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The determination of the bulk stress in a suspension of spherical particles to order c^2

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An exact formula is obtained for the term of order c^2 in the expression for the bulk stress in a suspension of force-free spherical particles in Newtonian ambient fluid, where c is the volume fraction of the spheres and $c \ll 1$. The particles may be of different sizes, and composed of either solid or fluid of arbitrary viscosity. The method of derivation circumvents the familiar obstacle, of non-absolutely convergent integrals representing the effect of all pair interactions in which one specified particle takes part, by the judicious use of a certain quantity which is affected by the presence of distant particles in a similar way and whose mean value is known exactly. The bulk stress is in general of non-Newtonian form and depends on the statistical properties of the suspension which in turn are dependent on the type of bulk flow.

The formula contains two functions which are parameters of the flow field due to two spherical particles immersed in fluid in which the velocity gradient is uniform at infinity. One of them, $p(\mathbf{r}, t)$, represents the probability density for the vector $\mathbf{r}$ separating the centres of the two particles. The variation of $p(\mathbf{r}, t)$ for a moving material point in $\mathbf{r}$-space due to hydrodynamic action is found in terms of a function $q(r)$, and this gives $p(\mathbf{r}, t)$ explicitly over the whole of the region of $\mathbf{r}$-space occupied by trajectories of one particle centre relative to another which come from infinity. In a region of closed trajectories, steady-state hydrodynamic action alone does not determine the relation between the values of $p(\mathbf{r}, t)$ for different material points. The function $q(r)$ is singular when the spheres touch, and the contribution of nearly-touching spheres to the bulk stress is evidently important. Approximate numerical values of all the relevant functions are presented for the case of rigid spherical particles of uniform size.

In the case of steady pure straining motion of the suspension, all trajectories in $\mathbf{r}$-space come from infinity, the suspension has isotropic structure and the stress behaviour can be represented (to order c^2) in terms of an effective viscosity $\mathring{\mu}$. It is estimated from the available numerical data that for a suspension of identical rigid spherical particles

$$\mathring{\mu}/\mu = 1 + 2{\cdot}5c + 7{\cdot}6c^2,$$

the error bounds on the coefficient of c^2 being about $\mp 0{\cdot}8$. In the important case of steady simple shearing motion, there is a region of closed trajectories of one sphere centre relative to another, of infinite volume. The stress system is here not of Newtonian form, and numerical results are not obtainable until the probability density $p(\mathbf{r}, t)$ can be made determinate in the region of closed trajectories by the introduction of some additional physical process, such as three-sphere encounters or Brownian motion, or by the assumption of some particular initial state.

In the analogous problem for an incompressible solid suspension it may be appropriate to assume that for many methods of manufacture $p(\mathbf{r}, t)$ is uniform over the accessible part of $\mathbf{r}$-space, in which event the solid suspension has 'Newtonian' elastic behaviour and the ratio of the effective shear modulus to that of the matrix is estimated to be $1 + 2{\cdot}5c + 5{\cdot}2c^2$ for a suspension of identical rigid spheres.

1. Introduction

We are concerned in this paper with the bulk rheological properties of a suspension of particles in a Newtonian fluid of uniform viscosity μ. It will be assumed (1) that the Reynolds number of the relative motion of the fluid near one particle is small compared with unity and the Stokes equations describe the motion of the fluid, (2) that the inertia of a particle in either translational or rotational motion may be neglected, and (3) that no external force or couple acts on a particle. These conditions are usually realized in practice by smallness of the particles. It is assumed also that a particle moves under the influence of hydrodynamic stresses at the particle surface only. The effects of Brownian motion of particles will not be included in the analysis.

The particles will be assumed to be spherical, and not necessarily of uniform size. (The principles of the calculation are applicable also to non-spherical particles, although the detailed working would then be more complex.) We shall be able to obtain detailed numerical results only for the important special case of rigid spherical particles, but in the general theory there is no additional difficulty in supposing the material of the particles to be a Newtonian fluid of viscosity μ'; the case of rigid particles is then obtained by taking the limit $\mu'/\mu \to \infty$, and for gas bubbles in liquid we put $\mu'/\mu = 0$. The spherical shape of a particle may be a consequence of the action of a strong surface tension at the interface, in which case the sphericity is permanent, or, in the absence of surface tension, it may be a consequence of the initial conditions, in which case it is only instantaneous because a fluid drop without surface tension deforms as the motion proceeds. We shall allow for both these possibilities, the latter being of interest primarily in the analogous problem for solid elastic media which is mathematically identical so far as the relation between the bulk stress and the instantaneous state of the suspension is concerned. The two cases coalesce as $\mu'/\mu \to \infty$, when the sphericity is permanent for any value of the surface tension.

The spatial distribution of particles throughout the ambient fluid is assumed to be random, with uniform average number density. Later we shall discuss the form of the probability distribution of particle configurations that is generated as a consequence of bulk motion of the suspension (in the case of particles which remain spherical).

Averages of the various flow quantities are defined with respect to an ensemble of realizations of the suspension for given conditions at the boundary of the dispersion. In particular, the mean (or bulk) velocity at a point $\mathbf{x}$, to be written as $\mathbf{U}(\mathbf{x})$, is an average over the ensemble of realizations, for some of which $\mathbf{x}$ lies in ambient fluid and for some inside a particle. The mean velocity $\mathbf{U}$ may also depend on time t.

The relative bulk velocity in a small neighbourhood of $\mathbf{x}$ can always be represented as the superposition of a pure straining motion, characterized by the rate-of-strain tensor

$$E_{ij} = \frac{1}{2}\left(\frac{\partial U_j}{\partial x_i} + \frac{\partial U_i}{\partial x_j}\right),$$

and a rigid-body rotation with angular velocity

$$\mathbf{\Omega} = \tfrac{1}{2}\nabla \times \mathbf{U}.$$

These two quantities E_{ij} and $\mathbf{\Omega}$ are continuous functions of $\mathbf{x}$ in general, and there will be a region about $\mathbf{x}$, of volume V say, in which E_{ij} and $\mathbf{\Omega}$ are approximately uniform. In such a region with statistically homogeneous kinematic flow conditions the bulk stress Σ_{ij} (also defined as an average of the stress over the ensemble of realizations for given $\mathbf{x}$ and t) will likewise be approximately uniform; and the local velocity gradient and stress will be stationary random functions of position within V. If now the linear dimensions of V (the macroscopic scale of the suspension) are large compared with the average distance between the particles (the microscopic scale), an ensemble average at the point $\mathbf{x}$ is identical with a spatial average over V for one realization, the latter sometimes being more convenient for analytical purposes.

It is known that, under the conditions described above, and for any concentration of particles, there is a relation between the deviatoric part of the bulk stress and the conditions at the surfaces of individual particles. This relation is

$$\Sigma_{ij} - \delta_{ij}\Sigma_{kk} = 2\mu E_{ij} + \Sigma_{ij}^{(p)} \tag{1.1}$$

(see, for example, Batchelor 1970), where the first term on the right-hand side is the deviatoric stress that would be generated in the ambient fluid in the absence of the particles, and the particle stress $\Sigma_{ij}^{(p)}$ is given, for particles which are force-free and couple-free, by

$$\Sigma_{ij}^{(p)} = \frac{1}{V}\sum S_{ij} \tag{1.2}$$

and
$$S_{ij} = \int_{A_0} \{(\sigma_{ik}x_j - \tfrac{1}{3}\delta_{ij}\sigma_{lk}x_l)n_k - \mu(u_i n_j + u_j n_i)\}\, dA. \tag{1.3}$$

The summation in (1.2) is over all the particles in V, A_0 is the surface of one of the particles, the unit (outward) normal there being $\mathbf{n}$, and u_i and σ_{ik} are the local velocity and stress. (When a surface tension acts at the interface, the stress in the integrand of (1.3) should be taken as the boundary value of the Newtonian stress in the ambient fluid.)

The integral denoted by S_{ij} has the same value for any other closed surface which lies entirely in the ambient fluid and encloses no particle other than that with surface A_0, and can be regarded as the additional force dipole strength of the region bounded by A_0 resulting from the replacement of ambient fluid in this region by the particle. S_{ij} depends on the size and shape and constitution of the particle and on the location of the adjoining particles, as well as on the bulk motion. For a given state of the suspension (that is, for a given distribution of the particles in V), and in the absence of Brownian motion effects, we may anticipate, from the linearity of the equations governing the flow near one particle, that S_{ij} and hence also $\Sigma_{ij}^{(p)}$ are linear functions of the bulk rate of strain E_{ij}. However, we leave open for exploration later the question whether the state of the suspension may itself depend on the nature of the bulk motion and its history.

In the case of a suspension which is so dilute that the fluid motion near one spherical particle is independent of the presence of the other particles, it is a simple matter to determine the force dipole strength S_{ij}. A spherical particle of radius a with centre at position $\mathbf{x}_0$ is here effectively alone in infinite fluid in which the velocity gradient tensor is uniform, with symmetrical and unsymmetrical parts represented by E_{ij} and Ω_i, at large distances from the particle; and the solution of the Stokes equations for the velocity $\mathbf{u}$ at position $\mathbf{x}_0+\mathbf{r}$ is found to be

$$\left.\begin{aligned} &u_i(\mathbf{x}_0+\mathbf{r})-U_i(\mathbf{x}_0)-\epsilon_{ijk}\Omega_j r_k \\ &\quad = E_{jk}r_j\left\{\delta_{ik}\left(1-\frac{\beta a^5}{r^5}\right)+\frac{r_i r_k}{r^2}\left(-\frac{5\alpha a^3}{2r^3}+\frac{5\beta a^5}{2r^5}\right)\right\} \quad \text{for} \quad r \geqslant a \\ &\quad\quad E_{jk}r_j\left\{\delta_{ik}(1-\beta)+\delta_{ik}\tfrac{25}{4}(\alpha-\beta)\left(\frac{r^2}{a^2}-1\right)-\frac{r_i r_k}{a^2}\tfrac{5}{2}(\alpha-\beta)\right\} \quad \text{for} \quad r \leqslant a, \end{aligned}\right\} \tag{1.4}$$

where $r = |\mathbf{r}|$. The parameters α and β in (1.4) are given by

$$\alpha = \frac{\mu'+\frac{2}{5}\mu}{\mu'+\mu}, \quad \beta = \frac{\mu'}{\mu'+\mu} \tag{1.5}$$

in the case of a liquid drop held spherical by surface tension (only the tangential component of stress then being continuous across the interface), and by

$$\alpha = \beta = \frac{\mu'-\mu}{\mu'+\frac{3}{2}\mu} \tag{1.6}$$

in the case of a liquid drop with zero surface tension at the interface which is only instantaneously spherical. We note for later use the expression for the rate of strain in the external fluid obtained from (1.4):

$$\begin{aligned} e_{ij}(\mathbf{x}_0+\mathbf{r}) = E_{ij}\left(1-\frac{\beta a^5}{r^5}\right)+E_{kl}\left(\frac{r_i r_k\delta_{jl}+r_j r_k\delta_{il}}{r^2}-\frac{r_k r_l}{r^2}\tfrac{2}{3}\delta_{ij}\right)\left(-\frac{5\alpha a^3}{2r^3}+\frac{5\beta a^5}{r^5}\right) \\ +E_{kl}\frac{r_k r_l}{r^2}\left(\frac{r_i r_j}{r^2}-\tfrac{1}{3}\delta_{ij}\right)\left(\frac{25\alpha a^3}{2r^3}-\frac{35\beta a^5}{2r^5}\right). \end{aligned} \tag{1.7}$$

The corresponding local stress in the external fluid can be written down, and then we find from (1.3) that for such an isolated spherical particle

$$S_{ij} = \tfrac{20}{3}\pi a^3\alpha\mu E_{ij}. \tag{1.8}$$

Hence for a dilute suspension the first approximation to the particle stress is

$$\Sigma_{ij}^{(p)} = 5c\alpha\mu E_{ij}, \tag{1.9}$$

where

$$c = \frac{1}{V}\Sigma\tfrac{4}{3}\pi a^3$$

is the volume fraction of the spherical particles (which need not be of the same size) in V. Thus the leading approximation to the particle stress for a dilute suspension of spherical particles is of the Newtonian form and corresponds to the addition of $\frac{5}{2}c\alpha\mu$ to the viscosity of the ambient fluid, as found first by Einstein (1906) for rigid spheres ($\alpha = 1$) and by Taylor (1932) for the conditions represented by (1.5).

There is in the literature a general belief, for which we shall later provide a proof, that the neglected effect of hydrodynamic interaction of the particles is of order c^2, in which case the full expression for the deviatoric part of the bulk stress in a dilute suspension of spheres is

$$\Sigma_{ij} - \tfrac{1}{3}\delta_{ij}\Sigma_{kk} = 2\mu E_{ij}(1 + \tfrac{5}{2}\alpha c) + O(c^2).$$

Measurements with suspensions of rigid spheres suggest that the term of order c^2 is negligible only for c less than about 0·02 (see for instance the survey by Rutgers 1962*a*). Many investigations, both theoretical and experimental, of the form and magnitude of the quadratic term have been made, but reliable information is still not available. So far as we know, no satisfactory method of calculating it has been published. It is often assumed, although without justification, that the term of order c^2 has the Newtonian form $2\mu E_{ij}kc^2$. Measurements have been made of the bulk shear stress for a steady simple shearing motion, from which an effective viscosity can be deduced, and some of the available data for this case suggest that k is about 12 for a suspension of equal-size rigid spheres (Rutgers 1962*b*) although other, and mostly smaller, values have been proposed; the different values may result in part from the fitting of a quadratic function over different ranges of values of c. Aside from its direct practical value in extending the range of concentrations for which the rheological properties of the suspension of spherical particles are known, information about the quadratic term would aid our understanding of the possible effect of hydrodynamic interactions at larger concentrations and perhaps for particles of different shape.

In this paper we give a new method of determining the bulk stress in a suspension of spherical particles correct to order c^2 which is free from hypothesis. The first and most essential part of the method is similar in type to that devised recently for the determination of the effect of hydrodynamic interactions on the average velocity of spheres falling through fluid under gravity (Batchelor 1972). In that problem, as here, the primary theoretical difficulty arises from the fact that the sum of the contributions to the quantity under discussion (which is S_{ij} in our case) due to the interaction of one sphere with each of the other spheres in the suspension taken one at a time is not an absolutely convergent integral. Only when this difficulty has been overcome is it possible to reduce the calculation of the c^2-term in the expression for the bulk stress to a consideration of the hydrodynamics of an encounter between just two spheres. Another important feature of the method is that it takes into account the non-uniformity of the probability density of the vector separation of the centres of two spheres which is produced by the bulk flow.

In the next three sections we describe the method and the results obtained for the particle stress in general form. It will be seen that numerical results for the particle stress are obtainable only when information about the interaction of two spherical particles in a linear flow field is available. In a companion paper (Batchelor & Green 1972, to be referred to hereafter as paper I) we have marshalled the known results concerning the interaction of two rigid spheres, and in the later sections of this paper we use this information to determine numerically the particle stress (to order c^2) for a suspension of rigid spherical particles of uniform size for certain types of bulk flow.

2. The expression for the bulk stress to order c^2 in terms of two-particle interactions

The mathematical expressions describing the statistical averages are simpler in the case of a suspension of spherical particles of uniform size, and we shall explain the general method in terms of this case. The generalization of the formal result obtained in this section to the case of a mixture of particle sizes will be seen to be straight-forward.

When the volume V contains N ($\gg 1$) spherical particles all of radius a, the summation in (1.2) is equivalent to N times the average value of S_{ij} for a given spherical particle of radius a over a large number of realizations (to be denoted by an overbar) and we may write

$$\begin{aligned}\Sigma_{ij}^{(p)} &= n\overline{S}_{ij}\\ &= 5c\alpha\mu E_{ij} + 5c\alpha\mu\left(\frac{\overline{S}_{ij}}{\frac{20}{3}\pi a^3\alpha\mu} - E_{ij}\right),\end{aligned} \tag{2.1}$$

where $n = N/V$ is the mean number density of the particles and $c = \frac{4}{3}\pi a^3 n$ is the volume fraction of the particles. The first term on the right-hand side of (2.1) is the particle stress obtained when hydrodynamic interactions between the particles are completely neglected, and so the second term represents the effect of those interactions.

The feature of the system that varies from one realization to another is the location of particles relative to that spherical particle for which the value of S_{ij} is being calculated (to be termed the reference particle), and we therefore introduce the probability density of a configuration of N particles which is defined by the N position vectors of the centres and will be denoted by $\mathscr{C}_N$. We write $P(\mathscr{C}_N)$ for the probability density of this configuration, and $P(\mathscr{C}_N|\mathbf{x}_0)$ for the *conditional* probability density which applies when the presence of an additional particle with centre at $\mathbf{x}_0$ is given. Since the N particles in V are identical we have the normalization relations

$$\int P(\mathscr{C}_N)\,d\mathscr{C}_N = \int P(\mathscr{C}_N|\mathbf{x}_0)\,d\mathscr{C}_N = N!,$$

where here and later each of these $3N$-dimensional integrals is taken over all possible values of the position co-ordinates of the centres of the N spherical particles of the configuration in V. (The notation and its interpretation and standard manipulations with it are all as in the earlier paper, Batchelor 1972).

The ensemble average of S_{ij} may then be expressed as

$$\bar{S}_{ij} = \frac{1}{N!}\int S_{ij}(\mathbf{x}_0, \mathscr{C}_N)\, P(\mathscr{C}_N|\mathbf{x}_0)\, d\mathscr{C}_N, \tag{2.2}$$

where $S_{ij}(\mathbf{x}_0, \mathscr{C}_N)$ denotes the value of the surface integral in (1.3) for a spherical particle with centre at $\mathbf{x}_0$ in the presence of a configuration of N other particles with locations specified by $\mathscr{C}_N$. The second of the two terms on the right-hand side of (2.1), representing the effect of particle interactions on the bulk stress, may likewise be written as

$$\frac{5c\alpha\mu}{N!}\int\left\{\frac{S_{ij}(\mathbf{x}_0, \mathscr{C}_N)}{\frac{20}{3}\pi a^3\alpha\mu} - E_{ij}\right\} P(\mathscr{C}_N|\mathbf{x}_0)\, d\mathscr{C}_N. \tag{2.3}$$

Now the probability that the centre of one particle of the configuration $\mathscr{C}_N$ lies within a distance of a few sphere radii from the reference particle with centre at $\mathbf{x}_0$ is of order na^3 (provided of course that the presence of one sphere does not change radically the probability density for a second sphere at such a distance), that is, of order c, which is small for a dilute suspension. And the probability that two particles of $\mathscr{C}_N$ simultaneously lie in this region surrounding the reference particle is of order c^2. We also observe that the quantity within curly brackets in (2.3) falls to zero as the distances of all the surrounding particles from $\mathbf{x}_0$ tend to infinity. It is therefore natural to suppose that we could obtain the first approximation to the effect of hydrodynamic interactions on the bulk stress by supposing that only *one* particle of the configuration $\mathscr{C}_N$ has a significant effect on the value of S_{ij} for the reference particle. This would correspond to replacing

$$\frac{1}{N!}\int \ldots P(\mathscr{C}_N|\mathbf{x}_0)\, d\mathscr{C}_N \quad \text{by} \quad \int \ldots P(\mathbf{x}_0+\mathbf{r}|\mathbf{x}_0)\, d\mathbf{r}$$

in (2.3), where $P(\mathbf{x}_0+\mathbf{r}|\mathbf{x}_0)\,\delta\mathbf{r}$ denotes the probability that the centre of a particle lies in the volume element $\delta\mathbf{r}$ about the point $\mathbf{x}_0+\mathbf{r}$ given that there is a particle with centre at $\mathbf{x}_0$. When $r/a \gg 1$ the locations of the two particles are presumably statistically independent and

$$P(\mathbf{x}_0+\mathbf{r}|\mathbf{x}_0) \approx P(\mathbf{x}_0+\mathbf{r}) = n;$$

and so a necessary condition for the 'natural' supposition to be correct is that the quantity

$$\frac{S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})}{\frac{20}{3}\pi a^3\alpha\mu} - E_{ij} \tag{2.4}$$

should be integrable with respect to $\mathbf{r}$, that is, that it should be of smaller order than a^3/r^3 when $a/r \ll 1$. Here $S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})$ stands for the force dipole strength of the reference particle in the presence of a second particle with centre at $\mathbf{x}_0+\mathbf{r}$.

To see whether this condition is satisfied we must consider the way in which two spherical particles interact when their separation is large. Each particle exerts zero resultant force on the fluid and acts as a force dipole, of strength given approximately by (1.8), which generates at distance r in unbounded fluid a disturbance velocity of order $\alpha E_{ij}a^3/r^2$ (see (1.4)), a disturbance velocity gradient of order $\alpha E_{ij} a^3/r^3$, etc. Such a disturbance motion at the position of the other particle gives it an additional translational velocity, and also requires a change of the distribution of stress at the surface of this second particle, to ensure satisfaction of the no-slip condition there in the presence of the disturbance rate of strain. The corresponding addition to the value of S_{ij} for each particle may be seen from (1.8) to be proportional to the disturbance rate of strain, and so to be of order $\alpha^2 \mu E_{ij} a^6/r^3$. It appears that the quantity (2.4) is (only just) not integrable, and that the straight-forward procedure suggested above is not permissible.† Consideration of two-particle interactions alone is not yet sufficient for the determination of the c^2-term in the expression for the bulk stress and we must return to (2.3).

The device that we adopt here, following the general procedure proposed earlier for problems of hydrodynamic interactions which lead to non-convergent integrals in the above manner (Batchelor 1972), is to look for a quantity, Q_{ij} say, whose mean value is known exactly and which has the same dependence on the position of one distant spherical particle as $S_{ij}/(\frac{20}{3}\pi a^3 \alpha\mu) - E_{ij}$, and then to reduce the expression for the difference between the mean values of

$$S_{ij}/(\tfrac{20}{3}\pi a^3 \alpha\mu) - E_{ij}$$

and of Q_{ij} to a consideration of the effect of only one particle of the configuration $\mathscr{C}_N$.

The appropriate choice of the function Q_{ij} is made evident by the fact that the contribution to the value of S_{ij} for a particle with centre at $\mathbf{x}_0$ due to the presence of a second particle with centre at $\mathbf{x}_0 + \mathbf{r}$ is proportional, when $a/r \ll 1$, to the rate of strain induced at $\mathbf{x}_0$ by that second particle. Noting the proportionality constant in (1.8), we choose

$$Q_{ij} = e_{ij}(\mathbf{x}_0, \mathscr{C}_N) - E_{ij},$$

where $e_{ij}(\mathbf{x}_0, \mathscr{C}_N)$ is the rate-of-strain tensor at point $\mathbf{x}_0$ in the suspension in the presence of the N spherical particles specified by $\mathscr{C}_N$. We have available the exact result

$$E_{ij} = \frac{1}{N!}\int e_{ij}(\mathbf{x}_0, \mathscr{C}_N) P(\mathscr{C}_N)\, d\mathscr{C}_N, \tag{2.5}$$

which allows us to write

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij} = \frac{5c\alpha\mu}{N!}\int \left[\left\{\frac{S_{ij}(\mathbf{x}_0, \mathscr{C}_N)}{\frac{20}{3}\pi a^3 \alpha\mu} - E_{ij}\right\} P(\mathscr{C}_N|\mathbf{x}_0) - \{e_{ij}(\mathbf{x}_0, \mathscr{C}_N) - E_{ij}\} P(\mathscr{C}_N)\right] d\mathscr{C}_N. \tag{2.6}$$

The right-hand side of (2.6) replaces (2.3) (to which it is identically equal) as the expression for the contribution to the deviatoric part of the bulk stress due to

† If the integration with respect to $\mathbf{r}$ is carried out in terms of polar co-ordinates, with the integration with respect to the radial co-ordinate over the infinite range being last in order, a finite value of the integral may be obtained, because it happens that the term of order a^3/r^3 in the expression for $S_{ij}(\mathbf{x}_0, \mathbf{x}_0 + \mathbf{r})$ for $a/r \ll 1$ has zero average over a spherical surface. However, this does not eliminate the difficulty, it merely conceals it. The integral of (2.4) over all $\mathbf{r}$-space is not absolutely convergent, and any finite value of the integral which is obtained by a particular order of integration with respect to the three scalar co-ordinates is without significance, unless the chosen order can be justified by some additional considerations.

hydrodynamic interactions. The change is apparently slight, but it is a vital one because when the configuration $\mathscr{C}_N$ consists of only one particle at position $\mathbf{x}_0+\mathbf{r}$ the two terms in the integrand have asymptotic forms (when $a/r \ll 1$) of order a^3/r^3 which cancel and in consequence the integral is absolutely convergent.

We can now assert that, since the probability of more than one particle centre of the configuration $\mathscr{C}_N$ lying within a distance of a few particle radii from $\mathbf{x}_0$ is of smaller order than c, and since particle centres outside this region have negligible effect on the integrand of (2.6), the contribution to the bulk stress due to interactions between spherical particles may be written as

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij} = 5c\alpha\mu \int \left[\left\{ \frac{S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})}{\frac{20}{3}\pi a^3 \alpha\mu} - E_{ij} \right\} P(\mathbf{x}_0+\mathbf{r}|\mathbf{x}_0) - \{e_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r}) - E_{ij}\} P(\mathbf{x}_0+\mathbf{r}) \right] d\mathbf{r} + o(c^2). \quad (2.7)$$

The integration is here over the whole of $\mathbf{r}$-space; but note that $P(\mathbf{x}_0+\mathbf{r}|\mathbf{x}_0) = 0$ when $r < 2a$ since two spherical particles do not overlap. The null term that was added to (2.3) to give the right-hand side of (2.6) is now not so innocuous and makes a contribution to the term of order c^2 in the expression for the particle stress which is not identically zero. What we have done in essence is to observe (1) that precisely the same apparent indeterminacy or divergence in the average value of $S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})$ over all particle pairs occurs in the average value of $e_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})$ over all particle pairs, and (2) that the exact value of the complete mean of e_{ij} at a given point is known from the specification of the problem; and this enabled us to construct a difference quantity involving $S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})$ whose average over all particle pairs is represented by an absolutely convergent integral.

We now consider the generalization of (2.7) to the case of a suspension of spherical particles of different size, and introduce a size distribution function $g(a)$, such that $g(a)\,\delta a$ is the fraction of the total number of particles in the suspension which have radii in the range δa about a and $\int_0^\infty g(a)\,da = 1$. The above formal arguments concerning the reduction to a consideration of the interaction of just two spherical particles in a linear velocity field obviously remain valid when the particles are of different size, provided that proper account is taken of the different types of particle pair which occur. For each type of pair there will be a contribution to the bulk stress of the form (2.7), and we can see how the radii of the two particles associated with $S_{ij}(\mathbf{x}_0, \mathbf{x}_0+\mathbf{r})$ separately enter the expression for the bulk stress by recalling the physical meaning of the two terms in the integrand. Thus, in a suspension of spherical particles of different sizes,

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij} = 5n\alpha\mu \int_0^\infty \int_0^\infty \int \tfrac{4}{3}\pi a^3 \left[\left\{ \frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} - E_{ij} \right\} P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) - \{e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b) - E_{ij}\} P(\mathbf{x}_0+\mathbf{r}, b) \right] g(a)\,g(b)\,d\mathbf{r}\,da\,db + o(c^2), \quad (2.8)$$

where the integration with respect to $\mathbf{r}$ is over all $\mathbf{r}$-space, n is again the total number of particles per unit volume, $S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)$ is the force dipole strength of a spherical particle of radius a with centre at $\mathbf{x}_0$ in the presence of a second particle of radius b with centre at $\mathbf{x}_0+\mathbf{r}$ (and with uniform velocity gradient in the fluid at infinity), $e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b)$ is the rate of strain at $\mathbf{x}_0$ in the presence of a particle of radius b with centre at $\mathbf{x}_0+\mathbf{r}$, $P(\mathbf{x}_0+\mathbf{r}, b)\, g(b)\, \delta b\, \delta\mathbf{r}$ is the probability that a particle with radius in the range δb about b has its centre in the range $\delta\mathbf{r}$ about the position $\mathbf{x}_0+\mathbf{r}$, and $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) g(b)$ is the corresponding probability density conditional on there being a particle of radius a at $\mathbf{x}_0$.

The relation (2.8) (or (2.7) if the particles are of uniform size) gives the contribution to the stress due to the presence of spherical particles correct to order c^2, and is the basic result in this paper. It allows the particle stress to be calculated explicitly when various one-particle and two-particle functions are known (in addition to the size distribution function $g(a)$, which can be regarded as a given property of a suspension). The function $e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b)$ representing the rate of strain in the presence of one spherical particle is already available from (1.7). For the two probability density functions we have

$$P(\mathbf{x}_0+\mathbf{r}, b) = n, \quad P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) \to n \quad \text{as} \quad r\to\infty, \tag{2.9}$$

but the form of $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a)$ is otherwise unknown. This conditional probability density is dependent on the flow due to two spherical particles in a linear flow field, as we shall show in the next section.

The remaining function in the integrand of (2.8) is the force dipole strength $S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)$. We have pointed out in paper I that, since S_{ij} is a symmetrical tensor with zero trace which is linear in E_{ij} and otherwise a function of $\mathbf{r}$ and scalar variables only, it may be written as†

$$\frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} = E_{ij}(1+K) + E_{kl}\left(\frac{r_i r_k \delta_{jl} + r_j r_k \delta_{il}}{r^2} - \frac{r_k r_l}{r^2}\tfrac{2}{3}\delta_{ij}\right) L + E_{kl}\frac{r_k r_l}{r^2}\left(\frac{r_i r_j}{r^2} - \tfrac{1}{3}\delta_{ij}\right) M, \tag{2.10}$$

where the non-dimensional scalar functions K, L, M are functions of the non-dimensional distance r/a, the radius ratio b/a, and the viscosity ratio μ'/μ. As already noted, the asymptotic form of the expression (2.10), after subtraction of E_{ij}, is the same to the order $(a+b)^3/r^3$ as that of $e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b) - E_{ij}$, that is,

$$K = o\left(\frac{(a+b)^3}{r^3}\right), \quad L \sim -\frac{5\alpha b^3}{2r^3}, \quad M \sim \frac{25\alpha b^3}{2r^3}, \tag{2.11}$$

as $r/(a+b)\to\infty$. Later we shall encounter the average value of S_{ij} over all directions of $\mathbf{r}$, which is

$$\begin{aligned}\frac{1}{4\pi r^2}\int_{r\,\text{const.}} \frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3\alpha\mu}\, dA(\mathbf{r}) &= E_{ij}(1+K+\tfrac{4}{3}L+\tfrac{2}{15}M),\\ &= E_{ij}(1+J)\end{aligned} \tag{2.12}$$

say, where J is also a function of r/a, b/a and μ'/μ.

† Paper I is concerned only with rigid spheres, but the fluidity of the spherical particles considered here makes no difference to the argument leading to (2.10) (or to (3.2) in the next section).

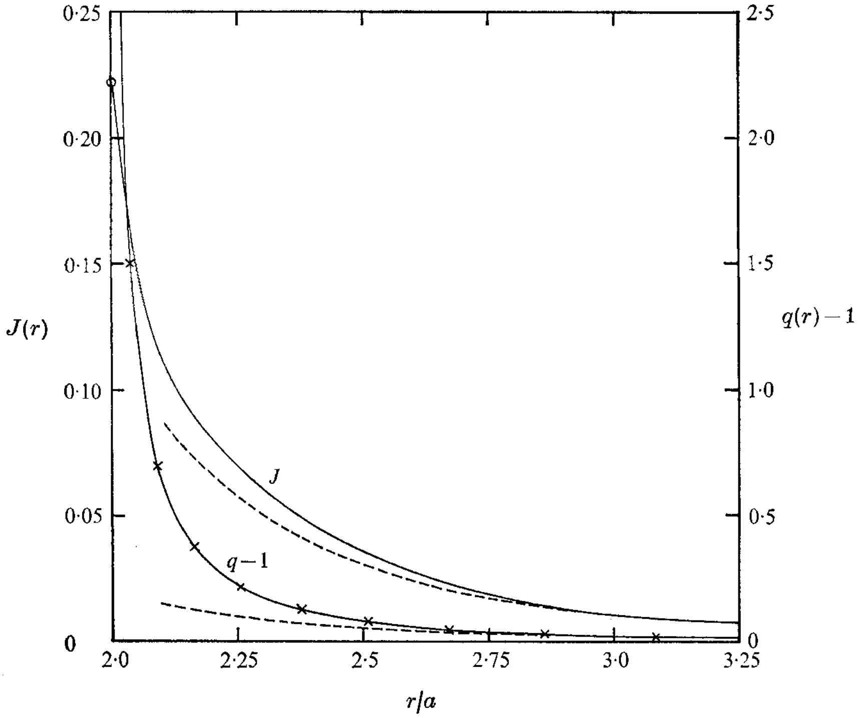

FIGURE 1. The broken lines show the far-field asymptotic forms of the functions $J(r)$ and $q(r)$ for the case of rigid spherical particles of uniform size. The continuous line for J has been drawn to fit this far-field form and the known inner limit $J = 0{\cdot}2214$ at $r/a = 2$. The continuous line for q has been drawn to fit numerical data for identical rigid spheres (shown as crosses) obtained by Lin, Lee & Sather (1970) and described in paper I.

In paper I we have surveyed the rather limited information about the functions K, L, M that is presently available from different sources for the case of two rigid spheres. Asymptotic forms (for large r) correct to the order $(a+b)^6/r^6$ are obtainable, and the limiting values as $r/(a+b) \to 1$ are known for the case $b/a = 1$. For the important function J it is found that

$$J = K + \tfrac{2}{3}L + \tfrac{2}{15}M \sim \frac{15a^3b^3}{2r^6} \tag{2.13}$$

as $r/(a+b) \to \infty$, and

$$J = 0{\cdot}2214 \quad \text{at} \quad b/a = 1, \quad r/a = 2. \tag{2.14}$$

The known values of the function $J(r)$ at the two ends of the range for the case of two equal rigid spheres are shown in figure 1, together with a plausible interpolation form which we shall use later for a numerical estimate of the particle stress (see also table 1).

We remind the reader that effects of Brownian motion have not been taken into account in the above derivation of the particle stress. When Brownian forces act on the spherical particles, the expression for the particle stress needs modification although it is unaffected to order c.

3. The probability distribution of the vector separation of two spherical particles

We consider here the probability density function for the separation vector $\mathbf{r}$ drawn from the centre of a spherical particle of radius a to the centre of a spherical particle of radius b. In accordance with the scheme of approximation for $c \ll 1$ already described, we regard these two particles as being not influenced by the presence of other particles in the suspension. Since no two particles overlap, we may write

$$P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) = \begin{cases} 0 & \text{for} \quad r < a+b \\ np\left(\dfrac{\mathbf{r}}{a}, \dfrac{b}{a}, \dfrac{\mu'}{\mu}, t\right) & \text{for} \quad r \geqslant a+b, \end{cases} \tag{3.1}$$

with the dependence of p on variables other than $\mathbf{r}$ and t normally taken as understood. The dimensionless function $p(\mathbf{r}, t)$ is determined, in part at least, by the hydrodynamics of an encounter between two particles, that is, by the influence that the presence of one particle exerts on the movement and relative position of the other by means of hydrodynamic stresses.† Other physical factors may be relevant, such as Brownian motion of the particles and electrical forces between neighbouring particles, both of which are likely to be important when the particles are very small. However, we shall consider here only the hydrodynamic effect, this being the effect that is present in *all* circumstances. No derivation of the probability distribution of the two-particle separation vector as determined by hydrodynamic action has yet appeared in the literature, although its relevance in the study of rheological properties of not-so-dilute suspensions has been recognized by Lin, Lee & Sather (1970), who also noted that it is related to the equation for the trajectory of one particle relative to another, and by Cox & Brenner (1971).

The hydrodynamic problem to be solved concerns the relative motion of two force-free spherical particles of internal viscosity μ' immersed in fluid whose velocity at large distances from the particles is a linear function of position which is a superposition of an angular velocity $\mathbf{\Omega}$ and a rate of strain E_{ij}. It is shown in paper I that the velocity of the centre of the particle of radius b relative to that of the particle of radius a, to be denoted by $\mathbf{V}(\mathbf{r})$, may be written without loss of generality as

$$V_i(\mathbf{r}) = \epsilon_{ijk}\Omega_j r_k + r_j E_{ij} - \left\{A\frac{r_i r_j}{r^2} + B\left(\delta_{ij} - \frac{r_i r_j}{r^2}\right)\right\} r_k E_{jk}, \tag{3.2}$$

where A and B are non-dimensional functions of the scalar variables r/a, b/a and μ'/μ. As $r \to a+b$, $A(r) \to 1$, since the component of $\mathbf{V}$ parallel to the line of centres must be zero in the limit. When r is large, the velocity of each particle is approximately the same as that of a fluid particle in a velocity field like (1.4) due to the other particle when alone in infinite fluid, whence we see that, as $r/(a+b) \to \infty$,

$$A(r) \sim \frac{5\alpha(a^3+b^3)}{2r^3}, \quad B(r) \sim O\left(\frac{a^5}{r^5}\right). \tag{3.3}$$

† Since the evolution of the probability density in time is involved, the considerations in this section are relevant only to the case of particles which *remain* spherical, that is, to the case in which α and β are given by (1.5.)

We shall need also the corresponding expression for the divergence of $\mathbf{V}$, viz.

$$\frac{\partial V_i}{\partial x_i} = -\left\{\frac{3(A-B)}{r^2}+\frac{1}{r}\frac{dA}{dr}\right\} r_j r_k E_{jk}. \tag{3.4}$$

The differential equation for the probability density function $p(\mathbf{r},t)$ may be found in the usual way from the condition that the number of particle pairs in $\mathbf{r}$-space is conserved and the fact that a 'material' point in $\mathbf{r}$-space representing a particular particle pair moves with velocity $\mathbf{V}$. This equation is

$$\frac{\partial p}{\partial t}+\mathbf{V}.\nabla p = -p\nabla.\mathbf{V}. \tag{3.5}$$

It will be noticed that the radial component of $\mathbf{V}$, viz.

$$V_r = \frac{\mathbf{r}.\mathbf{V}}{r} = \frac{1-A}{r} r_j r_k E_{jk}, \tag{3.6}$$

has the same dependence on the direction of $\mathbf{r}$ as $\nabla.\mathbf{V}$. We exploit this fact by writing (3.5) as

$$\frac{\partial p}{\partial t}+\mathbf{V}.\nabla p = pV_r\left\{\frac{3(A-B)}{r(1-A)}+\frac{1}{1-A}\frac{dA}{dr}\right\},$$

and then, if the function $q(r)$ is defined by

$$\frac{1}{q}\frac{dq}{dr} = \frac{3(A-B)}{r(1-A)}+\frac{1}{1-A}\frac{dA}{dr}, \tag{3.7}$$

the differential equation for $p(\mathbf{r},t)$ becomes

$$\left(\frac{\partial}{\partial t}+\mathbf{V}.\nabla\right)\left\{\frac{p(\mathbf{r},t)}{q(r)}\right\} = 0. \tag{3.8}$$

As defined, $q(r)$ contains an arbitrary multiplying constant and, if we choose this constant so that

$$q(r)\to 1 \quad \text{as} \quad r/(a+b)\to\infty,$$

the explicit expression for q is

$$q(r) = \frac{1}{1-A}\exp\left\{\int_r^\infty \frac{3(B-A)}{r(1-A)}\,dr\right\}. \tag{3.9}$$

The meaning of equation (3.8) is that the quantity p/q is constant for a 'material' point in $\mathbf{r}$-space whose velocity is given as a function of $\mathbf{r}$ and t by $\mathbf{V}$. That is, for a material point in $\mathbf{r}$-space which was at position $\mathbf{r}_0$ at time t_0,

$$p(\mathbf{r},t) = \frac{p(\mathbf{r}_0,t_0)}{q(r_0)}q(r). \tag{3.10}$$

For any material point in $\mathbf{r}$-space which comes from or goes to infinity we may choose $r_0=\infty$ and (in accordance with (2.9))

$$\{p(\mathbf{r}_0,t_0)\}_{r_0=\infty} = 1, \tag{3.11}$$

corresponding to the fact that particles which are far apart do not influence each other's position. It follows that for such a material point

$$p(\mathbf{r},t) = q(r). \tag{3.12}$$

This is a strong result, since it gives explicitly the probability density of the pair separation vector at all values of $\mathbf{r}$ occupied by material points which have come from infinity in $\mathbf{r}$-space, for any type of bulk flow (that is, regardless of the relative amount of pure straining and rigid rotation), steady or unsteady; and the probability density is independent of t and of the direction of $\mathbf{r}$ in the region composed of these material points which have come from infinity.

The use that can be made of the differential equation (3.8) evidently depends on the nature of the bulk flow. In the particular case of a steady pure straining motion, every point in the accessible part of $\mathbf{r}$-space (that is, the part for which $r \geqslant a+b$) lies on a trajectory of a material point in $\mathbf{r}$-space (or equivalently, a trajectory of one particle centre relative to another) which has come from infinity. As a consequence, $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a)$ may here be replaced by $nq(r)$ in the integrand of (2.8) over the whole of the region $r \geqslant a+b$, making possible a good deal of further progress, as we shall see. Unfortunately, not all the trajectories in other types of bulk flow come from infinity. It may happen that some of the trajectories are closed and occupy a region into which open trajectories from infinity do not penetrate; for instance, in the important case of steady simple shearing motion both observation (Darabaner & Mason 1967) and analysis given in paper I show the existence of 'bound' pairs of rigid spheres which move relative to each other along closed paths. Equation (3.10) tells us that p/q is constant for a material point in $\mathbf{r}$-space which is moving on such a closed trajectory, but the boundary condition (3.11) is not available here to enable us to determine the value of the constant. In particular, we have no means of determining the relation between the constant values of p/q for material points on different closed trajectories (or even for different material points on the same closed trajectory) in a steady bulk flow. This kind of indeterminacy resulting from purely convective effects in a region of closed trajectories is familiar in fluid mechanics, and can be overcome only by the consideration of the history of the flow before the particles began to move along closed trajectories or by the inclusion of some process, such as Brownian diffusion or occasional encounters between three particles, which transfers particles *across* these closed trajectories. Any steady-state distribution of the particles which is made determinate by such a process of transfer across trajectories will presumably depend on the type of (steady) bulk flow, since the shape of the trajectories depends on the type of bulk flow. In this paper we shall not consider further the problem of determining the probability density function $p(\mathbf{r},t)$ in the region of $\mathbf{r}$-space occupied by closed trajectories which have not come from infinity.

We conclude this section by noting the available information about the function $q(r)$.

There is first a simple integral identity which is a consequence of conservation of particle number. When a body of fluid containing sphere b flows towards sphere a, the hydrodynamic interaction of the two spherical particles causes the path of the centre of sphere b to deviate from the path taken by a material element of fluid in the absence of that sphere, and $\nabla . \mathbf{V}$ may be non-zero, in which case there is a higher or lower probability of finding the centre of sphere b in some parts of $\mathbf{r}$-space than in others. In particular, fluid may flow into the spherical shell $a \leqslant r < a+b$, but the centre of the sphere of radius b cannot enter that region; it is as if the spherical surface $r = a+b$ acted as a strainer for the centres of approaching particles. Now for a steady pure straining motion, all points in the region $a \leqslant r < a+b$ lie on streamlines which come from infinity, and all trajectories of the centre of sphere b come from infinity. Hence in this case the fluid instantaneously enclosed between the two surfaces $r = a$ and $r = a+b$ has been robbed of the sphere centres which it contained when it was at infinity, where the number density of sphere centres is uniform and $q = 1$, and the sphere centres taken from this fluid are piled up in the region $r \geqslant a+b$ (mostly near the inner boundary of this region). Thus we have the integral relation

$$\int_{a+b}^{\infty} \{q(r)-1\} 4\pi r^2 dr = \tfrac{4}{3}\pi\{(a+b)^3 - a^3\}. \tag{3.13}$$

It should be recognized that the reference to a bulk pure straining motion in this argument does not imply dependence of the relation (3.13) on the type of bulk flow; for, as noted earlier, the functions $A(r)$, $B(r)$ and $q(r)$ are all independent of the bulk flow. It is the application of (3.13), not the result itself, which is restricted to bulk flows for which all points in the region $r \geqslant a+b$ lie on open trajectories coming from infinity and for which as a consequence the probability density of the separation vector of two particles has the spherically symmetrical form everywhere.

The function $q(r)$ can be calculated explicitly from (3.9) when the functions $A(r)$ and $B(r)$ are known. In paper I we have gathered together the information about $A(r)$ and $B(r)$ that is obtainable *for rigid spheres*, by various methods, and for different parts of the range $a+b \leqslant r < \infty$. For the far-field region $r \gg a+b$ it is possible to obtain $A(r)$ and $B(r)$ correct to the order $(a+b)^6/r^6$ without difficulty, and the corresponding result for $q(r)$ is

$$q(r) - 1 \sim \frac{25}{2}\frac{a^3b^3}{r^6}. \tag{3.14}$$

In paper I, numerical values of $A(r)$ and $B(r)$ over all except large and small values of $(r-2a)/a$ for the case $b/a = 1$ were obtained from the data computed by Lin, Lee & Sather (1970); conveniently, the function $q(r)$ is also simply related to the functions which they computed explicitly and the derived results are shown in table 1 and figure 1. There is a singularity in $q(r)$ at $r = 2a$, and it is necessary to supplement the computations of Lin, Lee & Sather (1970) by an investigation of the analytical forms of $A(r)$ and $B(r)$ near this point. In paper I we have shown by lubrication-theory methods that, when $b/a = 1$,

$$A \sim 1 - 4{\cdot}077\xi, \quad B \sim 0{\cdot}4060 - \frac{0{\cdot}78}{\log \xi^{-1}} \tag{3.15}$$

as $\xi \to 0$, where $\xi = (r-2a)/a$; the coefficient of $(\log \xi^{-1})^{-1}$ here was obtained by matching the known asymptotic form to the values of the function B derived from the data of Lin, Lee & Sather. Substitution of these asymptotic forms in (3.9) gives

$$q(r) \sim \frac{q_0}{\xi^{0\cdot781}(\log \xi^{-1})^{0\cdot29}}, \tag{3.16}$$

where q_0 is a number which we may estimate to be 0·234 by making this asymptotic form fit the values of $q(r)$ at $r/a = 2\cdot0006$ and $2\cdot0025$ given in table 1. The relation (3.16) with $q_0 = 0\cdot234$ provides the best available description of the function $q(r)$ in the range $0 \leqslant \xi \leqslant 0\cdot0025$, but there are inaccuracies arising from the necessity to make a partial use of the computations by Lin, Lee & Sather of their functions $\mathscr{A}$ and f in this range, both of which have infinite gradients at $\xi = 0$.

r/a	$J(r)$	$q(r)$	
2·0	0·2214	∞	
2·0006	0·221	42·5	
2·0025	0·218	15·1	
2·005	0·214		10·6
2·0075	0·210		7·60
2·0100	0·207	5·80	
2·02	0·190		3·62
2·03	0·175		2·80
2·04	0·160		2·51
2·0401	—	2·500	
2·05	0·149		2·27
2·0907	—	1·694	
2·10	0·110		1·60
2·1621	—	1·372	
2·20	0·079		1·30
2·2553	—	1·213	
2·3709	—	1·127	
2·40	0·046		1·11
2·5103	—	1·076	
2·60	0·027		1·06
2·6749	—	1·047	
2·80	0·016		1·03
2·8662	—	1·028	
3·00	0·010		1·02
3·0862	—	1·018	

TABLE 1. Values of $J(r)$ and $q(r)$ for identical rigid spheres. The values of $J(r)$ have been read off the approximate curve shown in figure 1. The values of $q(r)$ shown in the column on the left-hand side have been obtained directly from the numerical data given by Lin, Lee & Sather (1970) ($q = 1/r^2 f^3 \mathscr{C}$ in their notation), and the values on the right-hand side at regular intervals of r/a have been read off a smooth curve through the accurate points. In the case of the value of $q(r)$ at $r/a = 2\cdot0006$, the value of the Lin, Lee & Sather function $\mathscr{C}$, which is equal to our $r(1-A)$, was obtained from the asymptotic form (3.15) since this is more accurate than the computed value.

An indication of the general accuracy of these results for $q(r)$ in the case of identical rigid spheres may be obtained by computing the value of the integral

$$\int_2^\infty (q-1)\frac{r^2}{a^2}\,d\frac{r}{a} \tag{3.17}$$

which, according to the identity (3.13), should equal 7/3. We divide the range of integration into three parts. In the part $r/a \geqslant 3{\cdot}0$, the far-field form (3.14) (with $b = a$) may be used to find a contribution 0·154 to the integral. For the part $2{\cdot}0025 \leqslant r/a \leqslant 3{\cdot}0$, a numerical integration using the values of $q(r)$ in table 1 gives a contribution 1·405. And for the part $2{\cdot}0 \leqslant r/a \leqslant 2{\cdot}0025$, an analytical integration using the near-field form (3.16) gives

$$\int_2^{2+\xi} q\frac{r^2}{a^2}d\frac{r}{a} = 2{\cdot}753\left\{\Gamma(0{\cdot}71) - \frac{\eta^{0\cdot 71}}{0{\cdot}71} + \frac{\eta^{1\cdot 71}}{1{\cdot}71} - \frac{\eta^{2\cdot 71}}{2!\times 2{\cdot}71} + \ldots\right\},$$
$$= 0{\cdot}596 \quad \text{when} \quad \xi = 0{\cdot}0025, \tag{3.18}$$

where $\eta = 0{\cdot}219 \log \xi^{-1}$ and Γ denotes the Gamma function. The corresponding contribution to the integral (3.17) is thus 0·586. The three contributions together give 2·15, whereas the known exact value is 2·33.

It is evident from these numerical values of q for the case of identical rigid spheres that a significant number of the sphere centres displaced from the fluid entering the region $a \leqslant r < 2a$ are located very close to the inner boundary $r/a = 2$. This suggests that in practice there may be departures from the theoretical formulae due to small surface irregularities and weak molecular or electrical forces between two very close spheres.

4. General aspects of the expression for the particle stress and comparison with other work

Our general expression for the particle stress in a suspension of spherical particles, correct to the order c^2, is given in (2.8), with (1.7), (2.10), (3.1) and (3.10) as auxiliary relations. The probability density function $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a)$ depends on $\mathbf{r}$ and t (as well as on b/a and μ'/μ) in a way which involves the history of the bulk flow, or in the case of a steady state, the type of bulk flow (that is, the particular combination of pure straining motion and rigid rotation). The expression for the bulk stress is in general of non-Newtonian form as a consequence of this dependence of P on variables other than r/a (and b/a and μ'/μ). A necessary condition for a Newtonian form for the bulk stress is isotropy of the micro-structure of the medium, and we have seen that the probability density of the vector $\mathbf{r}$ separating two particle centres lacks this spherical symmetry in general although it has it in the case of a bulk flow such that every trajectory of one particle centre relative to another is open and comes from infinity.

The expression (2.8) for the particle stress takes an illuminating form if we carry out the integration with respect to $\mathbf{r}$ explicitly over the region $r < a+b$, where $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) = 0$. We find from (1.7) that the average value of $e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b)$ over all directions of $\mathbf{r}$ is E_{ij} when $r > b$, showing that there is zero contribution to the integral in (2.8) from the range $b < r < a+b$. For the integral of the local rate of strain over the interior of the spherical particle of radius b we have

$$\int_{r<b} e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b)\, d\mathbf{r} = \int_{r=b} \tfrac{1}{2}(n_i\delta_{jk} + n_j\delta_{ik})\, u_k(\mathbf{x}_0+\mathbf{r}; \mathbf{x}_0, b)\, dA(\mathbf{r}),$$
$$= \tfrac{4}{3}\pi b^3(1-\alpha)\, E_{ij} \tag{4.1}$$

after use of the expression (1.4) (with a replaced by b) for the velocity distribution associated with a single spherical particle. Hence (2.8) may be written as

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij}$$
$$= 5c^2\alpha^2\mu E_{ij} + 5n^2\alpha\mu \int_0^\infty \int_0^\infty \int_{r \geqslant a+b} \tfrac{4}{3}\pi a^3 \left[\left\{ \frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} - E_{ij} \right\} p(\mathbf{r}, t) \right.$$
$$\left. - \{e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b) - E_{ij}\} \right] g(a)\, g(b)\, d\mathbf{r}\, da\, db + o(c^2). \quad (4.2)$$

Now the average value of the rate of strain over the ambient fluid of viscosity μ within a volume V of the suspension is equal to

$$\frac{E_{ij}}{1-c} - \frac{c}{1-c} \times \text{(average of } e_{ij} \text{ over the interior of particles within } V\text{)},$$

which may be seen from (4.1) to be

$$E_{ij}(1+\alpha c) \quad (4.3)$$

correct to order c. The first term on the right-hand side of (4.2) is thus simply the contribution of order c^2 to the particle stress due to this average increase in the ambient rate of strain experienced by each particle. This first term represents a kinematic type of interaction between particles, whereby the effect of adding another particle to the suspension is to replace some of the ambient fluid by a particle and so to increase the average rate of strain over the reduced volume of ambient fluid.

We obtain another view of the significance of the first term on the right-hand side of (4.2) by noting that, if the particles in the suspension are far apart from each other, with the distances between nearest neighbours being characterized by $l \gg a+b$ (a situation which is possible in a moving suspension only temporarily), the second term on the right-hand side of (4.2) is of smaller order than c^2. This follows from the fact that for such a suspension $p(\mathbf{r})$ is zero for $r/(a+b)$ less than a number of order $l/(a+b)$ and is of order unity for larger values of $r/(a+b)$; and since the integrand in (4.2) is of smaller order than $(a+b)^3/r^3$ when $(a+b)/r \ll 1$, the integral with respect to $\mathbf{r}$ is equal to $a^3b^3E_{ij}$ times a small number and the whole of the second term is $o(c^2)$. In a suspension of spherical particles well separated from each other, the interaction between the particles is (instantaneously) wholly of the above kinematic type, so far as the term of order c^2 in (4.2) is concerned.

The result, that the term of order c^2 in the expression for the bulk stress in a suspension of well-separated spherical particles has the Newtonian form and corresponds to a contribution to the effective viscosity equal to $\frac{5}{2}c^2\alpha^2\mu$, agrees with that found recently by Walpole (1972) by a quite different method for the case of spherical particles of equal size without surface tension (for which α has the form (1.6)). Walpole was concerned primarily with the analogous problem for elastic media (with compressibility), for which the assumed wide separation of the particles is a possible, although perhaps not a realistic, permanent property.

His method of solution depends critically on the assumption that the distributions of velocity and stress near one particle are the same as if that particle were immersed in fluid whose ambient rate of strain is uniform with the average value (for an incompressible medium) $E_{ij}(1+\alpha c)$, as is permissible if each particle is in the 'far-field' of influence of all other particles.

A link may also be made with the work by Hashin (1964*a*) on mathematical bounds to the effective viscosity of an isotropic suspension of particles of arbitrary shape and internal viscosity μ' (and with zero surface tension at the interface). By use of a variational principle Hashin found that the effective viscosity must lie between

$$\mu+\frac{c\mu}{\frac{2}{5}(1-c)+\mu/(\mu'-\mu)} \quad \text{and} \quad \mu'+\frac{(1-c)\mu'}{\frac{3}{5}c+\mu'/(\mu-\mu')},$$

without restriction on c. When $c \ll 1$, these bounds may be written as

$$\mu\{1+\tfrac{5}{2}c\alpha+\tfrac{5}{2}c^2\alpha^2+O(c^3)\}$$

and

$$\mu'\left\{1-\tfrac{5}{2}c\alpha\,\frac{2\mu'+3\mu}{3\mu'+2\mu}+\tfrac{5}{2}c^2\alpha^2\left(\frac{2\mu'+3\mu}{3\mu'+2\mu}\right)^2+O(c^3)\right\}.$$

We see that the first of these two bounds, which is the lower bound when $\mu' > \mu$ and the upper bound when $\mu' < \mu$, coincides with the actual effective viscosity for a suspension of spherical particles as far as the term of order c and with the actual effective viscosity for a suspension of well-separated spherical particles as far as the term of order c^2. The reason for this coincidence is not wholly clear, but may be connected with Hashin's choice of a trial stress distribution, for use in the variational principle, which is *uniform* within a particle; this is an actual property of the stress distribution for spherical particles without surface tension both in the approximation for small c which neglects all particle interactions (for see (1.4), which shows a linear velocity distribution within the sphere when (1.6) holds) and in an improved approximation which allows for interactions on the assumption that any one particle is in the far-field of influence of every other particle and so is still effectively immersed in fluid with uniform ambient rate of strain. So far as the influence of particle shape is concerned, Walpole (1972) gives reasons for believing that spheres represent an extreme case so that, if one of Hashin's bounds is to be realized by an actual isotropic suspension, it would necessarily be a suspension of spherical particles.

As a by-product of Hashin's results, we note that if our suspension of spherical particles has isotropic structure, as it does have when $p(\mathbf{r})$ is a function of r alone, the second term on the right-hand side of (4.2) is a multiple of E_{ij} which, in the case of particles without surface tension, must be positive if $\mu' > \mu$ and negative if $\mu' < \mu$. Our detailed result in §5 for the case $\mu'/\mu = \infty$ is consistent with this.

Bounds on the effective viscosity of an isotropic suspension of arbitrary concentration have also been obtained by Keller, Rubenfeld & Molyneux (1967), for particles which are permanently spherical and have internal viscosity μ' (so that the expressions for α and β in (1.5) are applicable). They constructed upper and lower bounds to the rate of dissipation within a sphere concentric with a particle and containing only that one particle, and then found upper and lower bounds to the mean rate of dissipation in the whole suspension by integration over all values of the radius of the outer spherical boundary weighted according to a probability density for the distance of the nearest neighbour to the reference particle. The upper and lower bounds coincide with the actual effective viscosity as far as the term of order c, as one would expect from the method. The upper and lower bounds to the coefficient of c^2 in the expression for $\mathring{\mu}/\mu$ depend significantly on the arrangement of the spheres, and are found in the case of sphere centres arranged (instantaneously) on a simple cubic lattice to be

$$\frac{375}{4\pi}\alpha^2 \quad \text{and} \quad -\frac{3375}{38\pi}\alpha^2.$$

It is difficult to extract specific results applicable to a random arrangement of spheres from the work of these authors.

The obstacle to analytical progress represented by the lack of absolute convergence of an integral of (2.4) over all particle pairs was recognized explicitly by Peterson & Fixman (1963) in a paper which, perhaps through being difficult to follow, has not received appropriate recognition in the literature on the rheology of suspensions. These authors appear to give essentially the same solution to this difficulty as that described in § 2 of this paper, and they obtain an expression for the bulk stress in a suspension of identical rigid spheres correct to order c^2 which is equivalent to the appropriate special form of (4.2) aside from one important difference. They took it for granted that all physically possible separations of two rigid spheres are equally probable, that is, that $p(\mathbf{r}) = 1$ for $r \geqslant a+b$, one consequence of which is that their bulk stress takes the Newtonian form. Their evaluation of the integral in the expression for the effective viscosity was also inaccurate (see § 7 for a further comment on this), but this is only a matter of detail.

A paper with the same general purpose as the present work has recently been published by Cox & Brenner (1971). These authors claim to obtain a formal expression for the bulk stress in a suspension of force-free rigid particles of arbitrary shape and concentration, and they expand this expression in powers of the concentration and of the ratio of the particle dimension to the length scale of the bulk flow. We do not understand the principles of their calculation sufficiently to be able to summarize them, but we note that there is no reference to integrals which are not absolutely convergent and that the coefficient of c^2 in their expression for the bulk stress appears to be different from our own. At an early stage of their calculation they take averages of interaction effects over all orientations of the particles concerned, and it is possible that this process is equivalent to a particular order of integration among the scalar variables of a multi-dimensional integral which is not absolutely convergent.

There have been many other attempts to determine the c^2-term in the expression for the bulk stress in a suspension of particles but none, so far as we know, which are free from hypotheses of uncertain validity.

5. The effective viscosity of the suspension in a steady pure straining motion

We have seen that evaluation of the integral in (2.8) or (4.2) is not yet possible for a general type of linear bulk flow (that is, for arbitrary relative amounts of pure straining and rigid rotation), owing to uncertainty about the form of the probability density function $p(\mathbf{r}, t)$ in the region of $\mathbf{r}$-space occupied by trajectories of one particle centre relative to another which are closed and do not come from infinity. For one particular type of bulk flow, viz. steady pure straining motion (for which $\mathbf{\Omega} = 0$), the difficulty disappears, because the trajectories of the centre of one spherical particle relative to another fill the *whole* of the accessible part of $\mathbf{r}$-space in that case. (This is self-evident, although lack of knowledge of the values of the functions A and B in the expression (3.2) for the relative velocity $\mathbf{V}$ for any except the case of rigid spheres considered in paper I makes a formal proof difficult.)

For this case of a bulk steady pure straining motion, then, the probability density function $p(\mathbf{r}, t)$ has the form $q(r)$ over the whole of the region $r \geqslant a+b$, and the integral with respect to $\mathbf{r}$ in the expression (4.2) for the particle stress becomes

$$\int_{r \geqslant a+b} \left[\left\{ \frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0 + \mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} - E_{ij} \right\} q\left(\frac{r}{a}, \frac{b}{a}\right) - \{e_{ij}(\mathbf{x}_0; \mathbf{x}_0 + \mathbf{r}, b) - E_{ij}\} \right] d\mathbf{r}. \quad (5.1)$$

The directional properties of the force dipole strength tensor S_{ij} are already known (formally) from (2.10), and it is convenient now to carry out the integration in (5.1) with respect to the direction of $\mathbf{r}$ in the manner indicated by (2.12). (This is a legitimate operation, because the integrand is of smaller order than $(a+b)^3/r^3$ when $(a+b)/r \ll 1$ and the way in which the integration with respect to $\mathbf{r}$ is carried out is immaterial.) The average value of $e_{ij}(\mathbf{x}_0; \mathbf{x}_0 + \mathbf{r}, b)$ over all directions of $\mathbf{r}$ is E_{ij} (when $r > b$), and so (4.2) may be rewritten as

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij} = 5c^2\alpha^2\mu E_{ij} + 20\pi n^2 \alpha\mu E_{ij} \int_0^\infty \int_0^\infty \tfrac{4}{3}\pi a^3 \int_{a+b}^\infty J q r^2\, dr\, g(a)\, g(b)\, da\, db + o(c^2), \quad (5.2)$$

where, it will be recalled,

$$J = K + \tfrac{2}{3}L + \tfrac{2}{15}M, \quad (5.3)$$

K, L, M being defined by (2.10) as functions of r/a and b/a alone.

Before going further with the manipulation of (5.2), we observe that the term of order c^2 in the expression for the particle stress now has the Newtonian form. This important conclusion has been established only for a steady bulk pure straining motion, and is of course a direct consequence of the isotropy of the two-particle structure of the suspension which in turn is a consequence of the open form of all trajectories of one particle centre relative to another.

The Newtonian stress form (5.2) implies that, to order c^2, the suspension can be characterized by an effective viscosity μ^* given by

$$\frac{\mu^*}{\mu} = 1 + \tfrac{5}{2}c\alpha + c^2 \left\{ \tfrac{5}{2}\alpha^2 + \frac{15\alpha}{2v^2} \int_0^\infty \int_0^\infty I\left(\frac{b}{a}\right) \tfrac{4}{3}\pi a^3 \tfrac{4}{3}\pi b^3 g(a)\, g(b)\, da\, db \right\}, \quad (5.4)$$

where $$I\left(\frac{b}{a}\right) = \frac{1}{b^3}\int_{a+b}^{\infty} J\left(\frac{r}{a},\frac{b}{a}\right) q\left(\frac{r}{a},\frac{b}{a}\right) r^2 dr, \tag{5.5}$$

and $$v = \frac{c}{n} = \int_0^{\infty} \tfrac{4}{3}\pi a^3 g(a)\, da$$

is the mean volume of a sphere.

We cannot proceed further with a discussion of the value of $\mathring{\mu}/\mu$ for a mixture of sphere sizes, since no information about the functions J and q is available for $b/a \neq 1$, except the asymptotic forms (2.13) and (3.14) for $r/(a+b) \gg 1$.

Enough is known about the functions q and J for the case $b/a = 1$, $\mu'/\mu = \infty$ to allow an estimate of $\mathring{\mu}/\mu$ for a suspension of identical rigid spheres, for which (5.4) and (5.5) reduce to

$$\frac{\mathring{\mu}}{\mu} = 1+\tfrac{5}{2}c + c^2\left\{\frac{5}{2}+\frac{15}{2}\int_2^{\infty} J(\zeta)q(\zeta)\zeta^2 d\zeta\right\}, \tag{5.6}$$

where $\zeta = r/a$. In §3 we have described the function $q(\zeta)$ over the whole of the range $2 \leqslant \zeta < \infty$: an (approximate) analytical asymptotic form near $\zeta = 2$ where q is infinite, an asymptotic form as $\zeta \to \infty$, and numerical values over the intermediate range (see table 1 and figure 1). The available picture of $J(\zeta)$ is less complete, in that we know only the value of $J(\zeta)$ at $\zeta = 2$ and the asymptotic form as $\zeta \to \infty$, and for values in the intermediate range it is necessary to use the rough interpolation between these two extremes shown in figure 1. We may now evaluate the integral in (5.6) by dividing the range of integration into three parts in exactly the same way that was done with the integral (3.17).

For the part of the range $2 \leqslant \zeta \leqslant 2{\cdot}0025$ we have

$$\int_2^{2\cdot0025} J(\zeta)q(\zeta)\zeta^2 d\zeta \approx J(2)\int_2^{2\cdot0025} q(\zeta)\zeta^2 d\zeta,$$
$$= 0{\cdot}2214 \times 0{\cdot}596 = 0{\cdot}132$$

in view of (2.14) and (3.18). For the central portion $2{\cdot}0025 \leqslant \zeta \leqslant 3{\cdot}0$ in which $J(\zeta)$ and $q(\zeta)$ are known only numerically (from table 1 and figure 1), we find by numerical integration that the contribution to the integral is 0·449. And for the outer part, $3{\cdot}0 \leqslant \zeta < \infty$, we may use the asymptotic forms (2.13) and (3.14) to find

$$\int_3^{\infty} J(\zeta)q(\zeta)\zeta^2 d\zeta \approx \frac{15}{2}\int_3^{\infty} \zeta^{-4} d\zeta = 0{\cdot}093.$$

Hence our estimate is

$$\frac{15}{2}\int_2^{\infty} J(\zeta)q(\zeta)\zeta^2 d\zeta \approx \tfrac{15}{2}(0{\cdot}132+0{\cdot}449+0{\cdot}093) = 5{\cdot}06, \tag{5.7}$$

whence $$\frac{\mathring{\mu}}{\mu} = 1+\tfrac{5}{2}c + 7{\cdot}6c^2. \tag{5.8}$$

By drawing the curve for J in figure 1 in different ways consistent with the end constraints, we find that the second of the above three contributions within brackets in (5.7) might be in error by about 0·06. There are also inaccuracies associated with the values of $q(r)$, especially near $r/a = 2$, which led to an error of 7·7 per cent in our evaluation of the integral (3.17). This suggests that the coefficient of c^2 in (5.8) is correct to within about 10 per cent. Further detailed work will be needed before the value of the coefficient of c^2 is known precisely. Our formula for $\mathring{\mu}$ shows exactly what quantities should be computed.

The quadratic term in the expression for $\mathring{\mu}/\mu$ is sometimes written as $k(2{\cdot}5c)^2$, with k being termed the Huggins constant, and our estimate (5.8) for rigid spheres of uniform size corresponds to

$$k = 1{\cdot}22.$$

These conclusions concerning a steady pure straining motion will apply also to an unsteady pure straining motion provided that the variation of the bulk flow does not prevent one sphere from escaping from the neighbourhood of another. Steady rotation of the principal axes of a two-dimensional pure straining motion relative to the fluid yields a steady simple shearing motion when viewed relative to rotating axes, so it is clear that in *some* kinds of time-dependent pure straining motions there are closed trajectories.

6. Steady simple shearing motion of the suspension

The important case of bulk flow having the form of steady simple shearing presents special difficulties which have yet to be overcome, and we shall not do more here than offer a few preliminary remarks. We choose the bulk velocity to have components $(\kappa x_2, 0, 0)$ relative to rectilinear coordinates (x_1, x_2, x_3), whence

$$\mathbf{E} = \begin{pmatrix} 0 & \frac{1}{2}\kappa & 0 \\ \frac{1}{2}\kappa & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \text{and} \quad \mathbf{\Omega} = (0, 0, -\tfrac{1}{2}\kappa). \tag{6.1}$$

The difficulties are associated with the existence of an extensive region of closed trajectories of one sphere centre relative to another. The existence of closed trajectories in steady simple shearing motion is known from both observation and theory, and an analytical description of them is given in paper I. (Figure 4 of that paper shows some of the closed trajectories for two rigid spheres of the same size.) The region occupied by closed trajectories is bounded internally by the spherical surface $r = a+b$ and externally by a surface of revolution about the x_2-axis which extends to infinity in the x_1- and x_3-directions and is asymptotically of the form $r_2 \sim r^{-\frac{3}{2}}$ for any value of the internal viscosity of a particle. The region of closed trajectories thus has infinite volume.

In the region occupied by open trajectories, the probability density function $p(\mathbf{r}, t)$ is equal to $q(r)$ everywhere. On the other hand, the relation between the constant values of $p(\mathbf{r}, t)/q(r)$ for different material points in the region of closed trajectories is not determinable from steady-state convective action in $\mathbf{r}$-space alone. In this region $p(\mathbf{r}, t)$ is determined by two-particle convective action from some assumed initial condition or by the steady-state balance of both two-particle convection and some additional process such as Brownian motion or three-particle encounters.

Whatever the means by which the indeterminacy is removed, considerations of symmetry show that the resulting probability density function $p(\mathbf{r}, t)$ must be an even function of $\mathbf{r}$ and of r_3.

For a bulk steady simple shearing motion represented by (6.1), the general expression (2.10) for the force dipole strength of one spherical particle in the presence of another reduces to

$$\frac{S_{ij}(\mathbf{x}_0, a; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} = \tfrac{1}{2}\kappa(\delta_{i1}\delta_{j2}+\delta_{i2}\delta_{j1})(1+K)+\kappa\left\{\frac{r_1}{2r^2}(r_i\delta_{j2}+r_j\delta_{i2}) + \frac{r_2}{2r^2}(r_i\delta_{j1}+r_j\delta_{i1}) - \frac{r_1 r_2}{r^2}\tfrac{2}{3}\delta_{ij}\right\}L + \kappa\frac{r_1 r_2}{r^2}\left(\frac{r_i r_j}{r^2}-\tfrac{1}{3}\delta_{ij}\right)M. \quad (6.2)$$

The expression for the particle stress also involves the rate of strain due to a single spherical particle, which in general is given by (1.7) and here reduces to

$$\frac{e_{ij}(\mathbf{x}_0; \mathbf{x}_0+\mathbf{r}, b)}{\frac{20}{3}\pi a^3 \alpha\mu} = \tfrac{1}{2}\kappa(\delta_{i1}\delta_{j2}+\delta_{i2}\delta_{j1})\left(1-\frac{\beta b^5}{r^5}\right)+\kappa\left\{\frac{r_1}{2r^2}(r_i\delta_{j2}+r_j\delta_{i2}) + \frac{r_2}{2r^2}(r_i\delta_{j1}+r_j\delta_{i1}) - \frac{r_1 r_2}{r^2}\tfrac{2}{3}\delta_{ij}\right\}\left(-\frac{5\alpha b^3}{2r^3}+\frac{5\beta b^5}{r^5}\right) + \kappa\frac{r_1 r_2}{r^2}\left(\frac{r_i r_j}{r^2}-\tfrac{1}{3}\delta_{ij}\right)\left(\frac{25\alpha b^3}{2r^3}-\frac{35\beta b^5}{2r^5}\right) \quad (6.3)$$

for $r > b$. These two expressions are to be substituted in (4.2). Since $p(\mathbf{r})$ is necessarily an even function of r_3, any term in (6.2) which is an odd function of r_3 makes zero contribution to the integral in (4.2); and any term in (6.3) which is an odd function of r_1, r_2 or r_3 makes zero contribution to the integral. Hence for steady simple shearing motion (4.2) becomes

$$\Sigma_{ij}^{(p)} - 5c\alpha\mu E_{ij} = 5c^2\alpha^2\mu E_{ij} + 5n^2\alpha\mu\kappa\int_0^\infty\int_0^\infty\int_{r\geqslant a+b}^\infty [\ldots]\tfrac{4}{3}\pi a^3 g(a)g(b)\,d\mathbf{r}\,da\,db + o(c^2), \quad (6.4)$$

in which the components of the tensor expression within the square brackets are as follows:

$\Sigma_{11}^{(p)}$	$\frac{r_1 r_2}{r^2}\left\{\tfrac{1}{3}L+\left(\frac{r_1^2}{r^2}-\frac{1}{3}\right)M\right\}p(\mathbf{r},t),$
$\Sigma_{22}^{(p)}$	$\frac{r_1 r_2}{r^2}\left\{\tfrac{1}{3}L+\left(\frac{r_2^2}{r^2}-\frac{1}{3}\right)M\right\}p(\mathbf{r},t),$
$\Sigma_{33}^{(p)}$	$\frac{r_1 r_2}{r^2}\left\{-\tfrac{2}{3}L+\left(\frac{r_3^2}{r^2}-\frac{1}{3}\right)M\right\}p(\mathbf{r},t),$
$\Sigma_{12}^{(p)}$, $\Sigma_{21}^{(p)}$	$\left\{\tfrac{1}{2}K+\frac{r_1^2+r_2^2}{2r^2}L+\frac{r_1^2 r_2^2}{r^4}M\right\}p(\mathbf{r},t)+\frac{\beta b^5}{2r^5} + \frac{r_1^2+r_2^2}{2r^2}\left(\frac{5\alpha b^3}{2r^3}-\frac{5\beta b^5}{r^5}\right)-\frac{r_1^2 r_2^2}{r^4}\left(\frac{25\alpha b^3}{2r^3}-\frac{35\beta b^5}{2r^5}\right),$
$\Sigma_{23}^{(p)}$, $\Sigma_{32}^{(p)}$, $\Sigma_{31}^{(p)}$, $\Sigma_{13}^{(p)}$	0.

The normal stresses are zero if the probability density function $p(\mathbf{r}, t)$ is an even function of each of r_1 and r_2, as it is when only the processes represented by equation (3.5) are involved, but this symmetry is likely to be lost when effects of Brownian motion or of three-particle encounters are introduced and the normal stresses will in general have different values. The most important stress component is the shearing stress $\Sigma_{12}^{(p)}$, and the quantity which in practice will be interpreted as an effective viscosity for steady shearing motion of the suspension is Σ_{12}/κ. For a suspension of identical spherical particles this ratio is given by

$$\frac{\Sigma_{12}}{\kappa\mu} = 1+\tfrac{5}{2}c\alpha+\tfrac{5}{2}c^2\alpha^2+\frac{15c^2\alpha}{4\pi a^3}\int_{r\geqslant 2a}\left[\tfrac{1}{2}Kp(\mathbf{r},t)+\frac{\beta a^5}{2r^5}+\frac{r_1^2+r_2^2}{2r^2}\left\{Lp(\mathbf{r},t)+\frac{5\alpha a^3}{2r^3}-\frac{5\beta a^5}{r^5}\right\}\right.$$
$$\left.+\frac{r_1^2r_2^2}{r^4}\left\{Mp(\mathbf{r},t)-\frac{25\alpha a^3}{2r^3}+\frac{35\beta a^5}{2r^5}\right\}\right]d\mathbf{r}+o(c^2). \quad (6.5)$$

In order to go further with the calculation of this shearing stress it will thus be necessary to use the available information about the functions K, L and M separately (and not simply in the combination represented by J) and, in addition, to investigate the form of the probability density $p(\mathbf{r},t)$ in the region of closed trajectories.

It is mathematically and physically possible for $p(\mathbf{r},t)/q(r)$ to be equal to unity everywhere, outside and inside the region of closed streamlines, in which case the particle stress has the Newtonian form (to order c^2) and the effective viscosity of the suspension has the same value as for a bulk steady pure straining motion. This form for $p(\mathbf{r},t)$ in the region of closed trajectories is permanent, so far as two-particle convective action alone is concerned, but it could be realized only by giving the particles the appropriate statistical distribution at some initial instant (as a 'thought' experiment one might imagine the suspension to be subjected to a steady pure straining motion for a time in order to establish the required initial state for the steady simple shearing motion). A more realistic initial condition might be $p(\mathbf{r},t_0) = 1$ everywhere in the region of closed trajectories, corresponding to the suspension being well stirred before being given the prescribed bulk motion. (This is analogous to the Eisenschitz assumption in the calculation of the particle stress in a dilute suspension of rod-like particles subjected to a steady simple shearing motion.) The function $p(\mathbf{r},t)$ at any subsequent t then follows from (3.10) and in principle the particle stress could be calculated. Such a calculation would be of limited value because it seems certain that in due course some additional process neglected in the above analysis would influence the relation between the values of $p(\mathbf{r},t)/q(r)$ for different material points in the region of closed trajectories and establish a steady state which is independent of the initial conditions. There appears to be no alternative but to consider the effect of either Brownian motion or three-particle encounters on the probability density function for the vector separation of two particles.

7. The analogous problem of elastic behaviour of a solid suspension

It is well known that the problem of determining the mean elastic stress in a 'suspension' of incompressible elastic particles embedded in an incompressible elastic matrix is mathematically identical in certain respects to that considered in this paper (Hashin 1964*b*). Rate of strain in the fluid suspension is the analogue of total strain in the elastic suspension. The Newtonian behaviour of the ambient fluid with viscosity μ corresponds to the matrix being composed of homogeneous isotropic elastic material with shear modulus μ, and the same holds for the particles. Surface tension at the boundary of a particle plays no part in the elastic problem, so in the case of spherical particles the relevant values of α and β are those given by (1.6).

The equivalence of the two problems holds provided the statistical properties of the particle arrangement in the suspension are given. The formal relation (2.8) or (4.2) between the bulk stress and the properties of two-particle interactions can then be employed in either of the two problems. However, the way in which the properties of the particle arrangement are determined is different in the two cases. In the fluid suspension case, the existence of the bulk motion has an important influence on the probability density $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a)$ and may even determine it fully, whereas in the solid suspension the existence of an infinitesimal strain has negligible effect on the statistical properties of the particle arrangement.

Thus when using (2.8) or (4.2) to calculate the elastic behaviour of a solid suspension of spherical particles, we ignore the dependence of $P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a)$ on the bulk motion described in § 3 and instead make an a priori assumption about the state of the suspension on the basis of available information about the way it was manufactured. In the absence of specific information, the most natural assumption is that the suspension was well stirred in a random fashion during manufacture and that all physically possible positions of one particle centre relative to another are equally probable, that is,

$$np(\mathbf{r}, t) \equiv P(\mathbf{x}_0+\mathbf{r}, b|\mathbf{x}_0, a) = n \tag{7.1}$$

for $r \geqslant a+b$. The spherical symmetry of this form for the probability density for the separation of two particle centres leads to a 'Newtonian' form for the term of order c^2 in the expression for the bulk stress, as in the case of a fluid suspension subjected to a bulk steady pure straining motion, and the relations in § 5 can be adapted to suit the present context simply by the formal step of putting $q(r) = 1$. In particular, (5.4), together with (5.5) in which $q = 1$, is now available as a rigorous expression for the effective shear modulus of an incompressible solid suspension of spherical particles of different sizes. Note that there is no restriction of this result for an elastic suspension to cases of pure strain.

We can go further and give approximate numerical results in the case of a solid suspension of rigid spheres of uniform size. For that case we see from (5.6) that the ratio of the effective shear modulus of the suspension to the shear modulus of the matrix material is

$$\frac{\overset{*}{\mu}}{\mu} = 1+\tfrac{5}{2}c+c^2\left\{\frac{5}{2}+\frac{15}{2}\int_2^\infty J(\zeta)\,\zeta^2 d\zeta\right\}, \tag{7.2}$$

where $\zeta = r/a$ and the function $J(\zeta)$ is known roughly from the interpolation shown in figure 1. The integrand here is not singular at $\zeta = 2$, unlike that in (5.6). For the part of the range $2 \leqslant \zeta \leqslant 3{\cdot}0$, we find by numerical integration that the contribution to the integral in (7.2) is 0·267. For $3{\cdot}0 \leqslant \zeta < \infty$, we may use the asymptotic form (2.13) for J, giving a contribution 0·093. Hence our estimate is

$$\frac{15}{2}\int_2^\infty J(\zeta)\,\zeta^2 d\zeta \approx \tfrac{15}{2}(0{\cdot}267+0{\cdot}093) = 2{\cdot}70,$$

whence

$$\frac{\overset{*}{\mu}}{\mu} = 1+\tfrac{5}{2}c+5{\cdot}2c^2. \tag{7.3}$$

As in §5, we find by varying the curve in figure 1 for J that the first of the contributions to the integral might be in error by 0·04, suggesting the coefficient of c^2 in (7·3) is correct to within about $\pm 0{\cdot}3$.

The numbers in (7.3) may be compared with those obtained by Peterson & Fixman (1963) for a fluid suspension of rigid spheres of uniform size. They assumed that for all linear bulk flows the probability density for the pair separation vector is given by (7.1), which, as we have seen, is incorrect for a fluid suspension but may be appropriate for a solid suspension. For the determination of the function J they used a far-field expansion (with a larger number of terms than in (2.13)), which is inevitably inaccurate in the important range of values of r/a near 2. Their estimate of the integral in (7.2) was 0·243 (whereas ours is 0·360), and their result for the numerical coefficient of c^2 in the effective viscosity (or shear modulus) was 4·3.

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