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The effect of Brownian motion on the bulk stress in a suspension of spherical particles

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The effect of Brownian motion of particles in a statistically homogeneous suspension is to tend to make uniform the joint probability density functions for the relative positions of particles, in opposition to the tendency of a deforming motion of the suspension to make some particle configurations more common. This smoothing process of Brownian motion can be represented by the action of coupled or interactive steady 'thermodynamic' forces on the particles, which have two effects relevant to the bulk stress in the suspension. Firstly, the system of thermodynamic forces on particles makes a direct contribution to the bulk stress; and, secondly, thermodynamic forces change the statistical properties of the relative positions of particles and so affect the bulk stress indirectly. These two effects are analysed for a suspension of rigid spherical particles. In the case of a dilute suspension both the direct and indirect contributions to the bulk stress due to Brownian motion are of order ϕ^2, where $\phi(\ll 1)$ is the volume fraction of the particles, and an explicit expression for this leading approximation is constructed in terms of hydrodynamic interactions between pairs of particles. The differential equation representing the effects of the bulk deforming motion and the Brownian motion on the probability density of the separation vector of particle pairs in a dilute suspension is also investigated, and is solved numerically for the case of relatively strong Brownian motion. The suspension has approximately isotropic structure in this case, regardless of the nature of the bulk flow, and the effective viscosity representing the stress system to order ϕ^2 is found to be

$$\mu^* = \mu(1 + 2{\cdot}5\phi + 6{\cdot}2\phi^2).$$

The value of the coefficient of ϕ^2 for steady pure straining motion in the case of weak Brownian motion is known to be 7·6, which indicates a small degree of 'strain thickening' in the ϕ^2-term.

1. Introduction

It has been known for some time that Brownian motion has an important effect on the rheological properties of a suspension of small particles. This is usually manifested as a dependence of one of the rheological parameters, for example the mean shear stress divided by the mean rate of shear, on the dimensionless ratio $\mu a^3 E/kT$, where μ is the viscosity of the (Newtonian) suspending fluid, a is a linear dimension of the particles, E is the relevant mean velocity gradient, k is Boltzmann's constant and T the absolute temperature. The parameter $\mu a^3 E/kT$ can be regarded as a measure of the ratio of the rate of change of some quantity due to convective or hydrodynamic effects and that due to Brownian diffusion. For steady simple shear flow of a dilute suspension of prolate spheroidal particles, for example, the ratio of mean shear stress to mean rate of shear varies monotonically between a stationary value at $\mu a^3 E/kT \ll 1$ and a second stationary value at $\mu a^3 E/kT \gg 1$ which is smaller, by a factor which is large in the case of long thin particles (Hinch & Leal 1972). 'Shear thinning' behaviour of this kind is readily explained by the tendency for the bulk flow to align the largest diameter of the particles preferentially with the mean streamlines, in opposition to the orientational spreading effect of Brownian motion. It is not at all easy to see what might be expected in the case of a suspension of spherical particles on which orientational diffusion of individual particles has no effect.

If a suspension of rigid spherical particles in a Newtonian fluid is so dilute that for hydrodynamic purposes each particle may be regarded as being alone in infinite fluid, the suspension is isotropic in structure and is characterized by an effective viscosity μ^* given, as found first by Einstein (1906), by

$$\mu^* = \mu(1+\tfrac{5}{2}\phi) \tag{1.1}$$

correct to the order of ϕ, the volume fraction of the particles. Brownian motion of an isolated particle has no influence on the velocity and stress in the fluid due to the presence of the particle in the bulk flow, and so the result (1.1) is independent of Brownian motion. Outside the small range of values of ϕ for which (1.1) is a good approximation (usually accepted as $\phi < 0{\cdot}02$), the effect of hydrodynamic interactions is important. We shall see that, when hydrodynamic interactions are relevant, so too is Brownian motion; both effects make their first appearance in the expression for the mean stress when terms of order ϕ^2 are considered.

This paper has both a general and a specific purpose. The general purpose is to give a theoretical analysis of the way in which Brownian motion affects the bulk stress in a suspension of (hydrodynamically) interacting rigid spherical particles which is being deformed, and in particular to derive an explicit expression for the rather mysterious direct contribution to the bulk stress made by Brownian motion. The specific purpose is to describe a calculation of the bulk stress in a dilute suspension correct to order ϕ^2 for the case of dominant Brownian motion ($\mu a^3 E/kT \ll 1$).

The specific calculation of the bulk stress to order ϕ^2 described herein is based on the work of two previous publications concerned with suspensions of spherical particles, one about the effect of hydrodynamic interaction of pairs of spheres, in the absence of Brownian motion, on the rheological properties of the suspension (Batchelor & Green 1972*b*) and the other about the effect of hydrodynamic interaction of spheres on the diffusional properties of spherical particles (Batchelor 1976). The result of the first paper was an expression for the bulk stress in the suspension, in the absence of Brownian motion, correct to order ϕ^2. The calculation could not be completed numerically for the particular case of a bulk steady simple shearing motion because the probability distribution of particle pairs is then not fully determinate in the absence of Brownian motion, but for a bulk pure straining motion it was found that the bulk stress is of Newtonian form with the effective viscosity

$$\mu^* = \mu\{1+\tfrac{5}{2}\phi+7{\cdot}6\phi^2+O(\phi^3)\}. \tag{1.2}$$

Extension of this calculation of the mean stress to order ϕ^2 to include the effect of Brownian motion of the particles requires use of the results obtained in the second of the two papers mentioned, in which the classical expression for the Brownian diffusivity of effectively isolated spherical particles was generalized to take account of hydrodynamic interactions between pairs of particles.

Our later discussion of the direct contribution to the bulk stress made by Brownian motion will be based on an important general result concerning Brownian motion. It is that the translational diffusional flux, due to Brownian motion, of a particle in a group of m hydrodynamically interacting particles is the same as that produced by certain steady forces acting on the particles, that on a particle at position $\mathbf{x}_i$ being

$$\mathbf{F}_i = -kT\frac{\partial \log P(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_m)}{\partial \mathbf{x}_i} \quad (i = 1, 2, \ldots, m), \tag{1.3}$$

where $P(\mathbf{x}_1, \ldots, \mathbf{x}_m)$ is the joint probability density function for the positions $\mathbf{x}_1, \ldots, \mathbf{x}_m$ of the m particles. (The expression (1.3) will be used only for values of $\mathbf{x}_1, \ldots, \mathbf{x}_m$ such that the spherical particles do not overlap geometrically. When overlapping positions of the particles are allowed, it is necessary to introduce additional intermolecular forces between particles; but for the case of rigid particles to be considered here we may avoid that by restricting the range of integration of $\mathbf{x}_1, \ldots, \mathbf{x}_m$ to non-overlapping values.) These thermodynamic forces reproduce the statistical bias in the random walks of the particles which results from the non-uniformity of the joint-probability density function. The idea of a 'thermodynamic force' as a determinate artifice for the calculation of diffusional fluxes has long been familiar in macromolecular science, and was used explicitly by Einstein (1905) in his pioneering work on Brownian motion of effectively isolated spherical particles (the case $m = 1$) in a very dilute suspension. Some explanation of, and justification for, the concept of the equivalent thermodynamic force is given in my recent paper (Batchelor 1976).

We are concerned here with a statistically *homogeneous* suspension, for which $P(\mathbf{x}_1, \ldots, \mathbf{x}_m)$ is invariant under translation of the configuration represented by the m points $\mathbf{x}_1, \ldots, \mathbf{x}_m$ and for which, as a consequence,

$$\sum_{i=1}^{m} \mathbf{F}_i = 0. \tag{1.4}$$

For a homogeneous suspension, diffusional flux does not have the common implication of transport of particles relative to spatial axes, but refers to movements of particles relative to each other. Putting it in concrete terms, if, as a consequence of special initial conditions or of the deforming action of a bulk flow, the particle configurations show a preference for, say, close groups, the effect of Brownian motion is to diffuse particles away from each other at a rate which can be calculated from (1.3) and the hydrodynamic relations giving the response of particles to imposed steady forces. This has consequences for the rheological properties of the suspension, because the exertion of forces with zero resultant on a group of particles, and hence on the suspension, contributes to the bulk stress.

The effects of electrical and Van der Waals forces between particles will not be included in our analysis.

2. The general expression for the bulk stress

We recall first the expression for the bulk stress in a homogeneous suspension of small force-free particles subjected to a statistically uniform deforming motion in the absence of Brownian motion (Batchelor 1970). The bulk stress $\mathbf{\Sigma}$ is here equal to the average contact or mechanical stress in the suspension, and an ensemble average, to be denoted by angle brackets, is equal to the average over a volume V containing $N\,(\gg 1)$ particles; hence

$$\begin{aligned}\mathbf{\Sigma}^H = \langle \boldsymbol{\sigma}^H \rangle &= \frac{1}{V}\int_V \boldsymbol{\sigma}^H dV \\ &= \frac{1}{V}\int_{V_f}(-p\mathbf{I}+2\mu\mathbf{e}^H)\,dV + \frac{1}{V}\sum_{i=1}^{N}\int_{V_i}\boldsymbol{\sigma}^H dV, \end{aligned} \tag{2.1}$$

where $\boldsymbol{\sigma}^H$ is the local contact stress, V_f is the volume of the fluid portion of V, V_i is the volume of a particle with centre at $\mathbf{x}_i$, and $\mathbf{e}^H$ is the rate-of-strain tensor at a point in the suspending fluid. The superscript H (for hydrodynamic) provides a reminder that the motion considered is due entirely to the bulk deformation imposed at the outer boundary. All material elements, both in the fluid and in the particles, are in equilibrium under the action of the mechanical stress system alone, whence we have

$$\mathbf{\Sigma}^H = \text{I.T.} + 2\mu\mathbf{E} + \frac{1}{V}\sum_i \mathbf{S}_i^H, \tag{2.2}$$

where I.T. denotes an isotropic term, $\mathbf{E}$ is the average rate-of-strain tensor in the suspension and, for rigid particles,

$$\mathbf{S}_i^H = \int_{A_i}\{(\mathbf{x}-\mathbf{x}_i)\,\boldsymbol{\sigma}^H.\mathbf{n} - \tfrac{1}{3}\mathbf{I}(\mathbf{x}-\mathbf{x}_i).\boldsymbol{\sigma}^H.\mathbf{n}\}\,dA \tag{2.3}$$

is the (deviatoric) force dipole strength of the particle with centre at $\mathbf{x}_i$ obtained from the distribution of contact stress in the suspending fluid over the particle surface A_i. The summation in (2.2) over a large number of identical particles in the volume V is equivalent to N times an average of $\mathbf{S}^H$ over all configurations of the surrounding particles, and we may write

$$\frac{1}{V}\sum_{i=1}^{N}\mathbf{S}^H = n\langle \mathbf{S}^H\rangle,$$

where $n\ (= N/V)$ is the number density of the particles.

These expressions will now be modified to include the effect of Brownian motion of the particles. The statistical properties of the relative positions of particles are of course affected by Brownian motion, and this leads indirectly to an effect on the bulk stress which will be considered later. In this section we are concerned with the direct or explicit change in the expression (2.2) with (2.3) for the bulk stress due to the existence of Brownian motion. This change is an *addition* to the above expression, because for the small particles under consideration the equations governing the fluid motion in the neighbourhood of a particle are linear and the stresses in the fluid due to bulk motion and due to the Brownian motion of particles are superposable.

The key to determination of the direct additional contribution to the bulk stress due to Brownian motion of particles is the principle referred to in the introduction, namely that, when the joint probability density of the positions of a number of particles is non-uniform, the resulting translational diffusion of the particles due to Brownian motion is the same as if, and has the same mechanical consequences as if, each particle were acted on by a certain steady force given by (1.2). According to this principle the additional bulk stress due directly to the existence of Brownian motion of the particles is simply the bulk stress that is generated by the application of coupled forces to particles suspended in fluid otherwise at rest. For the large group of N particles in a volume V of the suspension, the force on a particle of the group with centre at $\mathbf{x}_i$ is as given by (1.3) with $m = N$, and the sum of these forces for $i = 1, \ldots, N$ is zero in view of the statistical homogeneity of the suspension.

It is important to appreciate that the thermodynamic forces should be treated as interactive forces. The actual fluctuating thermal forces on particles which cause the diffusion are exerted by the fluid medium, but the statistical result of the Brownian motion of the particles is the same as if the particles exerted the fictitious steady forces (1.3) on each other. It is as if the particles interacted through the existence of an electric field, or, to construct a mechanical picture, as if the particles were joined to each other by elastic rods which transmit the force but which do not cause any hydrodynamic disturbance in the fluid, the electrical energy of the field or the elastic energy of the system of rods being $kT \log P(\mathbf{x}_1, \ldots, \mathbf{x}_N)$. This is not simply a permissible interpretation, it is essential to hypothesize a thermodynamic field or stress system throughout the medium which satisfies the relations

$$\left.\begin{aligned} \nabla . \boldsymbol{\tau} &= \mathbf{F}_i / V_i \quad \text{at points within a particle at } \mathbf{x}_i \\ &= 0 \qquad\quad \text{at points in the fluid,} \end{aligned}\right\} \tag{2.4}$$

where $\boldsymbol{\tau}$ is the local thermodynamic stress tensor.

We proceed now to consider the direct contribution to the bulk stress due to Brownian motion of the particles ($\boldsymbol{\Sigma}^B$ say), that is, the bulk stress in a suspension in which the mean rate of strain is zero and which is in motion solely as a consequence of the steady forces $\mathbf{F}_i$ exerted on the spheres. There are two kinds of local stress in this Brownian flow system, the mechanical or contact stress $\boldsymbol{\sigma}^B$ (of which the deviatoric part is $2\mu\mathbf{e}^B$ at points in the fluid) and the thermodynamic stress $\boldsymbol{\tau}$, both of which are stationary random functions of position in the suspension. Since inertia forces are negligible everywhere

$$\nabla . (\boldsymbol{\sigma}^B + \boldsymbol{\tau}) = 0. \tag{2.5}$$

The bulk stress is an average of the sum of all the different kinds of local stress, so

$$\boldsymbol{\Sigma}^B = \langle \boldsymbol{\sigma}^B \rangle + \langle \boldsymbol{\tau} \rangle.$$

By repeating the argument that leads to (2.2), we find

$$\begin{aligned} \langle \boldsymbol{\sigma}^B \rangle &= \frac{1}{V} \int_{V_f} \boldsymbol{\sigma}^B dV + \frac{1}{V} \sum_i \int_{V_i} \{\nabla . (\mathbf{x}\boldsymbol{\sigma}^B) - \mathbf{x}\nabla . \boldsymbol{\sigma}^B\}\, dV \\ &= \text{I.T.} + 2\mu\langle \mathbf{e}^B \rangle + \frac{1}{V} \sum_i \mathbf{S}_i^B, \end{aligned} \tag{2.6}$$

where $\mathbf{S}_i^B$ is related to $\boldsymbol{\sigma}^B$ in the way that $\mathbf{S}_i^H$ is related to $\boldsymbol{\sigma}^H$ in (2.3). (And note that whereas inclusion of the term $\mathbf{x}_i$ is arbitrary in (2.3), because

$$\int_{A_i} \boldsymbol{\sigma}^H . \mathbf{n}\, dA = 0,$$

it is essential in the corresponding expression for $\mathbf{S}_i^B$ since $\int_{A_i} \boldsymbol{\sigma}^B . \mathbf{n}\, dA$ is non-zero, being equal to $-\mathbf{F}_i$.) The mean rate of strain in the medium in this flow field is zero, so that $\langle \mathbf{e}^B \rangle = 0$ in (2.6).

To determine the mean thermodynamic stress, we may consider the consequences of a virtual small uniform strain of the configuration of particles in the suspension. The gain in energy of the thermodynamic field in a part of the suspension of volume V containing a large number of particles N may be expressed first as

$$V\mathbf{K} : \langle \boldsymbol{\tau} \rangle,$$

and second as

$$kT\delta \log P = kT \sum_{i=1}^{N} \frac{\partial \log P}{\partial \mathbf{x}_i} . \delta \mathbf{x}_i = -\sum_i \mathbf{F}_i . \mathbf{K} . \mathbf{x}_i,$$

whence we have

$$\langle \boldsymbol{\tau} \rangle = -\frac{1}{V} \sum_{i=1}^{N} \mathbf{x}_i \mathbf{F}_i \tag{2.7}$$

since the virtual strain $\mathbf{K}$ is arbitrary.

The bulk stress due to the thermodynamic forces in a suspension which is otherwise at rest is thus

$$\boldsymbol{\Sigma}^B = \langle \boldsymbol{\sigma}^B \rangle + \langle \boldsymbol{\tau} \rangle = \text{I.T.} + \frac{1}{V} \sum_i (\mathbf{S}_i^B - \mathbf{x}_i \mathbf{F}_i). \tag{2.8}$$

The last term in (2.8) is not affected by the choice of origin of the reference frame because $\sum_i \mathbf{F}_i = 0$. The contribution (2.8) to the bulk stress might be called the diffusion stress. As a partial check on the correctness of (2.8), we note that, if all the particles are members of isolated touching pairs of equal spheres with thermodynamic forces parallel to the line of centres, the mechanical stress $\boldsymbol{\sigma}^B$ is zero everywhere except at the contact point where there is a concentrated contact force $-\mathbf{F}_1$ on one sphere and $-\mathbf{F}_2$ on the other, so that

$$\begin{aligned} \mathbf{S}_1^B + \mathbf{S}_2^B &= -\tfrac{1}{2}(\mathbf{x}_2 - \mathbf{x}_1)\,\mathbf{F}_1 + \tfrac{1}{2}(\mathbf{x}_2 - \mathbf{x}_1)\,\mathbf{F}_2, \\ &= \mathbf{x}_1 \mathbf{F}_1 + \mathbf{x}_2 \mathbf{F}_2 \end{aligned}$$

since $\mathbf{F}_1 = -\mathbf{F}_2$. It appears therefore that $\boldsymbol{\Sigma}^B = 0$ in this case, which is what would be expected when Brownian motion cannot change the configuration of particles. This example also serves to reveal that the term $\mathbf{S}_i^B$ in (2.8) is a consequence of the finite size of the particles.

The bulk stress in a suspension of particles in Brownian motion which is being deformed is now obtained by superimposing the two contributions (2.2) and (2.8):

$$\begin{aligned} \boldsymbol{\Sigma} &= \boldsymbol{\Sigma}^H + \boldsymbol{\Sigma}^B \\ &= \text{I.T.} + 2\mu \mathbf{E} + \frac{1}{V} \sum_{i=1}^{N} (\mathbf{S}_i^H + \mathbf{S}_i^B - \mathbf{x}_i \mathbf{F}_i), \end{aligned} \tag{2.9}$$

where $\mathbf{S}^H$ and $\mathbf{S}^B$ are both given in terms of the mechanical stress at the surface of the particle by (2.3), but the stress distributions are of course different in the two cases. $\mathbf{S}^H$ corresponds to the stress generated in a suspension of force-free spheres without Brownian motion subjected to a deforming motion and $\mathbf{S}^B$ corresponds to the stress generated in the fluid by spheres moving solely under the influence of the thermodynamic forces.

We repeat that, in addition to the direct contribution to the bulk stress due to Brownian motion represented by the last two terms of (2.9), there is an indirect effect of Brownian motion through its influence on the joint-probability-density function $P(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ which appears as a weighting function in the integral expression for the ensemble average of quantities like $\mathbf{S}^H$.

3. An alternative form of the direct Brownian contribution to the bulk stress

We propose here to use the reciprocal theorem for Stokes flow first established by Lorentz (1906) to obtain another form of the contribution (2.8) due to the thermodynamic forces. The reciprocal theorem states that

$$\int \mathbf{u}' \,.\, \boldsymbol{\sigma}'' \,.\, \mathbf{n}\, dA = \int \mathbf{u}'' \,.\, \boldsymbol{\sigma}' \,.\, \mathbf{n}\, dA, \tag{3.1}$$

where $\mathbf{u}'$, $\boldsymbol{\sigma}'$ and $\mathbf{u}''$, $\boldsymbol{\sigma}''$ denote the fluid velocity and mechanical stress in two alternative Stokes flow systems for fluid occupying a certain region and the integrals are taken over the whole of the surface bounding this region. We choose a region of volume V with exterior boundary A and bounded internally by N equal rigid spheres with centres at $\mathbf{x}_1, \ldots, \mathbf{x}_N$ and surfaces $A_1, \ldots, A_N$, both V and N being large.

For the first flow system we choose

$$\mathbf{u}' = \mathbf{u}^H - \mathbf{E} \,.\, \mathbf{x}, \quad \boldsymbol{\sigma}' = \boldsymbol{\sigma}^H - 2\mu \mathbf{E};$$

that is, $\mathbf{u}'$ and $\boldsymbol{\sigma}'$ denote the change in the velocity and stress due to the presence of N force-free couple-free rigid spheres in fluid in which the velocity would otherwise be $\mathbf{E} \,.\, \mathbf{x}$ everywhere, where $\mathbf{E}$ is a constant rate-of-strain tensor (symmetrical and traceless). Thus

$$\mathbf{u}' = \mathbf{U}_i + \boldsymbol{\Omega}_i \times (\mathbf{x} - \mathbf{x}_i) - \mathbf{E} \,.\, \mathbf{x} \quad \text{on} \quad A_i, \tag{3.2}$$

where $\mathbf{U}_i$ and $\boldsymbol{\Omega}_i$ are the translational and rotational velocities of the sphere at $\mathbf{x}_i$ in the flow system represented by $\mathbf{u}^H$ and $\boldsymbol{\sigma}^H$.

For the second flow system in the same region we choose $\mathbf{u}'' = \mathbf{u}^B$, $\boldsymbol{\sigma}'' = \boldsymbol{\sigma}^B$, corresponding to spheres moving under the action of forces $\mathbf{F}_i$ $(i = 1, \ldots, N)$ and zero couple in fluid which is otherwise at rest, with $\sum_i \mathbf{F}_i = 0$ and

$$\int \boldsymbol{\sigma}^B \,.\, \mathbf{n}\, dA = -\mathbf{F}_i. \tag{3.3}$$

Now the contributions to the surface integrals in (3.1) from the outer boundary A increase less rapidly than V as V (and N) $\rightarrow \infty$, because the integrands are of bounded magnitude. We also have

$$\int_{A_i} \mathbf{u}^B \,.\, (\boldsymbol{\sigma}^H - 2\mu \mathbf{E}) \,.\, \mathbf{n}\, dA = 0$$

because the spheres are force-free and couple-free in the flow system represented by $\mathbf{u}^H$ and $\boldsymbol{\sigma}^H$. Hence (3.1) reduces to

$$\frac{1}{V} \sum_{i=1}^{N} \int_{A_i} \mathbf{u}' \,.\, \boldsymbol{\sigma}^B \,.\, \mathbf{n}\, dA = 0,$$

and on substitution from (3.2) and the use of (3.3) we find

$$\frac{1}{V}\mathbf{E}:\sum_{i=1}^{N}(\mathbf{S}_i^B-\mathbf{x}_i\mathbf{F}_i)+\frac{1}{V}\sum_{i=1}^{N}\mathbf{U}_i\,.\,\mathbf{F}_i = 0. \tag{3.4}$$

This interesting relation provides another interpretation of the last two terms in (2.9) representing the direct contribution to the bulk stress due to the thermodynamic or Brownian forces. For suppose that the homogeneous suspension of spheres is subjected to a deforming motion characterized by a uniform mean rate-of-strain $\mathbf{E}$. The rate of dissipation per unit volume in a steady viscometric flow of the suspension may be obtained from the bulk stress and the bulk rate of strain (Batchelor 1970), being equal to $\mathbf{E}:\mathbf{\Sigma}$, and it appears from (2.9) and (3.4) that the Brownian forces make a direct contribution

$$-\frac{1}{V}\sum_i \mathbf{U}_i\,.\,\mathbf{F}_i \tag{3.5}$$

to this rate of dissipation, where $\mathbf{U}_i$ is the translational velocity which a sphere at $\mathbf{x}_i$ would have in the absence of the Brownian forces. The rate of working by the Brownian forces is evidently the same as if each sphere was moved by those forces at such a velocity relative to the fluid as would keep it stationary when the whole suspension is subjected to a uniform deforming motion.

The relation (3.4) is also useful analytically. The sphere velocity $\mathbf{U}_i$ is obviously a linear function of $\mathbf{E}$, and may be written as

$$\mathbf{U}_i = \mathbf{E}\,.\,\mathbf{x}_i+\mathbf{E}:\mathbf{C}_i, \tag{3.6}$$

where the third-rank tensor $\mathbf{C}_i$ represents the effect of the presence of the surrounding spheres on the velocity of a sphere at $\mathbf{x}_i$ (in the absence of Brownian forces) and is chosen to be symmetrical and deviatoric in the first two suffixes that are contracted with those of $\mathbf{E}$. All terms in (3.4) are now linear in $\mathbf{E}$, and since $\mathbf{E}$ is an arbitrary tensor, aside from being symmetrical and having zero trace, we find

$$\sum_{i=1}^{N}(\mathbf{S}_i^B+\mathbf{C}_i\,.\,\mathbf{F}_i) = 0. \tag{3.7}$$

The expression (2.8) for the direct Brownian contribution to the bulk stress may thus be written as

$$\mathbf{\Sigma}^B = \text{I.T.}-\frac{1}{V}\sum_{i=1}^{N}(\mathbf{C}_i+\mathbf{x}_i\mathbf{I})\,.\,\mathbf{F}_i$$

and, on use of the expression (1.3) for $\mathbf{F}_i$,

$$= \text{I.T.}-\frac{kT}{V}\sum_i\nabla_i\,.\,\mathbf{C}_i+\frac{kT}{V}\sum_i\frac{\nabla_i\,.\{(\mathbf{C}_i+\mathbf{x}_i\mathbf{I})P\}}{P}, \tag{3.8}$$

in which ∇_i denotes the divergence operator with respect to $\mathbf{x}_i$ and is contracted with the last suffix of $\mathbf{C}_i$ and of $\mathbf{x}_i\mathbf{I}$.

Now the summation over an indefinitely large number of particles is equivalent to an average over all possible configurations of the position vectors $\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N$ of the N particles in V, and the second summation in (3.8) can thus be written as

$$\frac{kT}{VK}\sum_{i=1}^{N}\int\nabla_i\,.\{(\mathbf{C}_i+\mathbf{x}_i\mathbf{I})P\}\,d\mathscr{C}_N,$$

where $\mathscr{C}_N$ stands for the configuration $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$, the integration is over all possible values of these position vectors in V, and K is the normalizing factor $\int P\, d\mathscr{C}_N$. The integral clearly has the same value for $i = 1, 2, \ldots, N$, so, on taking $i = 1$ as representative,

$$= \frac{nkT}{K} \iint \nabla_1 . \{(\mathbf{C}_1 + \mathbf{x}_1 \mathbf{I}) P\} \, d\mathbf{x}_1 \, d\mathscr{C}_{N-1}$$

$$= \frac{nkT}{K} \int \left\{ \int_A (\mathbf{C}_1 . \mathbf{n} + \mathbf{x}_1 \mathbf{n}) P \, d\mathbf{x}_1 - \sum_j \int_{A'_j} (\mathbf{C}_1 . \mathbf{n} + \mathbf{x}_1 \mathbf{n}) P \, d\mathbf{x}_1 \right\} d\mathscr{C}_{N-1}, \tag{3.9}$$

where A is the (geometrical) outer boundary of V and A'_j is the closed boundary of one of the inner regions from which $\mathbf{x}_1$ is excluded by the requirement of no overlapping of spheres, $\mathbf{n}$ being the unit outward normal in both cases.

Consider the first of the two terms of (3.9), in which $|\mathbf{x}_1|$ is large (since it is implied that the origin is somewhere in the interior of V). Both $\mathbf{C}_1$ and P are functions of the configuration $\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N$, but if the order of integration be interchanged, so that the integration with respect to $\mathscr{C}_{N-1}$ is carried out first,

$$\int \mathbf{C}_1 P \, d\mathscr{C}_{N-1} \quad \text{and} \quad \int P \, d\mathscr{C}_{N-1}$$

are approximately constant for $\mathbf{x}_1$ on A; and then the integral of $\mathbf{n}$ with respect to $\mathbf{x}_1$ over A is zero and the integral of $\mathbf{x}_1 \mathbf{n}$ is isotropic. Thus only the second of the two terms in (3.9) survives, and

$$\mathbf{\Sigma}^B = \text{I.T.} - \frac{kT}{V} \sum_i \nabla_i . \mathbf{C}_i - \frac{nkT}{K} \sum_j \iint_{A'_j} (\mathbf{C}_1 . \mathbf{n} + \mathbf{x}_1 \mathbf{n}) P \, d\mathbf{x}_1 \, d\mathscr{C}_{N-1}. \tag{3.10}$$

The last term looks complicated but presents no problems for the dilute suspensions which we shall now consider.

The bulk stress is now the sum of (2.2) and (3.10), giving an alternative expression to (2.9).

4. The bulk stress to order ϕ^2

The above expression for the bulk stress in the suspension holds for all values of the particle volume fraction $\phi(=\frac{4}{3}\pi a^3 n)$. We propose now to adapt to the case $\phi \ll 1$ and, specifically, to obtain a form which is correct to the order of ϕ^2 and which will allow numerical evaluation.

If the suspension is so dilute that the fluid motion near each particle is effectively independent of the existence of other particles, the bulk straining motion cannot cause any statistical connections between the positions of particles and so $P(\mathbf{x}_1, \mathbf{x}_2, \ldots)$ becomes a product of functions of each of the position vectors $\mathbf{x}_1, \mathbf{x}_2, \ldots$. The thermodynamic force on the sphere at $\mathbf{x}_i$ then reduces to

$$\mathbf{F}_i \approx -kT \frac{\partial \log P(\mathbf{x}_i)}{\partial \mathbf{x}_i} = -kT \frac{\partial \log n}{\partial \mathbf{x}_i} = 0.$$

Consequently the direct contribution to the bulk stress due to Brownian motion is zero. The hydrodynamic force dipole strength $\mathbf{S}^H$ is the same for all particles and can be seen, from a knowledge of the flow due to a single sphere in a bulk deforming motion, to be

$$\mathbf{S}^H \approx \tfrac{20}{3}\pi a^3\mu \mathbf{E}, \quad = \mathbf{S}^H_0 \quad \text{say}, \tag{4.1}$$

showing that to order ϕ the bulk stress in a suspension of spheres is of Newtonian form with the effective viscosity $\mu(1+\frac{5}{2}\phi)$.

For larger values of ϕ the effect of hydrodynamic interaction of the particles must be allowed for. The probability that in a particular realization of the suspension there is one other particle within a certain distance of a given particle is proportional to ϕ, and the probability of there being two particles in this region is proportional to ϕ^2. This suggests that the first approximation to the effect of hydrodynamic interaction of particles may be obtained by considering only pairwise interaction of particles, and that the value of $\langle \mathbf{S}^H \rangle$ correct to order ϕ is obtained from the integral of $\mathbf{S}^H(\mathbf{r}) - \mathbf{S}^H_0$ (where $\mathbf{S}^H(\mathbf{r})$ is the force dipole strength of a sphere in the presence of another sphere whose centre is at separation $\mathbf{r}$, both spheres being force-free and embedded in the given bulk deforming motion) over all values of $\mathbf{r}$, with an appropriate probability weighting function. However, such an integral is not absolutely convergent, and it is necessary to recast the ensemble average before reducing it to an average over the separation of sphere pairs. It may be shown (Batchelor & Green 1972*b*) that, correct to order ϕ^2,

$$n\langle \mathbf{S}^H \rangle = n\mathbf{S}^H_0 + n^2 \int [\{\mathbf{S}^H(\mathbf{r}) - \mathbf{S}^H_0\} p(\mathbf{r}) - \tfrac{20}{3}\pi a^3 \mu \{\mathbf{e}(\mathbf{r}) - \mathbf{E}\}]\, d\mathbf{r}, \tag{4.2}$$

where $np(\mathbf{r})$ ($= P(\mathbf{x}+\mathbf{r}|\mathbf{x})$, the probability of a sphere centre being in unit volume at $\mathbf{x}+\mathbf{r}$ conditional on a second sphere centre being at $\mathbf{x}$) is the pair probability density function satisfying the condition $p(\mathbf{r}) \to 1$ as $\mathbf{r} \to \infty$, and $\mathbf{e}(\mathbf{r})$ is the rate of strain at position $\mathbf{r}$ relative to the centre of a sphere embedded in the bulk deforming motion. The components of $\mathbf{S}^H(\mathbf{r})$ have been calculated approximately from the hydrodynamic boundary-value problem for two force-free spheres in an otherwise uniform deforming motion (Batchelor & Green 1972*a*), and values of $p(\mathbf{r})$ have also been found for the particular case of a bulk steady pure straining motion, giving the result (1.2) for the effective viscosity of the suspension in the absence of Brownian motion.

Consider now the approximation, correct to order ϕ^2, to the direct contribution to the bulk stress due to Brownian motion as given by (3.10). We note first that, when the suspension is so dilute that a sphere interacts hydrodynamically with only one other sphere, the thermodynamic forces on two spheres with centres at $\mathbf{x}_1$ and $\mathbf{x}_2$ reduce to

$$\mathbf{F}_1 = -kT\frac{\partial \log P(\mathbf{x}_1, \mathbf{x}_2)}{\partial \mathbf{x}_1}, \quad \mathbf{F}_2 = -kT\frac{\partial \log P(\mathbf{x}_1, \mathbf{x}_2)}{\partial \mathbf{x}_2}.$$

Then since

$$P(\mathbf{x}_1, \mathbf{x}_2) = P(\mathbf{x}_1)\, P(\mathbf{x}_2|\mathbf{x}_1) = n^2 p(\mathbf{r}),$$

where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$, we have

$$\mathbf{F}_2 = -\mathbf{F}_1 = -kT\frac{\partial \log p(\mathbf{r})}{\partial \mathbf{r}}, \quad = \mathbf{F}(\mathbf{r}) \quad \text{say}. \tag{4.3}$$

We shall see in §5 that $p(\mathbf{r}) - 1$ is never of larger order than $(a/r)^3$ when $a/r \ll 1$, showing that $|\mathbf{F}|$ is of order $(a/r)^4$.

We shall also need to use the following expression for the relative velocity of two isolated force-free spheres immersed in a pure straining motion:

$$\mathbf{V}(\mathbf{r}) = \mathbf{U}_2 - \mathbf{U}_1 = \mathbf{r}\,.\,\mathbf{E} - \mathbf{r}\,.\,\mathbf{E}\,.\left\{\frac{\mathbf{rr}}{r^2}A(r) + \left(\mathbf{I} - \frac{\mathbf{rr}}{r^2}\right)B(r)\right\}, \tag{4.4}$$

where A and B are scalar functions of $r(=|\mathbf{r}|)$ (see Batchelor & Green 1972*a*). It then follows from the symmetry relation

$$\mathbf{U}_2 - \mathbf{E}\,.\,\mathbf{x}_2 = -(\mathbf{U}_1 - \mathbf{E}\,.\,\mathbf{x}_1)$$

that the tensors $\mathbf{C}_1$ and $\mathbf{C}_2$ defined by (3.6) are given, for this case of an isolated pair of spheres, by

$$\mathbf{C}_2 = -\mathbf{C}_1, \quad = \mathbf{C}(\mathbf{r}) \quad \text{say}, \tag{4.5}$$

where

$$C_{jkl}(\mathbf{r}) = -\frac{r_j r_k r_l}{2r^2}(A-B) + \tfrac{1}{6}r_l\delta_{jk}A - \tfrac{1}{4}(r_j\delta_{kl} + r_k\delta_{jl})B, \tag{4.6}$$

the first two suffixes being contracted with $\mathbf{E}$ in (3.6). The divergence with respect to the last suffix is then

$$\nabla_1\,.\,\mathbf{C}_1 = \nabla_2\,.\,\mathbf{C}_2 = \nabla_\mathbf{r}\,.\,\mathbf{C}(\mathbf{r})$$

and

$$\frac{\partial C_{jkl}(\mathbf{r})}{\partial r_l} = \tfrac{1}{2}W(r)\left(\frac{r_j r_k}{r^2} - \tfrac{1}{3}\delta_{jk}\right), \tag{4.7}$$

where

$$W(r) = -3(A-B) - r\frac{dA}{dr} = 3B - \frac{1}{r^2}\frac{d(r^3A)}{dr}. \tag{4.8}$$

It is known that

$$A(r) \sim 5(a/r)^3, \quad B(r) \sim \tfrac{16}{3}(a/r)^5, \quad W(r) \sim 75(a/r)^6 \tag{4.9}$$

as $a/r \to 0$.

The approximation to the first summation in (3.10) that takes account of pair interactions only is straightforward, in view of the rapid approach of $\nabla_\mathbf{r}\,.\,\mathbf{C}$ to zero as $a/r \to 0$, and gives

$$\frac{1}{V}\sum_{i=1}^{N}\nabla_i\,.\,\mathbf{C}_i = n^2\int_{r\geqslant 2a}\tfrac{1}{2}W(r)\left(\frac{\mathbf{rr}}{r^2} - \tfrac{1}{3}\mathbf{I}\right)p(\mathbf{r})\,d\mathbf{r} \tag{4.10}$$

correct to order ϕ^2, this integral being absolutely convergent.

Consider now the second summation in (3.10). When $\phi \ll 1$ a large fraction of the closed surfaces A_j' will be spheres of radius $2a$ enclosing one of the particles, and the probability of another sphere of the configuration $\mathscr{C}_{N-1}$ being nearby is small. For $\mathbf{x}_1$ on one of these spheres, say that with centre at $\mathbf{x}_2$, and on choosing the origin to be at the point of contact of the two spherical particles where the undisturbed fluid velocity is zero (as we must for consistency with the definition (3.6)), we have

$$\int_{A_j'}(\mathbf{C}_1\,.\,\mathbf{n} + \mathbf{x}_1\mathbf{n})\,P\,d\mathbf{x}_1 = \frac{1}{4}\int_{r=2a}\{\mathbf{C}(\mathbf{r})\,.\,\mathbf{n} + \tfrac{1}{2}\mathbf{rn}\}\,n^2p(\mathbf{r})\,d\mathbf{r}. \tag{4.11}$$

But when two spheres embedded in a pure straining motion are touching, the component of their relative velocity parallel to the line of centres is zero; that is, in view of (3.6) and (4.5),

$$\mathbf{r}\,.\,\mathbf{E}\,.\,\mathbf{r} + 2\mathbf{E} : \mathbf{C}\,.\,\mathbf{r} = 0$$

when $r = 2a$. It follows that the integrand of (4.11) is zero, and that the second summation in (3.10) is zero to leading order in ϕ.

The direct contribution to the bulk stress due to Brownian motion, correct to the order ϕ^2, is thus

$$\mathbf{\Sigma}^B = \text{I.T.} - \tfrac{1}{2}n^2kT\int_{r\geq 2a} W(r)\left(\frac{\mathbf{rr}}{r^2} - \tfrac{1}{3}\mathbf{I}\right)p(\mathbf{r})\,d\mathbf{r}. \quad (4.12)$$

The sum of the expressions (4.2) and (4.12) is the contribution to the bulk stress due to the presence of the particles, correct to the order ϕ^2. Further progress with the evaluation of these expressions requires information about the function $p(\mathbf{r})$. This brings in the indirect effect of Brownian motion on the bulk stress.

5. The equation for the pair-distribution function for a dilute suspension

The probability that sphere centres will be found simultaneously in unit volumes about the two points $\mathbf{x}_1$ and $\mathbf{x}_2$ is

$$P(\mathbf{x}_1, \mathbf{x}_2) = P(\mathbf{x}_1)\,P(\mathbf{x}_2|\mathbf{x}_1) = n^2p(\mathbf{r}),$$

where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$ and $p(\mathbf{r})$ is the pair-distribution function. In a suspension of equal spheres of radius a, the dimensionless quantity p is a function of $\mathbf{r}/a$, defined over the range $2 \leqslant r/a < \infty$, and perhaps also of t.

Suppose that the suspension is subjected to a bulk deforming motion characterized by the instantaneous bulk rate-of-strain tensor $\mathbf{E}$ and the bulk angular velocity $\mathbf{\Omega}$. Then if the suspension is dilute, and Brownian motion is absent, the differential equation for $p(\mathbf{r}, t)$ is the conservation relation

$$\frac{\partial p}{\partial t} + \nabla . (p\mathbf{V}) = 0, \quad (5.1)$$

where $\mathbf{V}(\mathbf{r})$ is the relative velocity of the members of an isolated pair of force-free spheres with relative position $\mathbf{r}$ in fluid whose velocity in the absence of the spheres is $\mathbf{x}\,.\,\mathbf{E} + \mathbf{\Omega}\times\mathbf{x}$. The relative velocity $\mathbf{V}$ can be written as

$$\mathbf{V}(\mathbf{r}) = \mathbf{r}\,.\,\mathbf{E} + 2\mathbf{E} : \mathbf{C} + \mathbf{\Omega}\times\mathbf{r}, \quad (5.2)$$

where the third-rank tensor $\mathbf{C}$ is the function of $\mathbf{r}$ already given in (4.6). The solution of (5.1) has been shown by Batchelor & Green (1972*b*) to be equivalent to the statement that $p(\mathbf{r}, t)/q(r)$ is constant for a 'material' point in $\mathbf{r}$-space whose velocity is given as a function of $\mathbf{r}$ and t by $\mathbf{V}$, where

$$q(r) = \frac{1}{1-A}\exp\left\{\int_r^\infty \frac{3(B-A)}{r(1-A)}\,dr\right\} \quad (5.3)$$

and has been evaluated.† In particular, for any material point in $\mathbf{r}$-space which comes from infinity, where $q = 1$ and $p(\mathbf{r})$ may be taken to be unity (no long-range statistical connexions), there is the very simple and powerful result

$$p(\mathbf{r}, t) = q(r). \quad (5.4)$$

† This is a convenient place for an admission that the relation (3.13) in the paper by Batchelor & Green (1972*b*), described there as 'a simple integral identity' for the function $q(r)$, may not be correct. The argument used to obtain it is false, and there is no reason now to think it is an identity, although numerically it is apparently not far from being correct. None of the other results or conclusions of the paper is affected.

In steady pure straining motion, all trajectories in **r**-space come from infinity; as a consequence, the pair-distribution function is independent of t and of the direction of **r**, and the bulk stress to order ϕ^2 is Newtonian in form (with the effective viscosity (1.2)). On the other hand, in steady simple shearing motion there is a region, with the interior boundary $r = 2a$, in which the trajectories are all closed, and the difficulty then arises that the above hydrodynamic relations are insufficient to determine the steady-state values of the constant $p(\mathbf{r}, t)/q(r)$ for the different material points on closed trajectories in this region.

If now we allow for Brownian motion of the particles, an additional term must be included in equation (5.1) to represent the effect of relative movement of the two spheres under the action of the equal and opposite thermodynamic forces on the spheres. The relative velocity of the two spheres due to these thermodynamic forces **F** and $-\mathbf{F}$ can be written as

$$(\mathbf{b}_{11}+\mathbf{b}_{22}-\mathbf{b}_{12}-\mathbf{b}_{21}) \,.\, \mathbf{F}, \tag{5.5}$$

where $\mathbf{b}_{11}$, $\mathbf{b}_{22}$, $\mathbf{b}_{12}$, $\mathbf{b}_{21}$ are mobility tensors defined and evaluated as functions of **r** in my previous paper (Batchelor 1976). The new form of (5.1) is then obtained simply by replacing **V** by the sum of **V** and the velocity (5.5), with **F** being given by (4.3). This is wholly equivalent to the more conventional procedure of introducing a relative Brownian diffusivity tensor

$$\mathbf{D}(\mathbf{r}) = kT(\mathbf{b}_{11}+\mathbf{b}_{22}-\mathbf{b}_{12}-\mathbf{b}_{21}) \tag{5.6}$$

and writing the equation as

$$\frac{\partial p}{\partial t}+\nabla \,.\, (p\mathbf{V}) = \nabla \,.\, (\mathbf{D} \,.\, \nabla p). \tag{5.7}$$

When use is made of the fact that the configuration of two spheres is symmetrical about the direction of **r**, the various mobility tensors can be written in terms of functions of r, and the final (exact) form for the diffusivity (5.6) is

$$\mathbf{D}(\mathbf{r}) = D_0\left\{\frac{\mathbf{rr}}{r^2}\, G(r)+\left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right) H(r)\right\}, \tag{5.8}$$

where $D_0 = kT/3\pi\mu a$. The two scalar functions $G(r)$ and $H(r)$ increase monotonically over the range $2 \leqslant r/a < \infty$, and their asymptotic forms are

$$G \sim 2(\rho-2), \quad H \to 0{\cdot}401 \quad \text{as} \quad \rho \to 2 \tag{5.9}$$

and

$$\left.\begin{aligned} G &= 1-\tfrac{3}{2}\rho^{-1}+\rho^{-3}-\tfrac{15}{4}\rho^{-4}+O(\rho^{-6}),\\ H &= 1-\tfrac{3}{4}\rho^{-1}-\tfrac{1}{2}\rho^{-3}+O(\rho^{-6}) \end{aligned}\right\} \tag{5.10}$$

for $\rho \gg 1$, where $\rho = r/a$.

The differential equation (5.7) is to be solved subject to the boundary conditions

$$\mathbf{r} \,.\, \mathbf{D} \,.\, \nabla p = 0 \quad \text{at} \quad \rho = 2$$

and

$$p \to 1 \quad \text{as} \quad \rho \to \infty,$$

the former of which excludes the possibility of relative diffusive flux of two touching spheres in the direction of the line of centres.

The relative importance of the convection and diffusion terms in (5.7) is measured by the ratio Ea^2/D_0, $= 3\pi\mu a^3 E/kT$, where E is a representative bulk velocity gradient, say one of the principal rates of strain. When $Ea^2/D_0 \gg 1$, the diffusion term is relatively small; but as is well known in fluid mechanics a highest-order differential of this kind can have a singular perturbing effect on the solution for the pair-distribution function. There is no reason to suppose that a small amount of Brownian diffusion would bring about a non-small change in the pair-distribution function in the case of a bulk flow consisting of a steady pure straining motion, and the solution (5.4) is presumably the first term in an expansion in powers of $(Ea^2/D_0)^{-1}$ which is valid for sufficiently small values of $(Ea^2/D_0)^{-1}$ in that case. On the other hand, in the case of a steady simple shearing motion, for which some of the trajectories in $\mathbf{r}$-space are closed, it seems likely that the existence of a small amount of Brownian diffusion, operating over the very long time needed to set up the steady state from arbitrary initial conditions, makes determinate the relation between the constant values of $p(\mathbf{r},t)/q(r)$ for different material points in the region of $\mathbf{r}$-space occupied by closed trajectories; there is an analogy here with the way in which a small amount of molecular transfer of momentum or heat makes determinate the distribution of vorticity or temperature in the region occupied by closed streamlines of a steady flow system. Investigation of this singular perturbing effect of a small amount of Brownian diffusion on the pair-distribution function in a steady simple shearing motion would be valuable, in view of the important role of this kind of bulk flow in practice and in experimental rheology, but the complex character of the closed trajectories due to the hydrodynamic velocity $\mathbf{V}$ alone (see Batchelor & Green 1972*a*) suggests it will be a difficult calculation.

We shall examine here the other extreme, $Ea^2/D_0 \ll 1$, at which Brownian motion effects are relatively strong. The first approximation to the pair-distribution function in these circumstances is obtained by dropping both terms on the left-hand side of (5.7), giving

$$p(\mathbf{r},t) = 1 \quad \text{for} \quad 2a \leqslant r < \infty.$$

If now we write

$$p(\mathbf{r},t) = 1 + p_1(\mathbf{r},t) + O((Ea^2/D_0)^2) \tag{5.11}$$

and substitute in (5.7), we obtain

$$\nabla.(\mathbf{D}.\nabla p_1) = \nabla.\mathbf{V} \tag{5.12}$$

as the equation for the perturbation of the uniform pair distribution. p_1 is evidently linear in $\mathbf{E}$, and must therefore be of the form

$$p_1 = -\frac{a^2}{D_0}\frac{\mathbf{r}.\mathbf{E}.\mathbf{r}}{r^2}Q(\rho), \tag{5.13}$$

where Q is a dimensionless function of $\rho(=r/a)$. Substitution of the expressions for p_1 and $\mathbf{D}$ from (5.13) and (5.8) in (5.12) then gives

$$a^2\nabla.\left[\mathbf{r}.\mathbf{E}.\left\{-\frac{\mathbf{rr}}{r^2}\frac{G}{r}\frac{dQ}{dr} - \left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right)\frac{2HQ}{r^2}\right\}\right] = \nabla.\mathbf{V}. \tag{5.14}$$

For $\nabla.\mathbf{V}$ we have from (5.2) and (4.7)

$$\nabla.\mathbf{V} = 2\mathbf{E}:(\nabla.\mathbf{C}) = W(\rho)\frac{\mathbf{r}.\mathbf{E}.\mathbf{r}}{r^2}, \tag{5.15}$$

where $W(\rho)$ is the combination of the functions A and B defined in (4.8). (Note that the bulk rotation makes no contribution $\nabla.\mathbf{V}$ and that as a consequence the pair distribution found from (5.14) for the case of strong Brownian motion is the same function of the bulk rate of strain $\mathbf{E}$ for all bulk flows with uniform velocity gradient. Clearly the same remark can be made about the bulk stress.) Then since $\mathbf{E}$ is an arbitrary tensor equation (5.14) reduces to

$$\frac{d}{d\rho}\left(\rho^2 G \frac{dQ}{d\rho}\right) - 6HQ = -\rho^2 W. \tag{5.16}$$

The boundary conditions on Q are

$$G\frac{dQ}{d\rho} = 0 \quad \text{at} \quad \rho = 2 \quad \text{and} \quad Q \to 0 \quad \text{as} \quad \rho \to \infty.$$

As $\rho \to \infty$ both G and H tend to unity, corresponding to an isotropic relative diffusivity tensor at large separations of the two spheres, and it follows from the asymptotic form (4.9) for $W(\rho)$ that the particular integral of (5.16) behaves as ρ^{-4} for $\rho \gg 1$, and that the complementary function behaves as ρ^{-3} and is dominant. This asymptotic variation of $Q(\rho)$ as ρ^{-3} (and of $p-1$ as r^{-3}) is a consequence of the quadrupole character of the source term $\nabla . \mathbf{V}$ (see (5.15)) in the diffusion equation (5.12). It follows that the integral $\int \mathbf{r}\nabla p \, d\mathbf{r}$ is not absolutely convergent as $\mathbf{r} \to \infty$; this is the reason why care was taken in § 3 to avoid proceeding at too early a stage to a two-particle approximation to the sum $\frac{1}{V}\sum_{i=1}^{N} \mathbf{x}_i \mathbf{F}_i$.

6. The pair-distribution function in the case of strong Brownian motion

We proceed now to a numerical solution of (5.16),† making use of the available numerical values of $G(\rho)$ and $H(\rho)$ (see tables 1 and 2 and figure 3 of Batchelor 1976). We also make use of the known values of $A(\rho)$ and $B(\rho)$ (see table 1 and the relations (4.6) and (5.17) of Batchelor & Green 1972*a*) to obtain values of $W(\rho)$ from the relation (4.8). Smooth curves were drawn through the tabulated values of G and H and W, and values at regular intervals of ρ, some of which are shown in table 1, were read off, the larger number of values needed for the numerical integration then being obtained by linear interpolation. In the range $2 < \rho < 2{\cdot}01$, where H and W vary rapidly, linear interpolation is not accurate and so numerical values of these two functions were derived from analytical forms consistent with all the available information.

In order to be able to make use of the inner boundary condition we first investigate the form of the solution near $\rho = 2$, which is a regular point of the equation. It is known (Batchelor & Green 1972*a*) that

$$A(\rho) \sim 1 - 4{\cdot}077\xi, \quad B(\rho) \to 0{\cdot}406, \quad \text{as} \quad \xi \to 0,$$

where $\xi = \rho - 2$, whence it follows from (4.8) and (5.9) that

$$W(\rho) \to 6{\cdot}372, \quad G(\rho) \sim 2\xi, \quad H(\rho) \to 0{\cdot}401, \quad \text{as} \quad \xi \to 0.$$

Near the point $\xi = 0$ the equation can therefore be written as

$$\xi\frac{d^2Q}{d\xi^2} + \frac{dQ}{d\xi} - 0{\cdot}301Q = -3{\cdot}186. \tag{6.1}$$

† I acknowledge here the help with the numerical solution of equation (5.16) received from Dr C. C. Lin, who has been engaged in a similar study of the effect of Brownian motion on a dilute suspension of spherical particles in collaboration with Prof. N. F. Sather at the Department of Chemical Engineering, University of Washington (Lin 1973).

ρ	G	H	W	Q
2·00	0	0·401	6·37	1·42
2·01	0·019	0·493	5·14	1·40
2·02	0·031	0·501	4·58	1·37
2·04	0·059	0·517	3·72	1·32
2·06	0·086	0·531	3·16	1·28
2·08	0·111	0·544	2·70	1·23
2·10	0·135	0·556	2·27	1·19
2·15	0·178	0·577	1·73	1·10
2·20	0·218	0·597	1·32	1·02
2·30	0·273	0·626	0·83	0·88
2·40	0·319	0·649	0·57	0·76
2·60	0·392	0·681	0·30	0·59
2·80	0·447	0·708	0·18	0·46
3·00	0·491	0·730	0·11	0·37
3·20	0·526	0·749	0·07	0·31
3·60	0·581	0·781	0·04	0·21
4·00	0·626	0·804	0·02	0·15

TABLE 1. Values of the pair-distribution function Q calculated from the two-sphere functions G, H, W at different separations ($\rho = r/a$).

The complementary function for this equation is

$$Q(\xi) = \alpha I_0(\eta) + \beta K_0(\eta), \tag{6.2}$$

where $\eta = 2(0{\cdot}301\xi)^{\frac{1}{2}}$ and I_0 and K_0 are the Bessel functions of imaginary argument usually denoted by those symbols, α and β being arbitrary constants. A particular integral of (6.1) is $Q = 3{\cdot}186/0{\cdot}301 = 10{\cdot}58$. The requirement that $2\xi(dQ/d\xi)$ be zero at $\xi = 0$ can be satisfied only if $\beta = 0$. A solution of (6.1) which satisfies the boundary condition at $\xi = 0$ is therefore

$$Q = 10{\cdot}58 + \alpha I_0(\eta). \tag{6.3}$$

But (6.1) is a valid approximation to (5.16) only if contributions to W of smaller order than ξ^0 are neglected. Hence what we learn from (6.3) is that

$$Q_0 = 10{\cdot}58 + \alpha, \quad Q_0' = 0{\cdot}301\alpha. \tag{6.4}$$

It is also useful for numerical purposes to note the asymptotic form of the solution of (5.16) as $\rho \to \infty$. From the asymptotic forms of G, H and W given in (5.10) and (4.9) we find that

$$Q(\rho) \sim \frac{\gamma}{\rho^3} + \frac{3\gamma - 25}{2\rho^4}, \tag{6.5}$$

where γ is an unknown constant.

The procedure adopted by R. W. O'Brien, who kindly carried out the numerical integration of equation (5.16) for me, was to assume a certain value for γ and to integrate back from $\rho = 4$ (values of Q being given with sufficient accuracy by (6.5) at larger values of ρ). The correct value of γ is then that for which the computed value of Q remains finite as $\rho \to 2$. It was found, by using the Milne predictor–corrector method in the range $2{\cdot}01 \leqslant \rho < 4$ and the Runge–Kutta method in the range $2 < \rho \leqslant 2{\cdot}01$, that Q became proportional to $\log(\rho - 2)^{-1}$ in this latter range with a coefficient whose value depended on γ. The value of γ for which this coefficient is zero was judged from trials to be 9·41. Table 1 shows the values of Q found in this way to satisfy equation

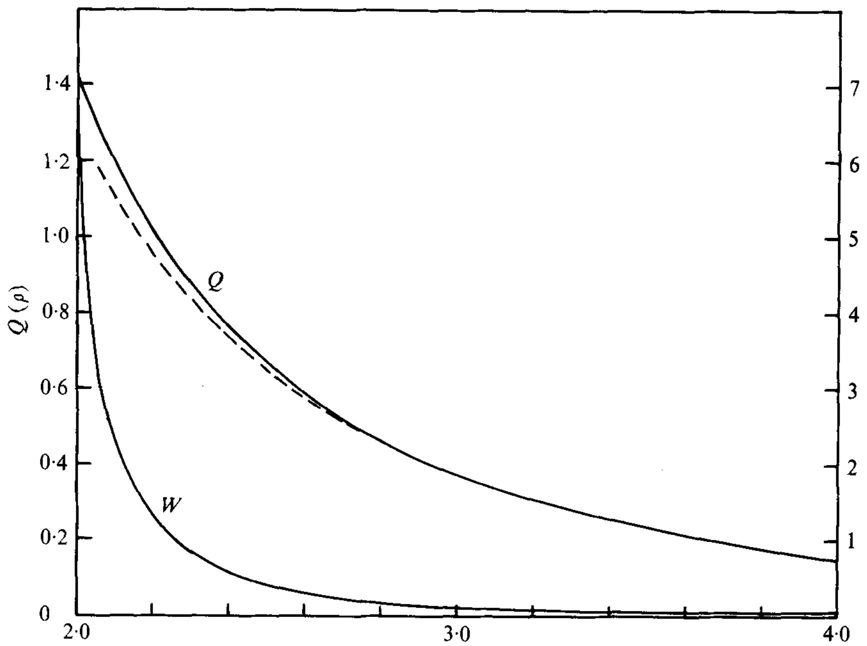

FIGURE 1. The scalar functions $W(\rho)$ and $Q(\rho)$ specifying $\nabla . \mathbf{V}$ and the pair-distribution function $p(\mathbf{r})$ respectively. The broken line is the asymptotic form $Q = (\gamma/\rho^3) + (3\gamma - 25)/2\rho^4$, with $\gamma = 9{\cdot}41$.

(5.16) and the boundary conditions at both ends of the range, corresponding to the choice $\gamma = 9{\cdot}41$. Figure 1 shows both W and Q as functions of ρ; it appears that the asymptotic form (6.5), with $\gamma = 9{\cdot}41$, is in fact a fair approximation to Q over the whole range. The pair-distribution function for the case $Ea^2/D_0 \ll 1$ is then given, correct to order Ea^2/D_0, by (5.11) and (5.13) with these values of Q.

7. The bulk stress to order ϕ^2 in the case of strong Brownian motion

The complete and exact expression for the bulk stress has been given in (2.9).

An approximate form of the term $n\langle \mathbf{S}^H \rangle$ in (2.9) correct to the order ϕ^2 is provided by (4.2). This term represents the hydrodynamic effects of the particles in the given bulk flow but is not completely independent of the existence of Brownian motion because Brownian diffusion affects the form of the particle pair-distribution function. In the case of relatively strong Brownian motion (i.e. $Ea^2/D_0 \ll 1$), the pair-distribution function is approximately uniform (see (5.11) and (5.13)) regardless of the nature of the bulk flow, and so the value of $n\langle \mathbf{S}^H \rangle$ correct to the orders of ϕ^2 and $(Ea^2/D_0)^0$ in the small quantities ϕ and Ea^2/D_0 is obtained from the expression (4.2) with $p = 1$. The integral term in (4.2) has previously been evaluated with $p = 1$ (Batchelor & Green 1972*b*) for use in the context of solid elastic composite materials for which the pair-distribution function might be uniform as a consequence of the method of manufacture, and the result is

$$n\langle \mathbf{S}^H \rangle = 2\mu(\tfrac{5}{2}\phi + 5{\cdot}2\phi^2)\,\mathbf{E}. \qquad (7.1)$$

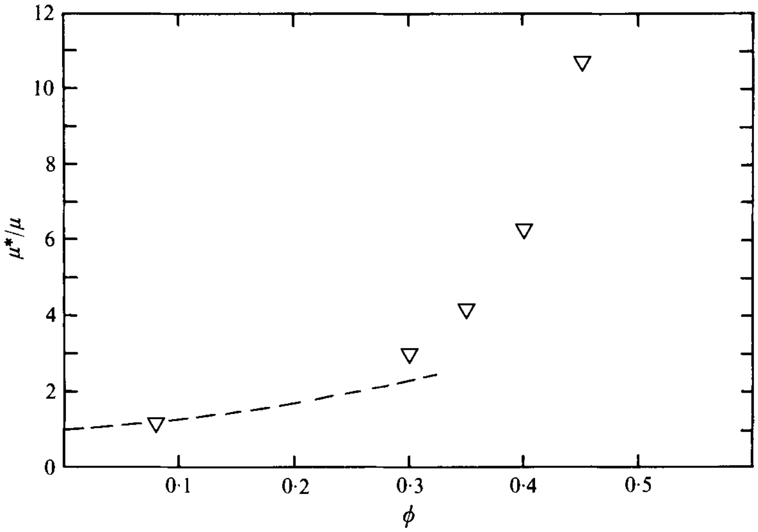

FIGURE 2. Measurements by Krieger (1972) of the effective viscosity of a suspension of rigid spherical particles in simple shearing flow at low rates of shear ($Ea^2/D_0 \ll 1$). The broken line is the theoretical relation (7.4) correct to order ϕ^2.

The Newtonian form of (7.1) is a consequence of the (approximate) isotropy of the distribution of particle pairs.

The approximate form, correct to order ϕ^2, of the last two terms in (2.9) representing the direct contribution to the bulk stress due to Brownian motion is given in (4.12). Here we need a better approximation to the pair-distribution function than $p = 1$, because with a uniform pair-distribution function the deviatoric part of the expression (4.12) is zero. Furthermore, the integral in (4.12) is multiplied by kT, which is large compared with $\mu a^3 E$ when Brownian motion effects are dominant, so the small departure from uniformity of the pair-distribution function leads to a direct contribution to the bulk stress which is independent of kT and is comparable with the (ϕ^2-term in the) hydrodynamic contribution (7.1). On substituting in (4.12) the expression for p given by (5.11) and (5.13), and remembering that $D_0 = kT/3\pi\mu a$, we find

$$\mathbf{\Sigma}^B = \text{I.T.} + \tfrac{9}{20}\phi^2\mu\mathbf{E}\int_2^\infty \rho^2 W(\rho)\,Q(\rho)\,d\rho. \tag{7.2}$$

A numerical integration using the values of the functions $W(\rho)$ and $Q(\rho)$ shown in table 1 and figure 1 gives the value of the integral in (7.2) as 4.3. The right-hand side of (7.2) is thus

$$\text{I.T.} + 2\mu(0{\cdot}97\phi^2)\,\mathbf{E}. \tag{7.3}$$

It appears from (7.1) and (7.3) that, when $Ea^2/D_0 \ll 1$, the deviatoric part of the bulk stress to order ϕ^2 is of Newtonian form, regardless of the form of the bulk flow, and is the same as that for a fluid with the viscosity

$$\mu^* = \mu(1 + \tfrac{5}{2}\phi + 6{\cdot}2\phi^2). \tag{7.4}$$

Newtonian behaviour of the stress to leading order in the small quantity Ea^2/D_0 is of course a general property of a system subjected to a small departure from a state of thermodynamic equilibrium, and is to be expected at all values of ϕ. However, the next approximation to the bulk stress, of order Ea^2/D_0, will not be of Newtonian form, and in particular there will be non-zero differences between the normal stresses. These normal stress differences could be found from an extension of the above perturbation calculation, but it is doubtful whether the labour would be justified since a quantity of order $\phi^2 Ea^2/D_0$ in the small quantities ϕ and Ea^2/D_0 is unlikely to be measurable.

Measured values of the effective viscosity of a suspension of spheres at small concentrations have not yet yielded an empirical value of the coefficient of ϕ^2. One of the best available sets of measurements at low rates of strain was made by Krieger (1972), who took care to minimize the effect of charges at the particle surfaces. His observations and the relation (7.4) are shown in figure 2, but there are too few observations at small concentrations to allow any conclusions from the comparison.

It appears, from a comparison of (7.4) with the expression (1.2) for the effective viscosity of the suspension when it is subjected to a steady bulk pure straining motion with $Ea^2/D_0 \gg 1$, that there is some 'strain thickening' in the ϕ^2-term, although the change is only about 20 %. Qualitatively the reason for the strain thickening is similar to that in the ϕ-term for the simpler case of a dilute suspension of rod-like particles without particle interactions (see figure 1 of the review by Leal & Hinch 1973). The effect of increasing the magnitude of the bulk rate of strain relative to the Brownian diffusivity is to increase the non-uniformity of the relevant particle probability distribution in each case, the pair-distribution function being increased at small separation in the case of the spheres (see the pair-distribution function for the case of negligible Brownian motion in figure 1 of Batchelor & Green 1972*b*) and the directional probability density being increased at directions near to that of the greatest principal rate of bulk strain in the case of the rods, and the result of this non-uniformity is to put more particles into configurations where they make a greater contribution to the bulk stress. The direct contribution to the bulk stress due to Brownian motion is zero in the limit $Ea^2/D_0 \to \infty$, and so changes with Ea^2/D_0 in the direction opposite to that of the indirect contribution, but it turns out that this is a smaller effect in both these cases.

It would be interesting to make a similar comparison of (7.4) with the bulk stress calculated to order ϕ^2 for large values of Ea^2/D_0 in the case of a steady simple shearing motion, and to see if there is any indication of the 'shear thinning' observed by Krieger in the range $0{\cdot}30 \leqslant \phi \leqslant 0{\cdot}45$. However, this will not be possible until the difficult calculation of the pair-distribution function for a simple shearing motion with $Ea^2/D_0 \gg 1$ has been completed. The pair-distribution function will not be isotropic in this latter case, and so the stress will not be of Newtonian form. Table 2 summarizes the present state of calculations of the bulk stress to order ϕ^2 in a suspension of spheres.

A final remark about the qualitative aspects of the direct contribution to the bulk stress due to Brownian motion may be useful. As we have seen, when $Ea^2/D_0 \gg 1$ the pair-distribution function is unaffected by the existence of a bulk rate of rotation and is given approximately in terms of the instantaneous bulk rate of strain by (5.11) and (5.13). Take for simplicity a case of two-dimensional bulk straining motion, with $E_{11} > 0$ and $E_{22} < 0$ and hydrodynamic trajectories of one sphere centre relative to another as indicated in figure 3. In the parts of the (r_1, r_2)-plane where $\nabla . \mathbf{V} < 0$, near the positive and negative r_2-axes (see (5.15)), the rate of generation of particle pairs

		$Ea^2/D_0 \ll 1$	$Ea^2/D_0 \gg 1$: Pure straining	$Ea^2/D_0 \gg 1$: Simple shearing
	Pair-distribution function $p(\mathbf{r})$	Approximately uniform ($p = 1$)	Non-uniform, isotropic	Non-uniform, non-isotropic
Contribution to coefficient of ϕ^2 in expression for μ^*/μ	Hydrodynamic part with $p = 1$	5·2	5·2	5·2
	Extra hydrodynamic part due to non-uniformity of p	0	2·4	?
	Direct contribution due to Brownian motion	1·0	0	0
	Total	6·2	7·6	?

TABLE 2. Theoretical results for the bulk stress to order ϕ^2 in a dilute suspension of spheres.

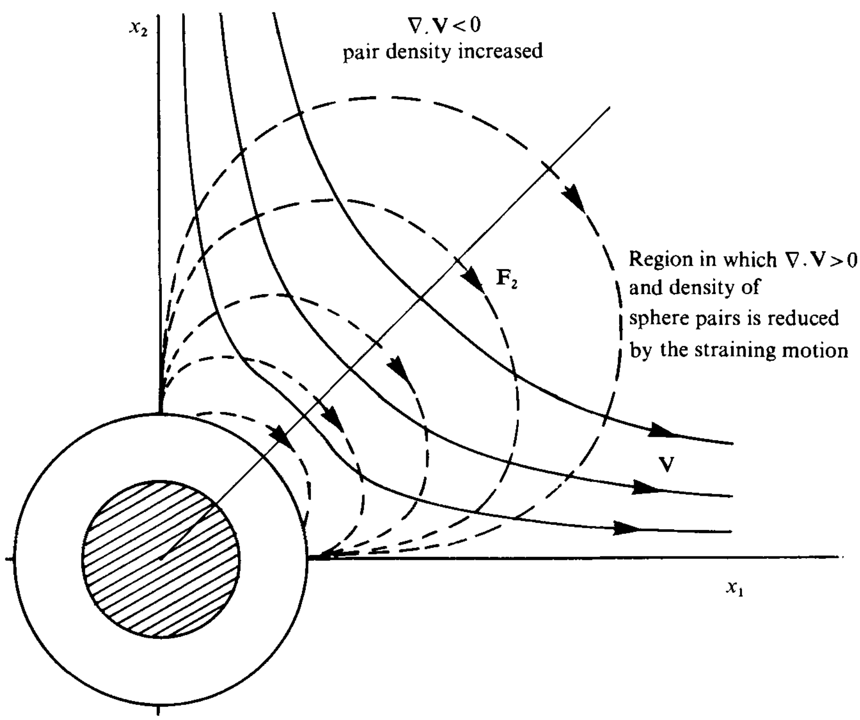

FIGURE 3. Sketch showing (in one quadrant only) the directions of the relative velocity $\mathbf{V}$ of two spheres in a two-dimensional pure straining motion and of the thermodynamic force $\mathbf{F}_2$ on the second sphere ($\mathbf{F}_1 = -\mathbf{F}_2$) in the case of low rates of strain ($Ea^2/D_0 \ll 1$). The force system opposes the straining motion in the manner of a Newtonian viscosity.

per unit volume of $\mathbf{r}$-space by hydrodynamic action is positive. In the absence of Brownian motion a material point coming from infinity on a trajectory enters a region of pair-density production and later moves away from the sphere at the origin through a region of pair-density destruction, the effects of which are to make $p > 1$ (and, less obviously, to make p a function of r alone) in the central region of the plane. But when Brownian motion is strong ($Ea^2/D_0 \ll 1$) most of this non-uniformity of p is eliminated by diffusion, leaving only a small excess in the source region near the r_2-axis and a small deficiency in the sink-region near the r_1-axis (see (5.13)). The direction of the flux of particle pairs due to Brownian diffusion, i.e. the direction of the thermodynamic force on one sphere, at any point is down the gradient of p and is indicated in figure 3. This force system generates a contribution to the average stress in the medium which the figure shows clearly to be a tension in the direction of the r_1-axis and a thrust in the direction of the r_2-axis, thus opposing the bulk deforming motion in the manner of a Newtonian viscous stress.

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