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The effects of Brownian rotations in a dilute suspension of rigid particles of arbitrary shape

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A set of constitutive equations is derived to describe the time-dependent flow of a dilute suspension of identical rigid particles of arbitrary shape which are influenced by Brownian couples. The form of the orientation probability distribution for small departures from isotropy is found. The case of weak flows with strong Brownian effects is studied in detail, and the viscoelastic approximation and second-order-fluid limit of the constitutive equation are derived for a general particle shape. A full numerical solution is given for ellipsoids. The general nearly spherical particle is also considered and constitutive equations for general flow strengths are obtained for this case.

1. Introduction

The first systematic study of the rheology of a dilute suspension of identical particles sufficiently small to be affected by Brownian motions would seem to be that by Giesekus (1962). In his paper he considers a dilute suspension of spheroids (i.e. ellipsoids with an axis of symmetry) and examines in detail the situation in which Brownian effects play a dominant role. In a series of papers, Leal and Hinch have extended the analysis to cover also the cases of weak Brownian motion (Leal & Hinch 1971; Hinch & Leal 1973), an intermediate regime of weak Brownian motion (Hinch & Leal 1972) and the entire range of flow strengths for nearly spherical particles (Leal & Hinch 1972). In every case, attention is confined to spheroidal particle shapes. The purpose of this paper is to develop a description which is not restricted to axially symmetric particles, and which will enable particles of a general shape to be treated.

Throughout we shall be concerned with identical, rigid, force-free particles in a suspension which is dilute and spatially homogeneous. Thus hydrodynamic interactions between the particles will be neglected, and there will be no Brownian forces tending to change the particle concentration in physical space. In fact, owing to the coupling between translation and rotation for, say, a screw-shaped particle, it is not *a priori* clear that we can ignore the translation of the particles. An order-of-magnitude argument demonstrates that the rotational effects are significantly larger than the translational ones, however (see the note at the end of §2.2), and therefore in what follows we shall concern ourselves with them only.

The particles will be taken to be sufficiently small for the Brownian couples on them to produce significant effects, and in consequence all physically reasonable motions of the suspension will correspond to a Reynolds number based on particle size which is small. The suspending fluid is taken to be Newtonian.

The paper is divided into five main sections. In § 2 we construct the basic apparatus needed to handle the orientation statistics for a general body. In § 3 this is applied to the case in which the distribution is nearly isotropic, and in §§ 4 and 5 explicit forms are given for the 'linear viscoelastic' and 'second-order-fluid' regimes. Numerical computations of these formulae for the particular body shape of an ellipsoid (with no symmetry) are given in § 6, and finally, in § 7, we consider the general near-sphere limit for the particle shape.

We do not discuss here particular flows of the suspension. The spirit of this paper is to indicate how the constitutive equation constructed for the suspension is connected with the more general phenomenological theories of complex materials. Also we make no apology for assuming that the tensors which characterize the motion of a particle in a linear flow are known. The problem of finding these for a general body shape is formidable, and outside the scope of this paper.

2. Basic formulation

2.1. *Orientation statistics*

The assumption of diluteness means that each particle of the suspension can be considered independently. In order to treat the microstructural kinematics, therefore, we need find only a method of describing the orientation of a single particle. Almost all previous studies of Brownian rotations have restricted attention to axisymmetric particles, for which the orientation statistics can conveniently be given in terms of a unit vector along the symmetry axis. Brenner (1967) discusses the Brownian motion of particles of a general shape. (He derives formulae for both the Brownian force and the Brownian couple on a particle: we shall be concerned only with the couples here.) His Euler-angle representation of orientation is, however, exceedingly cumbersome and use of such a representation produces results which are complicated (see Workman & Hollingsworth 1969) and difficult to extend to such problems as the one described here.

The method that we employ to specify the current orientation of a particle is to give the rotation matrix $R_{i\alpha}$ from some reference configuration to its present orientation. We adopt the convention that tensors to be evaluated in the reference state shall have Greek suffixes, while Latin suffixes are used in the current state. Thus as the particle rotates in response to the hydrodynamic forces on it, so the rotation matrix also changes. In other words, in the space of all possible linear transformations from one co-ordinate system to another, which in general involve stretches and rotations, we are concerned with the three-dimensional subspace represented by all orthogonal matrices $\mathbf{R}.\mathbf{R}^T = \mathbf{I}$. There is a large degree of redundancy in this representation of orientation space: $\mathbf{R}$ has nine components while the space considered requires only three; nevertheless this proves to be very much easier to handle than the Euler-angle representation, which uses just three variables.

Where the effects of Brownian motion are important, the orientation of any given particle of the suspension is only statistically determinate. We introduce an orientation probability distribution function $\mathcal{N}(\mathbf{R}, t)$ so that $\mathcal{N}\,d\tau$ gives at time t the proportion of particles whose orientations lie within a small region $d\tau$ of that specified by $\mathbf{R}$. ($d\tau$ can here be thought of as any convenient way of labelling a small volume of orientation space.)

$\mathcal{N}$ is normalized:

$$\int_{\text{orientations}} \mathcal{N}\, d\tau = 1 \quad \text{for all } t. \tag{2.1}$$

It must also satisfy a conservation law in orientation space:

$$\partial\mathcal{N}/\partial t + \nabla . \mathcal{F} = 0, \tag{2.2}$$

where $\mathcal{F}$ is the probability flux vector in orientation space and ∇ is the gradient operator in that space. The problem of finding an explicit representation of the ∇ operator is treated in appendix A. It is shown there that, if f is any scalar function of orientation, then

$$(\nabla f)_k = \epsilon_{kij} R_{i\alpha}\, \partial f/\partial R_{j\alpha}. \tag{2.3}$$

It is further demonstrated that (2.3) is valid irrespective of whether $\partial/\partial R$ is interpreted as a projection of a nine-dimensional gradient in the space of all linear transformations, or as a gradient defined only in our three-dimensional subspace.

2.2. *The particle material tensors*

With the assumption of diluteness, we may consider each particle of the suspension separately: as if it were in unbounded fluid with a prescribed velocity gradient at infinity. If, further, the particles are so small that on the microscale the Stokes equations are applicable, then as discussed by Hinch (1972), with some sign changes, linearity gives that

$$\begin{pmatrix} \mathbf{F} \\ \mathbf{L} \\ \mathbf{S} \end{pmatrix} = \mu V \begin{pmatrix} \mathbf{X} & \mathbf{P} & \mathbf{Q} \\ \mathbf{P}' & \mathbf{Y} & \mathbf{R} \\ \mathbf{Q}' & \mathbf{R}' & \mathbf{Z} \end{pmatrix} . \begin{pmatrix} \mathbf{u}-\mathbf{U} \\ \boldsymbol{\omega}-\boldsymbol{\Omega} \\ \mathbf{E} \end{pmatrix}, \tag{2.4}$$

where $\mathbf{F}$, $\mathbf{L}$ and $\mathbf{S}$ are the force, couple and stresslet exerted by the particle on the fluid, μ is the ambient fluid viscosity, V the volume of the particle, $(\mathbf{u}-\mathbf{U})$ and $(\boldsymbol{\omega}-\boldsymbol{\Omega})$ its velocity and angular velocity relative to those of the fluid at infinity, and $\mathbf{E}$ the symmetric part of the velocity gradient at infinity. The matrix of (tensor) coefficients is determined by the size and external shape of the particle. It is symmetric and positive definite. Nir, Weinberger & Acrivos (1975) construct variational bounds for the material tensors that appear. They also discuss the additional internal symmetries of the tensors which are the elements of the matrix. The evaluation of the six unknown tensors is achieved by the solution of appropriate low Reynolds number problems for the particle. For the most part we shall assume that these tensors are known, but in §7 an explicit determination for nearly spherical particles will be made. A recent paper by Youngren & Acrivos (1975) indicates a scheme by which they may be found numerically.

Throughout we shall be concerned with force-free particles with no external couples except those due to thermal agitations. We are interested in two effects: the particle angular velocity and the stresslet produced by the particle. By linearity we may add the separate contributions to these from the Brownian couples and the fluid straining motion at infinity. Thus we write

$$\boldsymbol{\omega} = \boldsymbol{\omega}^B + \boldsymbol{\omega}^H, \quad \mathbf{S} = \mathbf{S}^B + \mathbf{S}^H. \tag{2.5}$$

These two contributions are now considered separately.

Contribution from Brownian effects. As discussed by Brenner (1967) and Brenner & Condiff (1972), by an extension of Einstein's original argument the random Brownian couples may be replaced by an effective entropic couple:

$$\mathbf{L}^B = -kT\nabla \log \mathcal{N}.$$

As the particles are force-free, $\mathbf{F} = 0$ and $\mathbf{u}-\mathbf{U} = -\mathbf{X}^{-1}.\mathbf{P}.\boldsymbol{\omega}^B$, so that

$$\boldsymbol{\omega}^B = -D\mathbf{M}.\nabla \log \mathcal{N}, \tag{2.6}$$

where

$$D = kT/6\mu V, \quad \mathbf{M} = 6(\mathbf{Y}-\mathbf{P}'.\mathbf{X}^{-1}.\mathbf{P})^{-1}. \tag{2.7}$$

The non-dimensionalized mobility tensor $\mathbf{M}$ is independent of the size of the particle and $\|\mathbf{M}\|$ is $O(1)$ except for extreme body shapes. $\mathbf{M} = \mathbf{I}$ for a sphere. Also,

$$\mathbf{S}^B = 3\mu VD\mathbf{B}'.\nabla \log \mathcal{N},$$

where

$$B_{jpq} = -2(\mathbf{Y}-\mathbf{P}'.\mathbf{X}^{-1}.\mathbf{P})^{-1}_{jk}(\mathbf{R}-\mathbf{P}'.\mathbf{X}^{-1}.\mathbf{Q})_{kpq}, \tag{2.8}$$

and

$$B'_{kij} = B_{ijk}.$$

$\mathbf{B}$ is symmetric and traceless in its last two suffixes. It is, in fact, the tensor introduced by Bretherton (1962).

Contribution from the straining motion. Similarly, for the hydrodynamic contribution we obtain

$$\boldsymbol{\omega}^H = \boldsymbol{\Omega}+\tfrac{1}{2}\mathbf{B}:\mathbf{E}, \quad \mathbf{S}^H = \mu V\mathbf{C}:\mathbf{E}, \tag{2.9}$$

where

$$C_{ijlm} = Z_{ijlm} - Q'_{ijp}X^{-1}_{pk}Q_{klm} + \tfrac{1}{2}(R_{ijs} - Q_{ijp}X^{-1}_{pk}P_{ks})B_{slm}. \tag{2.10}$$

The particle tensor $\mathbf{C}$ is (essentially) that used by Batchelor (1970*a*). $\mathbf{C}$ is symmetric and traceless with respect to both its first and its second pair of suffixes. It is also symmetric under interchange of these pairs.

Note on the coupling between translation and rotation. In view of the coupling tensor $\mathbf{P}$, which is non-zero for screw-like particles, the Brownian rotation of the particles induces an additional translational velocity. It may then be thought that an additional term should appear in the probability conservation equation (2.2), viz. $(\partial/\partial\mathbf{x}).(\mathcal{N}\mathbf{u}^B)$. The following dimensional argument shows that this term is small in comparison with the rotational term $(\partial/\partial\boldsymbol{\theta}).(\mathcal{N}\boldsymbol{\omega}^B)$. If l is a particle length scale and L a macroscopic scale then $|\boldsymbol{\omega}^B| = O(D)$, and so $|\mathbf{u}^B| = O(Dl)$. Hence $|(\partial/\partial\mathbf{x}).(\mathcal{N}\mathbf{u}^B)| = O(Dl/L)$ while $|(\partial/\partial\boldsymbol{\theta}).(\mathcal{N}\boldsymbol{\omega}^B)| = O(D)$, which is larger by a factor $O(L/l)$. Now our underlying assumption throughout has been that l/L is small, and therefore to the accuracy of our averaging procedure the translation term is negligible. Note also that concentration gradients in physical space produce Brownian forces whose effects are similarly an order of magnitude smaller than those we have included.

2.3. *The form of the particle stress*

The stresslet exerted by just one particle on the fluid has now been derived as

$$\mathbf{S} = 3\mu VD\mathbf{B}'.\nabla \log \mathcal{N} + \mu V\mathbf{C}:\mathbf{E}.$$

As shown by Batchelor (1970*a*, equation 5.16), the total particle stress in a dilute suspension of total volume V_0 whose statistics are determinate is

$$\sigma^{(p)}_{ij} = \frac{1}{V_0}\sum_{\text{particles in } V_0}(S_{ij} + \tfrac{1}{2}\epsilon_{ijk}L_k).$$

Here the sum must be replaced by an average over orientations giving

$$\bar{\sigma}_{ij}^{(p)} = 3\mu D\Phi\langle(\boldsymbol{\epsilon}+\mathbf{B}').\nabla\log\mathcal{N}\rangle + \mu\Phi\langle\mathbf{C}\rangle:\mathbf{E},$$

where Φ is the volume concentration of particles and for any quantity ψ we define

$$\langle\psi\rangle \equiv \int_{\text{orientations}} \psi\mathcal{N}\,d\tau. \tag{2.11}$$

Now, in the first term,

$$\langle(\boldsymbol{\epsilon}+\mathbf{B}').\nabla\log\mathcal{N}\rangle = \int(\boldsymbol{\epsilon}+\mathbf{B}').\nabla\mathcal{N}\,d\tau$$
$$= \int\nabla.[\mathcal{N}(\boldsymbol{\epsilon}+\mathbf{B})]\,d\tau - \int\mathcal{N}\nabla.(\boldsymbol{\epsilon}+\mathbf{B})\,d\tau.$$

But $\mathcal{N}$ is a single-valued function of orientation and so the first integral vanishes by the divergence theorem and hence

$$\bar{\boldsymbol{\sigma}}^{(p)} = -3\mu D\Phi\langle\nabla.\mathbf{B}\rangle + \mu\Phi\langle\mathbf{C}\rangle:\mathbf{E}. \tag{2.12}$$

The noted symmetries of $\mathbf{B}$ and $\mathbf{C}$ ensure that the stress tensor is symmetric. This was to be expected, since no external couple acts on the suspension as a whole, and the random Brownian couples can make no systematic contribution to an antisymmetric bulk stress.

We can use (2.3) to evaluate $\nabla.\mathbf{B}$:

$$\nabla.\mathbf{B} = -2\mathbf{F}, \tag{2.13}$$

where

$$F_{ij} = \tfrac{1}{2}(\epsilon_{ikl}B_{kjl} + \epsilon_{kjl}B_{kil}). \tag{2.14}$$

Note that $\mathbf{F}$ is a symmetric traceless tensor depending only on the particle shape. Further, $F_{ij} = R_{i\alpha}R_{j\beta}F^0_{\alpha\beta}$, where $\mathbf{F}^0$ is independent of $\mathbf{R}$. We may thus put

$$\langle\mathbf{F}\rangle = \langle\mathbf{R}.\mathbf{R}\rangle\,\mathbf{F}^0,$$

with $\mathbf{F}^0$ evaluated in the reference state. $\langle\mathbf{C}\rangle$ may be dealt with similarly. We thus obtain the result

$$\bar{\sigma}_{ij}^{(p)} = 2\mu\Phi\{3DF^0_{\alpha\beta}\langle R_{i\alpha}R_{j\beta}\rangle + \tfrac{1}{2}C^0_{\alpha\beta\gamma\delta}\langle R_{i\alpha}R_{j\beta}R_{k\gamma}R_{l\delta}\rangle E_{kl}\}. \tag{2.15}$$

The first contribution here is the diffusion stress, while the second arises from the ambient straining motion.

2.4. *Derivation of the Fokker–Planck equation*

We see from (2.15) that in order to calculate the bulk stress it suffices to know $\mathcal{N}$ so as to be able to evaluate the second and fourth moments. The evolution of $\mathcal{N}$ is governed by (2.2) with the probability flux $\mathcal{F} = \mathcal{N}\boldsymbol{\omega} = \mathcal{N}(\boldsymbol{\omega}^B + \boldsymbol{\omega}^H)$. The probability conservation equation thus becomes by (2.6),

$$\partial\mathcal{N}/\partial t + \nabla.(\mathcal{N}\boldsymbol{\Omega} + \tfrac{1}{2}\mathcal{N}\mathbf{B}:\mathbf{E}) = D\nabla.(\mathbf{M}.\nabla\mathcal{N}). \tag{2.16}$$

This is the appropriate form of the Fokker–Planck equation for the problem. It is clear that the two contributions to $\boldsymbol{\omega}$ represent advection and diffusion of $\mathcal{N}$ in (2.16).

As before we can use (2.3) to give an explicit representation of the ∇ operator in (2.16). On writing $\boldsymbol{\Omega} = -\tfrac{1}{2}\boldsymbol{\epsilon}:\tilde{\boldsymbol{\Omega}}$, where $\tilde{\boldsymbol{\Omega}}$ is the antisymmetric vorticity tensor, and giving the suffixes in full, this becomes

$$\frac{\partial\mathcal{N}}{\partial t} + \tilde{\Omega}_{ij}R_{j\alpha}\frac{\partial\mathcal{N}}{\partial R_{i\alpha}} + \tfrac{1}{2}B_{kpq}E_{pq}\epsilon_{kij}R_{i\alpha}\frac{\partial\mathcal{N}}{\partial R_{j\alpha}} - \mathcal{N}E_{ij}F_{ij}$$
$$= DM_{kl}\epsilon_{kij}R_{i\alpha}\frac{\partial}{\partial R_{j\alpha}}\left[\epsilon_{lmn}R_{m\beta}\frac{\partial\mathcal{N}}{\partial R_{n\beta}}\right]. \tag{2.17}$$

Equations (2.15) and (2.17) together provide the constitutive equation for the suspension. In principle, given some initial conditions for $\mathscr{N}$ and a prescribed $\mathbf{E}(t)$ and $\tilde{\mathbf{\Omega}}(t)$, which may themselves be derived from the solution of an appropriate boundary-value problem, (2.17) can be integrated forwards in time to give a new $\mathscr{N}(t)$ and, through the angle averages in (2.15), a new $\boldsymbol{\sigma}$. Clearly, in general this is a formidable task. In order to make further analytic progress, we restrict attention from § 3 onwards to situations in which the orientation statistics are approximately uniform, and thus consider only small departures from the isotropic, Newtonian fluid structure.

We note in passing that some progress can be made in the general problem by means of a method of moments. In appendix C a useful exact result for the second moment of $\mathscr{N}$ in terms of the fourth moment is obtained. As usual in a moment technique, some truncation procedure for the progressively higher moments which arise is necessary to provide a closed system of equations.

3. Nearly isotropic orientation distributions

There are two circumstances in which we may expect *a priori* that to lowest order the orientations of the particles will be randomly distributed: first where Brownian effects play a dominant role, and second where the particles are nearly spherical and the flow is not exceptionally strong. In either case then, $\mathscr{N} \sim$ constant $= 1/8\pi^2$ by virtue of the normalization (2.1). We now consider the smallest perturbation from this case. Letting γ be a typical strain rate, in the former case we may define $\epsilon = \gamma/D \ll 1$. In the latter case, if $\epsilon \ll 1$ is a measure of the non-sphericity of the particles, then $\mathbf{B}$ and hence $\mathbf{F}$ are each $O(\epsilon)$. Hence expanding

$$\mathscr{N} = 1/8\pi^2 + \epsilon\mathscr{N}_1 + O(\epsilon^2), \tag{3.1}$$

substituting in (2.17) and retaining $O(\epsilon)$ terms gives

$$\frac{\partial\mathscr{N}_1}{\partial t} + \tilde{\Omega}_{ij} R_{j\alpha} \frac{\partial\mathscr{N}_1}{\partial R_{i\alpha}} - DM_{kl}\epsilon_{kij} R_{i\alpha} \frac{\partial}{\partial R_{j\alpha}} \left[\epsilon_{lmn} R_{m\beta} \frac{\partial\mathscr{N}_1}{\partial R_{n\beta}}\right] = \frac{1}{8\pi^2\epsilon} E_{ij} F_{ij}, \tag{3.2}$$

where the right-hand side is $O(1)$. (In the former case, $\|\tilde{\Omega}\|$ is $O(\gamma)$ and so the second term is also negligible to this order.)

Now the right-hand-side forcing in (3.2) may be written as $E_{ij} R_{i\alpha} R_{j\beta} F^0_{\alpha\beta}/8\pi^2\epsilon$. This suggests the substitution

$$\mathscr{N}_1 = (1/8\pi^2)\, \mathscr{A}_{ij\alpha\beta}(t)\, R_{i\alpha} R_{j\beta}, \tag{3.3}$$

where $\mathscr{A}$ is independent of $\mathbf{R}$, in close analogy with the near-sphere problem of Leal & Hinch (1972). Now in order to preserve the normalization we require $\int \mathscr{N}_1\, d\tau = 0$, so noting that $\int R_{i\alpha} R_{j\beta}\, d\tau = 8\pi^2 \delta_{ij}\delta_{\alpha\beta}$ (see appendix A), it suffices that $\mathscr{A}_{ii\alpha\alpha} = 0$. In fact we suppose that

$$\mathscr{A}_{ij\alpha\beta} = \mathscr{A}_{ji\alpha\beta} = \mathscr{A}_{ij\beta\alpha}, \quad \mathscr{A}_{ii\alpha\beta} = \mathscr{A}_{ij\alpha\alpha} = 0 \tag{3.4}$$

and verify *a posteriori* that these conditions are preserved by the equation for the time evolution of $\mathscr{A}$.

The algebra involved in substituting (3.3) in (3.2) is tedious but straightforward and leads to the equation

$$\partial\mathscr{A}_{ij\alpha\beta}/\partial t - \tilde{\Omega}_{ip} \mathscr{A}_{pj\alpha\beta} + \tilde{\Omega}_{pj} \mathscr{A}_{ip\alpha\beta} + K^{-1}_{\alpha\beta\gamma\delta} \mathscr{A}_{ij\gamma\delta} = \epsilon^{-1} E_{ij} F^0_{\alpha\beta}, \tag{3.5}$$

where $\mathbf{K}^{-1}$ is defined by (C 2).

It is easy to verify that this equation does preserve the symmetries (3.4) assumed for $\mathscr{A}$. Further, as all the terms appearing in (3.5) are independent of **R**, the quadratic form assumed for $\mathscr{N}_1$ in (3.3) is shown to be appropriate. By comparison with the analogous quadratic formula obtained by Leal & Hinch (1972) it is clear that, just as we can accommodate the greater complexity of non-axisymmetric bodies by use of a matrix **R** rather than a vector **p**, so we can specify the 'shape' of the probability distribution by the fourth-rank quantity $\mathscr{A}$ rather than their second-rank tensor **A**.

A particularly simple form of (3.5) arises when, to sufficient accuracy, the diffusion tensor is isotropic, i.e.

$$\mathbf{M} = \mathbf{I} + O(\epsilon), \tag{3.6}$$

which is found to be the case for nearly spherical particles and axisymmetric disks. In that case we may take $\mathscr{A}_{ij\alpha\beta} = \frac{1}{3}A_{ij}F^0_{\alpha\beta}$ (if $\mathbf{F} \neq 0$) and we then obtain

$$\mathscr{D}\mathbf{A}/\mathscr{D}t + 6D\mathbf{A} = 3\mathbf{E}\epsilon^{-1}, \tag{3.7}$$

where the Jaumann derivative $\mathscr{D}\mathbf{A}/\mathscr{D}t \equiv \partial\mathbf{A}/\partial t + \mathbf{A}.\tilde{\mathbf{\Omega}} - \tilde{\mathbf{\Omega}}.\mathbf{A}$. Equation (3.7) is identical to equation (5) of Leal & Hinch (1972), thus showing that for small departures from isotropy the orientation-space probability distribution for any nearly spherical particle shape is essentially the same as for axisymmetric near-spheres.

To complement (3.5) we need also the form of the stress in the nearly isotropic case. The angle averages appearing in (2.15) may now be computed correct to $O(\epsilon)$ from the known form for $\mathscr{N}_1$. For instance $\langle\mathbf{R}.\mathbf{R}\rangle = \langle\mathbf{R}.\mathbf{R}\rangle_0 + \epsilon\langle\mathbf{R}.\mathbf{R}\rangle_1 + O(\epsilon^2)$ (where by the notation $\langle\psi\rangle_n$ we mean $\int \psi\mathscr{N}_n d\tau$, $n = 0, 1, 2, \ldots$), and so from the results of appendix A,

$$\langle R_{i\alpha}R_{j\beta}\rangle = \tfrac{1}{3}\delta_{ij}\delta_{\alpha\beta} + \tfrac{1}{5}\epsilon\mathscr{A}_{ij\alpha\beta} + O(\epsilon^2),$$

and

$$\begin{aligned}\langle R_{i\alpha}R_{j\beta}R_{k\gamma}R_{l\delta}\rangle E_{kl} = {} & \tfrac{1}{60}E_{ij}[-2\delta_{\alpha\beta}\delta_{\gamma\delta} + 3(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})] \\ & + \tfrac{1}{210}\epsilon\{16(E_{in}\mathscr{A}_{jn\beta\gamma}\delta_{\alpha\delta} + E_{in}\mathscr{A}_{jn\beta\delta}\delta_{\alpha\gamma}) + 2(E_{in}\mathscr{A}_{jn\alpha\gamma}\delta_{\beta\delta} \\ & + E_{in}\mathscr{A}_{jn\alpha\delta}\delta_{\beta\gamma}) - 12(E_{in}\mathscr{A}_{jn\gamma\delta}\delta_{\alpha\beta} + E_{in}\mathscr{A}_{jn\alpha\beta}\delta_{\gamma\delta})\} \\ & + \{\text{same terms with } i, j \text{ interchanged}\} + \text{isotropic terms } + O(\epsilon^2).\end{aligned}$$

Care must be taken to retain consistently the important terms in (2.15), however, for when Brownian effects are dominant, the diffusion stress is apparently $O(\epsilon^{-1})$ greater than the hydrodynamic stress. We therefore restrict attention to this case first, and return to the near-sphere case in § 7.

4. The limit of linear viscoelasticity

Here we take very weak flows but place no restriction on their time variation. Thus $\epsilon = \gamma/D \ll 1$ and $O(\epsilon)$ terms are negligible. It follows that the probability distribution will adjust to changes on a time scale D^{-1}. Thus if we non-dimensionalize **E** and $\tilde{\mathbf{\Omega}}$ with respect to γ, and t with respect to D^{-1} then (3.5) becomes

$$\partial\mathscr{A}_{ij\alpha\beta}/\partial t + K^{-1}_{\alpha\beta\gamma\delta}\mathscr{A}_{ij\gamma\delta} = E_{ij}F^0_{\alpha\beta}, \tag{4.1}$$

and to this order of approximation

$$\bar{\sigma}^{(p)}_{ij} = 2\mu\Phi\gamma\{\tfrac{3}{5}F^0_{\alpha\beta}\mathscr{A}_{ij\alpha\beta} + \tfrac{1}{10}E_{ij}C^0_{\alpha\beta\alpha\beta} + O(\epsilon)\}. \tag{4.2}$$

Now as (4.1) is a linear equation, it can be solved by standard normal-mode techniques: the problem is that of diagonalizing $\mathbf{K}^{-1}$, resolving $\mathscr{A}$ and the right-hand side of (4.1)

N	$\lambda^{(N)}$	$\mathbf{T}^{(N)}$	$\mathbf{T}^{(N)\dagger}$
1	$4(D^1+D^2+D^3)$	$\mathrm{diag}\,(D^2D^3, D^3D^1, D^1D^2)$	$\mathrm{diag}\,(1,1,1)$
2, 3‡	$2(D^1+D^2+D^3)\pm k$	$\mathrm{diag}\,(T_{11}^{(\frac{2}{3})}$, cyclic permutations)	$\mathrm{diag}\,(D^1T_{11}^{(\frac{2}{3})}$, cyclic permutations)
4	$4(D^1+D^2+D^3)$	$\begin{pmatrix} . & -D^2 & . \\ D^3 & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & 1 & . \\ -1 & . & . \\ . & . & . \end{pmatrix}$
5	$4D^1+D^2+D^3$	$\begin{pmatrix} . & 1 & . \\ 1 & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & D^3 & . \\ D^2 & . & . \\ . & . & . \end{pmatrix}$
6, 8	Obtained from 4 by cyclic permutation		
7, 9	Obtained from 5 by cyclic permutation		

‡ Where $T_{11}^{(\frac{2}{3})} = [2D^1+2D^2-4D^3\mp k][2D^3+2D^1-4D^2\mp k]$
and $k^2 = 2[(D^1-D^2)^2+(D^2-D^3)^2+(D^3-D^1)^2]$.

TABLE 1. Spectrum of relaxation times and weight functions for the linear viscoelastic regime.

along the eigentensors of $\mathbf{K}^{-1}$ and thus, with an exponential time dependence for each normal mode, obtaining $\mathscr{A}$. Details may be found in Rallison (1976) and are available from the author on request. Then on substituting in (4.2) we have

$$\overline{\sigma}^{(p)} = 2\mu\Phi\gamma\left\{\tfrac{1}{10}C^0_{\alpha\beta\alpha\beta}\,\mathbf{E}(t)+\int_{-\infty}^{t} m(t-t')\,\mathbf{E}(t')\,dt'+O(\epsilon)\right\}, \tag{4.3}$$

where the memory function m is given by

$$m(\xi) = \sum_{N=1}^{9} w^{(N)}\exp\left(-\lambda^{(N)}\xi\right). \tag{4.4}$$

The weights $w^{(N)}$ are forced by $\mathbf{F}$, so that

$$w^{(N)} = \tfrac{3}{5}(\mathbf{F}^0 : \mathbf{T}^{(N)})(\mathbf{F}^0 : \mathbf{T}^{(N)\dagger})/(\mathbf{T}^{(N)} : \mathbf{T}^{(N)\dagger}), \tag{4.5}$$

where $\mathbf{T}^{(N)}$ and $\mathbf{T}^{(N)\dagger}$ are respectively the eigentensor and adjoint eigentensor of $\mathbf{K}^{-1}$ corresponding to the eigenvalue $\lambda^{(N)}$. In table 1 this diagonalization of $\mathbf{K}^{-1}$ is shown for a general mobility tensor $\mathbf{M}$ whose eigenvalues are D^i, $i = 1, 2, 3$.

From the form of the $\mathbf{T}^{(N)}$ it will be seen that, since $\mathbf{F}^0$ is symmetric and traceless, $w^{(N)}$ vanishes for $N = 1, 4, 6$ and 8. Thus in general the suspension will display five distinct relaxation times in the linear regime. Where the particles are orthotropic, however, the further symmetry of $\mathbf{F}^{(0)}$ implies in addition that $w^{(N)} = 0$ for $N = 3, 5$ and 7 and so only two time scales are apparent. Finally, in the degenerate case in which the particles are axisymmetric rotation about the symmetry axis (say the '1' axis) is irrelevant, and so only one diffusion coefficient can appear. In this final case there is just one relaxation time, $6D^2$ ($= 6D^3$), and either $w^{(2)}$ or $w^{(3)}$ is zero (depending on the choice of degenerate eigenvectors).

It is therefore possible to distinguish between different shapes of suspended rigid particles by observation of the linear relaxation spectrum. Further, we can compare the result here with the earlier literature concerning simple deformable particles (see, for instance, Lodge & Wu 1971; or the review article of Williams 1975). It is known that, for Rouse–Zimm type models of systems with large numbers of internal degrees of freedom, more than five time scales appear, corresponding to the various modes of deformation. It follows, then, that at this level rigid and deformable particles can be distinguished.

To facilitate comparison of the form of $\boldsymbol{\sigma}$ with the polymer literature, it is convenient to write (4.3) and (4.4) in terms of a complex viscosity μ^* which gives the ratio of $\boldsymbol{\sigma}$ and 2$\mathbf{E}$ when each varies as $e^{i\omega t}$. Clearly,

$$\frac{\mu^*-\mu}{\mu} = \Phi\left[\tfrac{1}{10}C^0_{\alpha\beta\alpha\beta}+\sum_N \frac{w^{(N)}}{\lambda^{(N)}+i\omega}\right].$$

This is very similar to comparable results for Rouse–Zimm chains (except that the second term becomes a sum over many more modes) but with the crucial difference that the first term does not appear in most such analyses. Thus in the high frequency limit, $\omega \to \infty$, we here predict a non-zero contribution to the viscosity of the suspension from the presence of the solute. It arises because the form of the hydrodynamics used here has incorporated a finite particle size, rather than a point friction force. Its appearance is necessary to explain many of the high frequency data obtained from dilute polymer solutions (see Fixman & Evans 1976).

5. The second-order-fluid limit

Here we again consider weak flows, though not so weak as in the viscoelastic limit. The further demand however is made that time variations are slow. With $\mathbf{E}$ and $\tilde{\boldsymbol{\Omega}}$ non-dimensionalized with respect to γ, and t scaled by γ^{-1}, we may take $\epsilon = \gamma/D \ll 1$ and (2.15) becomes

$$\begin{aligned}\bar{\sigma}^{(p)}_{ij} = 2\mu\Phi\gamma\{3F^0_{\alpha\beta}\langle R_{i\alpha}R_{j\beta}\rangle_1+\tfrac{1}{2}E_{pq}C^0_{\alpha\beta\gamma\delta}\langle R_{i\alpha}R_{j\beta}R_{p\gamma}R_{q\delta}\rangle_0 \\ +\epsilon[3\langle R_{i\alpha}R_{j\beta}\rangle_2 F^0_{\alpha\beta}+\tfrac{1}{2}E_{pq}C^0_{\alpha\beta\gamma\delta}\langle R_{i\alpha}R_{j\beta}R_{p\gamma}R_{q\delta}\rangle_1]+O(\epsilon^2)\}. \quad (5.1)\end{aligned}$$

Also, (3.5) becomes $K^{-1}_{\alpha\beta\gamma\delta}\mathscr{A}_{ij\gamma\delta} = E_{ij}F^0_{\alpha\beta}$. Hence by inverting $\mathbf{K}^{-1}$ by means, say, of the diagonalization discussed in §4, we obtain

$$\mathscr{A}_{ij\alpha\beta} = K_{\alpha\beta\gamma\delta}F^0_{\gamma\delta}E_{ij}, \quad (5.2)$$

where we require $K^{-1}_{\alpha\beta\mu\nu}K_{\mu\nu\gamma\delta} = \tfrac{1}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma}-\tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta})$. It is convenient to write

$$G^0_{\alpha\beta} = K_{\alpha\beta\gamma\delta}F^0_{\gamma\delta} \quad (5.3)$$

so that $\mathbf{G}$ is another symmetric traceless tensor determined solely by the particle shape.

We are now in a position to compute all the averages in (5.1) with the exception of $\langle \mathbf{RR}\rangle_2$. This could be found indirectly via an equation and solution for $\mathscr{N}_2$. In this case, however, it is much easier to use the second-moment equation of appendix C, which becomes at $O(\epsilon^2)$, with our non-dimensionalization,

$$\begin{aligned}K^{-1}_{\gamma\delta\alpha\beta}\langle R_{i\alpha}R_{j\beta}\rangle_2 = -\partial\langle R_{s\gamma}R_{t\delta}\rangle_1/\partial t+\tilde{\Omega}_{sm}\langle R_{m\gamma}R_{t\delta}\rangle_1-\tilde{\Omega}_{mt}\langle R_{s\gamma}R_{m\delta}\rangle_1 \\ -\tfrac{1}{2}\epsilon_{\alpha\mu\gamma}B^0_{\alpha\beta\theta}\langle R_{s\mu}R_{t\delta}R_{p\beta}R_{q\theta}\rangle_1 E_{pq}-\tfrac{1}{2}\epsilon_{\alpha\mu\delta}B^0_{\alpha\beta\theta}\langle R_{s\gamma}R_{t\mu}R_{p\beta}R_{q\theta}\rangle_1 E_{pq},\end{aligned}$$

where the $\langle\ \rangle_1$ averages on the right-hand side are known from (5.2). Writing

$$N^0_{\gamma\delta} = \epsilon_{\alpha\mu\gamma}B^0_{\alpha\beta\delta}G^0_{\beta\mu}+\epsilon_{\alpha\beta\gamma}B^0_{\alpha\beta\mu}G^0_{\mu\delta}+\epsilon_{\alpha\mu\delta}B^0_{\alpha\beta\gamma}G^0_{\beta\mu}+\epsilon_{\alpha\beta\delta}B^0_{\alpha\beta\mu}G^0_{\mu\gamma} \quad (5.4)$$

so that $\mathbf{N}$ is another symmetric tensor determined by the particle shape, and computing the angle averages, we find

$$\langle R_{i\alpha} R_{j\beta} \rangle_2 = -\tfrac{1}{5} K_{\alpha\beta\gamma\delta} G_{\gamma\delta} \left(\frac{\mathscr{D}\mathbf{E}}{\mathscr{D}t} \right)_{ij} - \tfrac{3}{35} K_{\alpha\beta\gamma\delta} N_{\gamma\delta} [\mathbf{E}.\mathbf{E} - \tfrac{1}{3}\mathbf{E}:\mathbf{E}\mathbf{I}]_{ij}$$

and so finally

$$\bar{\mathbf{\sigma}}^{(p)} = 2\mu\Phi\gamma\{c_1\mathbf{E} + \epsilon[c_2 \mathscr{D}\mathbf{E}/\mathscr{D}t + c_3(\mathbf{E}.\mathbf{E} - \tfrac{1}{3}\mathbf{E}:\mathbf{E}\mathbf{I})] + O(\epsilon^2)\}, \tag{5.5}$$

where the constants c_i are determined from the particle tensors as follows:

$$\left.\begin{aligned} c_1 &= \tfrac{2}{5} F^0_{\alpha\beta} G^0_{\alpha\beta} + \tfrac{1}{10} C^0_{\alpha\beta\alpha\beta}, \\ c_2 &= -\tfrac{2}{5} F^0_{\alpha\beta} K_{\alpha\beta\gamma\delta} G^0_{\gamma\delta}, \\ c_3 &= \tfrac{6}{35} G^0_{\alpha\beta} C^0_{\gamma\alpha\gamma\beta} - \tfrac{9}{35} F^0_{\alpha\beta} K_{\alpha\beta\gamma\delta} N^0_{\gamma\delta}. \end{aligned}\right\} \tag{5.6}$$

Equation (5.5) is a constitutive equation of the well-known second-order-fluid form. Note that, as the coefficients which appear are scalars, they are independent of our choice of particle reference axes, as indeed they must be. We may characterize such a fluid by its behaviour in steady simple shear, for which

$$\left.\begin{aligned} \sigma_{12} &= \mu\Phi\gamma c_1, \\ \sigma_{11} - \sigma_{33} &= \mu\Phi\gamma\epsilon(-c_2 + \tfrac{1}{2}c_3) \equiv \mu\Phi\gamma^2 N_1/D, \\ \sigma_{22} - \sigma_{33} &= \mu\Phi\gamma\epsilon(c_2 + \tfrac{1}{2}c_3) \equiv \mu\Phi\gamma^2 N_2/D. \end{aligned}\right\} \tag{5.7}$$

The viscometric functions c_1, N_1 and N_2 depend only on the particle shape. These results are a generalization of those of Giesekus (1962) for spheroids.

Once again a comparison of this result with that of previous workers on flexible-particle suspensions can be made. Since the second-order-fluid behaviour is determined solely by the three constants c_1, N_1 and N_2 it is clear that experimental determination of these can provide little precise information concerning the particles of the suspension. We note, however, that, in all cases where the hydrodynamics of a particle (flexible or rigid) has been treated by regarding its effect as a set of non-interacting point forces on the fluid, N_2 vanishes (e.g. Curtiss, Bird & Hassager 1976). The more sophisticated hydrodynamics of our analysis, represented by the use of resistance tensors (2.4), indicates that the Weissenberg hypothesis ($N_2 = 0$) is not valid generally, however.

6. The coefficients for ellipsoids

In view of the rather abstract analysis of this paper so far, it may be worth while to give a full solution for a particular particle shape. The ellipsoid is a natural choice here since Jeffery's (1922) solution of the Stokes equations for an ellipsoid is available, and in the particular case of a spheroid the answers obtained here can be checked against the previous work of Leal & Hinch (1972). The numerical solution presented for non-axisymmetric ellipsoids is believed to be new.

We consider an ellipsoid of semi-major axes (a, b, c) with unit vectors $\mathbf{p}^0$, $\mathbf{q}^0$ and $\mathbf{r}^0$ along those axes in the reference state. Then, as shown by Batchelor (1970*a*), the important tensors (with small changes of notation to conform with this paper) are

$$Y^0_{\alpha\beta} = 4[J_1 + 2I_1 b^2c^2/(b^2+c^2)^2]^{-1} p^0_\alpha p^0_\beta + \text{(2 similar terms)},$$

$$B^0_{\alpha\beta\gamma} = \frac{b^2 - c^2}{b^2 + c^2} p^0_\alpha q^0_\beta r^0_\gamma + \ldots + \ldots,$$

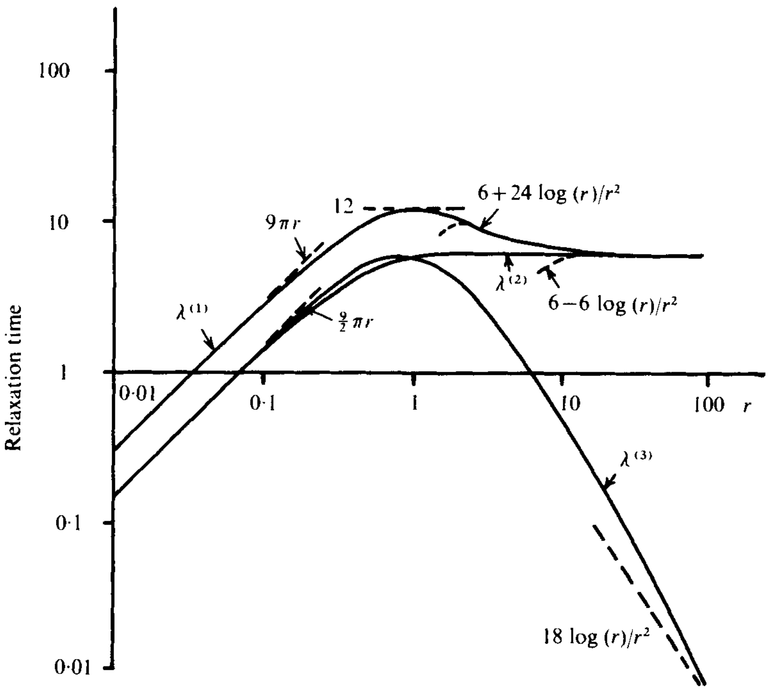

FIGURE 1. Relaxation times for spheroids. (Note that only $\lambda^{(3)}$ appears in the linear relaxation spectrum.)

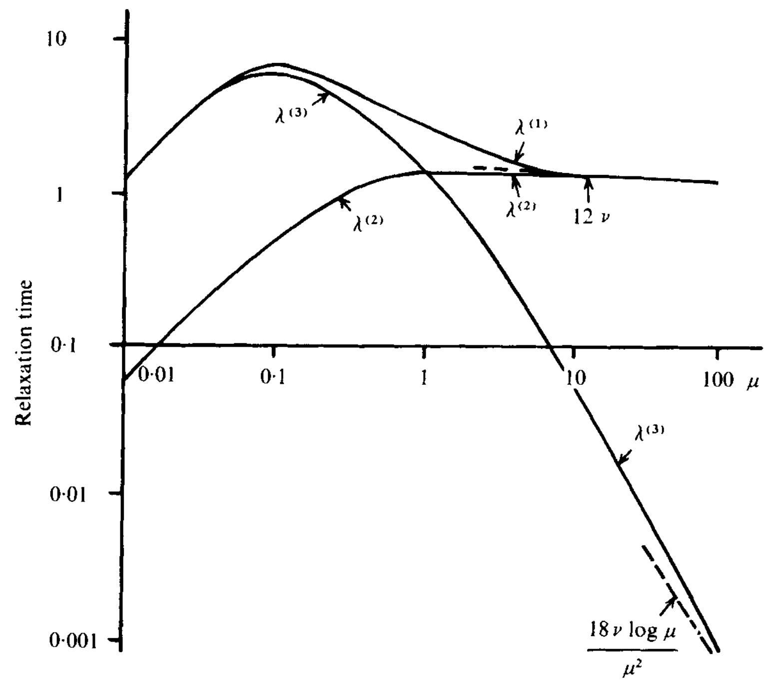

FIGURE 2. Relaxation times for ellipsoids with $b = \nu a$, $c = \mu a$, $\nu = 0{\cdot}1$. (Note that $\lambda^{(1)}$ does not appear in the linear viscoelastic spectrum.)

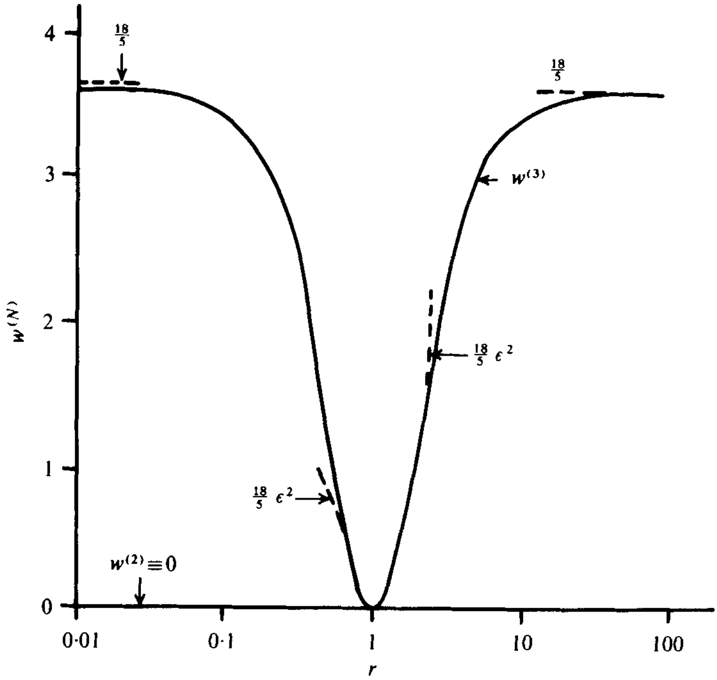

FIGURE 3. Weight functions for spheroids, $a = br$, $b = c$.

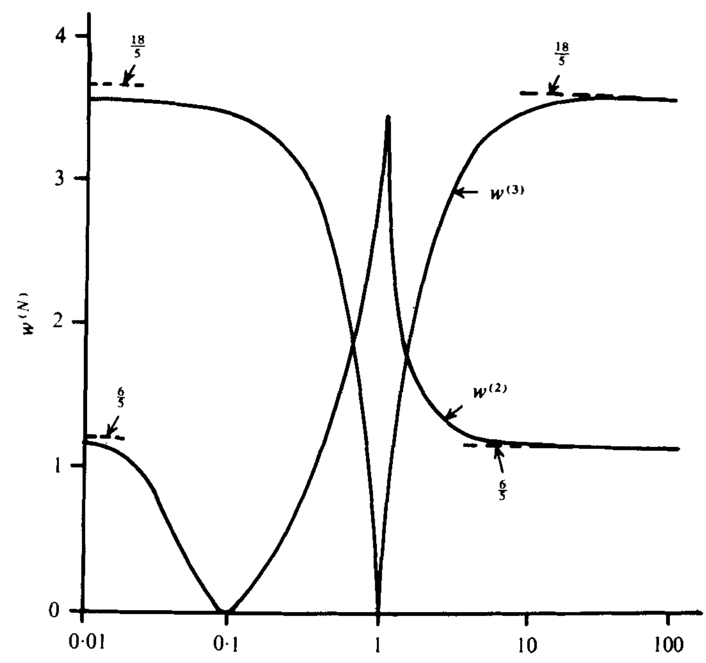

FIGURE 4. Weight functions for ellipsoids with $b = \nu a$, $c = \mu a$, $\nu = 0{\cdot}1$.

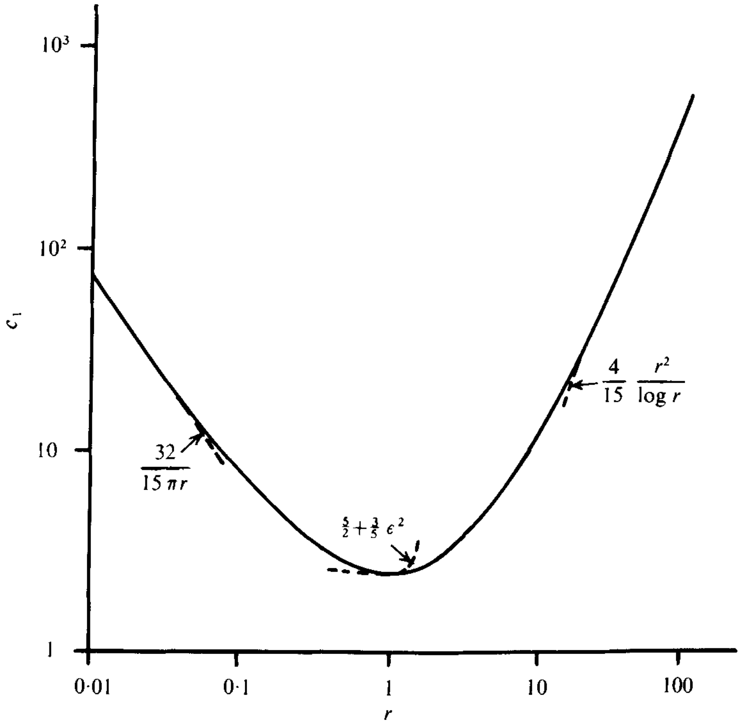

FIGURE 5. Viscosity dependence for spheroids.

$$C^0_{\alpha\beta\gamma\delta} = \frac{J_1(p^0_\alpha p^0_\beta - \frac{1}{3}\delta_{\alpha\beta})(p^0_\gamma p^0_\delta - \frac{1}{3}\delta_{\gamma\delta})}{\frac{1}{4}(J_1J_2+J_2J_3+J_3J_1)} + \frac{(q^0_\alpha r^0_\beta + q^0_\beta r^0_\alpha)(q^0_\gamma r^0_\delta + q^0_\delta r^0_\gamma)}{\frac{1}{2}I_1} + \ldots + \ldots,$$

where the I_i and J_i are elliptic integrals defined by Batchelor (1970*a*). These give

$$F^0_{\alpha\beta} = \operatorname{diag}\left(\frac{a^2-b^2}{a^2+b^2}+\frac{a^2-c^2}{a^2+c^2}, \ldots, \ldots\right)$$

and

$$M^0_{\alpha\beta} = \operatorname{diag}\left(\tfrac{3}{2}[J_1 + 2I_1 b^2c^2/(b^2+c^2)^2], \ldots, \ldots\right).$$

As this is an orthotropic body, only two relaxation times $\lambda^{(2)}$ and $\lambda^{(3)}$ appear in the linear relaxation spectrum (though $\lambda^{(1)}$ does appear in the inversion of $\mathbf{K}^{-1}$). These, and the coefficients c_i, can now all be computed after a numerical evaluation of the integrals I_i and J_i. The results for spheroids and a non-axisymmetric ellipsoid are shown graphically in figures 1–8. Figures 1 and 2 show the relaxation times (with $\lambda^{(1)}$ included for completeness) and figures 3 and 4 give the corresponding weight factors for the memory function in the linear viscoelastic limit. The viscometric functions for second-order-fluid behaviour are shown in figures 5–8. The results for spheroids agree with those of Leal & Hinch (1972) (with small corrections) though here we show the full shape dependence whereas their parameter D (as defined in Leal & Hinch 1971) is still shape dependent. Tables 2 and 3 give asymptotic results that may be obtained analytically for particles of given volume. These are shown on the figures for comparison with the numerical results. Note that, with our choice of reference axes, all particle tensors of the second rank that appear are of necessity diagonal. Only the diagonal components are given in the tables.

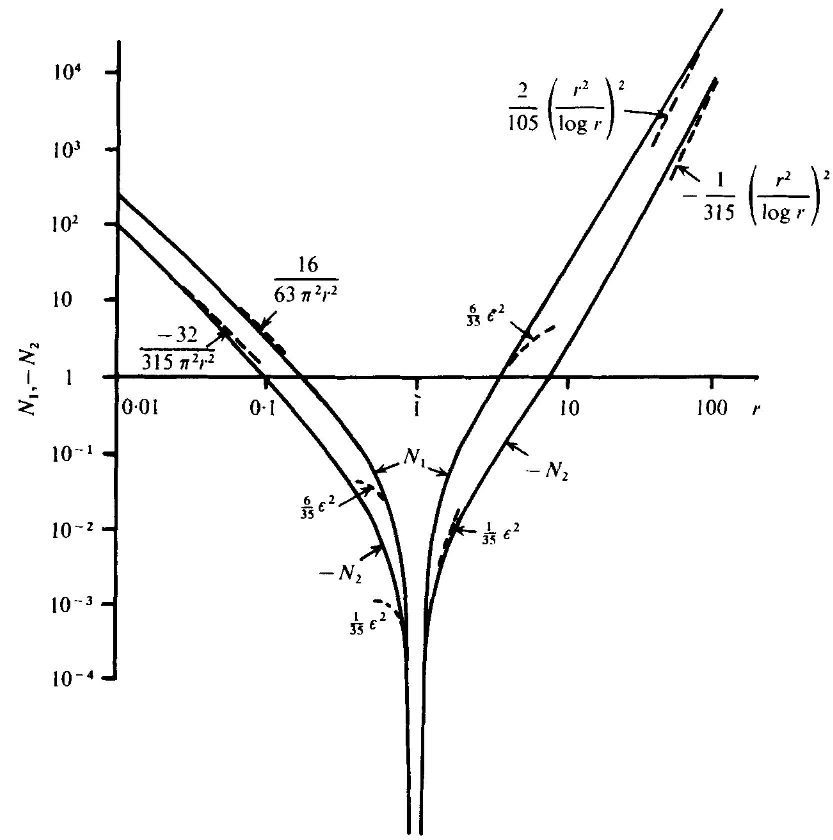

FIGURE 6. Normal-stress dependence for spheroids, $a = br$, $b = c$.

We may make the following observations from the results. First, in the linear visco-elastic regime, the weights corresponding to the two relaxation times are comparable in magnitude for all shapes *except* axisymmetric ellipsoids, where one vanishes. Thus, this case apart, both may be expected to appear physically in the linear relaxation spectrum.

Second, we note that the relaxation times for rods and 'tapes' of the same volume differ greatly in size. (We use the term 'tape' to describe an ellipsoid whose axes are all substantially different in length.) This difference arises from the different rotational mobility of each particle, which depends strongly on its length rather than its volume, and hence the ease with which it can execute modes of rotation. This can be understood from slender-body theory (see, for instance, Batchelor 1970*b*). If we label the a, b, c axes 1, 2, 3 respectively, then as $c \gg a \gg b$ the tape may be regarded as a slender body of aspect ratio $c/a = \mu$. Thus the mobility to rotations about the 1 or 2 axis is $3[c^3/(\log(c/a)\,abc)]^{-1} = 3\nu\log(\mu)/\mu^2$ as in table 3. Similarly, for rotation about the 3 axis the mobility is $3(a^2c/abc)^{-1} = 3\nu$. The asymptotic results for spheroids may be interpreted in the same way. The relaxation time $\lambda^{(3)}$ thus corresponds to rotations *of* the 'long' axis and $\lambda^{(2)}$ to rotations *about* it. The fact that the former mode has two degrees of freedom while the latter has one (or, effectively, none for spheroids) gives rise to the inequality of $w^{(2)}$ and $w^{(3)}$.

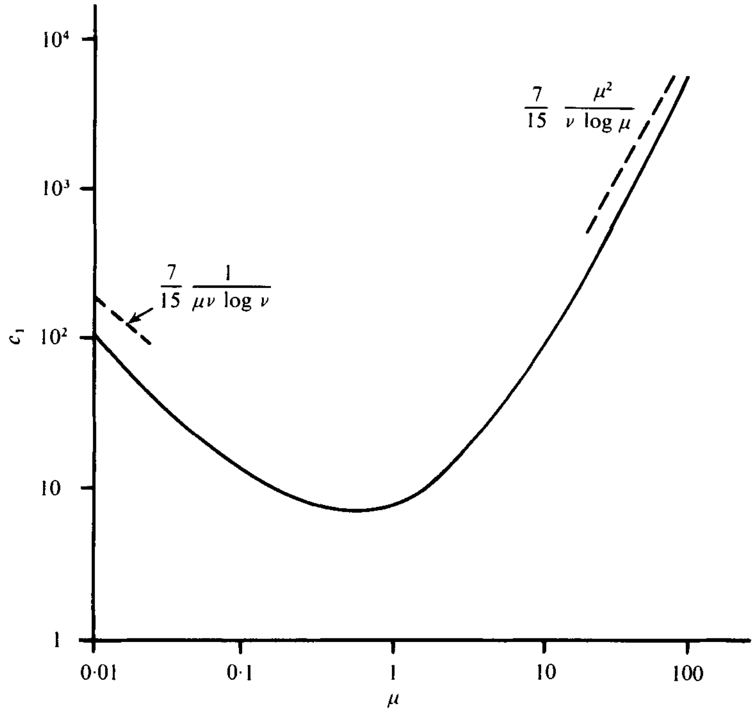

FIGURE 7. Viscosity dependence for ellipsoids with $b = \nu a$, $c = \mu a$, $\nu = 0{\cdot}1$.

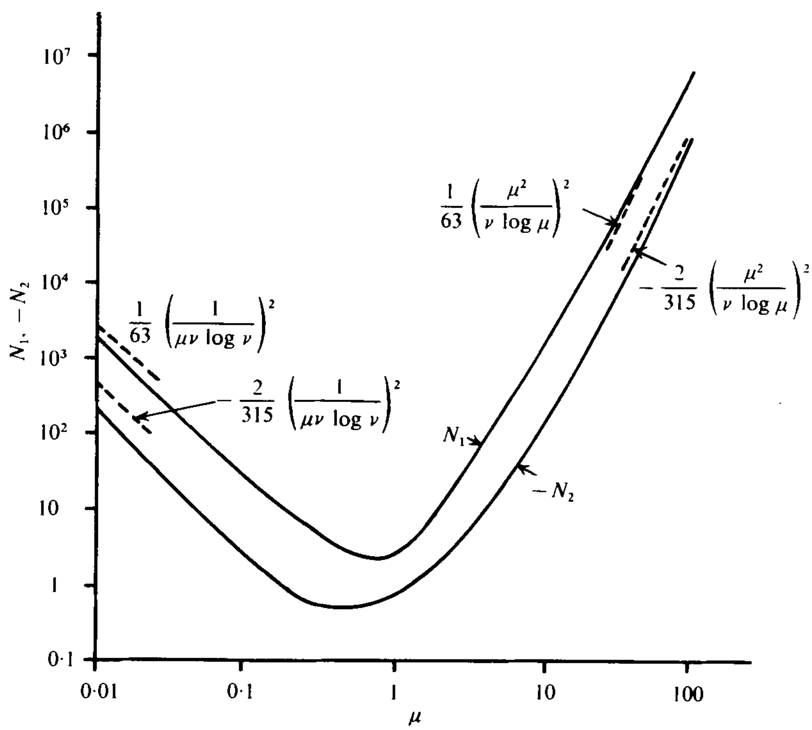

FIGURE 8. Normal-stress dependence for ellipsoids with $b = \nu a$, $c = \mu a$, $\nu = 0{\cdot}1$.

	$M^0_{\alpha\beta}$	$C^0_{\alpha\gamma\beta\gamma}$	$F^0_{\alpha\beta}$	$G^0_{\alpha\beta}$	$N^0_{\alpha\beta}$
Disks $r \to 0$	$\frac{3}{4}\pi r(1, 1, 1)$	$(4/9\pi r)\,(4, 13, 13)$	$(-2, 1, 1)$	$(2/9\pi r)\,(-2, 1, 1)$	$(4/9\pi r)\,(-2, 1, 1)$
Near-spheres $r = 1+\epsilon$	$(1, 1, 1)$	$\frac{25}{3}(1, 1, 1) + \frac{5}{6}\epsilon(2, -1, -1)$	$\epsilon(2, -1, -1)$	$\frac{1}{6}\epsilon(2, -1, -1)$	$O(\epsilon^2)$
Rods $r \to \infty$	$(\frac{3}{2}, 3\log(r)/r^2, 3\log(r)/r^2)$	$(r^2/9\log r)\,(4, 1, 1)$	$(2, -1, -1)$	$(r^2/18\log r)\,(2, -1, -1)$	$(r^2/9\log r)\,(-2, 1, 1)$

(*a*)

	$\lambda^{(2)}$‡	$\lambda^{(3)}$	$w^{(2)}$	$w^{(3)}$	c_1	N_1	N_2
$r \to 0$	$\frac{9}{2}\pi r$	$\frac{9}{2}\pi r$	0	$\frac{18}{5}$	$32/15\pi r$	$16/63\pi^2 r^2$	$-32/315\pi^2 r^2$
$r = 1+\epsilon$	$6+\frac{6}{5}\epsilon$	$6-\frac{6}{5}\epsilon$	0	$\frac{18}{5}\epsilon^2$	$\frac{5}{3}+\frac{3}{5}\epsilon^2$	$\frac{6}{35}\epsilon^2$	$-\frac{1}{35}\epsilon^2$
$r \to \infty$	6	$18\log(r)/r^2$	0	$\frac{18}{5}$	$\frac{4}{15}r^2/\log r$	$\frac{2}{105}(r^2/\log r)^2$	$-\frac{1}{315}(r^2/\log r)^2$

(*b*)

‡ Does not appear in the linear viscoelastic spectrum because of axial symmetry: $w^{(2)} = 0$.

TABLE 2. Spheroids: (*a*) material tensors, $a = br$, $b = c$; (*b*) relaxation times, weight functions and viscometric functions.

$M^0_{\alpha\beta}$	$C^0_{\alpha\beta\beta\gamma}$	$F^0_{\alpha\beta}$	$G^0_{\alpha\beta}$	$N^0_{\alpha\beta}$
$(3\nu\log(\mu)/\mu^2)(1, 1, \mu^2/\log\mu)$	$(\mu^2/9\nu\log\mu)(1, 1, 22)$	$(0, -2, 2)$	$(\mu^2/18\nu\log\mu)(-1, -1, 2)$	$(\mu^2/9\nu\log\mu)(3, -1, -2)$

(*a*)

$\lambda^{(2)}$	$\lambda^{(3)}$	$w^{(2)}$	$w^{(3)}$	c_1	N_1	N_2
12ν	$18\nu\log(\mu)/\mu^2$	$\frac{6}{5}$	$\frac{18}{5}$	$\frac{7}{15}\mu^2/\nu\log\mu$	$\frac{1}{63}(\mu^2/\nu\log\mu)^2$	$-\frac{2}{315}(\mu^2/\nu\log\mu)^2$

(*b*)

TABLE 3. Ellipsoids: (*a*) material tensors for 'tape' shape, $b = \nu a$, $c = \mu a$, $\nu \ll 1 \ll \mu$; (*b*) relaxation times, weight functions and viscometric functions. Note that the entries in this table can be extended to cover the cases $\mu = 1$, $\mu = \nu$ (which are spheroids) by use of table 2. Also the limit $\mu \ll \nu \ll 1$ can be derived from this table by the transformation $(\nu, \mu) \rightarrow (\mu/\nu, 1/\nu)$.

Finally, in the second-order-fluid regime, the second normal-stress difference (represented by N_2) is seen to be negative for all shapes except spheres. The fact that it is non-zero violates the Weissenberg hypothesis, though numerically it is smaller than the first normal-stress difference, typically by a factor of about 6.

7. Nearly spherical particles

7.1. *The shape tensors*

We consider a particle whose external shape is given by a surface S with equation

$$r = a(1+\epsilon f(\theta,\phi)+\epsilon^2 g(\theta,\phi)+O(\epsilon^3)), \quad r^2 = x^2+y^2+z^2, \tag{7.1}$$

where $\epsilon \ll 1$ and θ and ϕ are spherical polar angles. By means of a suitable choice for a, we demand that the particle volume

$$V = \tfrac{4}{3}\pi a^3. \tag{7.2}$$

By applying (7.2) at $O(\epsilon)$ and $O(\epsilon^2)$ we have

$$\left.\begin{aligned} \int_{r=1} f\,dS &= 0 \\ \text{and} \qquad \int_{r=1} (f^2+g)\,dS &= 0. \end{aligned}\right\} \tag{7.3}$$

Now, it is convenient to decompose f (and similarly g) into a sum of spherical surface harmonics. We write

$$f = \sum_{n=0}^{\infty} f_{(n)},$$

where $f_{(n)}$ is a harmonic of order n, i.e.

$$\nabla^2(r^n f_{(n)}) = \nabla^2(r^{-n-1}f_{(n)}) = 0.$$

The volume constraint (7.3*a*) gives $f_{(0)} = 0$, and further, $f_{(n)}$ corresponds merely to a translation of the 'centre' (or centre of reaction) of the near-sphere without deformation. We may therefore take $f_{(1)} = 0$ also. Now, following Barthès-Biesel & Acrivos (1973) we put

$$f_{(n)} \equiv \frac{(-)^n}{(2n-1)!!}\, T^{(n)}_{l_1\ldots l_n}\,\partial_{l_1}\ldots\partial_{l_n}\frac{1}{r} = T^{(n)}_{l_1\ldots l_n} r_{l_1}\ldots r_{l_n} r^{-n}, \tag{7.4}$$

where $\mathbf{T}^{(n)}$ is an nth-rank tensor which is symmetric with respect to interchange of its suffixes and traceless under any contraction. The set $\{\mathbf{T}^{(n)}|n \geqslant 2\}$ then represents the shape of the particle tensorially.

7.2. *The material tensors for near-spheres*

In order to construct a constitutive equation for a suspension of near-spheres, we need the material tensors which appear in (2.5). The problems of finding $\mathbf{P}$, $\mathbf{Q}$, $\mathbf{R}$, $\mathbf{X}$ and $\mathbf{Y}$ correct to $O(\epsilon)$ have been treated by Brenner (1964*a*, *b*) and by Taylor & Acrivos (1964). The final problem, that of finding $\mathbf{Z}$, is considered here in appendix B. Each material coefficient may be expanded as a power series in ϵ. We write, for instance,

$$\mathbf{C}^0 = \mathbf{C}^{0(0)} + \epsilon\mathbf{C}^{0(1)} + \epsilon^2\mathbf{C}^{0(2)} + O(\epsilon^3),$$

so that at leading order the particles are spheres and higher-order terms result from the deviation from sphericity. We now summarize the near-sphere results to the accuracy to which we shall need them:

$$\mathbf{X}^0 = (9/2a^2)\,\mathbf{I} + O(\epsilon), \quad \mathbf{Y}^0 = 6\mathbf{I} + O(\epsilon), \quad \mathbf{P}^0 = O(\epsilon^2),$$

$$\mathbf{Q}^0 = (9/7a)\,\epsilon\mathbf{T}^{(3)} + O(\epsilon^2), \quad R^0_{\alpha\beta\gamma} = 3\epsilon(\epsilon_{\beta\delta\gamma}T^{(2)}_{\alpha\delta} + \epsilon_{\alpha\delta\gamma}T^{(2)}_{\beta\delta}) + O(\epsilon^2)$$

and

$$Z^0_{\alpha\beta\gamma\delta} = \tfrac{5}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}) + \epsilon Z^{0(1)}_{\alpha\beta\gamma\delta} + \epsilon^2 Z^{0(2)}_{\alpha\beta\gamma\delta} + O(\epsilon^3),$$

where $\mathbf{Z}^{0(1)}$ is given by (B 10) and $Z^{0(2)}_{\alpha\beta\alpha\beta}$ by (B 17). Hence by (2.8),

$$B^0_{\alpha\beta\gamma} = -\epsilon(\epsilon_{\beta\delta\gamma}T^{(2)}_{\alpha\delta} + \epsilon_{\alpha\delta\gamma}T^{(2)}_{\beta\delta}) + O(\epsilon^2)$$

and so

$$\mathbf{F}^0 = 3\epsilon\mathbf{T}^{(2)} + O(\epsilon^2).$$

By (2.10)

$$\mathbf{C}^0 = \mathbf{Z}^0 + O(\epsilon^2),$$

and

$$C^{0(2)}_{\alpha\beta\alpha\beta} = Z^{0(2)}_{\alpha\beta\alpha\beta} - 9\mathbf{T}^{(2)} : \mathbf{T}^{(2)} - \tfrac{18}{49}\mathbf{T}^{(3)} : \mathbf{T}^{(3)} = \sum_{n=2}^{\infty} k_n \mathbf{T}^{(n)} : \mathbf{T}^{(n)}$$

using (B 7). The constants k_n are given by

$$k_n = \begin{cases} \tfrac{15}{7}, & n = 2, \\ \tfrac{425}{49}, & n = 3, \\ \dfrac{75(24n^3 - 20n^2 - 30n + 65)\,nn!}{2(2n-1)(2n+1)(2n+3)!!}, & n \geqslant 4. \end{cases}$$

Finally, from (2.7) we have $\mathbf{M}^0 = \mathbf{I} + O(\epsilon)$.

7.3. *Form of the constitutive equation*

We are now in a position to find the constitutive equation for a suspension of identical nearly spherical particles. We expect that the orientation statistics of such a suspension will be approximately uniform for all but the strongest flows, so that we are able to relax the restriction of dominant Brownian couples in this section and study moderate flow strengths. With the special forms of $\mathbf{C}^0$ and $\mathbf{F}^0$ appropriate for spheres, i.e.

$$C^{0(0)}_{\alpha\beta\gamma\delta} = \tfrac{5}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta}), \quad F^{0(0)}_{\alpha\beta} = 0,$$

(2.15) shows that

$$\overline{\sigma}^{(p)}_{ij} = 2\mu\Phi\{\epsilon F^{0(1)}_{\alpha\beta}[\langle R_{i\alpha}R_{j\beta}\rangle_0 + \epsilon\langle R_{i\alpha}R_{j\beta}\rangle_1] + \tfrac{5}{2}E_{ij} + \tfrac{1}{2}C^{0(1)}_{\alpha\beta\gamma\delta}E_{pq}[\langle R_{i\alpha}R_{j\beta}R_{p\gamma}R_{q\delta}\rangle_0 + \epsilon\langle R_{i\alpha}R_{j\beta}R_{p\gamma}R_{q\delta}\rangle_1] + \tfrac{1}{2}\epsilon^2 C^{0(2)}_{\alpha\beta\gamma\delta}\langle R_{i\alpha}R_{j\beta}R_{p\gamma}R_{q\delta}\rangle_0 + O(\epsilon^3)\}. \quad (7.5)$$

Thus, using the known forms of $\mathcal{N}_0$ and $\mathcal{N}_1$ in the angle averages, we obtain

$$\overline{\sigma}^{(p)}_{ij} = 2\mu\Phi\{\tfrac{5}{2}E_{ij} + \tfrac{1}{10}\epsilon C^{0(1)}_{\alpha\beta\alpha\beta}E_{ij} + \epsilon^2[\tfrac{2}{5}DF^{0(1)}_{\alpha\beta}\mathscr{A}_{ij\alpha\beta} + \tfrac{1}{10}C^{0(2)}_{\alpha\beta\alpha\beta}E_{ij} + \tfrac{3}{35}[(\mathscr{A}_{jl\beta\gamma}E_{il} + \mathscr{A}_{il\beta\gamma}E_{jl})\,C^{0(1)}_{\alpha\beta\alpha\gamma} - \tfrac{2}{3}\delta_{ij}E_{kl}\mathscr{A}_{kl\beta\gamma}C^{0(1)}_{\alpha\beta\alpha\gamma})] + O(\epsilon^3)\}. \quad (7.6)$$

With the nearly isotropic diffusion coefficient, (3.7) applies and so (7.6) becomes

$$\bar{\mathbf{\sigma}}^{(p)} = 2\mu\Phi\{\tfrac{5}{2}\mathbf{E} + \epsilon^2\mathbf{T}^{(2)} : \mathbf{T}^{(2)}[\tfrac{9}{5}D\mathbf{A} + K\mathbf{E} + \tfrac{3}{14}(\mathbf{A}.\mathbf{E} + \mathbf{E}.\mathbf{A} - \tfrac{2}{3}\mathbf{I}\mathbf{A} : \mathbf{E})] + O(\epsilon^3)\}, \quad (7.7)$$

where

$$K = \left(\sum_{n=2}^{\infty} k_n \mathbf{T}^{(n)} : \mathbf{T}^{(n)}\right) \Big/ (10\mathbf{T}^{(2)} : \mathbf{T}^{(2)})$$

and from (3.7)

$$\mathscr{D}\mathbf{A}/\mathscr{D}t + 6D\mathbf{A} = 3\mathbf{E}. \tag{7.8}$$

Equation (7.7) is the same as equation (6) of Leal & Hinch (1972). Indeed for the spheroids which they consider, $\mathbf{T}^{(2)} = \mathrm{diag}\,(\frac{2}{3}, -\frac{1}{3}, -\frac{1}{3})$ in the natural axes for the spheroid, and so (7.7) reduces exactly to their equation in that case. The rheological consequences of the constitutive equation deriving from (7.7) and (7.8) are studied in Leal & Hinch's paper. The fact that the same constitutive equation has arisen here indicates the following conclusions: first, only the second harmonic (i.e. the deformation corresponding to an ellipsoid) in the distorted sphere shape is important in determining the rheology (higher harmonics enter only through the scalar coefficient K, which slightly modifies at $O(\epsilon^2)$ the Einstein coefficient $\frac{5}{2}$ in the viscosity); and second, in this case, the results would be unaffected by a restriction to axial symmetry. The behaviour of a suspension of spheroidal near-spheres of suitable aspect ratio will be the same as that of any suspension of near-spheres.

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Appendix A. Properties of the rotation-matrix formalism

Expression for orientation-space gradients

Our aim here is to derive an expression for ∇ in terms of derivatives with respect to our chosen representation $\mathbf{R}$. Consider two frames of reference:

(i) a rotating frame S fixed in the particle;

(ii) a reference frame S^0, say S at $t = 0$.

Then for a line element rotating with the particle, starting at $\mathbf{x}^0$ and rotating to $\mathbf{x}$ by time t,

$$x_i = R_{i\alpha} x^0_\alpha.$$

Now if $d\varphi$ is an infinitesimal rotation,

$$d\boldsymbol{\varphi} \wedge \mathbf{x} = d\mathbf{x} = d\mathbf{R}\,.\,\mathbf{x}^0 = d\mathbf{R}\,.\,\mathbf{R}^{\mathrm{T}}.\,\mathbf{x}.$$

But $\mathbf{x}$ is arbitrary, and so we find $d\phi_i = -\frac{1}{2}\epsilon_{ijk} R_{k\alpha}\, dR_{j\alpha}$ and thus $\partial R_{i\alpha}/\partial \phi_k = -\epsilon_{kim} R_{m\alpha}$. Hence if f is any scalar *function of orientation*,

$$(\nabla f)_k \equiv \partial f/\partial \phi_k = \epsilon_{kij} R_{i\alpha}\, \partial f/\partial R_{j\alpha}. \tag{A 1}$$

At this stage we should be careful to distinguish between derivatives with respect to $R_{i\alpha}$ which are constrained in the space of all linear co-ordinate transformations to lie in the hypersurface consisting of pure rotations (such as the one above) and those which are not so restricted. (The situation here is directly analogous to that in the axisymmetric case, where the orientation-space gradient ∇ is given in terms of a unit vector $\mathbf{p}$, and is related to the unconstrained gradient operator $\partial/\partial\mathbf{p}$ by

$$\nabla \equiv (\mathbf{I} - \mathbf{pp})\,.\,\partial/\partial\mathbf{p}.)$$

We determine the relationship between the two operators by the following technique. Given some function $f(\mathbf{R})$ define a function $\tilde{f}(\mathbf{A})$ of all possible linear transformations $\mathbf{A}$

by $\tilde{f}(\mathbf{A}) = f(\mathbf{R})$, where $\mathbf{R}$ is (uniquely) derived from $\mathbf{A}$ by the polar decomposition theorem $\mathbf{A} = \mathbf{R}\mathbf{\Lambda}$, $\mathbf{R}$ is a pure rotation, $\mathbf{R}.\mathbf{R}^{\mathrm{T}} = \mathbf{I}$, and $\mathbf{\Lambda}$ is a pure stretch, $\mathbf{\Lambda} = \mathbf{\Lambda}^{\mathrm{T}}$. Then the elimination of $\mathbf{\Lambda}$ determines $\mathbf{R}$ in terms of $\mathbf{A}$.

Now

$$\frac{\partial \tilde{f}}{\partial A_{i\alpha}} = \frac{\partial f}{\partial R_{j\beta}} \frac{\partial R_{j\beta}}{\partial A_{i\alpha}}$$

and so

$$\left.\frac{\partial}{\partial R_{i\alpha}}\right|_{\mathbf{\Lambda}=\mathbf{I}} = P_{i\alpha j\beta} \left.\frac{\partial}{\partial R_{j\beta}}\right|_{\text{unrestricted}},$$

where the projection operator $P_{i\alpha j\beta} = (\partial R_{j\beta}/\partial A_{i\alpha})_{\mathbf{\Lambda}=\mathbf{I}}$. On performing the differentiation and making the substitution, we obtain

$$P_{i\alpha j\beta} = \tfrac{1}{2}(\delta_{\alpha\beta}\delta_{ij} - R_{j\alpha}R_{i\beta}). \tag{A 2}$$

Now using (A 1) and (A 2) and simplifying we find

$$(\nabla f)_k = \epsilon_{kij} R_{i\alpha}\, \partial f/\partial R_{j\alpha},$$

where $\partial/\partial R_{j\alpha}$ is now unconstrained, and thus this formula for ∇ is valid irrespective of whether we consider the whole space of possible transformations or the restricted one of rotations.

Orientation-space averages of products of rotations

In order to perform various averages, we need to evaluate such integrals as

$$I^{(2n)} = \int_{\text{orientations}} \mathbf{R} \ldots \mathbf{R}\, d\tau, \tag{A 3}$$

where the integrand consists of the external product of $2n$ rotation matrices. The cases $n = 1, 2$, and 3 suffice for our purposes.

Case $n = 1$:

$$I^{(2)} = \int R_{i\alpha} R_{j\beta}\, d\tau. \tag{A 4}$$

Since $I^{(2)}$ involves an integration over all orientations, it is clear that it must be independent of the particular choice of axes in the reference state. Further, it cannot depend on the choice of axes in the current configuration. It must therefore be isotropic with respect to both its Greek and its Latin suffixes, i.e.

$$I^{(2)}_{ij\alpha\beta} = \lambda \delta_{ij}\delta_{\alpha\beta} \quad \text{for some scalar} \quad \lambda.$$

Now contracting on i, j and α, β, (A 4) gives

$$9\lambda = 3\int d\tau = 3 \times (\text{volume of orientation space}) = 3 \times 8\pi^2.$$

(That the total volume of orientation space is $8\pi^2$ may be seen from, say, an Euler-angle parametrization: $d\tau = \sin\theta\, d\theta\, d\phi\, d\psi$). Hence

$$I^{(2)}_{ij\alpha\beta} = \tfrac{8}{3}\pi^2 \delta_{ij}\delta_{\alpha\beta}. \tag{A 5}$$

Case $n = 2$. Similarly, $I^{(4)}$ must be expressible as a sum of products of fourth-rank isotropic tensors of the two types. So we can write

$$I^{(4)}_{ijkl\alpha\beta\gamma\delta} = (\delta_{ij}\delta_{kl}, \delta_{il}\delta_{jk}, \delta_{ik}\delta_{jl}) \,.\, \mathcal{M} \,.\, (\delta_{\alpha\beta}\delta_{\alpha\delta},\ \delta_{\alpha\delta}\delta_{\beta\gamma},\ \delta_{\alpha\gamma}\delta_{\beta\delta})$$

for some 3×3 matrix $\mathcal{M}$. Now symmetry demands that the elements of $\mathcal{M}$ may be of only two types corresponding to the cases where the permutations of $ijkl$ and $\alpha\beta\gamma\delta$

correspond (the diagonal elements of $\mathcal{M}$) and where they do not (the off-diagonal elements). Then by means of a suitable contraction and use of (A 5) it is easy to show that

$$\mathcal{M} = \frac{8\pi^2}{30}\begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix}. \tag{A 6}$$

Case $n = 3$. Again we can construct a matrix formulation giving all possible products of the 15 isotropic sixth-rank tensors of each type. Of the 225 terms that appear, however, there are just three types. Analysis similar to that in the $n = 2$ case is able to generate the corresponding coefficients.

(i) Where the permutations of the Greek and Latin suffixes are the same the coefficient is $16 \times 8\pi^2/210$.

(ii) Where they differ in two pairs but are the same in the third the coefficient is $-5 \times 8\pi^2/210$.

(iii) Where they differ in all three pairs the coefficient is $2 \times 8\pi^2/210$.

Appendix B. Determination of $\mathbf{Z}$ for near-spheres

Formulation of the problem as a regular perturbation expansion

To find $\mathbf{Z}$ we must solve the system

$$\left.\begin{aligned} &\nabla.\boldsymbol{\sigma} = 0, \quad \nabla.\mathbf{u} = 0 \quad \text{outside} \quad S \\ \text{with} \quad &\boldsymbol{\sigma} = -p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^{\mathrm{T}}) \\ \text{and} \quad &\mathbf{u} = -\mathbf{E}.\mathbf{r} \quad \text{on} \quad S, \quad \mathbf{u} \to 0 \quad \text{as} \quad r \to \infty, \end{aligned}\right\} \tag{B 1}$$

where the particle surface is S and has outward normal $\mathbf{n}$. Then as shown by Batchelor (1970*a*),

$$S_{ik} = \int_S [\sigma_{ij}x_k n_j - \mu(u_i n_k + u_k n_i)]\,dS \tag{B 2}$$

and $\mathbf{S} = \mu\mathbf{Z}^0 : \mathbf{E}$ determines $\mathbf{Z}^0$.

It is obviously more convenient to replace the boundary condition on S with one on $r = a$. So by putting

$$\mathbf{u} = \mathbf{u}^{(0)} + \epsilon\mathbf{u}^{(1)} + \epsilon^2\mathbf{u}^{(2)} + O(\epsilon^3)$$

and expanding $\mathbf{u}$ as a Taylor series about $r = a$, we obtain a sequence of problems with boundary conditions on $r = a$:

$$\left.\begin{aligned} \mathbf{u}^{(0)} &= -\mathbf{E}.\mathbf{r}, \\ \mathbf{u}^{(1)} &= -\left(\mathbf{E}.\mathbf{r} + a\frac{\partial \mathbf{u}^{(0)}}{\partial r}\right)f, \\ \mathbf{u}^{(2)} &= -\left\{\left(\mathbf{E}.\mathbf{r} + a\frac{\partial \mathbf{u}^{(0)}}{\partial r}\right)g + af\frac{\partial \mathbf{u}^{(1)}}{\partial r} + \tfrac{1}{2}a^2f^2\frac{\partial^2 \mathbf{u}^{(0)}}{\partial r^2}\right\}, \end{aligned}\right\} \tag{B 3}$$

with each $\mathbf{u}^{(n)}$ tending to zero as $r \to \infty$ and satisfying the Stokes equations. Further, as shown by Batchelor (1970*a*), the integral in (B 2) may be taken over any surface enclosing the particle. With our new formulation this may be taken to be $r = a$. So $\mathbf{Z}^{0(n)}$ is obtained from the equation

$$S_{ik}^{(n)} = \int_{r=a} [\sigma_{ij}^{(n)}x_k n_j - \mu(u_i^{(n)}n_k + u_k^{(n)}n_i)]\,dS. \tag{B 4}$$

The zero-order solution

At this order the particle is spherical. The solution is well known to be

$$\left.\begin{aligned}\mathbf{u}^{(0)} &= -\mathbf{E}.\mathbf{r}a^5/r^5 - \tfrac{5}{2}\mathbf{r}\mathbf{r}.\mathbf{E}.\mathbf{r}(a^3/r^5 - a^5/r^7),\\ p^{(0)} &= -2\mu \times \tfrac{5}{2}a^3\mathbf{r}.\mathbf{E}.\mathbf{r}/r^5.\end{aligned}\right\} \tag{B 5}$$

Now as noted by Batchelor (1970*a*), the stresslet is given by the (-3) harmonic in the far-field form of the pressure. Thus

$$\mathbf{S}^{(0)} = \tfrac{5}{3}\mu 4\pi a^3\mathbf{E}$$

and so

$$Z^{0(0)}_{\alpha\beta\gamma\delta} = \tfrac{5}{2}(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma} - \tfrac{2}{3}\delta_{\alpha\beta}\delta_{\gamma\delta})$$

as expected.

Application of the reciprocal theorem

Before proceeding to the $O(\epsilon)$ solution, we establish a lemma via the reciprocal theorem. Consider the fluid domain bounded by $r = a$ and a surface at infinity. Then for two velocity and stress fields each satisfying the Stokes equations in the domain, vanishing sufficiently fast at infinity but satisfying different boundary conditions on $r = a$, we have

$$\int_{r=a} u_i'\sigma_{ij}n_j\,dS = \int_{r=a} u_i\sigma_{ij}'n_j\,dS. \tag{B 6}$$

The 'primed' field we choose here is one satisfying $\mathbf{u}' = -\mathbf{E}'.\mathbf{r}$ on $r = a$ for some symmetric traceless tensor $\mathbf{E}'$. The solution of the primed problem is then (B 5) with $\mathbf{E}$ replaced by $-\mathbf{E}'$. For the other field we choose the nth-order problem here. Then after some straightforward algebra, (B 6) and (B 4) give

$$E_{ik}'S_{ik}^{(n)} = -\frac{5\mu}{2a}E_{ik}'\int_{r=a}(r_iu_k^{(n)} + r_ku_i^{(n)} - \tfrac{2}{3}r_pu_p^{(n)}\delta_{ik})\,dS.$$

Thus as $\mathbf{E}'$ is arbitrary and $\mathbf{S}^{(n)}$ is symmetric and traceless, we must have

$$S_{ik}^{(n)} = -\frac{5\mu}{2a}\int_{r=a}(r_iu_k^{(n)} + r_ku_i^{(n)} - \tfrac{2}{3}r_pu_p^{(n)}\delta_{ik})\,dS. \tag{B 7}$$

The usefulness of (B 7) is that it means that we can compute $\mathbf{Z}^{(n)}$ simply from a knowledge of $\mathbf{u}^{(n)}$ at $r = a$. It is unnecessary to solve the full Stokes equations to find $\mathbf{u}^{(n)}$ everywhere as would be needed for use of (B 4).

The first-order solution

We now apply the result (B 7) to find $\mathbf{Z}^{(1)}$. From (B 7), (B 3) and (B 5) we have

$$S_{ik}^{(1)} = -\frac{25\mu}{2a}E_{lm}\int_{r=a} f\left[\frac{2r_ir_kr_lr_m}{a^2} - r_ir_m\delta_{kl} - r_kr_m\delta_{li}\right]dS. \tag{B 8}$$

Using the expansion (7.4) of f in spherical harmonics, we can exploit the orthogonality relation for such harmonics, which can be cast tensorially into the following form (Brenner 1964*a*): if $P^{(n)}_{l_1\ldots l_n} = (-)^n r^{n+1}\partial_{l_1}\ldots\partial_{l_n}r^{-1}(n!)^{-1}$ then

$$\int_{r=a} P^{(n)}_{l_1\ldots l_n}f_{(m)}\,dS = \begin{cases}[4\pi a^2/(2n+1)]\,T^{(n)}_{l_1\ldots l_n}, & m = n,\\ 0, & m \neq n.\end{cases}$$

Noting in particular that $P^{(0)} = 1$, $P^{(2)}_{ij} = \frac{1}{2}(3r_i r_j/r^2 - \delta_{ij})$ and

$$P^{(4)}_{ijkl} = \frac{1}{8}\left[\frac{35r_i r_j r_k r_l}{r^4} - \frac{5(\delta_{ik} r_j r_l + 5 \text{ similar terms})}{r^2} + (\delta_{ik}\delta_{jl} + 8 \text{ similar terms})\right], \quad \text{(B 9)}$$

it is clear from (B 8) that the only contributions to $\mathbf{Z}^{(1)}$ are from the second and fourth harmonics in f. On substituting we find that

$$Z^{0(1)}_{\alpha\beta\gamma\delta} = \tfrac{5}{14}[3(\delta_{\beta\gamma} T'^{(2)}_{\alpha\delta} + \delta_{\alpha\gamma} T'^{(2)}_{\beta\gamma} + \delta_{\beta\delta} T'^{(2)}_{\alpha\delta} + \delta_{\alpha\delta} T'^{(2)}_{\beta\gamma}) - 4(\delta_{\alpha\beta} T'^{(2)}_{\gamma\delta} + \delta_{\gamma\delta} T'^{(2)}_{\alpha\beta})] - \tfrac{40}{21} T'^{(4)}_{\alpha\beta\gamma\delta}. \quad \text{(B 10)}$$

Towards the second-order solution. We can again exploit the reciprocal-theorem result (B 7) to give $\mathbf{Z}^{(2)}$ when $\mathbf{u}^{(2)}$ is known on $r = a$. Unfortunately, (B 3) shows that for $\mathbf{u}^{(2)}$ on $r = a$ we need $\partial \mathbf{u}^{(1)}/\partial r$ there, and this means that the full $\mathbf{u}^{(1)}$ solution is required. The derivation of the $\mathbf{u}^{(1)}$ solution can be achieved via Lamb's solution of the Stokes equations in spherical harmonics, but the algebra involved is extremely tedious and will not be presented in full here: we give only a brief outline of the method used.

The full $\mathbf{u}^{(1)}$ *solution*

The problem for $\mathbf{u}^{(1)}$ is, from (B 1), (B 3) and (B 5),

$$\left.\begin{aligned} &\mu\nabla^2\mathbf{u}^{(1)} = \nabla p^{(1)}, \quad \nabla . \mathbf{u}^{(1)} = 0 \\ \text{with} \quad &\mathbf{u}^{(1)} \to 0 \quad \text{as} \quad r \to \infty \\ \text{and} \quad &\mathbf{u}^{(1)} = 5(\mathbf{r}\,\mathbf{r} . \mathbf{E} . \mathbf{r}/a^2 - \mathbf{E} . \mathbf{r}) f \quad \text{on} \quad r = a. \end{aligned}\right\} \quad \text{(B 11)}$$

To solve this problem we use the technique of Happel & Brenner (1965, §3.2). This involves expanding various functions of the $r = a$ boundary condition in spherical harmonics, and then exploiting Lamb's solution of the Stokes equations. By linearity we may consider the solution forced by each harmonic in f separately, so from now on we replace f by $f_{(n)}$ and perform a final summation to obtain the full $\mathbf{u}^{(1)}$.

In the notation of Happel & Brenner (1965), we require the expansions

$$\frac{\mathbf{r} . \mathbf{u}^{(1)}}{a} = \sum_{m=0}^{\infty} X_m, \quad -a\nabla . \mathbf{u}^{(1)} = \sum_{m=0}^{\infty} Y_m, \quad \mathbf{r} . \nabla \wedge \mathbf{u}^{(1)} = \sum_{m=0}^{\infty} Z_m, \quad \text{(B 12)}$$

each on $r = a$, where the X's, Y's and Z's are all spherical harmonics. Here this clearly gives

$$X_m = 0 \quad \text{for each} \quad m. \quad \text{(B 13)}$$

For the Y_m we need to express such functions as $\mathbf{r} . \mathbf{E} . \mathbf{r} f_{(n)}/a^2$ as a sum of spherical harmonics. Suitable functions are considered below.

(i)

$$r^{n+3}\mathbf{E} : \nabla\nabla(r^{-(n+1)} f_{(n)}). \quad \text{(B 14)}$$

This is a function of degree zero in r and $\nabla^2(r^{-(n+2)}(\text{i})) = 0$, so that it is a harmonic of order $n+2$.

(ii) Defining

$$\operatorname{tr}(\mathbf{E}\mathbf{T}^{(n)})_{l_1 \ldots l_{n-2}} \equiv E_{ij} T'^{(n)}_{ij l_1 \ldots l_{n-2}} \quad \text{(B 15)}$$

and noting that

$$r^{-(n-2)}\mathbf{E} : \nabla\nabla(r^n f_{(n)}) = n(n-1)\, r^{-(n-2)} \operatorname{tr}(\mathbf{E}\mathbf{T}^{(n)})_{l_1 \ldots l_{n-2}} r_{l_1} \cdots r_{l_{n-2}}$$

shows that this is clearly a harmonic of order $n-2$.

(iii) Define

$$Sd(\mathbf{ET}^{(n)})_{l_1\ldots l_n} \equiv \frac{1}{n}\sum_{r=1}^{n} E_{l_r p} T^{(n)}_{l_1\ldots p\ldots l_n} - \frac{2}{n(n-1)}\sum_{p=1}^{n-1}\sum_{r=p+1}^{n} \delta_{l_r l_p}\,\mathrm{tr}\,(\mathbf{ET}^{(n)})_{l_1\ldots l_n + l_r,\, l_p} \qquad \text{(B 16)}$$

where Sd, the 'symmetric deviator' of the product $\mathbf{E}.\mathbf{T}^{(n)}$, is essentially the same as that defined by Barthès-Biesel & Acrivos (1973). This is completely symmetric and traceless with respect to any pair of suffixes. So noting that

$$nr^n Sd(\mathbf{ET}^{(n)})_{l\ldots_1 l_n} r_{l_1}\ldots r_{l_n} = \frac{n(-)^n}{(2n-1)!!} Sd(\mathbf{ET}^{(n)})_{l_1\ldots l_n} \partial_{l_1}\ldots\partial_{l_n} r^{-1}$$

shows that the left-hand side is clearly a harmonic of degree n. It is now a straightforward matter to express the Y_m in terms of these harmonics. This gives $Y_m = 0$ except for $m = n-2$, n and $n+2$. Similarly, to find the Z_m, we exploit the fact that $\nabla\wedge(\mathbf{r}f_{(n)})$ is a vector spherical harmonic of order n, giving

$$Z_m = 0, \quad m \neq n-1, n+1,$$

$$Z_{n-1} = -\frac{5a}{2n+1} r^{n+2}\mathbf{E}:\nabla[r^{-(n+1)}\nabla\wedge(f_{(n)}\mathbf{r})],$$

$$Z_{n+1} = \frac{5a}{2n+1} r^{-n+1}\mathbf{E}:\nabla[r^{n}(f_{(n)}\mathbf{r})].$$

Lamb's solution for $\mathbf{u}^{(1)}$ is then (n)

$$\mathbf{u}^{(1)} = \sum_{m=1}^{\infty}\left[\nabla\wedge(\mathbf{r}\chi_{-l(m+1)}) + \nabla\Phi_{-(m+1)} - \frac{m-2}{\mu 2m(2m-1)} r^2\nabla p_{-(m+1)} + \frac{m+1}{\mu m(2m-1)}\mathbf{r}p_{-(m+1)}\right],$$

and the relations between the functions χ, Φ and p and Y and Z are given by Happel & Brenner (1965, §3.2).

A partial check may be made on these results by calculating (to $O(\epsilon)$) the force and couple on the particle. These may then be checked against the results of Brenner (1964*b*), which are derived by a use of the reciprocal theorem. The force on the particle is $-4\pi\nabla(r^3 p_{(-2)})$ and the couple is $-8\pi\mu\nabla(r^3\chi_{(-2)})$. Both these relations give the same answers for the tensors $\mathbf{Q}$ and $\mathbf{R}$ (in §7.2) as were given by Brenner. Further, the stresslet can be computed from the $p_{(-3)}$ term. This produces the same answer for $\mathbf{Z}^{0(1)}$ as that obtained in (B 10).

Finally, we may use this solution for $\mathbf{u}^{(1)}$ to compute $\partial\mathbf{u}^{(1)}/\partial r$ on $r = a$ and hence, by means of (B 3), find $\mathbf{u}^{(2)}$ there. Then we can use (B 7) to give $\mathbf{S}^{(2)}$ and with extensive use of the orthogonality relation (B 9) we find that

$$\left.\begin{aligned} Z^{0(2)}_{\alpha\beta\alpha\beta} &= \sum_{n=2}^{\infty} c_n \mathbf{T}^{(n)}:\mathbf{T}^{(n)}, \\ \text{where} \qquad c_n &= \frac{75(24n^3-20n^2-30n+65)\,nn!}{2(2n-1)(2n+1)(2n+3)!!}. \end{aligned}\right\} \qquad \text{(B 17)}$$

The full form of $\mathbf{Z}^{0(2)}$ has not been found. The contracted version in (B 17) is shown by (7.6) to be adequate for our purposes.

Appendix C. The second moment of the probability distribution

In this appendix we generate a useful exact result for the second moment of $\mathscr{N}$ first derived by Prager (1957) for the corresponding axisymmetric particle problem. This may be obtained by multiplying (2.17) by **RR** and integrating over all orientations. After two integrations by parts using the divergence theorem, we obtain the result

$$\begin{aligned}\partial\langle R_{s\gamma}R_{t\delta}\rangle/\partial t-\tilde{\Omega}_{sm}\langle R_{m\gamma}R_{t\delta}\rangle+\langle R_{s\gamma}R_{m\delta}\rangle\tilde{\Omega}_{mt}+DK^{-1}_{\gamma\delta\alpha\beta}\langle R_{s\alpha}R_{t\beta}\rangle \\ =-\tfrac{1}{2}\epsilon_{\alpha\mu\gamma}B^{0}_{\alpha\beta\theta}\langle R_{s\mu}R_{t\delta}R_{p\beta}R_{q\theta}\rangle E_{pq}-\tfrac{1}{2}\epsilon_{\alpha\mu\delta}B^{0}_{\alpha\beta\theta}\langle R_{s\gamma}R_{t\mu}R_{p\beta}R_{q\theta}\rangle E_{pq},\end{aligned} \quad \text{(C 1)}$$

where the particle tensor $\mathbf{K}^{-1}$ is given by

$$K^{-1}_{\alpha\beta\gamma\delta}=-3(\delta_{\beta\gamma}M^{0}_{\alpha\beta}+\delta_{\alpha\gamma}M^{0}_{\beta\delta})+4M^{0}_{\kappa\kappa}\delta_{\alpha\gamma}\delta_{\beta\delta}+2M^{0}_{\gamma\delta}\delta_{\alpha\beta}. \quad \text{(C 2)}$$

Equation (C 1) gives the evolution of $\langle\mathbf{RR}\rangle$ in terms of $\langle\mathbf{RRRR}\rangle$. We note that the time derivative represented by the first three terms of (C 1) is essentially a Jaumann derivative (as it must be for tensorial invariance). Also, by taking fourth and higher moments of (2.17) we could generate a hierarchy of equations for the evolutions of averages of products of rotations each involving the next higher average. If **E** is non-zero, then it is necessary to truncate the series at some point to obtain a closed set of equations.

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