J. Fluid Mech. (1982), *vol.* 119, *pp.* 379–408
Printed in Great Britain

Sedimentation in a dilute polydisperse system of interacting spheres. Part 1. General theory

By G. K. BATCHELOR

Department of Applied Mathematics and Theoretical Physics,
University of Cambridge

(Received 14 August 1981 and in revised form 19 January 1982)

Corrigendum Vol 137 pp 467-499

Small rigid spherical particles are settling under gravity through Newtonian fluid, and the volume fraction of the particles (ϕ) is small although sufficiently large for the effects of interactions between pairs of particles to be significant. Two neighbouring particles interact both hydrodynamically (with low-Reynolds-number flow about each particle) and through the exertion of a mutual force of molecular or electrical origin which is mainly repulsive; and they also diffuse relatively to each other by Brownian motion. The dispersion contains several species of particle which differ in radius and density.

The purpose of the paper is to derive formulae for the mean velocity of the particles of each species correct to order ϕ, that is, with allowance for the effect of pair interactions. The method devised for the calculation of the mean velocity in a monodisperse system (Batchelor 1972) is first generalized to give the mean additional velocity of a particle of species i due to the presence of a particle of species j in terms of the pair mobility functions and the probability distribution $p_{ij}(\mathbf{r})$ for the relative position of an i and a j particle. The second step is to determine $p_{ij}(\mathbf{r})$ from a differential equation of Fokker–Planck type representing the effects of relative motion of the two particles due to gravity, the interparticle force, and Brownian diffusion. The solution of this equation is investigated for a range of special conditions, including large values of the Péclet number (negligible effect of Brownian motion); small values of the Péclet number; and extreme values of the ratio of the radii of the two spheres. There are found to be three different limits for $p_{ij}(\mathbf{r})$ corresponding to different ways of approaching the state of equal sphere radii, equal sphere densities, and zero Brownian relative diffusivity.

Consideration of the effect of relative diffusion on the pair-distribution function shows the existence of an effective interactive force between the two particles and consequently a contribution to the mean velocity of the particles of each species. The direct contributions to the mean velocity of particles of one species due to Brownian diffusion and to the interparticle force are non-zero whenever the pair-distribution function is non-isotropic, that is, at all except large values of the Péclet number.

The forms taken by the expression for the mean velocity of the particles of one species in the various cases listed above are examined. Numerical values will be presented in Part 2.

1. Introduction

This paper is concerned with one of the classical problems of colloid science, viz. calculation of the average speed of fall of small particles in a statistically homogeneous dispersion acted on by a vertical body force proportional to the local density. The particles are suspended in Newtonian fluid of density ρ and viscosity η, and the dispersion is contained in a stationary vessel whose walls are far apart. The Reynolds number of the flow around one particle is assumed to be small, so that inertia forces may be neglected. If the concentration of particles is very small, and the particles are far apart from each other, the speed of fall of each particle is approximately the same as for an isolated particle. At higher concentrations the effect of interaction of the particles becomes significant. Here we investigate the effects of hydrodynamic interactions and interparticle forces between *pairs* of particles, and obtain formulae for the average fall speed of particles which are correct to the order of the first power of the volume fraction of the particles.

In the case of a dilute dispersion of identical particles it has been found (Batchelor 1972) that the average velocity relative to zero-volume flux axes (that is, relative to the containing vessel) is given by

$$\langle \mathbf{U} \rangle = \mathbf{U}^{(0)}\{1+S\phi+\mathrm{O}(\phi^2)\}, \tag{1.1}$$

where ϕ is the volume fraction of the particles, $\mathbf{U}^{(0)}$ is the fall velocity of a particle in isolation, and the sedimentation coefficient S has the value $-6{\cdot}55$ for rigid spherical particles which exert no direct force on each other except when touching.

In the more general case to be considered here, there are m different species of rigid spherical particle. The radius, density, number density, volume fraction, and velocity in isolation of each particle of species i will be denoted by

$$a_i, \rho_i, n_i, \phi_i, \mathbf{U}_i^{(0)} \quad (i = 1, 2, \ldots, m)$$

respectively. A uniform body force per unit mass $\mathbf{g}$ (which will be described as gravity although it might also represent centrifugal force) acts on the dispersion, and so

$$\mathbf{U}_i^{(0)} = \frac{2a_i^2(\rho_i-\rho)}{9\eta}\mathbf{g} \quad (i = 1, 2, \ldots, m) \tag{1.2}$$

and

$$\mathbf{U}_j^{(0)} = \gamma\lambda^2\mathbf{U}_i^{(0)}, \tag{1.3}$$

where

$$\lambda = \frac{a_j}{a_i}, \quad \gamma = \frac{\rho_j-\rho}{\rho_i-\rho}. \tag{1.4}$$

The effect of pairwise interactions of particles of species i and j on average fall speeds evidently depends on the statistics of relative positions of particles of these two species, in particular on the pair-distribution function $n_j p_{ij}(\mathbf{r})$ defined as the probability of finding the centre of a particle of species j in unit volume at position $\mathbf{r}$ relative to the centre of a particle of species i (p_{ij} being normalized so that $p_{ij}(\mathbf{r}) \to 1$ as $r \to \infty$). This pair-distribution function is determined, in a dilute dispersion, by the motion of the two particles through the suspending fluid due both to gravity and to any interactive force which may act between the two particles and by Brownian diffusion of the two particles.

The magnitude of the effect of Brownian diffusion relative to the effect of motion due to gravity is measured by the inverse of the Péclet number, and increases as the particle radii decrease. In the particular case of a dispersion of identical particles with no interactive force, the relative velocity of two neighbouring particles falling under gravity is zero (giving zero Péclet number regardless of the particle size) and there is no opposition, however large the particles may be, to the tendency for relative Brownian diffusion to make the pair-distribution function uniform. The previous investigation of sedimentation in a monodisperse system (Batchelor 1972) thus involved Brownian motion only indirectly, in that the existence of Brownian motion provided a justification for the assumption of a uniform pair-distribution function, and there was no need for any quantitative consideration of relative Brownian diffusion. The position is quite different in the present case of a polydisperse system, and the effect of Brownian motion plays a significant role in the analysis under all conditions except large values of the Péclet number.

It will be supposed that neighbouring particles exert a central force of molecular or electrical origin on each other and that the potential of the mutual force exerted between a particle of species i and a particle of species j whose centres have vector separation $\mathbf{r}$ is a function of r $(= |\mathbf{r}|)$ alone,† Φ_{ij} say, which is defined for $r > a_i + a_j$. The rigidity of the spheres prevents any closer approach of the two sphere centres than $r = a_i + a_j$. At some positive values of $r - (a_i + a_j)$ the force might be attractive. However, we shall assume later that a steady pair-distribution is set up in a sedimenting system, and this implies that the attractive force is not so strong as to cause permanent particle doublets to form. In the terminology of colloid science, the dispersion is stable.

The mean velocity of particles of species i correct to order ϕ $(= \phi_1 + \phi_2 + \ldots + \phi_m)$ depends on pair interactions only, and, since it is necessarily vertical like $\mathbf{U}_i^{(0)}$, may be written as

$$\langle \mathbf{U}_i \rangle = \mathbf{U}_i^{(0)} \left(1 + \sum_{j=1}^{m} S_{ij} \phi_j \right) \quad (i = 1, 2, \ldots, m). \tag{1.5}$$

The dimensionless sedimentation coefficient S_{ij} is a function of the size ratio λ, the (reduced) density ratio γ, the Péclet number of the relative motion of an i-particle and a j-particle, and some dimensionless measure of the interparticle potential Φ_{ij}. When $i = j$, S_{ij} is equal to the sedimentation coefficient S defined in (1.1) for a monodisperse system. Note (i) that the two parallel applied forces represented by $\mathbf{U}_i^{(0)}$ and $\mathbf{U}_j^{(0)}$ are involved in the determination of the pair-distribution function, on which S_{ij} depends, so that the contribution to $\langle \mathbf{U}_i \rangle$ due to pair interactions is not linear in $\mathbf{U}_i^{(0)}$ and $\mathbf{U}_j^{(0)}$ in general, despite the appearance of (1.5), and (ii) that the choice of one of the two applied forces, viz. $\mathbf{U}_i^{(0)}$, as a normalizing factor in the pair-interaction term in (1.5) may lead to S_{ij} having singular values in a case in which $\mathbf{U}_i^{(0)}$ has much smaller magnitude than $\mathbf{U}_j^{(0)}$.

The purpose of the paper is to show how S_{ij} may be determined from the interaction of two spheres of different size and density. In § 3 we give the formula for the direct contribution to the sedimentation coefficient due to gravity and mutual interaction forces, for a given pair-distribution function. Then in § 4 we derive the equation for the pair-distribution function, with allowance for the effects of gravity, hydrodynamic interactions, the interparticle force, and relative Brownian diffusion, and investigate

† In the case of particles with electrical charges attached to the surface and a surrounding cloud or 'double layer' of counter-ions in the fluid, the interparticle force of electrical origin might be affected by the streaming of the fluid past each particle, but we shall ignore such effects here.

the solution analytically in the illuminating limiting cases of large and small Péclet number and for some other special cases. It appears from this investigation that the pair-distribution function is non-uniform and non-isotropic in general. The resulting diffusive flux of particles of one species relative to those of another species tends to restore the uniformity of the pair-distribution function and thereby makes a direct contribution to the sedimentation coefficient which is described in § 5. This direct contribution due to Brownian motion, which is equivalent to that due to a (non-central) interactive 'thermodynamic' force, is significant in a polydisperse system whenever the Péclet number is not large, and remains significant, somewhat paradoxically, when the Péclet number is small and the pair-distribution function is approximately uniform in consequence of the dominant effect of Brownian motion.

In § 6 the results of §§ 3–5 are brought together in analytical formulae for S_{ij} in the various limiting or special cases of interest.

In Part 2 (Batchelor & Wen 1982), numerical values of the pair-distribution function and of the sedimentation coefficient in a number of particular cases will be presented.

2. The mobility coefficients for two spheres to which forces are applied

As explained above, the term of order ϕ in the expression for the mean velocity of spheres of species i is determined by interactions of pairs of spheres, with at least one particle of each pair being of species i. It is essential therefore to know how two spheres of different size move when they are acted on by given applied forces in fluid at rest at infinity. This is the basic deterministic hydrodynamic problem underlying the investigation of sedimentation velocities to order ϕ. We adopt here the specification and notation of the relevant parameters of this flow field given in an earlier paper (Batchelor 1976, § 4), and only the essential details will be repeated.

Suppose that an external force $\mathbf{F}_1$ acts through the centre, at position $\mathbf{x}_1$, of a sphere of radius a_1, and a force $\mathbf{F}_2$ acts similarly on a sphere of radius a_2 at $\mathbf{x}_2$. The two spheres are alone in fluid at rest at infinity, and inertia forces are negligible. The two forces generate superposable motions, and the resulting instantaneous velocities of the two spheres may be written as

$$\mathbf{U}_1 = \mathbf{b}_{11} \cdot \mathbf{F}_1 + \mathbf{b}_{12} \cdot \mathbf{F}_2, \quad \mathbf{U}_2 = \mathbf{b}_{21} \cdot \mathbf{F}_1 + \mathbf{b}_{22} \cdot \mathbf{F}_2, \tag{2.1}$$

where the $\mathbf{b}_{11}$, etc. are *mobility tensors* which depend only on the geometry of the two-sphere configuration. Since the sphere configuration is symmetrical about the direction of $\mathbf{r}(=\mathbf{x}_2-\mathbf{x}_1)$ we may write

$$\mathbf{b}_{\alpha\beta} = \frac{1}{3\pi\eta(a_\alpha + a_\beta)}\left\{A_{\alpha\beta}\frac{\mathbf{rr}}{r^2} + B_{\alpha\beta}\left(\mathbf{I} - \frac{\mathbf{rr}}{r^2}\right)\right\}. \tag{2.2}$$

where $\alpha, \beta = 1$ or 2, $r = |\mathbf{r}|$, $\mathbf{I}$ is the unit second-rank tensor, and the dimensionless scalar coefficients $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are functions of the two dimensionless variables

$$s = \frac{2r}{a_1 + a_2}, \quad \lambda = \frac{a_2}{a_1}. \tag{2.3}$$

These *two-sphere mobility functions* $A_{\alpha\beta}$ and $B_{\alpha\beta}$ play a central role in the calculation of sedimentation velocities to order ϕ.

Note that, as a consequence of the choice of non-dimensionalizing factors made in (2.2), $A_{\alpha\beta}$ and $B_{\alpha\beta}$ are finite at all values of λ, and

$$A_{\alpha\beta}, B_{\alpha\beta} \to \begin{matrix} 1 \\ 0 \end{matrix} \quad \text{as} \quad s \to \infty \quad \begin{matrix} \text{when} \quad \alpha = \beta \\ \text{when} \quad \alpha \neq \beta. \end{matrix}$$

It can be shown from the reciprocal theorem that $A_{\alpha\beta} = A_{\beta\alpha}$ and $B_{\alpha\beta} = B_{\beta\alpha}$. And by exchanging the roles of the two particles we find

$$A_{11}(s,\lambda) = A_{22}(s,\lambda^{-1}), \quad B_{11}(s,\lambda) = B_{22}(s,\lambda^{-1}), \tag{2.4}$$

$$\left.\begin{aligned} A_{12}(s,\lambda) &= A_{21}(s,\lambda) = A_{12}(s,\lambda^{-1}) = A_{21}(s,\lambda^{-1}), \\ B_{12}(s,\lambda) &= B_{21}(s,\lambda) = B_{12}(s,\lambda^{-1}) = B_{21}(s,\lambda^{-1}). \end{aligned}\right\} \tag{2.5}$$

A knowledge of the various asymptotic forms of these mobility functions will later be found useful. As is well known, series expansions in powers of s^{-1} can be found when $s \gg 1$ by the 'method of reflections'. Jeffrey (1982) has recently given a large number of terms, of which the following are sufficient for our present (analytical) purposes:

$$\left.\begin{aligned} A_{11} &= 1 - \frac{60\lambda^3}{(1+\lambda)^4 s^4} + \frac{32\lambda^3(15-4\lambda^2)}{(1+\lambda)^6 s^6} - \frac{192\lambda^3(5-22\lambda^2+3\lambda^4)}{(1+\lambda)^8 s^8} + O(s^{-10}) \\ B_{11} &= 1 - \frac{68\lambda^5}{(1+\lambda)^6 s^6} - \frac{32\lambda^3(10-9\lambda^2+9\lambda^4)}{(1+\lambda)^8 s^8} + O(s^{-10}) \end{aligned}\right\} \tag{2.6}$$

$$\left.\begin{aligned} A_{12} &= \frac{3}{2s} - \frac{2(1+\lambda^2)}{(1+\lambda)^2 s^3} + \frac{1200\lambda^3}{(1+\lambda)^6 s^7} + O(s^{-9}) \\ B_{12} &= \frac{3}{4s} + \frac{1+\lambda^2}{(1+\lambda)^2 s^3} + O(s^{-9}). \end{aligned}\right\} \tag{2.7}$$

It is to be expected from the nature of the method of reflections that increasing powers of s^{-1} in these series are associated generally with increasing powers of λ. It can be seen in particular from Jeffrey's series that the terms shown in (2.6) and (2.7) are sufficient to give expressions for A_{11} and B_{11} correct to order λ^3 when $\lambda \ll 1$ for a general value of s, viz.

$$\left.\begin{aligned} A_{11} &= 1 + \lambda^3(-60s^{-4} + 480s^{-6} - 960s^{-8}) + O(\lambda^4) \\ B_{11} &= 1 + \lambda^3(-320s^{-8}) + O(\lambda^4), \end{aligned}\right\} \tag{2.8}$$

and expressions for A_{12} and B_{12} correct to order λ^2, viz

$$\left.\begin{aligned} A_{12} &= (\tfrac{3}{2}s^{-1} - 2s^{-3}) + \lambda(4s^{-3}) + \lambda^2(-8s^{-3}) + O(\lambda^3) \\ B_{12} &= (\tfrac{3}{4}s^{-1} + s^{-3}) + \lambda(-2s^{-3}) + \lambda^2(4s^{-3}) + O(\lambda^3). \end{aligned}\right\} \tag{2.9}$$

Likewise, in view of (2.4) and (2.6), $A_{22}-1$ and $B_{22}-1$ are of order λ when $\lambda \ll 1$, and so $A_{11}-1$ and $B_{11}-1$ are of order λ^{-1} when $\lambda \gg 1$.

At the inner limit $s \to 2$, the fact that an applied force parallel to the line of centres produces the same common velocity of two touching spheres ($s = 2$) regardless of which sphere it acts on gives

$$A_{11}(2,\lambda) = \frac{2}{1+\lambda} A_{12}(2,\lambda) = \frac{1}{\lambda} A_{22}(2,\lambda). \tag{2.10}$$

Then standard lubrication theory shows that for two nearly touching spheres acted on by forces parallel to the line of centres

$$A_{11}-\frac{4}{1+\lambda}A_{12}+\frac{1}{\lambda}A_{22} \sim \frac{(1+\lambda)^3}{2\lambda^2}\xi \qquad (2.11)$$

as $\xi \to 0$, where $\xi = s-2$; and it may be shown that A_{11}, A_{12}, A_{22} are separately linear in ξ when $\xi \ll 1$. Simple lubrication theory does not give precise relationships between the values of B_{11}, B_{12}, B_{22} and their derivatives at $\xi = 0$, but it may be shown that, near $\xi = 0$, B_{11}, B_{12} and B_{22} are each of the form

$$\text{const.} + O\left(\frac{1}{\log \xi^{-1}}\right). \qquad (2.12)$$

For future reference we note that when $\mathbf{F}_1$ and $\mathbf{F}_2$ represent gravitational forces denoted by $6\pi\eta a_1 \mathbf{U}_1^{(0)}$ and $6\pi\eta a_2 \mathbf{U}_2^{(0)}$ respectively the relative velocity of the two sphere centres is

$$\mathbf{V}_{12}(\mathbf{r}) = \mathbf{U}_2-\mathbf{U}_1 = 6\pi\eta a_1 \mathbf{U}_1^{(0)}.(\mathbf{b}_{21}-\mathbf{b}_{11})+6\pi\eta a_2 \mathbf{U}_2^{(0)}.(\mathbf{b}_{22}-\mathbf{b}_{12}). \qquad (2.13)$$

The relative velocity of two distant spheres is

$$\mathbf{V}_{12}^{(0)} = \mathbf{U}_2^{(0)}-\mathbf{U}_1^{(0)} = (\lambda^2\gamma-1)\,\mathbf{U}_1^{(0)}, \qquad (2.14)$$

where the reduced density ratio

$$\gamma = (\rho_2-\rho)/(\rho_1-\rho) \qquad (2.15)$$

may take positive or negative values. Then on substituting for the mobility tensors from (2.2) the expression for $\mathbf{V}_{12}$ becomes

$$\mathbf{V}_{12}(\mathbf{r}) = \mathbf{V}_{12}^{(0)}.\left\{\frac{\mathbf{rr}}{r^2}L(s)+\left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right)M(s)\right\}, \qquad (2.16)$$

where

$$L(s) = \frac{\lambda^2\gamma A_{22}-A_{11}}{\lambda^2\gamma-1}+\frac{2(1-\lambda^3\gamma)A_{12}}{(1+\lambda)(\lambda^2\gamma-1)}, \qquad (2.17)$$

$$M(s) = \frac{\lambda^2\gamma B_{22}-B_{11}}{\lambda^2\gamma-1}+\frac{2(1-\lambda^3\gamma)B_{12}}{(1+\lambda)(\lambda^2\gamma-1)}. \qquad (2.18)$$

Note (i) that L and M are unchanged when λ and γ are replaced by λ^{-1} and γ^{-1}, and (ii) that when $\lambda = 1$ both L and M are independent of γ (because the relative velocity is then proportional to $\gamma-1$ at all separations). Near and far-field asymptotic forms for $L(s)$ and $M(s)$ may be found from those of A_{11}, B_{11}, etc.

The above mobility functions also occur in the expression for the relative diffusivity tensor for two spheres (Batchelor 1976), essentially because the relative diffusive flux due to Brownian motion can be represented as a consequence of equal and opposite thermodynamic forces acting on the two spheres. The relative diffusivity tensor, which we shall need to make use of when determining the pair-distribution function, is

$$\begin{aligned}\mathbf{D}(\mathbf{r}) &= kT(\mathbf{b}_{11}+\mathbf{b}_{22}-\mathbf{b}_{12}-\mathbf{b}_{21})\\ &= D_{12}^{(0)}\left\{G(s)\frac{\mathbf{rr}}{r^2}+H(s)\left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right)\right\},\end{aligned} \qquad (2.19)$$

where

$$D_{12}^{(0)} = \frac{kT}{6\pi\eta}\left(\frac{1}{a_1}+\frac{1}{a_2}\right), \qquad (2.20)$$

and

$$\left.\begin{aligned} G(s) &= \frac{\lambda A_{11}+A_{22}}{1+\lambda} - \frac{4\lambda A_{12}}{(1+\lambda)^2}, \\ H(s) &= \frac{\lambda B_{11}+B_{22}}{1+\lambda} - \frac{4\lambda B_{12}}{(1+\lambda)^2}. \end{aligned}\right\} \tag{2.21}$$

It follows from (2.4) and (2.5) that

$$G(s,\lambda) = G(s,\lambda^{-1}), \quad H(s,\lambda) = H(s,\lambda^{-1}), \tag{2.22}$$

and from (2.10), (2.11) and (2.12) that as $\xi \to 0$

$$G \sim \frac{(1+\lambda)^2}{2\lambda}\xi, \quad H(s)-H(2) \sim \frac{\text{const.}}{\log \xi^{-1}}. \tag{2.23}$$

By definition $G \to 1$ and $H \to 1$ as $s \to \infty$, and asymptotic developments of G and H correct to the order of s^{-8} (as $s \to \infty$) can be found from (2.6) and (2.7).

Numerical values of some of the mobility functions for some values of s and of λ have been available in the literature for many years, but computer-based calculations of the two-sphere flow field which will yield complete tables of values of A_{11}, A_{12}, B_{11}, B_{12} as functions of s for arbitrarily chosen values of λ have been devised only recently (Adler 1981; Jeffrey 1982). The results of the calculation made by Jeffrey (1982) have been used in the numerical evaluation of sedimentation velocities to be described in Part 2.

3. The general formula for the mean velocity of the particles of one species

In the dilute dispersion under consideration the probability of more than one particle being found in the neighbourhood of a given particle is negligible. The interactions to be considered are thus those arising when a particle of species i acted on by a force $\mathbf{F}_i$ finds in its neighbourhood, at relative position $\mathbf{r}$, a particle of species j acted on by a force $\mathbf{F}_j$. The forces $\mathbf{F}_i$ and $\mathbf{F}_j$ include not only the applied gravitational force but also a mutual interparticle force which depends on $\mathbf{r}$ and tends to zero as $r \to \infty$. The *additional* velocity of the particle of species i due to the presence of the particle of species j is then

$$\mathbf{b}_{11} \cdot \mathbf{F}_i + \mathbf{b}_{12} \cdot \mathbf{F}_j - \frac{\mathbf{F}_i^{(0)}}{6\pi\eta a_i}, \tag{3.1}$$

where the superscript (0) indicates the value for large separations, that is, for a particle effectively in isolation. Only gravity contributes to $\mathbf{F}_i^{(0)}$.

It is intuitively evident that the mean additional velocity of an i-species particle due to the presence of other particles in the suspension involves an integral of an expression like (3.1) over all positions of the particle of species j with the pair-distribution function $n_j p_{ij}(\mathbf{r})$ as a weighting factor. There is however the difficulty, of a type now familiar in the literature of suspension mechanics, that the mobility functions A_{12} and B_{12} contain terms of order r^{-1} and r^{-3} in their expansions in powers of r^{-1} for r large (see (2.7)) and so such an integral of the expression (3.1) is not convergent. Ways of overcoming the difficulty are known, and a formula involving only absolutely convergent integrals over all pair interactions has been derived for the mean sedimentation velocity in a monodisperse system (Batchelor 1972). Later this formula was generalized, in the context of a calculation of Brownian diffusion of particles down a concentration gradient, to the case of polydisperse systems (Batchelor 1976). Only the situation in which the forces $\mathbf{F}_i$ and $\mathbf{F}_j$ are independent of $\mathbf{r}$ was contemplated in that paper, but it is not difficult to see how the formula should be amended to allow for non-uniformity of $\mathbf{F}_i$ and $\mathbf{F}_j$.

From equation (7.5) of this latter paper (to which reference should be made for the interpretation of the various terms in (7.5)) we see that the mean additional velocity of a particle of species i due to pair interactions with particles of species j may be written as

$$n_j \int_{r \geqslant a_j} \{(\mathbf{b}_{11} \cdot \mathbf{F}_i + \mathbf{b}_{12} \cdot \mathbf{F}_j - \mathbf{U}_i^{(0)}) p_{ij}(\mathbf{r}) - \mathbf{u}(\mathbf{x} \mid \mathbf{x}+\mathbf{r}, a_j) - \tfrac{1}{6} a_i^2 \nabla_{\mathbf{r}}^2 \mathbf{u}(\mathbf{x} \mid \mathbf{x}+\mathbf{r}, a_j)\} \, d\mathbf{r} - \left(1 - \frac{a_i^2}{2a_j^2}\right) \phi_j \mathbf{U}_j^{(0)}, \tag{3.2}$$

where $\mathbf{u}(\mathbf{x} \mid \mathbf{x}+\mathbf{r}, a_j)$ denotes the velocity at point $\mathbf{x}$ in the fluid given that the centre of a sphere of radius a_j on which the force $\mathbf{F}_j^{(0)}$ acts is located at point $\mathbf{x}+\mathbf{r}$, and

$$\mathbf{U}_i^{(0)} = \frac{\mathbf{F}_i^{(0)}}{6\pi\eta a_i}, \quad \mathbf{U}_j^{(0)} = \frac{\mathbf{F}_j^{(0)}}{6\pi\eta a_j}.$$

It follows from the known expression for the fluid velocity distribution due to a single moving sphere that

$$\mathbf{u}(\mathbf{x} \mid \mathbf{x}+\mathbf{r}, a_j) + \tfrac{1}{6} a_i^2 \nabla_{\mathbf{r}}^2 \mathbf{u}(\mathbf{x} \mid \mathbf{x}+\mathbf{r}, a_j) = \mathbf{U}_j^{(0)} \cdot \left\{ \frac{3a_j}{4r} \left(\mathbf{I} + \frac{\mathbf{rr}}{r^2} \right) + \frac{a_j(a_i^2 + a_j^2)}{4r^3} \left(\mathbf{I} - \frac{3\mathbf{rr}}{r^2} \right) \right\}, \tag{3.3}$$

where $\mathbf{I}$ is the unit second-rank tensor. Then on substituting the expression (2.2) for $\mathbf{b}_{11}$ and $\mathbf{b}_{12}$ (with a_1 and a_2 replaced by a_i and a_j respectively) in (3.2), and remembering that

$$p_{ij}(\mathbf{r}) = 0 \quad \text{when} \quad r < a_i + a_j$$

for the rigid spheres considered here, we find for the change in mean velocity of a particle of species i due to pair interactions of all types

$$\langle \Delta \mathbf{U}_i \rangle = \sum_{j=1}^{m} \phi_j \left\{ \left(\frac{1+\lambda}{2\lambda} \right)^3 (\mathbf{U}_i^{(0)} \cdot \mathbf{J}' + \mathbf{U}_j^{(0)} \cdot \mathbf{J}'' + \mathbf{K}_{ij}) - \left(1 + \frac{3}{\lambda} + \frac{1}{\lambda^2} \right) \mathbf{U}_j^{(0)} \right\}, \tag{3.4}$$

where
$$\mathbf{J}' = \frac{3}{4\pi} \int_{s \geqslant 2} \left\{ A_{11} \frac{\mathbf{ss}}{s^2} + B_{11} \left(\mathbf{I} - \frac{\mathbf{ss}}{s^2} \right) - \mathbf{I} \right\} p_{ij}(\mathbf{s}) \, d\mathbf{s}, \tag{3.5}$$

$$\mathbf{J}'' = \frac{3}{4\pi} \frac{2\lambda}{1+\lambda} \int_{s \geqslant 2} \left[\left\{ A_{12} \frac{\mathbf{ss}}{s^2} + B_{12} \left(\mathbf{I} - \frac{\mathbf{ss}}{s^2} \right) \right\} p_{ij}(\mathbf{s}) - \left\{ \frac{3}{4s} \left(\mathbf{I} + \frac{\mathbf{ss}}{s^2} \right) + \frac{1+\lambda^2}{(1+\lambda)^2 s^3} \left(\mathbf{I} - \frac{3\mathbf{ss}}{s^2} \right) \right\} \right] d\mathbf{s}, \tag{3.6}$$

$$\mathbf{K}_{ij} = \frac{3}{4\pi} \int_{s \geqslant 2} \left[\left\{ A_{11} \frac{\mathbf{ss}}{s^2} + B_{11} \left(\mathbf{I} - \frac{\mathbf{ss}}{s^2} \right) \right\} \cdot \frac{(\mathbf{F}_i - \mathbf{F}_i^{(0)})}{6\pi\eta a_i} + \frac{2\lambda}{1+\lambda} \left\{ A_{12} \frac{\mathbf{ss}}{s^2} + B_{12} \left(\mathbf{I} - \frac{\mathbf{ss}}{s^2} \right) \right\} \cdot \frac{(\mathbf{F}_j - \mathbf{F}_j^{(0)})}{6\pi\eta a_j} \right] p_{ij}(\mathbf{s}) \, d\mathbf{s}, \tag{3.7}$$

and
$$\lambda = a_j / a_i, \quad \mathbf{s} = 2\mathbf{r}/(a_i + a_j).$$

The convergence of the integral $\mathbf{J}'$ is evident from the asymptotic forms for A_{11} and B_{11} given in (2.6); that of the integral $\mathbf{J}''$ is assured by the asymptotic form of p_{ij} found later; and that of $\mathbf{K}_{ij}$ is a consequence of the rapid decrease to zero, as $s \to \infty$, of the non-gravitational forces on the particles.

The right-hand side of (3.4) is linear in the forces $\mathbf{F}_i$, $\mathbf{F}_j$, for a given pair-distribution function, and it is convenient to recognize the separate contributions made by gravity ($\langle \Delta \mathbf{U}_i \rangle^{(G)}$) and by interparticle forces on the two spheres. The expression of $\langle \Delta \mathbf{U}_i \rangle$ in terms of the three integrals in (3.4) anticipates this decomposition.

When $\mathbf{F}_i$ and $\mathbf{F}_j$ represent gravitational forces, and so are independent of $\mathbf{s}$, we have

$$\mathbf{F}_i = \mathbf{F}_i^{(0)} = 6\pi\eta a_i \mathbf{U}_i^{(0)}, \quad \mathbf{F}_j = \mathbf{F}_j^{(0)} = 6\pi\eta a_j \mathbf{U}_j^{(0)}, \quad \mathbf{U}_j^{(0)} = \gamma\lambda^2 \mathbf{U}_i^{(0)}, \quad \text{and} \quad \mathbf{K}_{ij} = 0.$$

Hence
$$\langle \Delta \mathbf{U}_i \rangle^{(G)} = \mathbf{U}_i^{(0)} . \sum_{j=1}^{m} \phi_j \left\{ \left(\frac{1+\lambda}{2\lambda} \right)^3 (\mathbf{J}' + \gamma\lambda^2 \mathbf{J}'') - \gamma(\lambda^2 + 3\lambda + 1)\, \mathbf{I} \right\}. \tag{3.8}$$

On the other hand, when $\mathbf{F}_i$ and $\mathbf{F}_j$ represent mutual interparticle forces which tend to zero as $r \to \infty$, we have

$$\mathbf{F}_i = -\mathbf{F}_j, \quad = \mathbf{F}_{ij}(\mathbf{r}) \quad \text{say, and} \quad \mathbf{F}_i^{(0)} = -\mathbf{F}_j^{(0)} = 0,$$

and

$$\mathbf{K}_{ij} = \frac{1}{8\pi^2\eta a_i} \int_{s \geqslant 2} \left\{ \left(A_{11} - \frac{2}{1+\lambda} A_{12} \right) \frac{\mathbf{ss}}{s^2} + \left(B_{11} - \frac{2}{1+\lambda} B_{12} \right) \left(\mathbf{I} - \frac{\mathbf{ss}}{s^2} \right) \right\} . \mathbf{F}_{ij}\, p_{ij}(\mathbf{s})\, d\mathbf{s}. \tag{3.9}$$

The notion of interparticle forces causing a mean drift of the particles of one species may seem strange at first sight. A mean drift would of course be impossible in the familiar case in which the pair-distribution function is spherically symmetric, since $\mathbf{F}_{ij}(\mathbf{r}) = -\mathbf{F}_{ij}(-\mathbf{r})$ and the integral in (3.9) is then zero; but, as we shall see later, the pair-distribution function is in general unsymmetrical about a horizontal plane through $s = 0$ in a polydisperse sedimenting system, and a mean drift of particles of one species may then occur.

In the particular case of a *central* interparticle force derivable from a potential Φ_{ij} which is a function of r alone (e.g. a van der Waals force), we have

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{x}_i} \Phi_{ij}(r) = \frac{2}{a_i + a_j} \frac{\mathbf{s}}{s} \frac{d\Phi_{ij}}{ds}, \tag{3.10}$$

and the corresponding contribution to $\langle \Delta \mathbf{U}_i \rangle$ is seen from (3.4) and (3.9) to be

$$\langle \Delta \mathbf{U}_i \rangle^{(\mathrm{I})} = \frac{1}{8\pi^2\eta a_i^2} \sum_{j=1}^{m} \phi_j \frac{(1+\lambda)^2}{4\lambda^3} \int_{s \geqslant 2} \left(A_{11} - \frac{2}{1+\lambda} A_{12} \right) \frac{\mathbf{s}}{s} \frac{d\Phi_{ij}}{ds} p_{ij}(\mathbf{s})\, d\mathbf{s}. \tag{3.11}$$

We shall see later that the relative diffusion of the two particles due to Brownian motion is equivalent in its effect on the particle motions to a steady interparticle force, $\mathbf{F}_{ij}^{(B)}$ say, which in general is not directed along the line of centres. The corresponding contribution to $\langle \Delta \mathbf{U}_i \rangle$ is obtained by replacing $\mathbf{F}_{ij}$ by $\mathbf{F}_{ij}^{(B)}$ in (3.9), and will be considered in § 5.

It should be noted that the case $j = i$ is included in the summation in (3.4). Since $p_{ii}(\mathbf{r}) = p_{ii}(-\mathbf{r})$ there is no direct contribution to $\langle \Delta \mathbf{U}_i \rangle$ due to interparticle forces between two particles of species i. The term $j = i$ in the summation in (3.8) giving the contribution from gravitational forces is

$$\frac{3\phi_i}{4\pi}\mathbf{U}_i^{(0)}\cdot\int_{s\geqslant 2}\left[\left\{(A_{11}+A_{12})\frac{\mathbf{ss}}{s^2}+(B_{11}+B_{12})\left(\mathbf{I}-\frac{\mathbf{ss}}{s^2}\right)-\mathbf{I}\right\}_{\lambda=1}p_{ii}(\mathbf{s}) - \left\{\frac{3}{4s}\left(\mathbf{I}+\frac{\mathbf{ss}}{s^2}\right)+\frac{1}{2s^3}\left(\mathbf{I}-\frac{3\mathbf{ss}}{s^2}\right)\right\}\right]d\mathbf{s}-5\phi_i\mathbf{U}_i^{(0)}. \quad (3.12)$$

If p_{ii} is assumed to be unity, as was done in the previous investigation of sedimentation in a monodisperse system (Batchelor 1972), this becomes

$$\phi_i\mathbf{U}_i^{(0)}\left\{\int_2^\infty (A_{11}+2B_{11}-3+A_{12}+2B_{12}-3s^{-1})_{\lambda=1}s^2ds-5\right\}, \quad (3.13)$$

and the value of the integral was found in that paper to be $-1{\cdot}55$.

Since $\mathbf{U}_i^{(0)}$ and $\mathbf{U}_j^{(0)}$ are parallel to $\mathbf{g}$, and the pair-distribution function $p_{ij}(\mathbf{s})$ is necessarily symmetrical about the direction of $\mathbf{g}$, the change in mean velocity of the particles of species i given by (3.4) is a vector parallel to $\mathbf{U}_i^{(0)}$, as anticipated in (1.5).

4. The pair-distribution function

We come now to the other aspect of the problem, viz that concerned with the statistical structure of the dispersion. As a result of the singular circumstance that two identical spheres moving under gravitational forces alone have zero relative velocity at all relative positions in the fluid, the pair-distribution function for spheres in a dilute monodisperse system has the same form as in the absence of gravity; it is thus then the same as in the case of what the colloid scientists call structural equilibrium and is given immediately by the Boltzmann distribution for an equilibrium system. But in a polydisperse system the relative motion of the two spheres due to gravity causes non-uniformity of the pair-distribution function. Moreover it does so in a way which is not equivalent to the action of an interparticle force derivable from a potential, and so although there may be a statistically steady state we no longer have an equilibrium system to which the Boltzmann distribution is applicable. It is necessary in these new circumstances to obtain the pair-distribution function as the solution of a conservation equation of Fokker–Planck type†, as was done in the calculation of the effective viscosity of a suspension of (identical) spherical particles subjected to a deforming motion (Batchelor & Green 1972; Batchelor 1977).

† Colloid scientists have tended either to overlook this need or to dismiss it on the grounds that usually they are considering systems in which effects of convection are weak relative to those of Brownian motion (see, for instance, Peterson & Fixman 1963, Reed & Anderson 1976, and Dickinson 1980). In a sedimenting system, effects of motion due to gravity on the pair-distribution function are not always small in practice; and even when convection effects are dominated by those of Brownian motion, and the departure of the pair-distribution function from the Boltzmann distribution is small, this perturbation of the pair-distribution function is nevertheless the source of a non-negligible contribution to the mean velocity of particles in a polydisperse system. Solving the Fokker–Planck equation for the pair-distribution function is normally an unavoidable part of the investigation of properties of a dynamical system not in thermodynamic equilibrium.

4.1. *The differential equation for* p_{ij}

For this differential equation we shall need to know the velocity of the centre of a particle of species j relative to the centre of a particle of species i when the two particles are moving under the action of the specified gravitational and interparticle forces in fluid at rest at infinity. For the relative velocity $\mathbf{V}_{ij}(\mathbf{r})$ due to gravity alone we have the expression (2.16) (in which a_1 and a_2 should be replaced by a_i and a_j, and ρ_1 and ρ_2 by ρ_i and ρ_j). The contribution to the relative velocity due to a central interparticle force $\nabla_{\mathbf{r}}\Phi_{ij}(r)$ acting on the particle of species i and a corresponding force $-\nabla_{\mathbf{r}}\Phi_{ij}(r)$ acting on the particle of species j is

$$-(\mathbf{b}_{22}-\mathbf{b}_{21})\,.\,\nabla\Phi_{ij}-(\mathbf{b}_{11}-\mathbf{b}_{12})\,.\,\nabla\Phi_{ij},$$

which can also be written (as we see from (2.19)) as $-\mathbf{D}_{ij}\,.\,\nabla(\Phi_{ij}/kT)$, where $\mathbf{D}_{ij}(\mathbf{r})$ is the relative translational diffusivity of i and j particles. The total relative velocity due to deterministic forces is thus

$$\mathbf{V}_{ij}-\mathbf{D}_{ij}\,.\,\nabla(\Phi_{ij}/kT). \tag{4.1}$$

On taking account also of relative diffusion we find that the differential equation expressing the conservation of pairs made up of a sphere of species i and one of species j is

$$\partial p_{ij}/\partial t = -\nabla\,.\,(\mathbf{V}_{ij}p_{ij})+\nabla\,.\,\{p_{ij}\mathbf{D}_{ij}\,.\,\nabla(\Phi_{ij}/kT)\}+\nabla\,.\,(\mathbf{D}_{ij}\,.\,\nabla p_{ij}). \tag{4.2}$$

The terms of this linear equation for p_{ij} that are most important, through being non-zero over a wide range of values of $\mathbf{r}$, are the gravitational 'convection' term $-\nabla\,.\,(\mathbf{V}_{ij}p_{ij})$ and the diffusion term $\nabla\,.\,(\mathbf{D}_{ij}\,.\,\nabla p_{ij})$. A representative value of the ratio of the magnitude of these two terms is the Péclet number

$$\mathscr{P}_{ij} = \frac{\frac{1}{2}(a_i+a_j)\,V_{ij}^{(0)}}{D_{ij}^{(0)}},$$

where $V_{ij}^{(0)}$ and $D_{ij}^{(0)}$ denote (magnitudes of) the values of $\mathbf{V}_{ij}$ and $\mathbf{D}_{ij}$ for a widely separated particle pair and are given by (2.14) and (2.20) respectively. Note that, for given λ, $\mathscr{P}_{ij}$ is proportional to $(a_i+a_j)^4$. For the particular case $a_i = 0{\cdot}5\,\mu$m, $a_j = 1{\cdot}0\,\mu$m, $\rho_i = \rho_j = 2\rho$, and with water as the suspending fluid we find $\mathscr{P}_{ij} = 1{\cdot}5$ at normal temperatures. Since values of a_i between $0{\cdot}01\,\mu$m and $10\,\mu$m occur in practice it is clear that both large and small values of $\mathscr{P}_{ij}$ will be relevant.

The ratio of magnitudes of the term in equation (4.2) representing the effect of the interparticle force and the diffusion term is measured by

$$\Phi_{ij}^{(0)}/kT,$$

where $\Phi_{ij}^{(0)}$ is a representative value of the force potential Φ_{ij}. Effects of the interparticle force are often unimportant unless the gap between the spheres is small compared with each of the sphere radii.

The 'convection' term on the right-hand side of (4.2) can be written as

$$-\mathbf{V}_{ij}\,.\,\nabla p_{ij}-p_{ij}\nabla\,.\,\mathbf{V}_{ij},$$

of which the first term represents a true convective rate of change of p_{ij} and the second is a 'source' term resulting from compression of the continuum in $\mathbf{r}$-space representing probability density of sphere pairs. The source strength is proportional to $\nabla \cdot \mathbf{V}_{ij}$, which we find from (2.16) to be given by

$$\nabla \cdot \mathbf{V}_{ij}(\mathbf{r}) = \frac{\mathbf{V}_{ij}^{(0)} \cdot \mathbf{r}}{\frac{1}{2}(a_i + a_j)\, r} W(r), \tag{4.3}$$

where, on changing to the dimensionless variable $s = 2r/(a_i + a_j)$,

$$W(s) = \frac{2(L-M)}{s} + \frac{dL}{ds}. \tag{4.4}$$

This function $W(s)$ plays an important part in the calculation of $p_{ij}(\mathbf{r})$, and we note here for future use that its asymptotic development as $s \to \infty$, obtained from (2.17), (2.18), (2.6) and (2.7), is

$$W(s) = \frac{120\lambda^3(\gamma-1)}{(1+\lambda)^4(\gamma\lambda^2-1)\,s^5} + \frac{24\lambda^3}{(1+\lambda)^6 s^7}\left\{\frac{27(\gamma-\lambda^2)}{\gamma\lambda^2-1} - 80\right\} + \frac{12\,000\lambda^3(\gamma\lambda^3-1)}{(1+\lambda)^7(\gamma\lambda^2-1)\,s^8}$$
$$+ \frac{64\lambda^3}{(1+\lambda)^8 s^9}\left\{\frac{100(\gamma\lambda^4-1) + 63(\gamma-\lambda^4) - 405(\gamma-1)\lambda^2}{\gamma\lambda^2-1}\right\} + O(s^{-10}), \tag{4.5}$$

where $\lambda = a_j/a_i$ and $\gamma = (\rho_j - \rho)/(\rho_i - \rho)$.

We shall seek a steady-state solution of equation (4.2) satisfying the boundary condition

$$p_{ij}(\mathbf{r}) \to 1 \quad \text{as} \quad r \to \infty, \tag{4.6}$$

and a condition expressing the fact that the radial flux of sphere pairs is zero at the inner boundary $r = a_i + a_j$. Contributions to the flux of sphere pairs in $\mathbf{r}$-space are made by the relative velocity (4.1) and by diffusion, and the total flux is

$$\{\mathbf{V}_{ij} - \mathbf{D}_{ij} \cdot \nabla(\Phi_{ij}/kT)\}\, p_{ij} - \mathbf{D}_{ij} \cdot \nabla p_{ij}.$$

Now $\mathbf{r} \cdot \mathbf{V}_{ij} \to 0$ as $r \downarrow a_i + a_j$, in consequence of the rigidity of the spheres. The inner boundary condition is thus

$$\mathbf{r} \cdot \mathbf{D}_{ij} \cdot \{\nabla(\Phi_{ij}/kT)\, p_{ij} + \nabla p_{ij}\} = 0. \tag{4.7}$$

It will be noted from (2.23) that, as another consequence of sphere rigidity,

$$\mathbf{r} \cdot \mathbf{D}_{ij} \sim r - (a_i + a_j) \quad \text{as} \quad r \downarrow a_i + a_j;$$

and so, in cases in which the limiting value of $|\nabla \Phi_{ij}|$ as $r \downarrow a_i + a_j$ is finite, the condition to be satisfied at $r = a_i + a_j$ reduces to

$$\mathbf{r} \cdot \mathbf{D}_{ij} \cdot \nabla p_{ij} = 0, \tag{4.8}$$

and imposes a restriction on the rapidity with which p_{ij} varies near $r = a_i + a_j$.

At large values of the Péclet number the diffusion term in (4.2) is negligible by comparison with the convection term over a large region of $\mathbf{r}$-space. In that event, the order of the differential equation for p_{ij} in this region is one less. No inner boundary condition need be imposed on the solution of the equation in these circumstances.

Aside from the gravitational force in the expression for $\mathbf{V}_{ij}(\mathbf{r})$ there are no directional influences on the solution of (4.2). The solution satisfying the above boundary conditions will therefore be axially symmetric about the direction of $\mathbf{g}$.

We now investigate steady-state solutions of (4.2) in certain limiting or special cases.

Large Péclet number and $\Phi_{ij} = 0$

Larger values of $\mathscr{P}_{ij}$ will usually occur in practice as a consequence of $a_i + a_j$ being larger, and for such particles the range of action of the interparticle force may be a very small fraction of $a_i + a_j$. We shall neglect the effects of interparticle forces and of diffusion here. The resulting expression for the pair-distribution may consequently not be accurate at values of r very near $r = a_i + a_j$.

When $\mathscr{P}_{ij} \gg 1$ and $\Phi_{ij} = 0$ for $r > a_i + a_j$ the equation for the pair-distribution function is approximately

$$\frac{\partial p_{ij}}{\partial t} + \nabla \cdot (\mathbf{V}_{ij} p_{ij}) = 0. \tag{4.9}$$

(Retention of the time derivative creates no additional difficulty in this particular case.) This equation can be solved by the same kind of procedure as was used in the case of a dispersion of (identical) force-free spheres in a bulk linear deforming motion at high Péclet number (Batchelor & Green 1972). We note from (4.3) and (2.16) that $\nabla \cdot \mathbf{V}_{ij}$ can be written as

$$\nabla \cdot \mathbf{V}_{ij} = -\frac{\mathbf{r} \cdot \mathbf{V}_{ij}}{rq} \frac{dq(r)}{dr}, \tag{4.10}$$

where

$$\frac{d \log q}{dr} = \frac{W(r)}{\frac{1}{2}(a_i + a_j)\, L(r)}, \tag{4.11}$$

and so (4.9) becomes

$$\left(\frac{\partial}{\partial t} + \mathbf{V}_{ij} \cdot \nabla\right) \left\{\frac{p_{ij}(\mathbf{r}, t)}{q(r)}\right\} = 0. \tag{4.12}$$

Thus $p_{ij}(\mathbf{r}, t)/q(r)$ is constant for a 'material' point on a trajectory in $\mathbf{r}$-space. In the case of a trajectory coming from infinity, where $p_{ij} = 1$, the value of that constant is $1/q(\infty)$ and so we have

$$p_{ij}(\mathbf{r}, t) = q(r)/q(\infty), \tag{4.13}$$

at all points on that trajectory and thence at all points on all such trajectories. In the case of a trajectory which does not extend to infinity, (4.12) still gives the relation between the values of p_{ij} at any two points on the trajectory, but the relation between the values on two different trajectories is not determined by equation (4.9).

The occurrence of trajectories of finite length has been investigated by Wacholder & Sather (1974). They found that for each value of λ there is a range of values of γ for which some of the trajectories do not extend to infinity (except for $\lambda = 1$, when the range contracts to zero). One bound of the range of values of γ for which some of the trajectories are finite is given by $\gamma = \lambda^{-2}$ (this being the value for which two widely separated spheres have zero relative velocity). The other bound varies with λ in a way which is known only numerically and is given crudely by $\gamma = \lambda^{-1}$. In the important practical case of spheres of uniform density ($\gamma = 1$), and for any value of λ, all the trajectories extend to infinity. For finite trajectories to exist, the smaller of the two spheres must have a larger density.

When some of the trajectories in a flow field are finite, it is necessary to include the effect of relative diffusion of the two spheres (or perhaps the effect of three-particle interactions in certain circumstances) in the governing equation in order to make the pair-distribution function fully determinate. The effect of a small diffusivity here has a singular perturbing effect (exactly as in the case of steady simple shearing motion of a suspension of force-free spheres at large Péclet number), and the required analysis will not be straightforward. Since sedimenting systems in which some of the trajectories are finite are not typical, we shall set this problem aside and consider the high-Péclet-number form of the pair-distribution function only for cases in which all the trajectories extend to infinity and (4.13) consequently holds at all relative positions of the two spheres.

On returning to (4.11) and (4.13), we find

$$\log p_{ij}(\mathbf{s}) = \int_s^\infty \frac{W(s)}{L(s)}\,ds = \int_s^\infty \left\{\frac{2(L-M)}{sL} + \frac{1}{L}\frac{dL}{ds}\right\} ds, \tag{4.14}$$

which has the note-worthy property of depending on the separation magnitude s alone. A spherically symmetric pair-distribution function is generated, despite the directional character of the sedimentation of two spheres, essentially because $\mathbf{r}\,.\,\mathbf{V}_{ij}$ and $\nabla\,.\,\mathbf{V}_{ij}$ have the *same* dependence on the direction of $\mathbf{r}$, exactly as in the case of the pair-distribution function for a dispersion of force-free spheres in a bulk linear deforming motion. The solution (4.14) for the pair-distribution function in the absence of Brownian motion and interparticle force has also been obtained recently, by the same method, by Feuillebois (1980) in an investigation of sedimentation of rigid spheres of the same size (L and M, and hence also W and p_{ij}, being independent of γ in this case) and by Haber & Hetsroni (1981) in an investigation of sedimentation of liquid spheres having different sizes but the same density and a different internal viscosity from that of the suspending liquid.

The asymptotic form for p_{ij} (for $s \gg 1$) may be found from that for $W(s)$ given in (4.5) and that for $L(s)$ obtainable from (2.7) and (2.8), and to the order of s^{-6} is

$$\begin{aligned} p_{ij} = 1 &+ \frac{30(\gamma-1)\lambda^3}{(\gamma\lambda^2-1)(1+\lambda)^4}s^{-4} + \frac{72(\gamma-1)(\gamma\lambda^3-1)\lambda^3}{(\gamma\lambda^2-1)^2(1+\lambda)^5}s^{-5} \\ &+ \frac{4\lambda^3}{(1+\lambda)^6}\left\{\frac{45(\gamma-1)(\gamma\lambda^3-1)^2}{(\gamma\lambda^2-1)^3} + \frac{27(\gamma-\lambda^2)}{\gamma\lambda^2-1} - 80\right\}s^{-6} + O(s^{-7}). \end{aligned} \tag{4.15}$$

In the important case $\gamma = 1$, the first two non-uniform terms in (4.15) vanish and $p_{ij} - 1$ falls off rapidly, as s^{-6}, when $s \gg 1$.

At the other end of the range of values of s, near $s = 2$, A_{11}, A_{12}, A_{22}, and so also L, are each linear functions of ξ (where $\xi = s-2$), and B_{11}, B_{12}, B_{22}, and so also M, are each linear functions of $(\log \xi^{-1})^{-1}$ (see (2.11) and (2.12)). Also, it follows from (2.10) that $L = O(\xi)$ near $\xi = 0$, whence we find from (4.14) that

$$p_{ij} \sim \frac{\text{const.}}{\xi^x(\log \xi^{-1})^y} \tag{4.16}$$

near $\xi = 0$, where x and y are determined by the constants in the asymptotic forms (as $\xi \to 0$) of A_{11}, A_{12}, A_{22} and B_{11}, B_{12}, B_{22} (and x is usually positive). The singularity in p_{ij} at $\xi = 0$ revealed by (4.16) is similar to that found for the case of a dispersion of force-free spheres in a bulk pure straining motion (Batchelor & Green 1972), although there is no reason to suppose that the values of x and y are the same.

It is evident that (4.16) cannot be a valid approximation at all small values of ξ because the neglected diffusion term in (4.2) is in fact of larger order, by one power of ξ^{-1}, near $\xi = 0$ if p_{ij} has the form (4.16); nor does (4.16) satisfy the inner boundary condition (4.8). Thus diffusion cannot be neglected near the inner boundary, and there exists a 'boundary layer' in which effects of convection and diffusion are of comparable magnitude. It is a boundary layer with more than the ordinary mathematical complexity, because the radial diffusivity varies as ξ and the distribution of p_{ij} outside the boundary layer with which a match must be made, viz. (4.16), is itself singular at $\xi = 0$. No analysis of this boundary layer has been made, but it is clear that the effect of diffusion must be to transfer sphere pairs away from the inner boundary and so to reduce the magnitudes of p_{ij} and $\partial p_{ij}/\partial r$ near $\xi = 0$. It seems likely, from order-of-magnitude estimates of the convection and diffusion terms near $\xi = 0$, that the boundary layer thickness is of order $(a_i + a_j)\,\mathscr{P}_{ij}^{-1}$.

4.3. *The limits* $\lambda \to 1$, $\gamma \to 1$, $D_{ij}^{(0)} \to 0$ (*with* $\Phi_{ij} = 0$)

On taking these three limits we arrive at the case of a dispersion of spheres identical in radius and density sedimenting with zero diffusivity of the spheres due to Brownian motion. It appears however that the pair-distribution function corresponding to this multiple limit is not unique, and depends on which of the three limits is taken last. It is worth-while to examine the different limiting forms of $p_{ij}(\mathbf{r})$, because they are relevant to practical situations in which one of the three limits is realized less perfectly than the other two.

Take first the case in which the limit $D_{ij}^{(0)} \to 0$ is taken last. This may be regarded as a mathematical description of an accurately monodisperse system sedimenting with a small but non-zero diffusivity of the spheres. When $\lambda = 1$ and $\gamma = 1$ we have $\mathbf{V}_{ij} = 0$, and so the equation (4.2) for the steady-state pair-distribution function (with neglect again of the interparticle force) reduces to

$$\nabla \cdot (\mathbf{D}_{ij} \cdot \nabla p_{ij}) = 0.$$

The solution satisfying the condition of zero radial flux at the inner boundary is

$$p_{ij}(r) = 1 \quad \text{for} \quad r > a_i + a_j, \tag{4.17}$$

regardless of how small $D_{ij}^{(0)}$ may be. This is of course the solution for dominant Brownian motion – dominant here because of the circumstance that the convection term is zero for identical spheres. This solution was adopted in the previous calculation of the mean sedimentation velocity in a monodisperse system (Batchelor 1972).

Suppose now that the limit $\gamma \to 1$ is taken last. If we put $D_{ij}^{(0)} = 0$, the equation for p_{ij} reduces to (4.9), and since when $\lambda = 1$ all the trajectories extend to infinity the solution is given by (4.14). And if $\lambda = 1$ we see from (2.17) and (2.18) (and some use of (2.4)) that

$$L(r) = (A_{11} - A_{12})_{\lambda=1}, \quad M(r) = (B_{11} - B_{12})_{\lambda=1}. \tag{4.18}$$

The pair-distribution function is thus independent of γ, and it is unnecessary to take the limit $\gamma \to 1$. The function $p_{ij}(\mathbf{r})$ has been calculated for this case by Feuillebois (1980) using the known values of the functions $A_{11}(r)$, $A_{12}(r)$, $B_{11}(r)$, $B_{12}(r)$ for $\lambda = 1$.

The effect of varying γ here is to vary the speed with which one of the two spheres moves relative to the other along its trajectory but not to change the trajectory itself.

Finally, suppose that the limit $\lambda \to 1$ is taken last. With $D_{ij}^{(0)} = 0$ the equation for p_{ij} is again (4.9) and since when $\gamma = 1$ all trajectories extend to infinity the solution is again (4.14). Now in the neighbourhood of $\lambda = 1$ we may put

$$A_{11}(\lambda) = A_{11}(1) + (\lambda - 1)\,(\partial A_{11}/\partial \lambda)_{\lambda=1} + O((\lambda-1)^2),$$

and, in view of the relation (2.4),

$$A_{22}(\lambda) = A_{11}(1) - (\lambda - 1)\,(\partial A_{11}/\partial \lambda)_{\lambda=1} + O((\lambda-1)^2),$$

and similarly for B_{11} and B_{22}. We then see from (2.17) and (2.18) that when $\gamma = 1$

$$\left.\begin{aligned} \lim_{\lambda\to 1} L(r) &= \left(A_{11} - \frac{\partial A_{11}}{\partial \lambda} - \tfrac{3}{2}A_{12}\right)_{\lambda=1}, \\ \lim_{\lambda\to 1} M(r) &= \left(B_{11} - \frac{\partial B_{11}}{\partial \lambda} - \tfrac{3}{2}B_{12}\right)_{\lambda=1}, \end{aligned}\right\} \tag{4.19}$$

and these functions of r must be substituted in the expression (4.14) for p_{ij}. The trajectories have different shapes in the two cases $\lambda = 1$, $\gamma \to 1$ and $\gamma = 1$, $\lambda \to 1$, and this is the essential reason for the different forms of the pair-distribution function in the two cases. The existence of the difference between these two limits is obvious when the asymptotic form (4.15) is considered.

This third case in which the limit $\lambda \to 1$ is taken last provides a mathematical description of a dispersion of spheres of accurately uniform density and a small variation of radius sedimenting at high Péclet number. The variation of radius must not be too small, because it would be difficult then to satisfy in practice the condition of high Péclet number (since identical spheres have zero relative velocity). We can see the practical limitations by considering a dispersion of equal-density spheres, some of which have radius a and some radius $a + \delta a$, where $\delta a \ll a$. The difference between the free-fall speeds of the two types of sphere is

$$|\mathbf{U}_2^{(0)} - \mathbf{U}_1^{(0)}| \approx \frac{2\delta a}{a} U_0,$$

where U_0 is the free-fall speed of either type of sphere, and so the Péclet number for pair interactions involving one sphere of each type is

$$\mathscr{P} = \frac{2aU_0}{D_0}\frac{\delta a}{a}, \tag{4.20}$$

where D_0 is the relative diffusivity at large separations. For particles of relative density 2 gm/cm^3 in water or of density 1 gm/cm^3 in air at room temperature we have

$$\mathscr{P} = 16 \frac{\delta a}{a} (a\,\mu\mathrm{m})^4,$$

showing that for a size variation of 10 percent the Péclet number is large (i.e. 10 or more) for particles no smaller in radius than 1·6 μm. We also see incidentally that for particles of radius 1 μm a size difference of a few percent is sufficient to give $\mathscr{P}$ a value of about unity, which suggests that in an experiment with a supposedly monodisperse system the pair-distribution function might not have the form (4.17) appropriate to exactly identical spheres. It is evidently important to have accurate observations of the size variation in dispersions of spheres of radius 1 μm and above.

It might happen that a dispersion contains two species of particle which differ slightly in radius *and* in density. Provided that $\lambda - 1$ and $\gamma - 1$ are not so small that the Péclet number is not large there is then the question, will the pair-distribution function be closer to that found from (4.14) with (4.18) (which assumes $\lambda = 1$) or to that found from (4.14) with (4.19) (which assumes $\gamma = 1$)? Inspection of the asymptotic form for p_{ij} in (4.15) suggests that a simple comparison of the magnitudes of $\lambda - 1$ and $\gamma - 1$ would enable a decision to be made.

The recent work of Haber & Hetsroni (1981) on sedimentation in a dispersion of liquid spheres of different sizes but having the same density and zero Brownian diffusivity shows yet another way of approaching the limit of identical rigid spheres with zero Brownian motion, although this is not a new limit. These authors found that when $\lambda = 1$ (and $\gamma = 1, D_{ij}^{(0)} = 0$), taking the limit in which the viscosity of the two interacting droplets (η_1) approaches infinity gives a pair-distribution function different from unity (and they supposed that there was consequently some doubt about the validity of the assumption, viz. $p_{ij} = 1$, that I made for a monodisperse system in 1972). But in fact the only consequence of changing η_1/η is to change the mobility functions $A_{11}, B_{11}, \ldots$, and the limit operations $\eta_1/\eta \to \infty$ and $\lambda \to 1$ commute. The limiting value of $p_{ij}(\mathbf{r})$ found by these authors by putting $\lambda \to 1$ and $\eta_1/\eta \to \infty$ in that order is thus the same as that found above by putting $\gamma = 1$, $D_{ij}^{(0)} = 0$, $\lambda \to 1$. (The asymptotic form for p_{ij} given by Haber & Hetsroni does not actually agree with the form taken by (4.15) when $\gamma = 1$ and $\lambda \to 1$, but that is because their mobility functions appear to be incorrect.)

4.4. *Structural equilibrium*

When the spheres are truly identical, both in density and in radius, the relative velocity of two isolated spheres due to the gravitational forces on the spheres is zero and the convection term disappears from equation (4.2). In these circumstances retention of the effect of interparticle forces presents no difficulty. The steady-state solution of (4.2) that satisfies the outer boundary condition (4.6) and the inner boundary condition (4.8) is then the equilibrium or Boltzmann distribution

$$p_{ij}(\mathbf{r}) = \exp\{-\Phi_{ij}(\mathbf{r})/kT\}. \tag{4.22}$$

Thus at relative sphere positions near $r = a_i + a_j$ where $\Phi_{ij} < 0$ (the value of Φ_{ij} at large r being zero) there is an excess density of sphere pairs and at positions where $\Phi_{ij} > 0$ there is a deficiency, with consequences for the mean speed of fall of particles which are qualitatively evident from the fact that two identical spheres fall more quickly when they are close together than when they are far apart.

There is also an approximation to equilibrium in a region of strong interparticle force near $r = a_i + a_j$ when the i and j spheres are not identical. Inspection of the various terms in (4.2) suggests that if Φ_{ij} is changing rapidly in a (small) range of values of r near $r = a_i + a_j$ the full equation (for arbitrary values of λ, γ and $\mathscr{P}_{ij}$) can be satisfied only if the radial gradient of p_{ij} is also of large magnitude. In that event equation (4.2) reduces approximately to

$$\frac{d}{dr}\left[\frac{\mathbf{r}\,.\,\mathbf{D}_{ij}\,.\,\mathbf{r}}{r^2}\left\{p_{ij}\frac{d(\Phi_{ij}/kT)}{dr} + \frac{\partial p_{ij}}{\partial r}\right\}\right] = 0. \tag{4.23}$$

Integration and use of the condition of zero flux of sphere pairs across the inner boundary then gives

$$p_{ij}(\mathbf{r}) = F(\theta, \phi) \exp\{-\Phi_{ij}(\mathbf{r})/kT\} \tag{4.24}$$

near $r = a_i + a_j$, where θ, ϕ are polar and azimuthal co-ordinates of $\mathbf{r}$, corresponding to a *locally* valid Boltzmann distribution in a region where the effects causing a departure from equilibrium are relatively weak.

The function $F(\theta, \phi)$ is presumably determined by some kind of matching of this solution with that valid outside the region of strong interparticle force. However, it will not be a simple matching process, because at values of r such that (4.24) approximates to its asymptotic value $F(\theta, \phi)$ the radial gradient of the expression (4.24) is no longer large and (4.23) is not a valid approximation to the full equation.

4.5. *Small Péclet number*

In this case $\frac{1}{2}(a_i + a_j)\, V_{ij}^{(0)}/D_{ij}^{(0)} \ll 1$ and the convection term in (4.2) is in general small compared with the diffusion term. Thus the governing equation reduces approximately to (4.23) and we recover again the Boltzmann distribution (4.22). (The solution (4.24) holds over a wide range of values of r in this case and the constant F must be assigned the value unity to satisfy the outer boundary condition.) We shall investigate here an improved approximation to $p_{ij}(\mathbf{r})$ which takes some account of the effect of convection in a steady state. It will be seen later that a knowledge of this improved approximation is needed for the correct prediction of the mean speed of sedimentation of each particle species in the limit $\mathscr{P}_{ij} \to 0$.

The appropriate form of perturbation of the Boltzmann distribution at small values of $\mathscr{P}_{ij}$ is

$$p_{ij}(\mathbf{r}) = \exp\{-\Phi_{ij}(r)/kT\}\{1 + \mathscr{P}_{ij} p_{ij}^{(1)}(\mathbf{r}) + O(\mathscr{P}_{ij})\}. \tag{4.25}$$

If we substitute this expression for p_{ij} in the (steady-state form of) equation (4.2) and neglect terms of order $\mathscr{P}_{ij}^2$ we are left with

$$\mathscr{P}_{ij} \nabla_{\mathbf{r}} \cdot (e^{-\Phi_{ij}/kT}\, \mathbf{D}_{ij} \cdot \nabla_{\mathbf{r}} p_{ij}^{(1)}) = \nabla_{\mathbf{r}} \cdot (\mathbf{V}_{ij}\, e^{-\Phi_{ij}/kT}). \tag{4.26}$$

The scalar function $p_{ij}^{(1)}(\mathbf{r})$ is evidently axially symmetric about the vertical direction, and we try the form

$$p_{ij}^{(1)}(\mathbf{r}) = \frac{\mathbf{r} \cdot \mathbf{V}_{ij}^{(0)}}{r V_{ij}^{(0)}} Q(s). \tag{4.27}$$

On substituting in (4.26), and using the expressions for $\mathbf{D}_{ij}$, $\mathbf{V}_{ij}$ and $\nabla \cdot \mathbf{V}_{ij}$ given in (2.19), (2.16) and (4.3) respectively, we find after some straightforward working that (4.26) is satisfied by this expression for $p_{ij}^{(1)}$ provided $Q(s)$ is a solution of

$$\frac{d}{ds}\left(s^2 G \frac{dQ}{ds}\right) - \frac{d(\Phi_{ij}/kT)}{ds} s^2 G \frac{dQ}{ds} - 2HQ = s^2 W - \frac{d(\Phi_{ij}/kT)}{ds} s^2 L, \tag{4.28}$$

where G, H, L and W are all scalar functions of s and λ, and L and W also depend on γ.

The outer boundary condition to be imposed on Q is

$$Q \to 0 \quad \text{as} \quad s \to \infty,$$

and the inner boundary condition (4.8) reduces to

$$G\, dQ/dr = 0 \quad \text{at} \quad s = 2. \tag{4.29}$$

At small Péclet number the applied forces $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$ represent perturbations of an equilibrium system dominated by Brownian and interparticle forces, and we may expect that p_{ij} is a linear function of both $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$. This linearity is obscured here by the inclusion of the factor $\lambda^2\gamma-1$ in the definitions of the scalar functions L and M specifying the relative velocity of the two spheres (see (2.17) and (2.18)), but it may be seen that $(\lambda^2\gamma-1)\,L$ and $(\lambda^2\gamma-1)\,W$ are linear functions of γ and hence that $(\lambda^2\gamma-1)\,Q$, where $Q(s)$ satisfies the above equation and boundary conditions, is linear in γ. Thus the perturbation term in (4.25) is a linear function of γ, or, equivalently, a linear function of $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$ as expected.

Leaving aside the factors in (4.26) containing Φ_{ij}, which are significantly different from unity only when the gap between the two spheres is very small, (4.26) or (4.28) is essentially a pure diffusion equation, made more complicated than the usual type by the diffusivity being different for the radial and transverse directions and being a function of r. The right-hand side represents a source, which owes its existence to the fact that the relative trajectories are not volume preserving (i.e. $\nabla\,.\,\mathbf{V}_{ij}\neq 0$). The function $W(s)$ representing the magnitude of $\nabla\,.\,\mathbf{V}_{ij}$ varies as s^{-5} at large values of s in general, and as s^{-7} in the particular case $\gamma = 1$ (see (4.5)), and the particular integral of (4.28) is correspondingly of order s^{-3} in general and of order s^{-5} for spheres of equal density. Both G and H approach unity as $s\rightarrow\infty$, and the complementary function for Q is of order s^{-2} when $s \gg 1$, as would be expected for a solution with the dipole structure (4.27). For further information about $Q(s)$ it will be necessary to solve (4.28) numerically.

It has been seen that the pair-distribution function is spherically symmetric in both limits, $\mathscr{P}_{ij}\rightarrow\infty$ and $\mathscr{P}_{ij}\rightarrow 0$, although for quite different physical reasons (and in the case $\mathscr{P}_{ij}\rightarrow\infty$ the spherical symmetry was established only when $\Phi_{ij} = 0$). The departure from spherical symmetry is small in the case $\mathscr{P}_{ij}\ll 1$ because diffusive smoothing is then strong, and it is small in the case $\mathscr{P}_{ij}\gg 1$ (with $\Phi_{ij} = 0$) owing to the circumstance that $\nabla\,.\,\mathbf{V}_{ij}$ has the same dependence on the direction of $\mathbf{r}$ as $\mathbf{r}\,.\,\mathbf{V}_{ij}$. There is no reason to expect that at a general value of $\mathscr{P}_{ij}$ the departure from spherical symmetry will be small (although $p_{ij}(\mathbf{r})$ is necessarily symmetrical about the direction of $\mathbf{g}$).

4.6. *Pairs of spheres with very different radii or densities*

The cases $\lambda\ll 1$ and $\lambda\gg 1$ are of limited direct interest in practice, but analytical results may be obtained and will be useful as known end points to those found numerically for different values of λ. For the purpose of this subsection we shall suppose that interparticle forces have negligible effect when $r-(a_i+a_j)$ is comparable with or greater than the smaller of the two sphere radii.

When one of the two spheres has a relatively small radius, say $\lambda = a_j/a_i \ll 1$, the gravitational relative velocity $\mathbf{V}_{ij}$ is approximately the sum of $\mathbf{U}_j^{(0)}-\mathbf{U}_i^{(0)}$ and the value of $\mathbf{u}+\frac{1}{6}a_j^2\nabla^2\mathbf{u}$ at position $\mathbf{x}_j$ where $\mathbf{u}$ is the fluid velocity due to the motion of an isolated bigger sphere with centre at $\mathbf{x}_i$. Both these contributions to $\mathbf{V}_{ij}$ have zero divergence. We see this explicitly from (4.5) which can be regarded as giving an asymptotic development of W for small values of λ (for a general value of s) correct to order λ^2, just as (2.6) and (2.7), from which (4.5) was derived, yielded the asymptotic developments (2.8) and (2.9) correct to order λ^2 or better. Thus, when made non-dimensional by division by $2V_{ij}^{(0)}/(a_i+a_j)$, $\nabla\,.\,\mathbf{V}_{ij}$ is zero to order λ^2, for all values of $\mathbf{r}$

except those for which $r-(a_i+a_j)$ is small compared with the small radius a_j and for which the method of reflections on which (2.6), (2.7) and (4.5) are based cannot be expected to give a convergent series.

The equation for p_{ij} reduces in these circumstances to

$$\frac{\partial p_{ij}}{\partial t}+\mathbf{V}_{ij}\,.\,\nabla p_{ij}=\nabla\,.\,(\mathbf{D}\,.\,\nabla p_{ij}), \tag{4.30}$$

that is, to the equation for convection and (non-isotropic) diffusion in an incompressible fluid, except at values of $s-2$ small compared with λ. There is now no source term, nor is any non-uniformity of p_{ij} specified by the boundary conditions, and so $p_{ij}(\mathbf{r}) \approx 1$. Furthermore, since the term omitted from (4.30) is $p_{ij}\nabla\,.\,\mathbf{V}_{ij}$, and $\nabla\,.\,\mathbf{V}_{ij}$ (when made non-dimensional) is known to be of order λ^3 when $\lambda \ll 1$, the solution of the full equation is

$$p_{ij}(\mathbf{r}) = 1+O(\lambda^3) \tag{4.31}$$

when $\lambda \ll 1$, for a given value of $\mathscr{P}_{ij}$. This holds at all values of the Péclet number. The asymptotic development of p_{ij} in (4.15) for the case of large Péclet number is consistent with (4.31).

By definition we have $p_{ij}(\mathbf{r}) = p_{ji}(-\mathbf{r})$, that is, $p_{ij}(\mathbf{r},\gamma,\lambda) = p_{ij}(-\mathbf{r},\gamma^{-1},\lambda^{-1})$, whence it follows from (4.31) that

$$p_{ij}(\mathbf{r}) = 1+O(\lambda^{-3}) \tag{4.32}$$

when $\lambda \gg 1$, for any given value of the Péclet number.

The limiting cases $\gamma\to 0$ and $|\gamma|\to\infty$ are likewise worth consideration. It is necessary here only to put $\gamma = 0$ or $|\gamma|\to\infty$ in the expressions for $L(s)$ and $M(s)$ in (2.17) and (2.18), and to use the resulting (finite) expression for $W(s)$ in the calculations of $p_{ij}(\mathbf{r})$. The order of the two limit operations $\gamma\to 0$, $\lambda\to\infty$, is significant, since the products $\lambda^2\gamma$ and $\lambda^3\gamma$ occur in (2.17) and (2.18).

5. The direct contribution to mean particle velocities due to Brownian motion

The asymmetry of the pair-distribution function about a horizontal plane through $r = 0$ found explicitly in the case of small Péclet number shows the existence of direct contributions to the mean velocity of each species of particle due to interparticle forces and to Brownian diffusion, and the latter contribution in particular warrants separate consideration.

This asymmetry of $p_{ij}(\mathbf{r})$ at small Péclet number can readily be seen to be a consequence of the combined effects of convection and diffusion represented in equation (4.2). Consider for example a case in which $\gamma\lambda^2 > 1$ and the particle of species j falls downward relative to the particle of species i. The exclusion of the trajectories from the region $r < a_i+a_j$ crowds the trajectories together over much of the upper half-space, corresponding to $\nabla\,.\,\mathbf{V}_{ij} < 0$ there, whereas in the mirror image system in the lower half-space the trajectories move apart from each other and $\nabla\,.\,\mathbf{V}_{ij} > 0$. The negative values of $\nabla\,.\,\mathbf{V}_{ij}$ in the upper half-space and positive values in the lower half-space act as a diffusive source and sink respectively, giving the whole distribution of $p_{ij}(\mathbf{r})$ the character of diffusion from an upwardly directed dipole source at the centre of the field. The diffusive effects are dominant at small Péclet number, and negligible at large Péclet number (when the pair-distribution function at any point is determined solely by the values of $\nabla . \mathbf{V}_{ij}$ on the trajectory through that point, and is spherically symmetric if all the trajectories come from infinity), and at finite Péclet number we must expect to find larger values of p_{ij} in the upper half-space than in the lower half-space.

The flux of a particle of species j (or i) relative to a particle of species i (or j) that results from diffusive levelling thus in general has a vertical component which is mostly downward (or upward). The steady-state gradients of p_{ij} are of course feeble in the case of small Péclet number, but the product of a small gradient by the relatively large Brownian diffusivity is not a small quantity, as we shall see explicitly. The final step in the argument is to recognize that a relative flux of the two kinds of particle in a certain direction implies the existence of an absolute flux (i.e. a flux relative to the container walls) of each of the two species which must be taken into account in a calculation of mean particle velocities.

We leave intuitive considerations now and make a precise calculation of the direct contribution to the mean velocity of the particles of species i due to Brownian diffusion (the indirect contribution being that resulting from the influence of Brownian motion on the pair-distribution function) for arbitrary values of λ, γ and the Péclet number.

In a previous paper (Batchelor 1976) it was shown that if two particles with the labels i and j are alone in infinite fluid and the joint probability density of the positions of their centres is

$$P(\mathbf{x}_i, \mathbf{x}_j) = n_i n_j p_{ij}(\mathbf{r}),$$

where $\mathbf{r} = \mathbf{x}_j - \mathbf{x}_i$, then the diffusive flux of the spheres due to Brownian motion is the same as if spheres i and j move under the action of steady interparticle forces $\mathbf{F}_{ij}^{(B)}(\mathbf{r})$ and $-\mathbf{F}_{ij}^{(B)}(\mathbf{r})$ respectively, where

$$\mathbf{F}_{ij}^{(B)} = -kT\frac{\partial \log P(\mathbf{x}_i, \mathbf{x}_j)}{\partial \mathbf{x}_i} = kT \,.\, \nabla_{\mathbf{r}} \log p_{ij}(\mathbf{r}). \tag{5.1}$$

Reference to § 2 shows that when couple-free spheres i and j are acted on by forces $\mathbf{F}_{ij}^{(B)}$ and $-\mathbf{F}_{ij}^{(B)}$ the sphere i acquires the velocity

$$\mathbf{b}_{11} \,.\, \mathbf{F}_{ij}^{(B)} - \mathbf{b}_{12} \,.\, \mathbf{F}_{ij}^{(B)} = kT(\mathbf{b}_{11} - \mathbf{b}_{12}) \,.\, \nabla_{\mathbf{r}} \log p_{ij}(\mathbf{r}) \tag{5.2}$$

(and there is a corresponding velocity of the sphere j, which in general is not equal and opposite). The mean velocity of a sphere of species i due to relative Brownian diffusion of i and j particles is now obtained by integrating (5.2) over all values of $\mathbf{r}$ with $n_j p_{ij}(\mathbf{r})$ as a weighting function, as anticipated in § 3 by the inclusion of a Brownian contribution to the interparticle force $\mathbf{F}_{ij}$ in (3.9).

The specific Brownian contribution to the change in mean velocity of a particle of species i due to all pair interactions is thus

$$\langle \Delta \mathbf{U}_i \rangle^{(B)} = kT \sum_{j=1}^{m} \tfrac{1}{4}(a_i + a_j)^2 n_j \int_{s \geq 2} (\mathbf{b}_{11} - \mathbf{b}_{12}) \,.\, \nabla_{\mathbf{s}} p_{ij}\, d\mathbf{s}. \tag{5.3}$$

There is at first sight a difficulty here over the convergence of this integral. At large Péclet number $p_{ij} - 1$ has been found to be of order s^{-4} when $s \gg 1$ (see (4.15)), whereas at small Péclet number the departure of p_{ij} from its equilibrium form is given by the solution of equation (4.28) and is of order s^{-2}. Thus, since $\mathbf{b}_{11} - \mathbf{b}_{12}$ is of order s^0 for s

large, it seems that the integral in (5.3) is not absolutely convergent as $s \to \infty$ at small values of the Péclet number. However, the difficulty is not a real one. Equation (4.28), and its vector parent (4.26), is an approximate form of the governing equation for $p_{ij}(\mathbf{r})$ in which the convection term $\mathbf{V}_{ij} . \nabla p_{ij}$ is neglected, and, like other such low-Péclet-number approximations to convection-diffusion equations, is not valid for indefinitely large values of s. As s increases the second-derivative diffusion term in (4.2) ultimately becomes smaller than the first-derivative convection term, however small the Péclet number may be, and the high-Péclet-number form (4.9), in which only convection terms are retained, becomes the appropriate approximation to (4.2) at sufficiently large values of s, the solution for $p_{ij}-1$ then being of order s^{-4}.

It might nevertheless be thought that the integral in (5.3) could not be evaluated for small Péclet numbers without a knowledge of the way in which $p_{ij}(\mathbf{s})-1$ changes at large s from the solution of (4.28), which is of order s^{-2} and for which the integral is not absolutely convergent, to some different form of smaller magnitude resulting from convection effects. But that problem also may be seen not to exist by writing

$$\int_{s\geqslant 2} (\mathbf{b}_{11}-\mathbf{b}_{12}) . \nabla p_{ij} d\mathbf{s} = \int_{s\geqslant 2} \nabla . \{(\mathbf{b}_{11}-\mathbf{b}_{12})(p_{ij}-1)\} d\mathbf{s} - \int_{s\geqslant 2} \nabla . (\mathbf{b}_{11}-\mathbf{b}_{12})(p_{ij}-1)\, d\mathbf{s}. \quad (5.4)$$

The asymptotic forms of $A_{11}, A_{12}, \ldots$ given in § 2 show that $\nabla . (\mathbf{b}_{11}-\mathbf{b}_{12})$ is of order s^{-5} for s large, and so the second integral on the right-hand side is convergent when the low-Péclet-number approximation is used for $p_{ij}-1$. The first integral may be transformed to the sum of two surface integrals, one over a surface 'at infinity' which is zero because, as we have seen, $p_{ij}-1$ is of order s^{-4} when s is sufficiently large however small the Péclet number may be, and the other over the sphere $s = 2$ which is zero because

$$\mathbf{s} . (\mathbf{b}_{11}-\mathbf{b}_{12}) = \frac{s}{6\pi\eta a_i}\left(A_{11} - \frac{2}{1+\lambda} A_{12}\right) \to 0 \quad \text{as} \quad s \to 2$$

in view of (2.10).

We may thus rewrite (5.3) as

$$\langle \Delta \mathrm{U}_i \rangle^{(B)} = \frac{3}{4\pi a_i} \sum_{j=1}^{m} \frac{\phi_j D_{ij}^{(0)}(1+\lambda)}{2\lambda^2} \int_{s\geqslant 2} \left\{ \frac{A_{11}-B_{11}}{s} + \frac{1}{2}\frac{dA_{11}}{ds} - \frac{2(A_{12}-B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda}\frac{dA_{12}}{ds} \right\} \frac{\mathbf{s}}{s} (1-p_{ij})\, d\mathbf{s}. \quad (5.5)$$

At large Péclet number this direct contribution due to Brownian motion is small relative to the direct contribution due to gravity, and in any event the integral tends to zero as $\mathscr{P}_{ij} \to \infty$ because the pair-distribution function is spherically symmetric in the limit. At small Péclet number, $1-p_{ij}$ is proportional to $\mathscr{P}_{ij}$ (for see (4.25)) and so $\langle \Delta \mathrm{U}_i \rangle^{(B)}$ is proportional to $\mathbf{V}_{ij}^{(0)}$ with a constant of proportionality of order unity. Thus at small Péclet number $\langle \Delta \mathrm{U}_i \rangle^{(B)}$ is comparable with $\langle \Delta \mathrm{U}_i \rangle^{(G)}$, unless the value of $\gamma\lambda^2$ is near to unity, in which case it is much smaller. These latter statements may be expected also to hold when the Péclet number is neither small nor large.

When I generalized the formula found for the sedimentation velocity in a mono-disperse system (Batchelor 1972) to the case of a suspension of particles of different size for use in a discussion of down-gradient diffusion in a polydisperse system (Batchelor 1976), I overlooked this direct contribution to $\langle \Delta \mathbf{U}_i \rangle$ due to Brownian diffusion. The omission will be made good in a later paper on diffusion in a polydisperse system (Batchelor 1982).

6. Specific formulae for the sedimentation coefficient

We now bring together the results of §§3–5 in order to obtain formulae for the mean velocity of the particles of species i in the various limiting or special cases for which the pair-distribution function was investigated in §4. The final results will be expressed in terms of the sedimentation coefficient S_{ij} defined by (1.5). Except where the contrary is stated, the formulae allow for the effects of three different forces acting on each particle: (*a*) the gravitational force, which gives an isolated particle the velocity $\mathbf{U}_i^{(0)}$ and a pair of isolated particles the relative velocity $\mathbf{V}_{ij}(r)$, (*b*) the interparticle central force represented by the potential $\Phi_{ij}(r)$, and (*c*) the effective Brownian interparticle force $\mathbf{F}_{ij}^{(B)}(\mathbf{r})$ described in §5. All three make (additive) direct contributions to the change in the mean particle velocity $\langle \Delta \mathbf{U}_i \rangle$, and so to the sedimentation coefficient, as indicated by the notation

$$S_{ij} = S_{ij}^{(G)} + S_{ij}^{(I)} + S_{ij}^{(B)}. \tag{6.1}$$

And all three have a further indirect effect on the mean particle velocity through their influence on the probability distribution of the relative position of two particles.

For the direct contribution to $\langle \Delta \mathbf{U}_i \rangle$ due to gravity we have the expression (3.8). To convert this to a contribution to S_{ij} we note that, since $p_{ij}(\mathbf{r})$ is symmetrical about the vertical axis, each of the tensors $\mathbf{J}'$ and $\mathbf{J}''$ given by (3.5) and (3.6) has one of its principal axes in the vertical direction, whence

$$S_{ij}^{(G)} = \left(\frac{1+\lambda}{2\lambda}\right)^3 \left(\frac{\mathbf{g}\cdot\mathbf{J}'\cdot\mathbf{g}}{g^2} + \gamma\lambda^2 \frac{\mathbf{g}\cdot\mathbf{J}''\cdot\mathbf{g}}{g^2}\right) - \gamma(\lambda^2+3\lambda+1). \tag{6.2}$$

For the interparticle-force contribution $\langle \Delta \mathbf{U}_i \rangle^{(I)}$ we have the expression (3.11), and again the symmetry of $p_{ij}(\mathbf{r})$ about the vertical may be invoked to justify retaining only the vertical component of (3.11), whence

$$\langle \Delta \mathbf{U}_i \rangle^{(I)} = \frac{1}{8\pi^2 \eta a_i} \sum_{j=1}^{m} \frac{\phi_j \mathbf{V}_{ij}^{(0)}}{V_{ij}^{(0)}} \frac{(1+\lambda)^2}{4\lambda^3} \int_{s\geqslant 2} \left(A_{11} - \frac{2}{1+\lambda} A_{12}\right) \frac{\mathbf{s}\cdot\mathbf{V}_{ij}^{(0)}}{sV_{ij}^{(0)}} \frac{d\Phi_{ij}}{ds} p_{ij}(\mathbf{s})\, d\mathbf{s}$$

and, on using the explicit expressions for $\mathscr{P}_{ij}$ and $D_{ij}^{(0)}$ (see (2.20)),

$$S_{ij}^{(I)} = \frac{3}{8\pi} \frac{\gamma\lambda^2 - 1}{\mathscr{P}_{ij}} \frac{(1+\lambda)^2}{4\lambda^2} \int_{s\geqslant 2} \left(A_{11} - \frac{2}{1+\lambda} A_{12}\right) \frac{\mathbf{s}\cdot\mathbf{V}_{ij}^{(0)}}{sV_{ij}^{(0)}} \frac{d(\Phi_{ij}/kT)}{ds} p_{ij}(\mathbf{s})\, d\mathbf{s}. \tag{6.3}$$

For the Brownian-diffusion contribution $\langle \Delta \mathbf{U}_i \rangle^{(B)}$ we have the expression (5.5). The symmetry of $p_{ij}(\mathbf{r})$ about the vertical shows that only the vertical component of (5.5) is non-zero and hence that

$$S_{ij}^{(B)} = \frac{3}{4\pi} \frac{\gamma\lambda^2 - 1}{\mathscr{P}_{ij}} \frac{(1+\lambda)^2}{4\lambda^2} \int_{s\geqslant 2} \left\{\frac{A_{11}-B_{11}}{s} + \frac{1}{2}\frac{dA_{11}}{ds} - \frac{2(A_{12}-B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda}\frac{dA_{12}}{ds}\right\} \frac{\mathbf{s}\cdot\mathbf{V}_{ij}^{(0)}}{sV_{ij}^{(0)}} (1-p_{ij})\, d\mathbf{s}. \tag{6.4}$$

Evaluation of the integrals in (6.2)–(6.4) requires a knowledge of the pair-distribution function, and this is available only in the special cases considered in § 4.

6.1. *Large Péclet number and* $\Phi_{ij} = 0$

Here all effects of interparticle forces are being ignored (as may be permissible when the large value of the Péclet number is a consequence of large size of the particles). The effect of Brownian diffusion on the pair-distribution function is negligible, except perhaps when $s-2 \ll 1$, and the expression (4.14) found for $p_{ij}(\mathbf{s})$ is spherically symmetric. In these circumstances $\langle \Delta \mathbf{U}_i \rangle^{(B)}$ is zero, as explained at the end of the previous section. Thus the only contribution to the sedimentation coefficient is $S_{ij}^{(G)}$, given by (6.2). The integration over the surface of a sphere of radius s in the expressions (3.5) and (3.6) can be carried out, giving $\mathbf{J}'$ and $\mathbf{J}''$ as proportional to the unit tensor $\mathbf{I}$. The sedimentation coefficient is then

$$S_{ij}(\lambda, \gamma) = \int_2^\infty \left[\left(\frac{1+\lambda}{2\lambda}\right)^3 (A_{11} + 2B_{11} - 3)\, p_{ij} + \tfrac{1}{4}\gamma(1+\lambda)^2 \left\{(A_{12} + 2B_{12})\, p_{ij} - \frac{3}{s}\right\}\right] s^2 ds - \gamma(\lambda^2 + 3\lambda + 1), \quad (6.5)$$

where $\lambda = a_j/a_i, \quad \gamma = (\rho_j - \rho)/(\rho_i - \rho), \quad s = 2r/(a_i + a_j).$

The pair-distribution function to be substituted in (6.5) is given by (4.14). A_{11}, A_{12}, B_{11} and B_{12} are all functions of s and λ, and the quantities L and M on which p_{ij} depends are functions of s, λ and γ (see (2.17) and (2.18)). When $\lambda = 1$, L and M, and hence also p_{ij}, do not depend on γ, and we see from (6.5) that S_{ij} is a linear function of γ in this particular case.

6.2. *Identical spheres*

This case is relevant to sedimentation in a polydisperse system since some of the pair interactions involve two particles of the same species. There is no effect of 'convection' on the pair-distribution function in this case, and p_{ij} is given by the Boltzmann distribution (4.22). The direct contribution to $\langle \Delta \mathbf{U}_i \rangle$ due to the interparticle force is zero for a pair of identical particles, for which $p_{ij}(\mathbf{r}) = p_{ij}(-\mathbf{r})$, as remarked in § 3, and $\langle \Delta \mathbf{U}_i \rangle^{(B)} = 0$ for the same reason. Hence, since p_{ij} is spherically symmetric, the sedimentation coefficient is again given by (6.5) (with λ and γ put equal to unity). The suffixes i and j are now redundant, and

$$S = \int_2^\infty \left\{(A_{11} + 2B_{11} - 3 + A_{12} + 2B_{12})_{\lambda=1} \exp(-\Phi/kT) - \frac{3}{s}\right\} s^2 ds - 5,$$

$$= -6{\cdot}55 + \int_2^\infty (A_{11} + 2B_{11} - 3 + A_{12} + 2B_{12})_{\lambda=1} \{\exp(-\Phi/kT) - 1\} s^2 ds \quad (6.6)$$

on using the known numerical result for the integral in the case $\Phi = 0$ (Batchelor 1972).

Values of the sedimentation coefficient for a monodisperse system have been calculated for representative forms of the interparticle potential function $\Phi(r)$ by several authors, to be referred to in Part 2 when further such calculations are being described.

Often the interparticle force potential Φ is different from zero only when $s-2$ is small, and in such cases a useful approximation to (6.6) may be made. According to the data for the two-sphere mobility functions with $\lambda = 1$ (Batchelor 1972)†,

† In table 1 of this paper λ_1 denotes $A_{11} + A_{12}$ and λ_2 denotes $B_{11} + B_{12}$. Note incidentally the misprint in the heading to the last column of the table where $1 + (r/a)$ should be $1 + (a/r)$.

$A_{11}+2B_{11}-3+A_{12}+2B_{12}$ varies by only 6 percent over the range $2 < s < 2{\cdot}2$, and as an approximation we may regard it as constant and equal to $1{\cdot}32$ over that range. We then have

$$S \approx -6{\cdot}55+0{\cdot}44\alpha, \tag{6.7}$$

where

$$\alpha = 3\int_2^\infty (e^{-\Phi/kT}-1)\,s^2 ds = \frac{n}{\phi}\int_{r\geqslant 2}(p-1)\,d\mathbf{r}. \tag{6.8}$$

The parameter α is the excess number of close partners to a given sphere (the excess, that is, relative to the number for a uniform pair-distribution function) divided by the average number of sphere centres in the volume $\frac{4}{3}\pi a^3$. An interpretation of α which may be useful for observational purposes is obtained by regarding these close sphere pairs as doublets (of the temporary kind – our whole investigation is based on the premise that the dispersion is stable), the excess fraction of the total number of spheres which are partners in doublets at any time being $\alpha\phi$. The coefficient of α in (6.7) comes from the fact that the fall speed of two identical nearly-touching spheres, averaged over all orientations of the line of centres, exceeds that of two spheres which are far apart by 44 %.

6.3. *Small Péclet number*

Here the pair-distribution was found to be

$$p_{ij}(\mathbf{r}) = \exp\left(-\frac{\Phi_{ij}}{kT}\right)\left\{1+\mathscr{P}_{ij}\frac{\mathbf{r}\,.\,\mathbf{V}_{ij}^{(0)}}{rV_{ij}^{(0)}}\,Q(s)\right\}, \tag{6.9}$$

correct to the order of $\mathscr{P}_{ij}$, where the scalar function $Q(s)$ satisfies the differential equation (4.28). We seek an expression for the mean velocity of particles of species i which is correct to leading order in $\mathscr{P}_{ij}$, that is, correct to order $\mathscr{P}_{ij}^0$.

The direct contribution to S_{ij} due to gravity is given by (6.2), in which the values of $\mathbf{J}''$ and $\mathbf{J}'$ correct to order $\mathscr{P}_{ij}^0$ are found by substituting in (3.5) and (3.6) an expression for p_{ij} which contains only the leading term of (6.9) and so is spherically symmetric. The integrations with respect to the direction of $\mathbf{s}$ in $\mathbf{J}'$ and $\mathbf{J}''$ can be carried out, giving

$$S_{ij}^{(G)} = \left(\frac{1+\lambda}{2\lambda}\right)^3\int_2^\infty (A_{11}+2B_{11}-3)\exp\left(-\frac{\Phi_{ij}}{kT}\right)s^2 ds$$
$$+\gamma\left(\frac{1+\lambda}{2}\right)^2\int_2^\infty\left\{(A_{12}+2B_{12})\exp\left(-\frac{\Phi_{ij}}{kT}\right)-\frac{3}{s}\right\}s^2 ds-\gamma(\lambda^2+3\lambda+1). \tag{6.10}$$

The second direct contribution, due to the central interparticle force, is given by (6.3). The magnitude of $S_{ij}^{(I)}$ is not determined by the Péclet number alone (Φ_{ij}/kT also being involved), and we therefore try to obtain as much accuracy as possible by substituting the whole of the expression of (6.9) for p_{ij} in (6.3). The leading term in (6.9) is spherically symmetric and makes no contribution to the integral in (6.3), and after carrying out the integration with respect to the direction of $\mathbf{s}$ we find

$$S_{ij}^{(I)} = \tfrac{1}{2}\lambda(\gamma\lambda^2-1)\int_2^\infty\left(\frac{2A_{12}}{1+\lambda}-A_{11}\right)\frac{d\exp\left(-\Phi_{ij}/kT\right)}{ds}\,Q(s)\,s^2 ds. \tag{6.11}$$

It appears therefore that, if Φ_{ij}/kT is of order unity, as is often the case in practice, the small departure of the pair-distribution function from spherical symmetry is responsible for a value of $S_{ij}^{(I)}$ which is of the same order of magnitude as $S_{ij}^{(G)}$ (although the numerical value might be smaller in consequence of the small range of action of interparticle forces). Note in particular that $S_{ij}^{(I)}$ does not tend to zero as $\mathscr{P}_{ij} \to 0$ for a given value of $\Phi_{ij}^{(0)}/kT$. If the j-spheres have a larger fall speed in isolation ($\mathbf{V}_{ij}^{(0)}$ directed downwards) and so are more numerous just above an i-sphere than just below it ($Q < 0$), and if the interparticle force is generally repulsive ($d(-\Phi_{ij})/ds > 0$), then, since $2A_{12}/(1+\lambda) - A_{11} < 0$, (6.11) shows that the contribution to $\langle \Delta \mathbf{U}_i \rangle^{(I)}$ is in the same sense as $\mathbf{V}_{ij}^{(0)}$; that is, the j-spheres are pushing the i-spheres *downwards*.

Incidentally, we may confirm from (6.11) that $S_{ij}^{(I)}$ tends to zero as the range of action of the interparticle force tends to zero (so that $\exp(-\Phi_{ij}/kT) \to 1$ for $s > 2$). The function $Q(s)$ is finite at $s = 2$, and so, since $2A_{12}/(1+\lambda) - A_{11} = 0$ at $s = 2$ (see (2.10)), the integral in (6.11) is zero in the limit. It may similarly be shown from (6.3), using the local Boltzmann distribution (4.24) valid near $s = 2$, that $S_{ij}^{(I)}$ tends to zero at arbitrary Péclet number when the force exerted between the i and j-spheres reduces to an exclusion of separations closer than the touching position. We have of course taken this for granted in the previous discussion of cases in which $\Phi_{ij} = 0$ for $s > 2$.

The third direct contribution to S_{ij} is due to Brownian diffusion, and is given by (6.4). Here we certainly need to substitute the whole of the expression (6.9) for p_{ij}. The spherically symmetric term of leading order in (6.9) makes no contribution, and after carrying out the integration with respect to the direction of $\mathbf{s}$ we find

$$S_{ij}^{(B)} = (\gamma\lambda^2 - 1)\left(\frac{1+\lambda}{2\lambda}\right)^2 \int_2^\infty \left\{\frac{A_{11} - B_{11}}{s} + \frac{1}{2}\frac{dA_{11}}{ds} - \frac{2(A_{12} - B_{12})}{(1+\lambda)s} - \frac{1}{1+\lambda}\frac{dA_{12}}{ds}\right\} \exp\left(-\frac{\Phi_{ij}}{kT}\right) Q(s)\, s^2 ds. \quad (6.12)$$

Thus S_{ij} is the sum of the expressions (6.10)–(6.12). When the i and j-spheres are identical, this expression for S_{ij} reduces to that given in (6.6).

As mentioned in §4, $(\gamma\lambda^2 - 1)Q$ is a linear function of γ, because in this case of small Péclet number the effects of the forces applied to the i and j particles are independent perturbations of an equilibrium system. We may therefore write

$$(\gamma\lambda^2 - 1)\, Q(s, \gamma, \lambda) = Q'(s, \lambda) + \gamma Q''(s, \lambda), \quad (6.13)$$

where Q' and Q'' are independent of γ (and $Q' = -Q''$ when $\lambda = 1$). We may also introduce new sedimentation coefficients S'_{ij}, S''_{ij} which do not depend on γ and are defined by the relation

$$6\pi\eta a_i \langle \mathbf{U}_i \rangle = \mathbf{F}_i^{(0)} + \sum_{j=1}^{m} \phi_j (S'_{ij} \mathbf{F}_i^{(0)} + \lambda^{-3} S''_{ij} \mathbf{F}_j^{(0)}), \quad (6.14)$$

where $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$ are the applied forces. The factor λ^{-3} has been inserted in (6.14) for convenience in our particular case in which $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$ represent gravitational forces proportional to the sphere volumes. Then from a comparison with (1.5), we see that

$$S_{ij} = S'_{ij} + \gamma S''_{ij}. \quad (6.15)$$

The explicit expressions for S'_{ij} and S''_{ij} can be obtained from (6.10)–(6.12) by replacing $(\gamma\lambda^2 - 1)Q$ by $Q' + \gamma Q''$ and then identifying the coefficients of γ^0 and γ. Note that, although in the present paper the applied forces are parallel, the expressions for S'_{ij} and S''_{ij} found in this way are valid for arbitrary directions of $\mathbf{F}_i^{(0)}$ and $\mathbf{F}_j^{(0)}$.

These sedimentation coefficients S'_{ij} and $\lambda^{-3}S''_{ij}$ defined by (6.14) enter into the expressions for the spatial flux of particles of one species due to Brownian diffusion in the presence of gradients of number density of the particles of the various species in a polydisperse system (Batchelor 1982).

6.4. *Two species of spheres with very different radii or densities*

It was shown in § 4 that, when $\lambda \ll 1$ or $\lambda \gg 1$, $p_{ij}-1$ is small, being of order λ^3 when $\lambda \ll 1$ and of order λ^{-3} when $\lambda \gg 1$, for any given value of the Péclet number, provided only that the effects of interparticle forces are negligible at values of $r-(a_i+a_j)$ comparable with the smaller of a_i and a_j. We may use this result now to obtain some asymptotic expressions for S_{ij} which likewise are independent of the Péclet number.

We consider first the direct contribution due to gravity given by (6.2). The tensors $\mathbf{J}'$ and $\mathbf{J}''$ in that equation can be written as

$$\mathbf{J}' = \mathbf{I}\int_2^\infty (A_{11}+2B_{11}-3)\,s^2 ds + \frac{3}{4\pi}\int_{s\geqslant 2}\left\{(A_{11}-1)\frac{\mathbf{ss}}{s^2}+(B_{11}-1)\left(\mathbf{I}-\frac{\mathbf{ss}}{s^2}\right)\right\}(p_{ij}-1)\,d\mathbf{s} \tag{6.16}$$

$$\mathbf{J}'' = \mathbf{I}\frac{2\lambda}{1+\lambda}\int_2^\infty\left(A_{12}+2B_{12}-\frac{3}{s}\right)s^2 ds + \frac{3}{4\pi}\frac{2\lambda}{1+\lambda}\int_{s\geqslant 2}\left\{A_{12}\frac{\mathbf{ss}}{s^2}+B_{12}\left(\mathbf{I}-\frac{\mathbf{ss}}{s^2}\right)\right\}(p_{ij}-1)\,d\mathbf{s}, \tag{6.17}$$

and the orders of magnitude of all these integrals may be estimated.

The behaviours of A_{11}, B_{11}, A_{12}, B_{12} when $\lambda \ll 1$ are shown in (2.8) and (2.9), whence we find

$$\int \lim_{\lambda\to 0}\left(\frac{A_{11}+2B_{11}-3}{\lambda^3}\right)s^2 ds = \int_2^\infty\left(-\frac{60}{s^2}+\frac{480}{s^4}-\frac{1600}{s^6}\right)ds = -20 \tag{6.18}$$

and

$$A_{12}+2B_{12}-\frac{3}{s} = O(\lambda^3). \tag{6.19}$$

Use of the above result for $p_{ij}-1$ then shows that when $\lambda \ll 1$

$$\mathbf{J}' \sim -20\lambda^3\mathbf{I}, \quad \mathbf{J}'' = O(\lambda^4), \tag{6.20}$$

and

$$S_{ij}^{(G)} = -\tfrac{5}{2}-\gamma+O(\lambda). \tag{6.21}$$

On the other hand, when $\lambda \gg 1$, we may use the result noted in § 2 that $A_{11}-1$ and $B_{11}-1$, and hence also $A_{11}+2B_{11}-3$, are of order λ^{-1} when $\lambda \gg 1$. We also know from (2.5) that A_{12} and B_{12} are unchanged when λ is replaced by λ^{-1}, whence it follows from (6.19) that $A_{12}+2B_{12}-3s^{-1}$ is of order λ^{-3} when $\lambda \gg 1$. Hence when $\lambda \gg 1$

$$\mathbf{J}' = O(\lambda^{-1}), \quad \mathbf{J}'' = O(\lambda^{-3}), \tag{6.22}$$

and the contribution to S_{ij} due directly to gravity is

$$S_{ij}^{(G)} = -\gamma(\lambda^2+3\lambda+1)+O(\lambda^{-1}). \tag{6.23}$$

These two expressions for $S_{ij}^{(G)}$, (6.21) and (6.23), can be given a physical interpretation. When a sphere of radius a_i is falling through a dispersion there are two direct consequences of the presence of spheres of radius a_j in the fluid. One is that there is a net volume flux within a spherical surface of radius $a_j + a_i$ surrounding each j sphere equal to the sum of $\frac{4}{3}\pi a_j^3 \mathbf{U}_j^{(0)}$ due to the motion of the rigid sphere itself and $\frac{4}{3}\pi a_j^3(3\lambda^{-1}+\frac{3}{2}\lambda^{-2})\,\mathbf{U}_j^{(0)}$ due to the motion of the fluid in the spherical shell surrounding the rigid sphere. This downward volume flux must be balanced by an equal upward flux in the remainder of the system, and so the mean velocity in the fluid accessible to the centre of an i sphere is

$$-(1+3\lambda^{-1}+\tfrac{3}{2}\lambda^{-2})\,\phi_j\,\mathbf{U}_j^{(0)}, \quad = -\gamma(\lambda^2+3\lambda+\tfrac{3}{2})\,\phi_j\,\mathbf{U}_i^{(0)}.$$

The other is that the motion of the j spheres generates an environment for each i sphere in which the Laplacian of the fluid velocity at any point is non-zero. As explained in the paper on sedimentation in a monodisperse system (Batchelor 1972), this affects the motion of an i sphere (and the additional buoyancy force resulting from the greater density of the medium due to the presence of the j spheres is a part of this effect) and the change in the mean velocity of an i sphere which takes all accessible positions with equal probability is

$$\tfrac{1}{2}\lambda^{-2}\phi_j\,\mathbf{U}_j^{(0)}, \quad = \tfrac{1}{2}\gamma\phi_j\,\mathbf{U}_i^{(0)},$$

if we neglect further hydrodynamic interactions. Thus the total change in the mean velocity of an i sphere which takes all accessible positions with equal probability and which does not change its environment by its presence is

$$-\gamma(\lambda^2+3\lambda+1)\,\phi_j\,\mathbf{U}_i^{(0)}. \tag{6.24}$$

This is simply the last bracketed term in (3.4). No assumption about the magnitude of λ has been made in the argument leading to (6.24). When $\lambda \ll 1$ it accounts for the second term on the right-hand side of (6.21) and when $\lambda \gg 1$ it accounts for the whole of the explicit part of (6.23).

However, it is not quite true that a *large* i sphere does not disturb the environment in which it is placed. One of the consequences of the presence of the i sphere for a neighbouring smaller sphere is that the ambient velocity gradient at the position of the small sphere is non-zero and that the rate of energy dissipation in the fluid by viscosity is increased by the presence of the small sphere. All elements of the fluid surrounding the large sphere dissipate energy, not as a fluid of viscosity η, but as a fluid of viscosity η containing, on average, n_j spheres of radius a_j per unit volume, and we know from the Einstein formula that the effective viscosity of such a mixture is $\eta(1+\frac{5}{2}\phi_j)$ correct to the order of ϕ_j. The larger spheres are therefore falling through a fluid medium whose effective viscosity is $\eta(1+\frac{5}{2}\phi_j)$, and the corresponding fractional change in the fall speed of the larger spheres is $-\frac{5}{2}\phi_j$. Note that it is not necessary for the validity of this explanation that there be a large number of small spheres in the neighbourhood of the large sphere; provided the probable number of small spheres in unit volume outside the large sphere is uniform, it does not matter how small this number is. Thus the first term on the right-hand side of (6.21) is also accounted for.

There are also the contributions $S_{ij}^{(I)}$ and $S_{ij}^{(B)}$ given by (6.3) and (6.4) respectively. $S_{ij}^{(I)}$ is evidently small provided that, as has already been assumed, the interparticle force is negligible at sphere gaps comparable with the smaller of a_i and a_j. For $S_{ij}^{(B)}$

we note that the expression within curly brackets in (6.4) is seen from (2.8) and (2.9) to be of order λ^3 when $\lambda \ll 1$. Hence, remembering the result concerning $p_{ij}-1$, we find

$$S_{ij}^{(B)} = O(\lambda^4), \tag{6.25}$$

when $\lambda \ll 1$, at any given value of the Péclet number. And when $\lambda \gg 1$ we use the fact that $A_{11}-1$ and $B_{11}-1$ behave as λ^{-1} (as shown in § 2) to find

$$S_{ij}^{(B)} = O(\lambda^{-2}). \tag{6.26}$$

It appears therefore that, both when $\lambda \ll 1$ and when $\lambda \gg 1$, the sedimentation coefficient is dominated by the effect of gravity. At any Péclet number we have

$$S_{ij} = -\tfrac{5}{2}-\gamma+O(\lambda) \qquad \text{when} \quad \lambda \ll 1, \tag{6.27}$$

and

$$S_{ij} = -\gamma(\lambda^2+3\lambda+1)+O(\lambda^{-1}) \quad \text{when} \quad \lambda \gg 1. \tag{6.28}$$

The limiting cases $\gamma \to 0$ or $|\gamma| \to \infty$ are quite straightforward. It was noted in § 4 that $L(s)$ and $M(s)$, and hence also p_{ij} for a given Péclet number, approach finite limits as $\gamma \to 0$ or $|\gamma| \to \infty$. The mobility functions do not depend on γ, and it is evident therefore from (3.4) that, in the absence of any dependence of interparticle force effects on γ, S_{ij} is asymptotically linear in γ as $|\gamma| \to \infty$ for a given value of $\mathscr{P}_{ij}$. At small Péclet number S_{ij} has already been seen to be a linear function of γ for all γ; and at large Péclet number we see from (6.5) that

$$S_{ij} \sim \gamma\left[\tfrac{1}{4}(1+\lambda)^2\int_2^\infty \left\{(A_{12}+2B_{12})\,(p_{ij})_{|\gamma|\to\infty}-\frac{3}{s}\right\}s^2ds-(\lambda^2+3\lambda+1)\right] \tag{6.29}$$

as $|\gamma| \to \infty$.

I am grateful to Dr J. M. Rallison and Mr C.-S. Wen for their comments on a draft of this paper.

REFERENCES

ADLER, P. M. 1981 Interaction of unequal spheres. I. Hydrodynamic interaction. Colloidal forces. *J. Colloid Interface Sci.* **84**, 461–474.

BATCHELOR, G. K. 1972 Sedimentation in a dilute dispersion of spheres. *J. Fluid Mech.* **52**, 245–268.

BATCHELOR, G. K. 1976 Brownian diffusion of particles with hydrodynamic interaction. *J. Fluid Mech.* **74**, 1–29.

BATCHELOR, G. K. 1977 The effect of Brownian motion on the bulk stress in a suspension of spherical particles. *J. Fluid Mech.* **83**, 97–117.

BATCHELOR, G. K. 1982 Diffusion in a polydisperse system. *J. Fluid Mech.* (submitted).

BATCHELOR, G. K. & GREEN, J. T. 1972 The determination of the bulk stress in a suspension of spherical particles to order c^2. *J. Fluid Mech.* **56**, 401–427.

BATCHELOR, G. K. & WEN, C.-S. 1982 Sedimentation in a dilute polydisperse system of interacting particles. Part 2. Numerical results. *J. Fluid Mech.* (in the press).

DICKINSON, E. 1980 Sedimentation of interacting colloidal particles. *J. Colloid Interface Sci.* **73**, 578–581.

FEUILLEBOIS, F. 1980 Certain problemes d'écoulements mixtes fluide-particules solides. Doctoral dissertation presented to Paris VI University.

HABER, S. & HETSRONI, G. 1981 Sedimentation in a dilute dispersion of small drops of various sizes. *J. Colloid Interface Sci.* **79**, 56–75.

Jeffrey, D. J. 1982 Two unequal rigid spheres in low-Reynolds-number flow. Part 3. The mobility functions. *J. Fluid Mech.* (submitted).

Peterson, J. M. & Fixman, M. 1963 Viscosity of polymer solutions. *J. Chem. Phys.* **39**, 2516–2523.

Reed, C. C. & Anderson, J. L. 1976 Analysis of sedimentation velocity in terms of binary particle interactions. Article in *Colloid and Interface Science*, vol. IV, ed. M. Kerker. Academic Press.

Wacholder, E. & Sather, N. F. 1974 The hydrodynamic interaction of two unequal spheres moving under gravity through quiescent viscous fluid. *J. Fluid Mech.* **65**, 417–437.