (62) when $r\sqrt{\phi} \gg 1$ while Eq. (63) requires the stronger condition $\log \phi \gg 1$ and the latter may well not be satisfied before the denominator in Eq. (63) becomes zero. Fig. 1 shows how the different expressions behave, using the same quantities as Batchelor (in effect plotting specific viscosity divided by concentration against the logarithm of the concentration, with Eq.

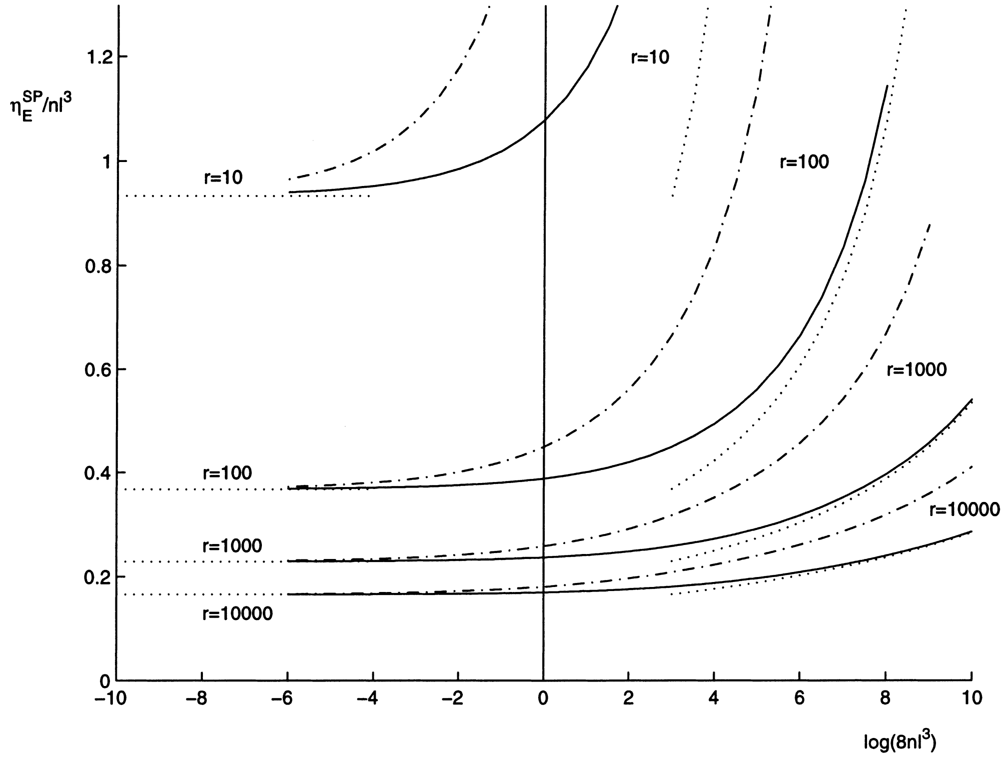

Fig. 1. Scaled specific extensional viscosity as a function of scale concentration (variables as in [63]).

(58) used to express concentration ϕ in terms of $n\ell_p^3$). The dotted lines show the two limiting cases, Eq. (62) and Eq. (64), the chain-dotted line is Batchelor's interpolation formula, Eq. (63) and the full line is the modified interpolation formula, Eq. (65) which can be seen to do a much better job of joining to two dotted lines for each value of aspect ratio, *r*. The predictions of Eq. (62) are in general agreement with the experimental results of Mewis and Metzner [68], as Batchelor [69] and Metzner [70] also report. The problems [46] of using a spinning experiment (stretching a jet of liquid) to measure extensional viscosity do not arise here since the liquid in question is Newtonian (or close to that). Kizior and Seyer [71] find that dependence of extensional viscosity on concentration and fibre aspect ratio is well described by Eq. (62) but the actual values of extensional viscosity are low. Since the experimental values are obtained from a jet thrust experiment, this discrepancy is not too serious. The only results which appear to test the interpolation formula are those of Pittman and Byram [72]. They find that Batchelor's interpolation formula, Eq. (63), overestimates the extensional viscosity by a factor of about 2. This suggests that the modified interpolation formula Eq. (65) would be better.

Developments of Batchelor's work are to be found in the thesis of Evans [44]. See also particularly the work of Shaqfeh and Fredrickson [73] and of Mackaplow and Shaqfeh [75] discussed in Section 5.4 below.

5.3. Semi-dilute Brownian fibre suspensions

Doi and Edwards [76,67]; see also [12,77] attempt to deal with the semidilute régime in a different way (since they consider Brownian fibres while Batchelor deals with non-Brownian fibres). This work is intended for solutions of rod-like polymers but is, as we have remarked, relevant to suspensions of Brownian fibres also. Interaction between the particles is modelled by a reduced rotational diffusion coefficient. This has the character of a ‘mean-field approximation’, by which we mean that the effect of other fibres on an individual fibre is modelled by replacing the viscosity (or other property) of the suspending liquid by an average viscosity (or other property) of the suspension as a whole. Strictly speaking the rotary diffusivity, D_r, in Eq. (29) depends on the distribution of fibre orientations, i.e. on Ψ, so that, the equation becomes non-linear. Linearization is effected by using an appropriate modified rotary diffusivity which is an approximate average value for the non-dilute suspension. If the rotary diffusivity in a dilute solution is D_{r0}, this is first modified to take account of the non-diluteness of the suspension

$$D_r = \beta D_{r0}(nl^3)^{-2} \tag{66}$$

and then this is averaged over all fibre orientations.

In their second paper [76] Doi and Edwards obtain expressions for viscosity and normal stress differences algebraically in the limit of small shear rate and numerically for higher shear rates. The low strain rate approximation is

$$\eta = \frac{\phi k_B T}{10\overline{D_r}}\left(1 + 0.0710\left(\frac{\dot{\gamma}}{\overline{D_r}}\right)^2\right)^{-0.525} \tag{67}$$

with the coefficients obtained by curve fitting. $\overline{D_r}$ is an approximation to the average rotational diffusivity, D_r which depends on the shear rate, $\dot{\gamma}$.

As well as viscosity, Doi and Edwards [76] obtain the normal stress predictions

$$N_1 = \frac{\phi k_B T \dot{\gamma}^2}{30\overline{D_r}^2}\left(1 + 0.0558\left(\frac{\dot{\gamma}}{\overline{D_r}}\right)^2\right)^{-0.874}, \tag{68}$$

$$N_2 = -\frac{\phi k_B T \dot{\gamma}^2}{105\overline{D_r}^2}\left(1 + 0.0550\left(\frac{\dot{\gamma}}{\overline{D_r}}\right)^2\right)^{-0.931} \tag{69}$$

with $\overline{D_r}$ as before.

Chaffey and Porter [78] discuss the Doi and Edwards expressions for viscosity and first normal stress difference and also the work of Brenner [2] on the hydrodynamics of the individual fibres. It does not appear that they add anything fundamental to theoretical studies although they do extend the Doi and Edwards results to higher shear rates. It should be noted that there is an important misprint in their expression for N_1 which is given as depending linearly on $\dot{\gamma}$ in ([78], Eq. (19)); the dimensionless form of this ([78], Eq. (20)) is correct.

Ironically, the linear dependence of N_1 on $\dot{\gamma}$ is just what experiment [9] requires. The one theoretical prediction of this linearity of first normal stress difference for a fibre suspension is that of Carter [79,80]. He derived

$$N_1 = K\eta_s\phi\dot{\gamma}\frac{\phi r^{3/2}}{\log 2r - 1.8} \tag{70}$$

(where K is a constant) on the basis of Jeffery’s maximum energy dissipation as well as the assumption that collisions between the fibres are the major cause of non-zero normal stresses in steady shear flow.

This linear dependence of N_1 on $\dot{\gamma}$ is, of course, not consistent with classical simple fluid theory in the limit of vanishingly small shear rate, though we recall that the Leslie–Ericksen theory for nematic liquid crystals shows the same behaviour.

A thorough discussion of the experimental evidence, reviewing prior work and reporting the results of extensive experimental work of Hur [5], is given by Zirnsak, Hur and Boger [9]. As well as agreement with Carter's theory as far as shear rate dependence of N_1 is concerned, they note that no theory gives the observed dependence of N_1 on the viscosity, η_s of the suspending liquid. Observation shows an increase in N_1 with η_s, but this increase is considerably less than linear (an eightfold increase in η_s gives rise only to a doubling in N_1). Carter's theory predicts a linear dependence, while other theories predict that N_1 will be independent of η_s. In making these comparisons, it is to be remembered [9] that the rotary diffusivity D_r depends on η_s.

One point made by Koch [81] is that, because of symmetry of the flow, linearity and reversibility (of Stokes flow), normal stress differences in simple shear cannot arise from purely hydrodynamic causes. The predictions of normal stress differences here arise from Brownian forces, which are not regarded as purely hydrodynamic. Other features of suspension flow which can give rise to non-zero normal stress differences are contact between fibres, inertia and (obviously) a non-Newtonian suspending liquid.

Cathey and Fuller [82] discuss the Doi and Edwards theory and apply it to measurements on solutions of a rigid-rod polymer (collagen) in an opposed jet apparatus. They note that the arbitrary constant which Doi and Edwards, originally expected to be of order one, needs to be about 10^4 to fit their results, and cite other work estimating values between 10^3 and 10^6. They find that their results at high rates of strain are in agreement with Batchelor's theory (used to predict the increase in viscosity as a function of concentration). In addition, the dependence on rate of strain for different concentrations collapses onto one graph with use of the scaling of Doi and Edwards. Ng et al. [83] make a similar comparison for a xanthan gum solution and find reasonable agreement. It should be noted that the equation for extensional viscosity ([83], p. 296) uses length/radius as the aspect ratio, rather than length/diameter used here, Eq. (55), and by most authors (being the ratio of major to minor axis of an ellipsoid).

Berry and Russel [84] take a slightly different approach from Doi and Edwards which, by taking into account interactions between pairs of fibres, should cover the concentration range between dilute and semi-dilute. This gives a second order correction to the viscosities and normal stresses as series in the fibre concentration *(n* fibres per unit volume) and in the Péclet number. In fact their small parameters are *Pé* and

$$\epsilon = \frac{1}{\log(2h/R_p)}, \tag{71}$$

which occurs in the combination $\epsilon n \ell_p^3$. The range of validity which Berry and Russel claim for their series approximations is

$$6 \le \tfrac{4}{3}\pi n \ell_p^3 \epsilon \le 24. \tag{72}$$

5.4. Semi-dilute non-Brownian fibre suspensions

Dinh and Armstrong [27] have developed an equation in which Batchelor's theory is used to modify the force exerted on a fibre by the suspending liquid in a way which tries to take account of the presence of other particles. They also use solutions of the evolution equation for particle orientation and hence for the orientation distribution function to write down a constitutive equation which involves the deformation from an initially isotropic state (randomly oriented fibres). The result for uniaxial extension shows stress growth to the value given by Batchelor's theory. For start-up of simple shear they obtain shear and normal stress growth functions which tend to the behaviour of the suspending liquid for large time. In steady shear flow the fibres line up with the flow and their effect, according to the approximation used, vanishes. This happens because the fibre thickness is neglected as far as hydrodynamic interaction is concerned and so a fibre lined up with the flow direction in simple shear feels no force and therefore remains lined up in this direction and does not affect the flow at all. The results of Dinh and Armstrong are therefore not correct for steady simple shear but may be useful in studying other flows; they do have something to say about the start-up of simple shear. Malamataris and Papanastasiou [85] derive a closed form constitutive equation based on the Dinh and Armstrong work, with the same limitations. In effect they obtain a closure approximation following the ideas of Currie [86].

One feature of the results of Dinh and Armstrong [27] and Malamataris and Papanastasiou [85] is that in shear and extension the transient viscosities (stress growth coefficients) depend on strain (relative to an initial configuration). Dependence on rate of strain only arises through strain being a product of rate of strain and time. The limiting values for large strain give the steady flow values (the viscosities) and these are best expressed as specific viscosities. In simple shear

$$\eta^{\mathrm{SP}} = 0 \tag{73}$$

from which it is seen that, as we have remarked already, the suspended fibres contribute nothing to the viscosity. In uniaxial extension we have

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{\pi n \ell_{\mathrm{p}}^{3}}{6 \log(h/R_{\mathrm{p}})}, \tag{74}$$

which agrees with Batchelor's result, Eq. (62). Note that this is incorrectly given by Malamataris and Papanastasiou ([85], p. 460) as $\pi/6$, omitting the factor $n\ell_{\mathrm{p}}^{3}/\log(h/R_{\mathrm{p}})$ and the error is repeated by Zirnsak [9]; the correct results (consistent with the theory) are given in the original paper by Dinh and Armstrong [27]. Recall that the average inter-fibre spacing, h, is given by one of Eqs. (56) and (57) while the number of fibres per unit volume, n, is related to the concentration ϕ by Eq. (58). Dinh and Armstrong show the effect on shear viscosity of the choice of equation for h and remark that, in the expected range of validity of the theory, the difference is not great.

For small strain, at the start of flow, when there is an assumed isotropic distribution of fibres, the fibre suspension behaves as a Newtonian liquid. Hence we have, in simple shear,

$$\eta^{\mathrm{SP}} = \frac{\pi n \ell_{\mathrm{p}}^{3}}{90 \log(h/R_{\mathrm{p}})}, \tag{75}$$

and, in uniaxial extension (corresponding to a Trouton ratio of 3),

$$\eta_{\mathrm{E}}^{\mathrm{SP}} = \frac{\pi n \ell_{\mathrm{p}}^{3}}{30 \log(h/R_{\mathrm{p}})}, \tag{76}$$

which are correctly given [27,85,9] although ([85], Fig. 1) is clearly scaled by the limiting value of Eq. (75).

Normal stress differences in simple shear are also discussed in these papers [27,85,9]; these are zero initially (Newtonian behaviour with an isotropic fibre distribution) and in steady shear (no effect of fibres). The second of these results is associated with the major defect of the model (as a description of real fibre suspensions where an effect is seen in steady simple shear). The first result emphasizes that non-Newtonian behaviour is a result of flow-induced alignment (or at least anisotropy) for a fibre suspension in a Newtonian liquid. This is generally true.The idea of ‘shielding’ and multiple interactions between particles is discussed by Goddard [87] (who in turn cites classical treatments involving ‘self-consistent’ models). At the time, no way of treating the collective effect of large numbers of mutually interacting particles was evident, so Goddard turned to a ‘nearest neighbour’ approach as an alternative to Batchelor’s [69] method, which has drawbacks in the occurrence of divergent integrals. The work of Shaqfeh and Fredrickson [73] presents a treatment that seems to achieve Goddard’s aim and is a significant development in the analysis of semi-dilute suspensions.

Acrivos and Shaqfeh [88] earlier studied the effective elongational viscosity of a non-dilute suspension of aligned slender rods. While this work gives an attractive physical interpretation, it is oversimplified and essentially superseded by the work of Shaqfeh and Fredrickson [73] which we now discuss. Shaqfeh and Fredrickson use the idea of ‘multiple scattering’ to deal with the effects of many fibres and so avoid the limitations inherent in asymptotically valid approaches which give, in practice, power series in concentration ϕ (or, more appropriately for fibres, in $n\ell_{\mathrm{p}}^3$). This new approach can justly claim to give a rigorous derivation of the stress in a semi-dilute suspension for arbitrary orientation distribution. The results are often discussed in terms of a ‘screening length’ which is a length associated with the transition between what a fibre sees as pure suspending fluid very near to itself and a suspension (with average properties such as a viscosity which may be anisotropic) far from itself. Looked at another way, the disturbance to the flow field caused by an individual fibre is screened by neighbouring fibres and so does not affect the flow field beyond the screening length. Batchelor’s notion [63] of a cell is of this type but Shaqfeh and Fredrickson obtain the screening length from detailed calculations of the interactions between many fibres. The mean spacings, h, of Doi and Edwards, given in Eqs. (56) and (57), are screening lengths. Shaqfeh and Fredrickson obtain the value given in Eq. (57) for all flows (not just for fully aligned flows) and reduce this by a factor $\sqrt{\ln(1/\phi)}$. The reason for the difference between the two approaches in isotropic fibre suspensions is that high aspect ratio fibres move along streamlines in linear flows and so they do not tend to cross one another. This makes the Doi–Edwards constraints irrelevant to semi-dilute non-Brownian suspensions. These ideas were first noted by Evans [44], and by Koch and Shaqfeh [74].

The stress is given, in this approach (for non-Brownian fibres), by

$$\sigma = \eta_{\text{fibre}}\left[\langle \boldsymbol{uuuu}\rangle - \tfrac{1}{3}\boldsymbol{I}\langle \boldsymbol{uu}\rangle\right] : \boldsymbol{D} + 2\eta_{\mathrm{s}}\boldsymbol{D} \tag{77}$$

and the aim of the work is to calculate η_{fibre}. The results obtained are, for isotropic suspensions (randomly oriented fibres),

$$\frac{\eta_{\text{fibre}}}{\eta_{\mathrm{s}}} = \frac{4\phi r^2}{3\ln(1/\phi)}\left[1 - \frac{\ln\ln(1/\phi)}{\ln(1/\phi)} + \frac{C}{\ln(1/\phi)} + \cdots\right], \tag{78}$$

where $C = 0.6634$ for slender cylindrical fibres and $C = -0.202$ for slender ellipsoids. For a suspension of fully aligned fibres, Shaqfeh and Fredrickson obtain

$$\frac{\eta_{\text{fibre}}}{\eta_{\mathrm{s}}} = \frac{4\phi r^2}{3[\ln(1/\phi) + \ln\ln(1/\phi) + C + \cdots]}, \tag{79}$$

where $C = 0.1585$ for slender cylindrical fibres and $C = 1.034$ for slender ellipsoids. The numerical values of C in all four cases are those given by Mackaplow and Shaqfeh [75].

It should be noted that, in spite of the significance of the work of Shaqfeh and Fredrickson [73], it is in practice restricted to semi-dilute systems and does not describe concentrated systems accurately (as Shaqfeh and Fredrickson themselves note — the restriction arises from the use of slender-body theory). This leads Dupret and Verleye [33] to describe the work as basically useless for the practical simulation of moulding processes. While this may be an exaggeration, the limitations of the work, together with the sophistication of the mathematical derivation and the complexity of the results, do mean that models used in composites processing do not use the ideas or results developed here. It is to be regretted that simpler, erroneous models such as that of Dinh and Armstrong, seem more attractive to engineers.

6. Effect of a non-Newtonian suspending liquid

Theoretical studies here, too, are scarce and are confined to slightly non-Newtonian fluids. Leal [89] studied slender rod-like particles suspended in a second-order fluid and the same fluid was studied by Kaloni and Stastna [90] with spherical particles. Brunn [91,92] used a Giesekus fluid model (for quasi-stationary flow) and Goddard [93,94] considered a power-law fluid. These results are not useful for direct comparison with experimental work, since the constitutive equations used are of a different character from those which describe well the constant-viscosity elastic fluids discussed below. A contrary view is implied by Ganani and Powell [95] who report results for short glass fibres in a polyisobutylene/cetane solution and obtain a second-order fluid coefficient as a function of volume fraction.

The general prediction seems to be that the increases in stress in extensional flows are not as large as for Newtonian suspending liquids. The question of whether this decrease in stress is accompanied by a decrease in the Trouton ratio is not settled. (The Trouton ratio is defined [96] as the ratio of extensional viscosity to shear viscosity at the same value of the rate of strain — by which we mean the same value of the second invariant of the rate of strain tensor). The fluids in question are shear thinning, so that the shear viscosity decreases with increasing shear rate.

An exception to this is the work of Harlen and Koch [97] who consider extensional flow of fibres suspended in a dilute polymer solution where there is no shear thinning (a Boger fluid). Theoretical results for simple shear flow were obtained by Harlen and Koch [98] who considered fibre orientation and rheology for fibres suspended in an Oldroyd B fluid. Iso, Koch and Cohen [99,100] observed experimentally the competition between elastic stresses and fibre interactions in controlling the orientation distribution. They showed for weakly elastic fluids [99] that this could be modelled successfully using the low Deborah number theory of Leal [89] and the high Deborah number theory of Harlen and Koch [98] each of which predict that fibres will tend to align with the vorticity axis (i.e. across the flow) in simple shear. For highly elastic fluids Iso, Cohen and Koch [100] find a different behaviour, with fibres tending to line up with the flow. Bartram, Goldsmith and Mason [101] found the same behaviour at high shear rates and Johnson, Salem and Fuller [102] similarly found for high elasticity fluids at high shear rates a tendency for orientation away from the vorticity axis to be preferred. Some numerical simulation work at high Deborah number by Binous and Phillips [103] on the sedimentation of spherical and non-spherical particles may be indicative of an useful approach in the investigation of highly elastic fluids.

To some readers, a review of the rheology of a class of materials with no mention of linear viscoelasticity, must seem strange. In fact little work has been done on this and what there is seems uniformly to indicate that fibre suspensions in Newtonian liquids are not ‘elastic’ in the sense that adding fibres does not affect the storage modulus, as measured in oscillatory shear. Zirnsak et al. [9] report that there is no significant difference between the storage modulus G' of a suspension of glass fibres in a Newtonian liquid and that of the suspending liquid. Earlier work by Ganani [95] and by Carter [79] is in agreement with this. In a recent paper, Harlen and Koch [104] do not address this explicitly, but show how, over many cycles of oscillation in an elastic suspending liquid, the tendency is for fibres to line up in the flow direction and hence minimize their effect on the suspension rheology.

7. Flow of composites

One major area of application of this work is the flow of polymer melts containing reinforcing fibres or, in other words, the processing of composites (to produce fibre-reinforced polymeric materials). The results for slightly non-Newtonian liquids do not seem likely to have much direct relevance, since polymer melts can hardly be described as *slightly* non-Newtonian. Curiously the modelling and simulation of these flows, which the composites industry requires, does not often involve non-Newtonian suspending liquids (and certainly not elastic suspending liquids). Hence the work on Newtonian liquids is relevant to applications that actually feature in the literature, with non-dilute suspensions being important. The choice of closure approximation (Section 3.3 above) is a frequent topic in this area of research, particularly in association with the development of numerical simulation tools for the flow of composites [33,35].

In work on composites (and in particular their processing) fibre orientation distribution is an important physical quantity rather than just something that influences the rheology. The orientation distribution of the fibres in the product (typically produced by some moulding process) affects the properties and serviceability of the product. Hence the evolution of the fibre orientation distribution is important [105] and we need to understand transient or non-equilibrium situations. In other words, rheology is not the only thing of interest, nor even the priority for understanding (though obviously the orientation distribution, the rheology and the flow are all coupled).

There is a brief introduction to this area of application by Folkes and Siddiqui [106]. A recent symposium [107] collects together some recent ideas on the rheology and flow of fibre suspensions, with particular reference to composites [81,108–114]. The papers cover short-fibre, discontinuous-long-fibre and continuous-long-fibre reinforcement, as well as some fundamental studies in rheology and non-Newtonian fluid mechanics.

The approach taken by Folgar and Tucker [115] (see also Tucker [35]) is the basis of most treatments of semi-dilute and moderately concentrated composites. There are superficial similarities with the equations for Brownian particles discussed above (Section 5.3). Folgar and Tucker deal with the fibre–fibre interactions by means of an empirically adjustable rotary diffusion term directly in the Jeffery equation for a single fibre.

$$D_{\mathrm{r}} = C_{\mathrm{I}}\dot{\gamma}. \tag{80}$$

In both Eqs. (66) and (80) the adjusted rotary diffusion coefficient has an arbitrary constant to be determined empirically. The key difference from Doi and Edward's Brownian fibre result is that Tucker's hydrodynamic rotary diffusivity is proportional to the shear rate.

There is a good deal of evidence which indicates that this approach gives accurate predictions in many circumstances. There are essentially two choices to be made (on the basis of experimental evidence, theoretical reasoning or in an ad hoc manner). The constant C_{I} has to be chosen and a closure approximation needs to be made. Work of Koch and Shaqfeh and coworkers has confirmed the basic assumption of Folgar and Tucker. Rahnama, Koch and Shaqfeh [8] introduce the idea of an anisotropic rotary diffusivity. This is therefore a tensor and it is dependent on the orientation of the particular fibre, the type of flow, and the fibre orientation distribution. Rahnama, Koch, Iso and Cohen [116] calculated the rotary diffusivity for simple shear and compared predictions with experimental results of Stover, Koch and Cohen [7] and Anczurowski and Mason [6]. Shaqfeh and Koch [117] calculated the diffusivity for extensional flows and Rahnama, Koch and Cohen [118] tested experimentally the predicted dispersion of orientation for extensional flow. Koch [119] gives a summary of this work and suggests a model diffusivity tensor for all linear flows. Finally we note that the hydrodynamic diffusivity is rather small and so an 'effective Péclet number' based on the effective diffusivity would still be large.

A number of workers, notably those associated with Koch and Shaqfeh have used numerical simulation as an effective tool in investigating non-dilute fibre suspensions. Sundararajakumar and Koch [81] discuss the effect of mechanical contact between fibres in simple shear and compare this with earlier work [8] on hydrodynamic interactions. Using a renormalized Green's function, following Shaqfeh and Fredrickson [73], they show [81] that in the case of weak hydrodynamic interactions an effective rotary diffusion coefficient may be used. This provides a link between the work on semi-dilute suspension viscosity and on the evolution of the fibre orientation distribution.

Gibson and Toll [120] adopt a rather pragmatic (phenomenological) approach in the first part of their paper, treating the response to squeezing flow using power-law relations between relevant stress and rate of strain components. A variational approach (reminiscent of that used for converging flow by Binding [121]) is used to estimate the contributions of shear and extension in the squeezing flow (by minimizing the dissipation). In the second part of their paper, a micro-mechanical approach is used to analyse the flow in a way that allows for non-local effects, which become relevant for non-homogeneous flows of suspensions of long fibres. The same issues might arise (in principle at least) for liquids consisting of long molecules, if the molecular lengths are comparable with lengths over which the flow field changes appreciably. Non-local effects are commonly excluded by one of the basic 'simple fluid' axioms.

Another connection between areas one might regard as unconnected has been made by Becraft and Metzner [122]. They find that behaviour of glass fibre filled polyolefines in shear is well described by a modification by Doraiswamy and Metzner [123] of Doi's theory for liquid-crystalline polymers [77]. The connection is made because liquid-crystalline behaviour is associated with high concentrations and it is with such concentrations (up to 40% by weight) that Becraft and Metzner are concerned. We have here a combination of effects — a non-dilute suspension in a non-Newtonian liquid. This paper [123] also contains a discussion of fibre orientation and inhomogeneity in fibre concentration. Extrudate appearance (roughness, the effect of fibres) is also discussed.

The term 'hyperconcentrated suspension' is introduced by Pipes et al. [124] to describe the situation where the fibres are all lined up and the suspending liquid is regarded more as a lubricant. This takes us into unfamiliar territory and an essentially empirical approach is adopted. A Carreau equation is used for the viscosity $\eta = \eta_0(1 + \lambda\dot{\gamma})^{(n-1/2)}$ and the anisotropic material response is described in terms of in-plane and transverse shearing viscosities and longitudinal and transverse elongational viscosities. Such an approach does not give us a constitutive equation from which we can predict the rheology of the suspension in other flows; it would be more satisfactory to describe the material response in a way which does not use different equations for different flow geometries. Perhaps there are ideas in the section of the paper of Goddard [87] on highly concentrated suspensions which offer more fundamental insight in this extreme of high concentration (see also [125]).

8. Discussion

There are a number of other recent papers which include reviews of the rheology of fibre suspensions; see, for example [9,126]. There are many earlier reviews including those by Ganani and Powell [127], Metzner [70], Jeffrey and Acrivos [128] and Maschmeyer and Hill [129]. For an industrial perspective, reviews by Jinescu [130] and Beazley [131] may be mentioned and one of the best recent papers reviewing fibre suspensions from the point of view of composites is that by Dupret and Verleye [33].

As well as shear and extensional flows, work has been done on flow past a sphere, a problem which has been used as a standard test for non-Newtonian CFD codes and which also has applications in falling-ball rheometry [60,132–135]. Sink flow [136,137] and die entry flow (converging or contraction flow) [138,112] have also been studied either theoretically or experimentally. Other non-ideal flows studied included spinning [72,139] and lubrication flows [140,141]. The radial migration of spherical and rod-like particles in torsional flow is studied by Feng and Joseph [142]. An influence of orientation on the direction of migration is discovered and interaction between particles, especially aggregation of particles, are discussed.

The idea of a non-local theory has been mentioned above (Section 7, [120]). Schiek and Shaqfeh [143–145] develop this and discuss how variations in the velocity gradient on a length scale comparable with the fibre length necessitates this approach. They also point out how flow boundaries have a similar effect. An even more unusual flow is observed when an external force is brought into play. This can lead to chaotic behaviour of suspensions [146,147]. Another situation where modern dynamical system theory arises is reported by Szeri, Milliken and Leal [148]. Flows which are unsteady in the Lagrangean sense are analysed using tools from the theory of periodically forced nonlinear differential equations. The question addressed is whether a random initial orientation is maintained or an ordered state evolves. Use of a four-roll mill allows this to be studied experimentally. A less exotic unusual (or unexpected) behaviour is observed under some circumstances in the flow of long fibres. The fibre orientation is observed to be across flow rather than along it. This is mentioned by Tucker [35] and by McClelland and Gibson [149].

Simulation can be carried out at various levels of refinement, from molecular dynamics to the numerical solution of discretized continuum equations. The issues surrounding this became evident during the six month programme on ‘The Dynamics of Complex Fluids’ at the Isaac Newton Institute in Cambridge in 1996 (see, for example, [150,151]). Other recent work develops direct simulations of fibre suspension flows with industrial applications in mind [152,153,154]. The simulations on molecular or microstructural length scales now begin to offer the possibility of replacing a constitutive equation (in the familiar continuum mechanical form) by a direct simulation which may be expected to avoid the approximations, empiricisms and ad hoc assumptions behind most constitutive equations. This is surely progress to be welcomed but the question of whether it spells the imminent end of constitutive equations is by no means settled. There are limitations to what can successfully be simulated; Mackaplow and Shaqfeh [75] mention that the molecular dynamics simulations of Claeys and Brady [155] run into problems with large fibre aspect ratio. However that is not the main reason for expressing the opinion that constitutive equations, rather than the results of numerical simulation, are a highly desirable tool for our understanding of the behaviour of materials.

The area of colloidal suspensions such as discussed by Solomon and Boger [156] is interesting. They discuss a colloidal suspension of nonspherical particles when van der Waals and electrostatic forces, as well as Brownian forces, affect the rheology. This serves as a reminder that length scales are always important in developing appropriate rheological equations of state.

Finally, the ideas in fibre suspension rheology which we choose to highlight are

1. Without flow-induced orientation (anisotropy) a fibre suspension (in a Newtonian liquid) is Newtonian — but one needs to make the suspension flow in order to discover whether it is Newtonian or not, so that this remark can only give what is, in some sense, limiting behaviour.
2. If one takes the magnitude of the storage modulus from linear viscoelasticity as a measure of elasticity, the absence of effects in oscillatory shear must be interpreted as an absence of elasticity in the fluid. Coupled with the large effects in extensional flow, this gives a clear sign that high extensional viscosity should not be taken as evidence of elasticity.
3. While numerical simulation is extremely valuable as a research tool, it does not do away with the need for constitutive equations (however approximate). Computational cost is only one reason for making this claim. A constitutive equation offers the rheologist information in a form which is much easier to comprehend; only a very large series of graphs could contain as much information. Numerical simulation will, of course, answer specific questions most effectively and will in certain situations be the tool of choice.

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