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Diffusion in a dilute polydisperse system of interacting spheres

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When m different species of small particles are dispersed in fluid the existence of a (small) spatial gradient of concentration of particles of type j is accompanied, as a consequence of Brownian motion of the particles, by a flux of particles of type i. The flux and the gradient are linearly related, and the tensor diffusivity $\boldsymbol{D}_{ij}$ is the proportionality constant. When the total volume fraction of the particles is small, $\boldsymbol{D}_{ij}$ is approximately a linear function of the volume fractions $\phi_1, \phi_2, \ldots, \phi_m$, with coefficients which depend on the interactions between pairs of particles. The complete analytical expressions for these coefficients given here for the case of spherical particles are a linear combination of the second virial coefficient for the osmotic pressure of the dispersion (measuring the effective force acting on particles when there is a unit concentration gradient) and an analogous virial coefficient for the bulk mobility of the particles. Extensive calculations of the average velocities of the different species of spherical particles in a sedimenting polydisperse system have recently been published (Batchelor & Wen 1982) and some of the results given there (viz. those for small Péclet number of the relative motion of particles) refer in effect to the bulk mobilities wanted for the diffusion problem. It is thus possible to obtain numerical values of the coefficient of ϕ_k in the expression for $\boldsymbol{D}_{ij}$, as a function of the ratios of the radii of the spherical particles of types i, j and k. The numerical values for 'hard' spheres are found to be fitted closely by simple analytical expressions for the diffusivity; see (4.6) and (4.7). The dependence of the diffusivity on an interparticle force representing the combined action of van der Waals attraction and Coulomb repulsion in a simplified way is also investigated numerically for two species of particles of the same size. The diffusivity of a tracer particle in a dispersion of different particles is one of the many special cases for which numerical results are given; and the result for a tracer 'hard' sphere of the same size as the other particles is compared with that found by Jones & Burfield (1982) using a quite different approach.

1. Introduction

This is a sequel to some earlier papers on diffusion and sedimentation of small particles suspended in fluid, and we begin with a brief recapitulation of this previous work.

Gradient diffusion in a monodisperse system

Some years ago in a paper on Brownian diffusion of particles in fluid (Batchelor 1976) I showed that the mean particle flux down a small concentration gradient due to diffusion is the same as if each of the particles is acted on by a steady applied force

$$\overset{*}{\boldsymbol{F}} = -\frac{1}{1-\phi}\left(\frac{\partial \mu}{\partial n}\right)_{p,\,T} \nabla n \tag{1.1}$$

and the fluid is force-free, where n is the local mean number density of particles, ϕ is the particle volume fraction, and μ is the local chemical potential of a particle. The axes of reference here are such that the mean flux of volume, of particles and fluid together, across any geometrical surface in the dispersion is zero. The mean particle velocity $\langle \boldsymbol{U} \rangle$ resulting from this fictitious applied force (sometimes termed a 'thermodynamic force') is proportional to $\overset{*}{\boldsymbol{F}}$, since $\overset{*}{\boldsymbol{F}}$ represents a small perturbation of the equilibrium state of uniform concentration. Hence we may write $\langle \boldsymbol{U} \rangle$ as

$$\langle \boldsymbol{U} \rangle = \frac{B(\phi)}{6\pi\eta a}\overset{*}{\boldsymbol{F}}, \tag{1.2}$$

where B is a concentration-dependent bulk mobility coefficient, a is a length characteristic of a particle, and η is the viscosity of the suspending fluid. The tensor diffusivity $\boldsymbol{D}$ representing the effect of Brownian motion is defined by the equality of the two expressions for the flux of particle number ($\boldsymbol{f}$), viz.

$$\boldsymbol{f} = n\langle \boldsymbol{U} \rangle = -\boldsymbol{D}\cdot\nabla n,$$

and hence is given by

$$\boldsymbol{D} = \frac{B\boldsymbol{I}}{6\pi\eta a}\frac{\phi}{1-\phi}\left(\frac{\partial\mu}{\partial\phi}\right)_{p,\,T}, \tag{1.3}$$

where $\boldsymbol{I}$ denotes the unit second-rank tensor.

This expression is valid for arbitrary values of ϕ. The only restriction is that, as in all non-equilibrium transport theories, the magnitude of the intensity gradient (∇n) must be small in some sense.

When $\phi \ll 1$, both $\phi(\partial\mu/\partial\phi)_{p,\,T}$ and $B(\phi)$ may be expanded in series of positive powers of ϕ, and coefficients of ϕ^q in these series depend on interactions of a group of $q+1$ particles. We may write

$$\phi\left(\frac{\partial\mu}{\partial\phi}\right)_{p,\,T} = kT\{1+(\beta-1)\phi+O(\phi^2)\} \tag{1.4}$$†

and

$$B(\phi) = 1+S\phi+O(\phi^2), \tag{1.5}$$

where β and S depend on interactions between pairs of particles (β being related to the second virial coefficient for the osmotic pressure of the dispersion). Then

$$\boldsymbol{D} = \boldsymbol{D}^{(0)}\{1+(\beta+S)\phi+O(\phi^2)\}, \tag{1.6}$$

where

$$\boldsymbol{D}^{(0)} = \frac{kT}{6\pi\eta a}\boldsymbol{I} \tag{1.7}$$

is the classical expression for the diffusivity of a very dilute dispersion of independent spheres of radius a first derived by Einstein.

It is known from standard methods of evaluating the configuration integral for a dispersion in equilibrium (Hill 1960) that

$$\beta = 8$$

in the case of spheres which are rigid and exert no force on each other when they are not touching (so-called 'hard' spheres). It is also known from an analysis of the problem of gravitational sedimentation in a monodisperse system of spheres of this same type (Batchelor 1972) that

$$S = -6.55.$$

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† β as defined here is minus the quantity denoted by β in the previous paper on diffusion (Batchelor 1976).

Thus it was found (Batchelor 1976) that

$$\boldsymbol{D} = \boldsymbol{D}^{(0)}(1+1.45\phi) \tag{1.8}$$

correct to order ϕ, for rigid spheres which exert no force on each other except when touching.

There is no difficulty in principle in calculating the values of β and S, and thereby the coefficient of ϕ in (1.8), for spheres which do exert a (central) force on each other when the distance between their centres exceeds $2a$. Numerical values for a particular form of the interaction potential are given in §5.

Gradient diffusion in a polydisperse system

In the same paper (Batchelor 1976) I gave some of the general formulae needed for the case of a polydisperse system in which there are m different species of particle, the properties of particles of species i being denoted by $a_i, v_i, n_i, \phi_i, \mu_i$ (where v_i is the particle volume, and μ_i depends on $n_1, n_2, \ldots$ and not on n_i alone). The mean flux of particles of any species due to diffusion in the presence of gradients of concentration of all species was shown to be the same as if each of the particles of species i is acted on by a steady applied force

$$\overset{*}{\boldsymbol{F}_i} = \boldsymbol{F}_i + \frac{v_i}{1-\phi}\sum_{j=1}^{m} n_j \boldsymbol{F}_j \tag{1.9}$$

and the fluid is force-free, where $\phi = \sum_{j=1}^{m} \phi_j$ and

$$\boldsymbol{F}_i = -\sum_{j=1}^{m}\left(\frac{\partial \mu_i}{\partial n_j}\right)_{p,\,T} \nabla n_j. \tag{1.10}$$

Again the axes of reference are such that the mean flux of material volume is zero.

The applied forces $\overset{*}{\boldsymbol{F}_1}, \overset{*}{\boldsymbol{F}_2}, \ldots$ represent independent perturbations of an equilibrium state with isotropic structure and in place of (1.2) we have

$$\langle \boldsymbol{U}_i \rangle = \frac{1}{6\pi\eta a_i}\sum_{j=1}^{m} B_{ij}\overset{*}{\boldsymbol{F}_j}, \tag{1.11}$$

where the bulk mobility coefficient B_{ij} depends on $\phi_1, \phi_2, \ldots, \phi_m$ and on the particle size ratios typified by

$$\lambda_{ij} = \frac{a_j}{a_i}.$$

The diffusivity $\boldsymbol{D}_{ij}$ giving the flux of number of particles of species i due to the existence of a gradient of concentration of species j in a polydisperse system is defined by

$$\boldsymbol{f}_i = n_i\langle \boldsymbol{U}_i \rangle = -\sum_{j=1}^{m} \boldsymbol{D}_{ij}\cdot\nabla n_j, \tag{1.12}$$

and is found by substituting (1.9), (1.10) and (1.11) in (1.12) to be

$$\boldsymbol{D}_{ij} = \frac{\boldsymbol{I}}{6\pi\eta a_i}\sum_{k=1}^{m} B_{ik}\phi_i\left\{\lambda_{ij}^3\left(\frac{\partial \mu_k}{\partial \phi_j}\right)_{p,\,T} + \frac{\lambda_{ik}^3}{1-\phi}\sum_{l=1}^{m}\lambda_{lj}^3\phi_l\left(\frac{\partial \mu_l}{\partial \phi_j}\right)_{p,\,T}\right\}. \tag{1.13}$$

This expression is valid for arbitrary values of the particle volume fractions $\phi_1, \phi_2, \ldots, \phi_m$.

When $\phi \ll 1$, $\mu_i - kT\log\phi_i$ and B_{ij} may be replaced by the first few terms of their expansions in powers of ϕ_k. Terms of the first degree in ϕ_k in these series represent the effects of interactions between pairs of particles. We shall see in the next section that in place of (1.4) we have

$$\left(\frac{\partial \mu_i}{\partial \phi_j}\right)_{p,\,T} = kT\left\{\frac{\delta_{ij}}{\phi_i} - \lambda_{ij}^{-3} + \beta_{ij}\left(\frac{1+\lambda_{ij}}{2\lambda_{ij}}\right)^3 + O(\phi)\right\}, \tag{1.14}$$

where $\delta_{ij} = 1$ when $i = j$ and zero otherwise, and β_{ij} reduces to the constant β in (1.4) when $i = j$.

The bulk mobility coefficient B_{ij} describes the mean velocity of an i particle resulting from the application of a steady force to each j particle in the presence of force-free particles of species k ($\neq i$ or j), and the relevant pair interactions (viz. those between two particles of which at least one is acted on by a force) in which an i particle takes part depend on whether $j = i$ or $j \neq i$. If $j = i$, the relevant pair interactions are (i) those between two i particles on each of which a force acts, the contribution to B_{ij} then being the same as for a monodisperse system with volume fraction ϕ_i, and (ii) those between an i particle on which a force acts and a force-free k particle, the number of such interactions being proportional to ϕ_k, where k takes all values from 1 to m excluding i; and if $j \neq i$, the relevant pair interactions are those between a force-free i particle and a j particle on which a force acts, the number of such interactions being proportional to ϕ_j. Hence we may write

$$B_{ij} = \delta_{ij}\left(1 + \sum_{k=1}^{m} K'_{ik}\phi_k\right) + \lambda_{ij}^{-3} K''_{ij}\phi_j + O(\phi^2), \tag{1.15}$$

where the coefficients K'_{ij} and K''_{ij} depend only on λ_{ij} and

$$K'_{ii} + K''_{ii} = S \quad (i = 1, 2, \ldots, m). \tag{1.16}$$

Substitution of (1.14) and (1.15) in (1.13) then gives, after some algebra,

$$\boldsymbol{D}_{ij} = \boldsymbol{D}_i^{(0)}\left\{\delta_{ij} + \beta_{ij}\phi_i\left(\frac{1+\lambda_{ij}}{2}\right)^3 + \delta_{ij}\sum_{k=1}^{m} K'_{ik}\phi_k + K''_{ij}\phi_i\right\} \tag{1.17}$$

correct to order ϕ, where $\boldsymbol{D}_i^{(0)}$ is the diffusivity of independent particles of species i. The diagonal element of the diffusivity matrix is thus

$$\boldsymbol{D}_{ii} = \boldsymbol{D}_i^{(0)}\left\{1 + (\beta + S)\phi_i + \sum_{k(\neq i)} K'_{ik}\phi_k\right\}, \tag{1.18}$$

and the off-diagonal element is

$$\underset{(i \neq j)}{\boldsymbol{D}_{ij}} = \boldsymbol{D}_i^{(0)}\phi_i\left\{\beta_{ij}\left(\frac{1+\lambda_{ij}}{2}\right)^3 + K''_{ij}\right\}. \tag{1.19}$$

The relation (1.17) holds for any particle shape provided λ_{ij}, the ratio of the characteristic lengths a_i and a_j, is interpreted as $(v_j/v_i)^{\frac{1}{3}}$. In the important case in which the i-particles have much smaller volume fraction than any other species, so that each i-particle is effectively isolated from its fellows – being then a 'tracer' particle – we may put $\phi_i = 0$ in (1.18) and (1.19) to obtain

$$\boldsymbol{D}_{ii} = \boldsymbol{D}_i^{(0)}\left(1 + \sum_{k(\neq i)} K'_{ik}\phi_k\right), \quad \underset{(i \neq j)}{\boldsymbol{D}_{ij}} = 0. \tag{1.20}$$

An explicit expression for β_{ij} in terms of the potential of the force exerted between two spherical particles of radii a_i and a_j can readily be derived using the methods developed in statistical mechanics. Numerical values of the bulk mobility coefficients K'_{ij} and K''_{ij} on the other hand are difficult to obtain accurately, and none were available in 1976. However the position has now changed because in some recent work on sedimentation of spheres in a dilute polydisperse system (Batchelor 1982; Batchelor & Wen 1982) values of the related sedimentation coefficients have been calculated for many values of the parameters on which they depend.

The purposes of this note are to show how this recent work on sedimentation may be used to obtain complete analytical expressions for the mobility coefficients K'_{ij} and K''_{ij} entering into the expression (1.17) for the diffusivity and to present some numerical values of the diffusivity of each species of spherical particle in a dilute polydisperse system.

2. The 'second virial coefficient' for a polydisperse system

Here we obtain an expression for the constant β_{ij} in (1.14) representing the effect of interactions of pairs of particles on the thermodynamic force. The derivation uses arguments to be found in text-books on statistical mechanics (see, for example, Hill 1960, Landau & Lifschitz 1968 or McQuarrie 1973) and will be indicated briefly for the benefit of fluid dynamicists not familiar with such arguments. β_{ij} is (a numerical multiple of) the 'second virial coefficient' giving the correction to the perfect-gas law due to the finite size and range of interaction of the gas molecules, or to the ideal-solution expression for the osmotic pressure in solutions of non-electrolytes. In most text-books β_{ij} is specified only for identical particles.

The starting point is the following standard expression for the Gibbs free energy of a volume V of the dispersion, in equilibrium, containing $N_0(\gg 1)$ fluid molecules each of volume v_0 and $N_i(\gg 1)$ spherical particles each of volume v_i $(i = 1, 2, \dots, m)$:

$$G = N_0 \psi_0 + \sum_{i=1}^{m} N_i(\psi_i + kT \log \phi_i/e) + kT \log Q_N^{-1}, \tag{2.1}$$

where

$$N = \sum_i N_i, \quad V = N_0 v_0 + \sum_i N_i v_i, \quad \phi_i = N_i v_i / V.$$

In (2.1) ψ_0 is the chemical potential (i.e. the free energy per molecule) of the fluid in the pure state, and ψ_i, like ψ_0, is a function only of the temperature and pressure. The effect of interactions between the particles is contained in Q_N, the configuration integral given by

$$Q_N = \frac{1}{V^N} \int \dots \int \exp\left\{\frac{-\Phi(\boldsymbol{x}_1, \dots, \boldsymbol{x}_N)}{kT}\right\} \mathrm{d}\boldsymbol{x}_1 \dots \mathrm{d}\boldsymbol{x}_N, \tag{2.2}$$

where $\Phi(\boldsymbol{x}_1, \dots, \boldsymbol{x}_N)$ is the potential energy of the forces exerted between the N particles at positions $\boldsymbol{x}_1, \dots, \boldsymbol{x}_N$ and the integration is over the volume V in each case. An expression for G of the same form (2.1) applies to a solution of solute molecules and also to the molecules of a gas (ψ_0 and ψ_i being zero in this latter case). The fact that the colloidal particles of interest here are much bigger than molecules is of no consequence. The chemical potential of the particles of species i is defined as

$$\begin{aligned} \mu_i &= \left(\frac{\partial G}{\partial N_i}\right)_{p,T} \\ &= \psi_i + kT\left(\log \phi_i - \frac{N v_i}{V} + \frac{\partial \log Q_N^{-1}}{\partial N_i}\right), \end{aligned} \tag{2.3}$$

and the coefficient of ∇n_j in the expression (1.10) for the thermodynamic force can then be determined when Q_N is known.

In the limit $N/N_0 \to 0$, the particle interaction energy Φ is small for all except a negligible fraction of the possible particle configurations represented in (2.2) and it is evident that $Q_N^{1/N} \to 1$, $\log Q_N^{1/N} \to 0$. When $N/N_0 \ll 1$, $\log Q_N^{1/N}$ is a small quantity of order N/N_0 which represents the effect of interactions between isolated pairs of particles (and so must involve two species symmetrically), the correction term of order N^2/N_0^2 represents the effect of interactions between particles in groups of three, and so on. Bearing in mind that G must be a homogeneous function of the first degree in $N_0, N_1, \ldots$, we see that $\log Q_N^{-1/N}$ can be written as

$$\log Q_N^{-1/N} = \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} \beta_{ij} \frac{N_i N_j}{N N_0} \frac{4\pi}{3v_0} \left(\frac{a_i + a_j}{2}\right)^3 + O(N^2/N_0^2) \tag{2.4}$$

when $N/N_0 \ll 1$, where $a_i = (3v_i/4\pi)^{\frac{1}{3}}$. The corresponding approximate expression for μ_i is

$$\mu_i = \psi_i + kT\left\{\log \phi_i - nv_i + \sum_{j=1}^{m} \beta_{ij} \phi_j \left(\frac{a_i + a_j}{2a_j}\right)^3 + O(\phi^2)\right\}, \tag{2.5}$$

where $n = N/V$. This yields (1.14) on differentiation with respect to ϕ_j.

It can be seen by inspection of (2.2), and confirmed from the rigorous arguments given in the text-books, that when the particles in a dilute dispersion are all spheres of species i, and only pair interactions are allowed for,

$$Q_N^{1/N} = 1 + \tfrac{3}{2}\phi_i \int_0^\infty \left\{\exp\left(\frac{-\Phi_{ii}}{kT}\right) - 1\right\} s^2 \, \mathrm{d}s + O(\phi_i^2), \tag{2.6}$$

where $\Phi_{ii}(s)$ is the potential of the (central) force exerted between two spheres of radius a_i with distance sa_i between their centres (and $\Phi_{ii} = \infty$ when $0 \leqslant s < 2$ in the case of rigid spheres). Then if a single spherical particle of species j is introduced into this dispersion of particles of species i, the new value of Q_N is obtained by multiplying the old value by a factor

$$1 + 3\phi_i \left(\frac{a_i + a_j}{2a_i}\right)^3 \int_0^\infty \left\{\exp\left(\frac{-\Phi_{ij}}{kT}\right) - 1\right\} s^2 \, \mathrm{d}s \tag{2.7}$$

(as may be seen by carrying out the integration with respect to this additional particle before the other N integrations in (2.2)), where s now denotes the distance between the two sphere centres divided by $\frac{1}{2}(a_i + a_j)$ and $\Phi_{ij}(s)$ is the potential of the force exerted between a sphere of species i and a sphere of species j. Comparison of (2.6) and (2.7) with (2.4) shows that both correspond to

$$\beta_{ij} = 3 \int_0^\infty \left\{1 - \exp\left(\frac{-\Phi_{ij}}{kT}\right)\right\} s^2 \, \mathrm{d}s, \tag{2.8}$$

in which i and j may take the same or different values.

In the case of 'hard' spheres for which $\Phi_{ij} = 0$ when $s \geqslant 2$ and $\Phi_{ij} = \infty$ when $0 \leqslant s < 2$, this reduces to

$$\beta_{ij} = 8$$

as quoted in §1. And in the case of rigid spheres of radii a_i and a_j which do exert a force on each other at positions for which $s > 2$ we have

$$\beta_{ij} = 8 + 3 \int_2^\infty \left\{1 - \exp\left(\frac{-\Phi_{ij}}{kT}\right)\right\} s^2 \, \mathrm{d}s. \tag{2.9}$$

Values of β_{ij} for some particular forms of the function $\Phi_{ij}(s)$ in the range $s \geqslant 2$ are given in §5.

3. The identification of the bulk mobility coefficients with sedimentation coefficients for a dilute polydisperse system

The bulk mobility coefficients K'_{ij} and K''_{ij} whose values we seek here are defined by the two relations (1.11) and (1.15), which together become

$$\langle U_i \rangle = \frac{1}{6\pi\eta a_i}\left\{\overset{*}{F}_i + \sum_{j=1}^{m} \phi_j \left(K'_{ij}\overset{*}{F}_i + \lambda_{ij}^{-3} K''_{ij}\overset{*}{F}_j\right)\right\}. \tag{3.1}$$

In this relation, $\overset{*}{F}_i$ denotes a steady force applied to each of the particles of species i, where i takes all values from 1 to m, and $\langle U_i \rangle$ is the mean velocity of a particle of species i generated by these steady forces. $\overset{*}{F}_i$ is a thermodynamic force which generates the same particle flux as the actual Brownian diffusion down the concentration gradient, and it must have small magnitude if our assumption that the diffusive flux is linear in the concentration gradients is to be valid.

Now in the sedimenting system in which particles move under the action of real applied forces having different values for different species, the effect of the applied forces is a small perturbation of the system, with consequent linearity of the mean particle velocity in each of the applied gravitational forces, only for small values of the Péclet number (a measure of the relative magnitude of effects of particle 'convection' and diffusion on the statistical structure of the dispersion, that is, in this case of a dilute dispersion, on the pair-distribution function). For an interaction between an i and a j particle the Péclet number of the relative motion of the two particles may be defined as

$$\mathbb{P}_{ij} = \frac{\frac{1}{2}(a_i + a_j)\,|U_j^{(0)} - U_i^{(0)}|}{D_i^{(0)} + D_j^{(0)}}, \tag{3.2}$$

where $U_i^{(0)}$ and $U_j^{(0)}$ are the velocities of isolated i and j particles moving under the action of the applied forces $F_i^{(0)}$ and $F_j^{(0)}$ and $D_i^{(0)} + D_j^{(0)}$ is the relative diffusivity of the two particles when they are far apart.† (The value of $\mathbb{P}_{ij}$ for the diffusive system is given, aside from factors of order unity, by

$$a_i a_j \left(\frac{|\nabla\phi_j|}{a_j \phi_j} - \frac{|\nabla\phi_i|}{a_i \phi_i}\right),$$

and is small when the change in particle concentration of each species over one particle radius is a small fraction of the concentration – this is the quantitative form of the condition for the diffusive flux of particles to be proportional to the concentration gradients). And in the sedimenting system the forces applied to the particles of the different species are parallel.

In the first of the two recent papers on sedimentation in a dilute polydisperse system (Batchelor 1982), analytical formulae for the sedimentation velocities of the different species were given. It was shown there (see (6.14) in that paper) that for pair interactions with $\mathbb{P}_{ij} \ll 1$ the mean velocity of particles of species i is given by

$$\langle U_i \rangle = \frac{1}{6\pi\eta a_i}\left\{F_i^{(0)} + \sum_{j=1}^{m} \phi_j \left(S'_{ij}F_i^{(0)} + \lambda_{ij}^{-3} S''_{ij}F_j^{(0)}\right)\right\}, \tag{3.3}$$

where $F_i^{(0)}$ denotes the external force applied to each particle of species i and the

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† Note that there is no dependence of the sedimentation velocity to order ϕ on the Péclet number in the case of a monodisperse system of spheres because two identical spheres acted on by identical forces have zero relative velocity, regardless of their vector separation, and the Péclet number for a pair of particles is zero for any magnitude of the applied force.

sedimentation coefficients S'_{ij} and S''_{ij} are independent of the applied forces. Explicit expressions for S'_{ij} and S''_{ij} in the case of spherical particles were found. The practical application of the results of that paper is to systems sedimenting under gravity with applied forces $\boldsymbol{F}_1^{(0)}$, $\boldsymbol{F}_2^{(0)}, \ldots$ which are parallel, and parallelism of the applied forces was essential for validity of the results for Péclet numbers which are not small, but at small Péclet number $\boldsymbol{F}_1^{(0)}$, $\boldsymbol{F}_2^{(0)}, \ldots$ are independent perturbations of the system with linearly additive effects and the expressions obtained for S'_{ij} and S''_{ij} are valid for arbitrary directions of the applied forces.

The expression (3.1) describes the mean velocity of a particle of species i when steady forces of small magnitude and arbitrary direction representing the diffusive consequences of concentration gradients are applied to the particles of the various species. Likewise the expression (3.3) describes the mean velocity of a particle of species i when steady external forces (representing gravity although no analytical use is made of that fact), of sufficiently small magnitude to make the Péclet number small, are applied to the particles of the different species. Hence we may identify the expressions for the mean particle velocity in the two systems, showing that

$$K'_{ij} = S'_{ij}, \quad K''_{ij} = S''_{ij}. \tag{3.4}$$

The diffusivity tensor $\boldsymbol{D}_{ij}$ is then obtained, correct to order ϕ, by substituting the known expressions for S'_{ij} and S''_{ij} in place of K'_{ij} and K''_{ij} in (1.17). Henceforth the identification (3.4) will be accepted without further comment.

It was noted (Batchelor 1982) that each of the sedimentation coefficients S'_{ij}, S''_{ij} is the sum of three contributions with different physical meanings and may conveniently be written as

$$S'_{ij}{}^{,''} = S'_{ij}{}^{,''(\mathrm{G})} + S'_{ij}{}^{,''(\mathrm{I})} + S'_{ij}{}^{,''(\mathrm{B})}. \tag{3.5}$$

The contributions $S'^{(\mathrm{G})}_{ij}$, $S''^{(\mathrm{G})}_{ij}$ due directly to gravity (directly, meaning 'for given structure of the dispersion'; there is also an indirect effect of gravitational forces, through their influence on the statistical properties of the configuration of spheres) are given by

$$S'^{(\mathrm{G})}_{ij} = \left(\frac{1+\lambda_{ij}}{2\lambda_{ij}}\right)^3 \int_2^\infty (A_{11}+2B_{11}-3)\exp\left(\frac{-\Phi_{ij}}{kT}\right) s^2\,\mathrm{d}s, \tag{3.6}$$

$$S''^{(\mathrm{G})}_{ij} = \left(\frac{1+\lambda_{ij}}{2}\right)^2 \int_2^\infty \left\{A_{12}+2B_{12})\exp\left(\frac{-\Phi_{ij}}{kT}\right) - \frac{3}{s}\right\} s^2\,\mathrm{d}s - (\lambda_{ij}^2+3\lambda_{ij}+1), \tag{3.7}$$

where A_{11}, A_{12}, A_{22}, B_{11}, B_{12}, B_{22} are the two-sphere mobility functions of $s(=2r/(a_i+a_j))$, where r is the distance between the centres of an i and a j sphere) and also depend on $\lambda_{ij}\,(=a_j/a_i)$.

The contributions $S'^{(\mathrm{I})}_{ij}$, $S''^{(\mathrm{I})}_{ij}$ due directly to the interactive force exerted between an i and a j particle, which is represented by the potential Φ_{ij} (defined for $s > 2$ – within radii a_i and a_j the material of the two spheres is assumed to be rigid), are given by

$$S'_{ij}{}^{,''(\mathrm{I})} = \tfrac{1}{2}\lambda_{ij} \int_2^\infty \left(\frac{2A_{12}}{1+\lambda_{ij}} - A_{11}\right) \frac{\mathrm{d}\exp(-\Phi_{ij}/kT)}{\mathrm{d}s} Q'^{,''}\, s^2\,\mathrm{d}s. \tag{3.8}$$

Here Q' and Q'' are functions of s and λ_{ij} representing the perturbations of the Maxwell–Boltzmann form of the pair-distribution function due to the applied forces $\boldsymbol{F}_i^{(0)}$ and $\boldsymbol{F}_j^{(0)}$ respectively; see the appendix for more details. It should be noted that Q' and Q'' are normalized quantities of order unity.

The contributions $S_{ij}'^{(\mathrm{B})}$, $S_{ij}''^{(\mathrm{B})}$ are due directly to Brownian diffusion and are given by

$$S_{ij}'^{,\prime\prime(\mathrm{B})} = \left(\frac{1+\lambda_{ij}}{2\lambda_{ij}}\right)^2 \int_2^\infty \left\{\frac{A_{11}-B_{11}}{s} + \frac{1}{2}\frac{\mathrm{d}A_{11}}{\mathrm{d}s} - \frac{2(A_{12}-B_{12})}{(1+\lambda_{ij})s} - \frac{1}{1+\lambda_{ij}}\frac{\mathrm{d}A_{12}}{\mathrm{d}s}\right\} \times \exp\left(\frac{-\Phi_{ij}}{kT}\right) Q'^{,\prime\prime} s^2 \,\mathrm{d}s. \quad (3.9)$$

As explained in the paper (Batchelor 1982), the interparticle force and Brownian diffusion make direct and non-negligible contributions to the mean velocity of the particles of one species in consequence of the departure from spherical symmetry of the pair-distribution function for i and j particles. The departure from spherical symmetry is small, being of order $\mathbb{P}_{ij}$, but the contribution to the mean particle velocity is a product of the Brownian diffusivity and this departure from spherical symmetry and is not an algebraically small quantity. The existence of this direct contribution due to Brownian diffusion was overlooked in my first attempt to generalize the formulae for the dependence of the diffusivity on particle concentration to the case of a polydisperse system (Batchelor 1976).

For further explanation of the meaning of the symbols occurring in the expressions for S_{ij}' and S_{ij}'' and of the physical processes underlying the relations reference should be made to Batchelor (1982). In §§4 and 5 we shall make use of the numerical values of S_{ij}' and S_{ij}'' given in the second of the two recent papers on sedimentation in a polydisperse system (Batchelor & Wen 1982).

From this point onwards we shall denote a_j/a_i by λ without the suffixes.

4. Rigid spheres with zero interaction potential

Rigid spheres which exert no force on each other when not touching (i.e. $\Phi_{ij} = 0$ for $s > 2$) provide a simple case which is of some practical interest and for which a fairly complete set of numerical results is available. For this case the diffusivity is given by (1.18) and (1.19) with

$$\beta_{ij} = 8, \quad S = -6.55, \quad (4.1)$$

$$\left.\begin{aligned} K_{ij}' &= S_{ij}' = S_{ij}'^{(\mathrm{G})} + S_{ij}'^{(\mathrm{B})}, \\ K_{ij}'' &= S_{ij}'' = S_{ij}''^{(\mathrm{G})} + S_{ij}''^{(\mathrm{B})}, \end{aligned}\right\} \quad (4.2)$$

where from (3.7)

$$S_{ij}'^{(\mathrm{G})} = -\left(\frac{1+\lambda}{2\lambda}\right)^3 \int_2^\infty (3-A_{11}-2B_{11})\, s^2 \,\mathrm{d}s, \quad (4.3)$$

$$S_{ij}''^{(\mathrm{G})} = -\left(\frac{1+\lambda}{2}\right)^2 \int_2^\infty \left(\frac{3}{s}-A_{12}-2B_{12}\right) s^2 \,\mathrm{d}s - (\lambda^2+3\lambda+1), \quad (4.4)$$

and $S_{ij}'^{(\mathrm{B})}$, $S_{ij}''^{(\mathrm{B})}$ are given by (3.9) with $\Phi_{ij} = 0$.

Numerical values of $S_{ij}'^{(\mathrm{G})}$, $S_{ij}''^{(\mathrm{G})}$, $S_{ij}'^{(\mathrm{B})}$ and $S_{ij}''^{(B)}$ have been calculated by Batchelor & Wen (1982) for a number of different values of λ, and are reproduced in table 1. These numerical values were found from accurate data for the two-sphere mobility functions and should be correct to within ∓ 0.01. Table 1 and figure 1 show the corresponding values of K_{ij}' and $K_{ij}'' + \lambda^2 + 3\lambda + 1$ as functions of λ. In the earlier paper on diffusion (Batchelor 1976) the values of the two integrals in (4.3) and (4.4) (denoted there by C and D respectively) were given only for $\lambda = 1$.

λ	$S'^{(G)}_{ij}$	$S'^{(B)}_{ij}$	K'_{ij}	$S''^{(G)}_{ij}+\lambda^2+3\lambda+1$	$S''^{(B)}_{ij}$	$K''_{ij}+\lambda^2+3\lambda+1$
0	−2.50	0	−2.50	0	0	0
0.125	−2.34	0.03	−2.31	0.01	−0.01	0
0.25	−2.24	0.07	−2.17	0.04	−0.04	0
0.5	−2.09	0.15	−1.94	0.12	−0.12	0
1	−1.83	0.27	−1.56	0.28	−0.27	0.01
2	−1.45	0.35	−1.10	0.48	−0.47	0.01
4	−1.04	0.41	−0.63	0.64	−0.68	−0.04
8	−0.69	0.45	−0.24	0.75	−0.88	−0.13

TABLE 1. The bulk mobility coefficients K'_{ij} $(=S'_{ij})$ and K''_{ij} $(=S''_{ij})$ as functions of λ $(=a_j/a_i)$ for the case of rigid spheres with zero interaction potential.

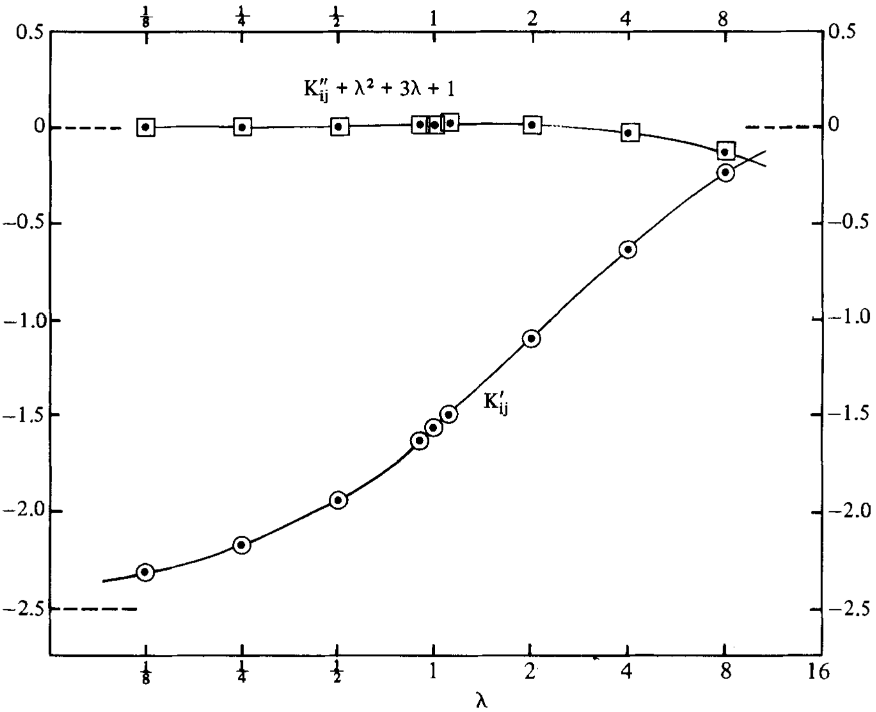

FIGURE 1. Calculated values of the bulk mobility coefficients K'_{ij}, K''_{ij} as functions of $\lambda(=a_j/a_i)$ for the case of rigid spheres with zero interaction potential. The broken lines are theoretical asymptotes.

As was pointed out by Batchelor & Wen (1982), the calculated values of K'_{ij} in table 1 are fitted well by the simple empirical relation

$$K'_{ij}=-\frac{2.5}{1+0.6\lambda}. \tag{4.5}$$

It also appears that $K''_{ij}+\lambda^2+3\lambda+1$ is negligible except when $\lambda \gg 1$, and that it is then of small magnitude by comparison with λ^2 (see the last column of table 1) and even smaller compared with the term $\frac{1}{8}(1+\lambda)^3\beta_{ij}$ in (1.17). Thus for most practical purposes it may be sufficient to put

$$K''_{ij}=-(\lambda^2+3\lambda+1),$$

and to write (1.18) and (1.19) in the approximate forms

$$\boldsymbol{D}_{ii} = \boldsymbol{D}_i^{(0)}\left(1+1.45\phi_i - \sum_{k(\neq i)} \frac{2.5\phi_k}{1+0.6\lambda_{ik}}\right) \tag{4.6}$$

$$\underset{(i\neq j)}{\boldsymbol{D}_{ij}} = \boldsymbol{D}_i^{(0)}\phi_i(\lambda^3+2\lambda^2) \tag{4.7}$$

for the case of rigid spheres with zero interaction potential, where $\lambda = a_j/a_i$ and $\lambda_{ik} = a_k/a_i$.

It will happen often that a dispersion contains just two different species of particle, with the labels i and j, in which case the flux of number of i particles is

$$\begin{aligned} \boldsymbol{f}_i &= -\boldsymbol{D}_{ii}\cdot\nabla n_i - \boldsymbol{D}_{ij}\cdot\nabla n_j, \\ &= \frac{kT}{6\pi\eta a_i}\left\{-\left(1+1.45\phi_i - \frac{2.5\phi_j}{1+0.6\lambda}\right)\nabla n_i - (\lambda^3+2\lambda^2)\,\phi_i\,\nabla n_j\right\} \end{aligned} \tag{4.8}$$

if we use the approximate expressions (4.6) and (4.7). The flux of number of j particles is given by exactly the same expression with suffixes i and j exchanged and λ replaced by λ^{-1}. The roles of the i and j particles appear more symmetrically in the corresponding expression for the flux of particle volume, viz.

$$\boldsymbol{q}_i = \tfrac{4}{3}\pi a_i^3\,\boldsymbol{f}_i = \frac{kT}{6\pi\eta a_i}\left\{-\left(1+1.45\phi_i - \frac{2.5\phi_j}{1+0.6\lambda}\right)\nabla\phi_i - (1+2\lambda^{-1})\,\phi_i\,\nabla\phi_j\right\}. \tag{4.9}$$

The case of a 'tracer' particle of radius a_i diffusing in a dispersion containing numerous particles of radius a_j is of special interest in practice. This corresponds to a two-particle system for which $\phi_i \ll \phi_j$, and, as given in (1.20),

$$\boldsymbol{D}_{ii} = \boldsymbol{D}_i^{(0)}(1+K'_{ij}\phi_j), \quad \underset{(i\neq j)}{\boldsymbol{D}_{ij}} = 0. \tag{4.10}$$

The numerous j particles are here acting solely as passive obstacles to the migration of an i particle, and the existence of a gradient of concentration of j particles has no influence on the flux of i particles. No divergent or non-absolutely convergent integrals arise in the expression for the corresponding sedimentation coefficient S'_{ij} because the relevant hydrodynamic interactions are weak.

The graph of K'_{ij} in figure 1 shows the way in which this tracer diffusivity varies with λ. When $\lambda \ll 1$, we have $K'_{ij} = -2.5$, as expected from the fact that the only consequence of the presence of very small j particles is to increase the effective viscosity of the fluid surrounding the migrating i particle by the factor $1+\frac{5}{2}\phi_j$ (Batchelor 1982). When $\lambda = 1$, we have $K'_{ij} = -1.56$ (instead of the value -1.83 which was found in 1976 through my oversight of the contribution $S'^{(B)}_{ij}$ to the sedimentation coefficient S'_{ij}), showing the reduction in the diffusivity of a tracer sphere due to the presence in the dispersion of other spheres which differ from the tracer sphere only in some non-dynamical property. And as $\lambda \to \infty$ we have $K'_{ij} \to 0$, not simply from extrapolation of the values in table 1 but also from an analytical argument (Batchelor 1982). This last result for the diffusivity is a little surprising, and at first sight it might seem to conflict with the result, originally established by Maxwell (see Jeffrey 1973), that the diffusivity of solute molecules or heat in a medium is changed, by a factor $1-\frac{3}{2}\phi$, owing to the presence of fixed impermeable spheres distributed with statistical homogeneity and volume fraction ϕ. However, there is no contradiction because in the present case the large spheres are free to move and this lessens the resistance that they offer to the migrating small spheres. It is probable that the change in the diffusivity of a tracer particle due to the presence of force-free spheres of large radius a_j is not zero to higher orders in ϕ_j.

5. Rigid spheres with a non-zero interaction potential

The spheres here are supposed to prevent any closer approach of their two centres than $r = a_i + a_j$ and in addition to exert on each other a force given by the pair-wise interaction potential $\Phi_{ij}(r)$ which is defined for $a_i + a_j < r < \infty$ and approaches zero as $r \to \infty$. Precise results for the effect of the interparticle force on the diffusivity in a dilute monodisperse system have not yet been presented, so far as I know, and since this case is of course relevant to diffusion in a polydisperse system, inasmuch as some interactions involve identical particles, we take it first.

Gradient diffusion in a monodisperse system

The diffusivity is given by (1.6), and we need to find the values of the virial coefficient β and the sedimentation (or bulk mobility) coefficient S. For β we have, from (2.9),

$$\beta = 8 - 3\int_2^\infty \left\{\exp\left(-\frac{\Phi}{kT}\right) - 1\right\} s^2\,\mathrm{d}s, \tag{5.1}$$

the suffixes to Φ being superfluous here. It will be convenient, following Batchelor & Wen (1982), to write

$$\alpha = 3\int_2^\infty \left\{\exp\left(-\frac{\Phi}{kT}\right) - 1\right\} s^2\,\mathrm{d}s \tag{5.2}$$

and to note that, since the pair-distribution function in a diffusing (or sedimenting) dilute monodisperse system has the Maxwell–Boltzmann form, $\alpha\phi$ is the mean number of particles to be found within a sphere of radius $R(\gg a)$ centred on a given particle, minus the number in a dispersion of the same concentration with $\Phi = 0$. It is understandable that this quantity α should be connected with the second virial coefficient for the chemical potential, because this virial coefficient is a measure of that part of unit volume of the dispersion from which an additional particle is excluded.

For S we have an integral expression involving $\Phi(s)$ and the two-sphere mobility functions (see formula (6.5) in Batchelor 1982). However, it is unnecessary to consider this expression in detail because it was shown by Batchelor & Wen (1982) that, provided $|\Phi|/kT$ falls to a small value when the gap between two spheres becomes as large as about a quarter of a sphere radius, S is given with reasonable accuracy by the approximate relation

$$S = -6.55 + 0.44\alpha, \tag{5.3}$$

essentially because the mobility functions vary only slightly over the range of values of s for which $\exp(-\Phi/kT) - 1$ is different from zero. For instance, it was found, for a particular form of the function $\Phi(s)$ such that $\Phi = 0$ when $s > 2.2$, that the difference between the values of S given by (5.3) and the full expression is less than one percent. If there is electrostatic repulsion between charged particles with thick double layers, it may happen that Φ/kT is still significantly different from zero at separations near $s = 3$, and in such cases it will be necessary to evaluate S from the full expression. No numerical results of this kind are yet available, although there would be no difficulty in obtaining them once the function $\Phi(s)$ is known.

The expression (1.6) for the gradient diffusivity is

$$\boldsymbol{D} = \boldsymbol{D}^{(0)}\{1+(\beta+S)\phi+O(\phi^2)\}$$

and from (5.1), (5.2) and (5.3) we have

$$\beta+S \approx 1.45-0.56\alpha, \tag{5.4}$$

giving a very simple relation between the diffusivity and the number of close particle pairs per unit volume resulting from the interparticle force. Positive values of α correspond to a mainly attractive interparticle force and more close pairs than in the case $\Phi = 0$; and this leads (*a*) to a resultant attractive force on a particle towards a region of higher particle density and so to a smaller diffusivity, and (*b*) to a larger bulk mobility (because close pairs fall under gravity more quickly than a well-separated pair) and so to a larger diffusivity, effect (*a*) being numerically larger. And conversely for negative values of α corresponding to a mainly repulsive force and fewer close pairs than in the case $\Phi = 0$ (which can be thought of, so far as effect (*a*) is concerned, as equivalent to an increase in the volume of the region near one sphere from which another sphere is excluded by the repulsive force associated with the rigidity of the spheres).

The value of α can be calculated from (5.2) if the interparticle force potential $\Phi(s)$ is known. Many combinations of an attractive van der Waals force and an electrostatic repulsion of charged spheres with double-layer screening occur in practice and could be considered. However, our purpose here is to provide illustrative, rather than comprehensive, values of the diffusivity showing the dependence on the interparticle potential, and only the simple family of potential functions constructed by Batchelor & Wen (1982) will be considered. According to this model of the interparticle force, Φ has different behaviours in three ranges. First,

$$\frac{\Phi}{kT} = \frac{\Phi_0}{kT} \gg 1 \quad \text{when} \quad 0 < \xi(=s-2) < \xi_0, \tag{5.5}$$

corresponding to a strong electrostatic repulsion which prevents two spheres from approaching closer than a centre-to-centre distance of $2a+\xi_0 a$, $\xi_0 a$ being a measure of the double-layer thickness. Second,

$$\Phi = -\frac{A}{12\xi(1+11.2\xi a\lambda_{\mathrm{d}}^{-1})} \quad \text{when} \quad \xi_0 \leqslant \xi \leqslant 0.2, \tag{5.6}$$

corresponding to a van der Waals attraction between two spheres of radius a with a 'retarded' potential, and no electrostatic repulsion, outside the double layer, where A is the composite Hamaker constant, taken as equal to $1.25kT$ (the value for polystyrene spheres in water) in the calculations, and λ_{d} is the dispersion wave-length, usually assumed to be 0.100 μm. Third,

$$\Phi = 0 \quad \text{when} \quad \xi > 0.2, \tag{5.7}$$

corresponding to the rapid decrease of the magnitude of the van der Waals potential which is known to occur when the gap between the surfaces of the two spheres approaches a sphere radius. ξ_0 is a free parameter which may be varied between 0 and 0.2 to show the effect of variation of the thickness of the double layer which screens the Coulomb repulsion. For discussion of the reasons for choosing this simplified form of $\Phi(s)$ reference should be made to Batchelor & Wen (1982).

Batchelor & Wen (1982) give numerical values of α calculated from (5.2), with this assumed form for $\Phi(s)$, as a function of ξ_0 for several values of a/λ_{d}, and these are reproduced in table 2. The corresponding values of the coefficient of ϕ in the expression (5.4) for the diffusivity are shown graphically in figure 2 for several different sphere radii. Note that very small values of ξ_0, representing a very thin double layer and leading to values of α above about 12, are unlikely to be realistic because in such a case numerous multiple aggregates, as well as doublets, would form, in conflict with the assumed stability of the dispersion.

It appears that the effect of the interparticle force on the diffusivity can be considerable, and that the coefficient of ϕ in (5.4) varies in figure 2 from about -3.5 at small values of ξ_0 with $a = 0.1$ μm to about $+2.9$ at $\xi_0 = 0.2$. An attempt to predict values of the diffusivity accurately from the theory clearly requires a knowledge of the electrical conditions in the dispersion. We need to know that the height of the Coulomb barrier is large, as assumed in the above model, and we need to know its location.

Some measurements of the sedimentation coefficient S for spherical particles whose double-layer thicknesses were known approximately have been reported in the literature, and Batchelor & Wen (1982) show that the values expected from the theory agree reasonably with those observed. Measurements of the diffusivity of sterically stabilized silica spheres (with $a = 0.021$ μm) dispersed in cyclohexane made by Kops-Werkhoven & Fijnaut (1981) give 1.3 ∓ 0.2 for the coefficient of ϕ in (5.4); however, a close comparison with the theoretical value is not possible in this case without an estimate of the effective value of α for sterically stabilized particles.

Gradient diffusion in a polydisperse system

The diffusivity $\boldsymbol{D}_{ij}$ giving the flux of i particles due to the existence of a spatial gradient of concentration of j particles is of the form (1.17), and we need to be able to find the values of the virial coefficient β_{ij} and the bulk mobility coefficients $K'_{ij}(= S'_{ij})$ and $K''_{ij}(= S''_{ij})$. For β_{ij} we have, from (2.9),

$$\beta_{ij} = 8 - \alpha_{ij},$$

where

$$\alpha_{ij} = 3\int_2^\infty \left\{\exp\left(-\frac{\Phi_{ij}}{kT}\right) - 1\right\} s^2\,\mathrm{d}s. \tag{5.8}$$

Again we note that, since the pair-distribution function for i and j particles has the Maxwell–Boltzmann form (although to a different degree of approximation, in a polydisperse system, as we saw in §3), $\alpha_{ij}\phi_j$ can be interpreted as the mean number of j particles to be found within a sphere of radius $R(\gg a_i + a_j)$ centred on a given i particle, minus the number in a dispersion with the same concentration and $\Phi_{ij} = 0$. The coefficient β_{ij} can be calculated when the potentials of the force exerted between two spheres of the same species ($i = j$) and between two spheres of different species ($i \neq j$) are known.

The sedimentation coefficients S'_{ij} and S''_{ij} are given by (3.5)–(3.9), and likewise can be evaluated when $\Phi_{ij}(s)$ is given. This is a much larger computational task, however, because the differential equation for the pair-distribution function – more specifically, for the perturbation of the Maxwell–Boltzmann form of the pair-distribution function, as described in the Appendix – must first be solved. Batchelor & Wen (1982) have made this calculation of S'_{ij} and S''_{ij} for the case of two spheres of the same size (the i and j species being distinguished by a difference in some other particle property), and for the simplified form of interparticle force potential described earlier in this section, and we shall use their results here to get a general impression of the effect of the interparticle force on the diffusivity. It was assumed that the interparticle

	$a = 0.1\ \mu\mathrm{m}$			$a = 0.5\ \mu\mathrm{m}$			$a = 1\ \mu\mathrm{m}$			$a = 2\ \mu\mathrm{m}$		
ξ_0	α	K'_{ij}	K''_{ij}	α	K'_{ij}	K''_{ij}	α	K'_{ij}	K''_{ij}	α	K'_{ij}	K''_{ij}
0.008	—	—	—	—	—	—	—	—	—	2.39	−1.03	−4.44
0.010	—	—	—	—	—	—	3.79	−0.86	−3.98	0.96	−1.42	−4.70
0.012	—	—	—	6.09	−0.55	−3.25	1.79	−1.30	−4.44	0.54	−1.50	−4.81
0.014	—	—	—	3.26	−1.09	−3.99	1.10	−1.42	−4.63	0.34	−1.53	−4.86
0.016	13.23	0.47	−1.07	2.11	−1.28	−4.32	0.75	−1.48	−4.73	0.22	−1.55	−4.90
0.018	8.68	−0.45	−2.21	1.51	−1.40	−4.48	0.54	−1.52	−4.79	0.12	−1.57	−4.93
0.020	6.44	−0.68	−3.00	1.15	−1.44	−4.60	0.39	−1.54	−4.84	0.05	−1.58	−4.95
0.025	3.63	−1.22	−3.73	0.63	−1.51	−4.76	0.15	−1.57	−4.91	−0.08	−1.60	−4.99
0.030	2.49	−1.35	−4.11	0.35	−1.56	−4.84	−0.01	−1.59	−4.96	−0.19	−1.61	−5.03
0.040	1.32	−1.50	−4.47	−0.01	−1.60	−4.95	−0.25	−1.62	−5.04	−0.37	−1.63	−5.08
0.050	0.70	−1.57	−4.68	−0.26	−1.63	−5.04	−0.43	−1.64	−5.10	−0.52	−1.65	−5.14
0.060	—	−1.61	−4.83	—	−1.65	−5.11	—	−1.66	−5.16	—	−1.66	−5.19
0.070	−0.05	—	—	−0.65	—	—	−0.76	—	—	−0.81	—	—
0.080	—	−1.65	−5.05	—	−1.68	−5.24	—	−1.68	−5.28	—	−1.68	−5.29
0.100	−0.80	−1.68	−5.23	−1.14	−1.70	−5.36	−1.20	−1.70	−5.39	−1.23	−1.70	−5.40
0.120	—	−1.70	−5.39	—	−1.71	−5.48	—	−1.71	−5.50	—	−1.71	−5.51
0.150	−1.78	−1.72	−5.61	−1.90	−1.73	−5.66	−1.92	−1.73	−5.67	−1.93	−1.73	−5.67
0.200	−2.65	−1.75	−5.96	−2.65	−1.75	−5.96	−2.65	−1.75	−5.96	−2.65	−1.75	−5.96

TABLE 2. Values of the parameter α measuring the number of close pairs of particles (see (5.2) and (5.8)) and of the bulk mobility coefficients K'_{ij} $(= S'_{ij})$ and K''_{ij} $(= S''_{ij})$, for a dispersion of two species of spherical particle of the same size $(a_i = a_j = a)$ which exert a force on each other. ξ_0 is the parameter in the expression for the interparticle force potential that measures the position of a high Coulomb barrier around each sphere of both species. At larger sphere separations than $(2+\xi_0)\,a$ the interparticle force is a van der Waals attraction; see (5.5), (5.6) and (5.7).

force potential is numerically the same function of s for an i and a j sphere as for two i spheres. Batchelor & Wen gave reasons for concluding that the effect of the interparticle force on the functions $Q'(s)$ and $Q''(s)$, which represent the perturbation about the Maxwell–Boltzmann form of the pair-distribution function, is small; and they took the values of these functions, which occur in the expressions for $S_{ij}^{\prime,\prime\prime(\mathrm{I})}$ and $S_{ij}^{\prime,\prime\prime(\mathrm{B})}$ (see (3.8) and (3.9)), to be the same as for the case $\Phi_{ij} = 0$.

Reference should be made to Batchelor & Wen (1982) for the calculated values of the separate contributions to S'_{ij} and S''_{ij} represented by (3.6), (3.7), (3.8) and (3.9). Table 2 shows the resulting values of S'_{ij} (or K'_{ij}) and S''_{ij} (or K''_{ij}) for a range of values of ξ_0, measuring the location of the high Coulomb barrier, and for four values of the common sphere radius a.

The quantity α_{ij} in this case in which $\Phi_{ij}(s)$ is assumed to be the same when $i \neq j$ as when $i = j$ is of course identical with α (see (5.2)), the values of which also are given in table 2. Note also that for this case $\lambda = 1$ there is the identity

$$\begin{aligned} K'_{ij} + K''_{ij} &= S \\ &\approx -6.55 + 0.44\alpha. \end{aligned} \tag{5.9}$$

With just the two species of particle, and $a_i = a_j$, the expression (1.18) for the diagonal element of the diffusivity matrix giving the flux of i particles becomes

$$\begin{aligned} \boldsymbol{D}_{ii} &= \boldsymbol{D}_i^{(0)}\{1 + (\beta + S)\,\phi_i + K'_{ij}\,\phi_j\} \\ &= \boldsymbol{D}_i^{(0)}\{1 + (1.45 - 0.56\alpha)\,\phi_i + K'_{ij}\,\phi_j\}, \end{aligned} \tag{5.10}$$

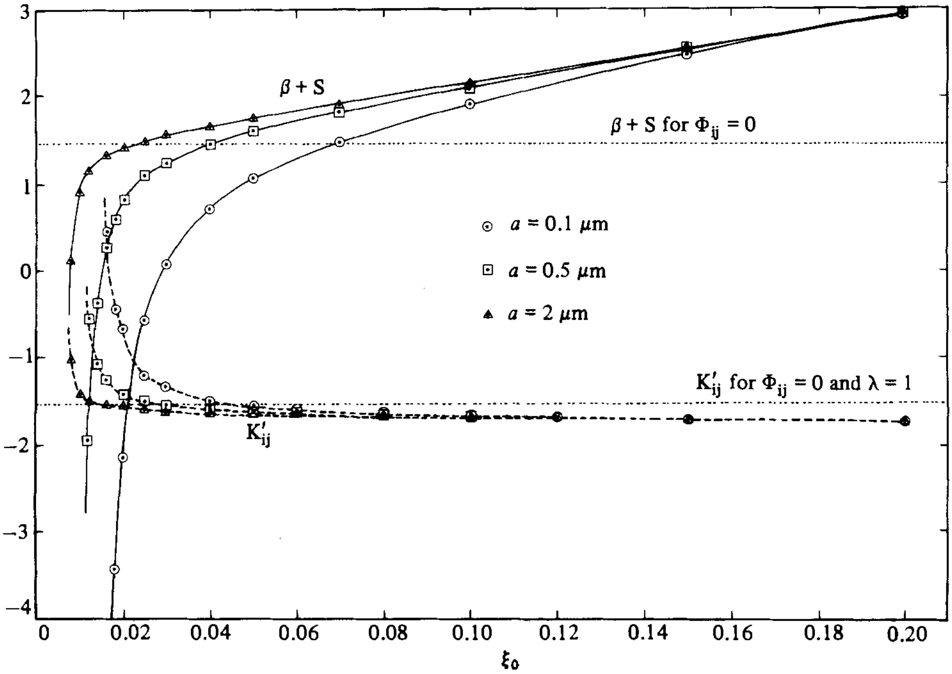

FIGURE 2. The monodisperse diffusivity coefficient $\beta+S$ ($\approx 1.45-0.56\alpha$) as a function of the parameter ξ_0 specifying the location of the high Coulomb barrier surrounding each sphere; and K'_{ij} as a function of ξ_0 for a dispersion of i and j spheres of the same size ($\lambda = 1$). For the dependence on the diffusivity on K'_{ij} see (5.10), (5.11) and (5.12).

and the non-diagonal element given by (1.19) becomes

$$\underset{(i\neq j)}{\boldsymbol{D}_{ij}} = \boldsymbol{D}_i^{(0)}\phi_i(\beta+K''_{ij}) = \boldsymbol{D}_i^{(0)}\phi_i(1.45-0.56\alpha-K'_{ij}). \qquad (5.11)$$

With the aid of table 2 for the values of α and of K'_{ij} and K''_{ij}, both elements of the diffusivity matrix can be found numerically. The coefficients of ϕ_i and ϕ_j in (5.10) are shown in figure 2; and the coefficient of ϕ_i in (5.11) is the difference between these two plotted quantities. The value of each coefficient for $\Phi_{ij} = 0$ is shown for comparison, from which it appears that the effect of the interparticle force is significant, although not dominant, just as in the case of a monodisperse system. The opposing effects of van der Waals attraction and Coulomb repulsion cancel approximately when ξ_0 lies between 0.04 and 0.07 for sphere radii in the range 0.1–2.0 μm.

The case of an i-type tracer particle, labelled in some way, diffusing in a dispersion of spherical particles of the same size with volume fraction ϕ_j corresponds to $\phi_i \to 0$ in (5.10) and (5.11). The diffusivity of the tracer particle is thus

$$\boldsymbol{D}_{ii} = \boldsymbol{D}_i^{(0)}(1+K'_{ij}\phi_j), \quad \underset{(i\neq j)}{\boldsymbol{D}_{ij}} = 0, \qquad (5.12)$$

and the numerical value of K'_{ij} is given in figure 2. The value of K'_{ij} differs appreciably from its value for $\Phi_{ij} = 0$ (viz. $K'_{ij} = -1.56$) only for quite small values of ξ_0, smaller than about 0.025.

6. Other work on concentration-dependent diffusivities

There are many published papers on the first-order dependence of the diffusivity on concentration for particles in a monodisperse system, and a few which attempt to extend the analysis to particular cases of a polydisperse system. So far as I know, no other writers have chosen to exploit the exact expressions (1.3) and (1.13) for the diffusivity together with the virial expansions of the chemical potential of the particles and the bulk mobility of the particles. This approach linking diffusion with sedimentation analytically yielded the first correct deduction of the diffusivity of monodisperse particles (and by correct I mean analytically correct, not simply with improved numerical accuracy of the hydrodynamic functions) and it has now made possible a set of numerical results for polydisperse systems which go far beyond what has been found by other methods. The resolution of the problem into two component parts, one the virial expansion of the chemical potential, which gives the concentration dependence of the thermodynamic force driving the particles down the concentration gradient and which is known already from text-books on statistical mechanics, and the other the virial expansion of the bulk mobility, which is an essentially hydrodynamic quantity giving the response of the particles to applied forces, seems to me to be physically clear and to provide a convenient frame-work for numerical calculation.

Other researchers have mostly chosen to use complex and sophisticated techniques from statistical mechanics which blur the division of the problem into the above two parts. This preference for methods developed in statistical mechanics may be a reflection of the theoretical physics background of the authors; and it may also arise from their wish to obtain information about the displacement of marked particles over a wide range of times after being at specified positions in the dispersion, such information being relevant to observations of the light scattered from particles and not obviously obtainable from the approach I have adopted.

Felderhof (1978) gives a brief review of the contributions to the calculation of the diffusivity of a monodisperse system of spherical particles up to that date, and he notes the reasons why the various published results differ analytically and numerically. Felderhof also shows how the result (1.8) for 'hard' spheres can be recovered approximately (the difference being due to Felderhof's use of an expansion of the two-sphere mobility functions in inverse powers of the separation of the two spheres in place of the more accurate numerical solution of the two-sphere flow field) from a consideration of the Smoluchowski equation for the joint probability density of the positions of a group of N particles.

The development of the experimental technique of photon correlation spectroscopy (the photons being scattered from light incident on particles) has stimulated several very recent theoretical investigations of the diffusion of tracer particles in a dispersion of other particles of the same size (Hanna, Hess & Klein 1982; Jones & Burfield 1982; Pusey & Tough 1982*a*, *b*). Tracer diffusion can be regarded as a special case of diffusion in a polydisperse system even when $a_i = a_j$ (in which case the term self-diffusion is also appropriate) as we have noted. Much of the analysis in these papers is concerned with the dependence of the statistical properties of the displacement of a tracer particle on the time t measured from the instant of its release at a specified point.

Now, at values of t such that

$$\frac{m}{6\pi\eta a} \ll t \ll \frac{(a\phi^{-\frac{1}{3}})^2}{D_i^{(0)}}, \tag{6.1}$$

where the left-hand member of the inequality is the Brownian relaxation time and the right-hand member is a measure of the time required for the tracer particle to diffuse over a distance comparable with the spacing of the passive j-particles, the velocity of the tracer particle is a stationary function of time and half the rate of increase of mean-square displacement of the particle defines a diffusivity. This diffusivity depends on the configuration of nearby j-spheres (actually on the position of the nearest neighbour only in our case of a dilute dispersion), which is constant at times satisfying (6.1), and so is not isotropic. However, the average of the diffusivity over all positions of the nearest j-sphere, weighted with an appropriate pair-distribution function, is a more meaningful quantity, and is referred to as the 'short-time' tracer diffusivity by Pusey & Tough (1982*a*, *b*) and other authors concerned with the interpretation of light-scattering measurements. It seems to be agreed that the pair-distribution function that corresponds to the conditions of the experiments has the Maxwell–Boltzmann form, as it would do if the tracer particle was part of an equilibrium system at the instant of 'release' ($t = 0$).

At times t comparable with $(a\phi^{-\frac{1}{3}})^2/D_i^{(0)}$, the velocity of the tracer particle is no longer a stationary random function of time because the particle is moving into different surroundings. However, when

$$t \gg (a\phi^{-\frac{1}{3}})^2/D_i^{(0)} \tag{6.2}$$

the particle has had many encounters with j-spheres and its velocity is again a stationary random function of position and again half the rate of increase of mean-square displacement defines a diffusivity. This is the 'long-time' diffusivity in the terminology of Pusey & Tough (1982*a*, *b*) and Jones & Burfield (1982), whereas in my formulation, which presupposes that the pair-distribution function and other parameters of the structure of the dispersion have reached a steady state, it is simply *the* tracer diffusivity.

We may thus compare the results obtained here for the tracer diffusivity (with $a_i = a_j$) with the diffusivity found by these authors for what they designate as 'long times', when 'memory effects' are significant.

I do not understand the cited papers well enough to be able to compare their analytical results with mine, and unfortunately the approximations made in the hydrodynamic data by most of the authors obscures a comparison of the numerical end-products. Jones & Burfield (1982) appreciated the importance of moderately accurate hydrodynamic data, although even they used a small number of terms of series expansions of the two-sphere mobility functions which would be significantly in error at nearly-touching positions of the two spheres. Jones & Burfield report finding that a tracer sphere of radius a_i, in a dispersion of 'hard' j-spheres for which $a_j = a_i$, at 'long times' after release has the scalar diffusivity

$$D_i^{(0)}\{1+(-C-0.08)\phi_j\},$$

where C is the integral in the expression for $S_{ij}'^{(G)}$ in (4.3) with $\lambda = 1$. The tracer diffusivity found here on the other hand (see (4.10) and (4.2)) is $D_i^{(0)}(1+K_{ij}'\phi_j)$, where

$$K_{ij}' = -C+S_{ij}'^{(B)} \tag{6.3}$$

when $\lambda = 1$. There is thus agreement on the appearance of the integral C (for which Jones & Burfield adopt the approximate value 1.73, instead of the more accurate value 1.83 given in my 1976 paper, but that is not relevant to our comparison). According to table 1 the value of $S_{ij}'^{(B)}$ for $\lambda = 1$ is 0.27. This represents in my formulation the contribution due to the non-equilibrium form of the pair-distribution function, whereas Jones & Burfield find -0.08 for the contribution due to what they term 'memory effects'. The difference between 0.27 and -0.08 is not large, and might arise from the less accurate hydrodynamic data used by Jones & Burfield. The positive sign of $S'^{(B)}_{ij}$ in my formulation is a consequence of the fact that the smoothing of the pair-distribution function by Brownian motion assists the tracer particle to move down the concentration (or probability) gradient, as explained in the context of the sedimentation problem (Batchelor & Wen 1982).

In my first brief investigation of diffusion in a polydisperse system (Batchelor 1976) I overlooked the fact that the non-zero relative velocity of two interacting spheres of different species caused by different thermodynamic forces acting on the two spheres (the relative velocity being non-zero even when the two spheres are of the same size), and the resulting small non-zero value of the Péclet number for the relative motion, lead to a small departure from the equilibrium form of the pair-distribution function and thereby to direct contributions of order unity, viz. $S^{(I)}_{ij}$ and $S^{(B)}_{ij}$, to the bulk mobility coefficient (in ways made clear in my paper on sedimentation, Batchelor 1982).† As a consequence of this oversight, I took the pair-distribution function to have the equilibrium or Maxwell–Boltzmann form, and so – unwittingly – I obtained what is referred to in the recent papers cited above as the 'short-time' tracer diffusivity. My result in 1976 for the magnitude of the isotropic diffusivity of a tracer particle in a dispersion of j-spheres of the same size was

$$D_i^{(0)}(1-C\phi_j),$$

where C is the integral referred to in (6.3). This result was wrong for the 'long-time' tracer diffusivity that I thought I was calculating, but is right for the 'short-time' tracer diffusivity that other people later calculated.

No quantitative results for diffusivities in a polydisperse system other than the above-mentioned results for tracer diffusion in a dispersion of particles of the same size as the tracer particle appear to have been published.

Ackerson (1978), Jones & Burfield (1982), Pusey & Tough (1982*a*, *b*) and Hanna *et al.* (1982) have all noted that, in their formulations of diffusion problems, 'memory effects', or differences between short and long time behaviour, do not arise in the calculation of the gradient (or 'collective', as they term it) diffusivity in a monodisperse system. I am not sure what meaning can be given to short-time gradient diffusion in a monodisperse system, since the choice of the initial sphere configuration seems to be quite arbitrary, but if they mean that departures from the equilibrium form of the pair-distribution function do not develop I do of course agree. The equivalent statement in my formulation is that the steady-state pair-distribution function has the equilibrium form at all times, for the reason (not noticed by these authors, so far as I can tell) that two identical spheres moving under the action of equal applied forces

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† Pusey & Tough (1982*a*, *b*) recognized that there must be some error in the value of the tracer diffusivity of a 'hard' sphere given in my 1976 paper (and that there is an equivalent omission in the quite different formulation of Jones 1979), although they were not aware that it was an oversight which can be, and has now been, made good within the context of my approach. They ascribed my error to an assumption stated at the beginning of my paper, viz. that the configuration of particles does not change significantly during the time-interval characteristic of the Brownian diffusion process. Like Marqusee & Deutch (1980), they supposed that this assumption precludes consideration of long-time effects such as the development of a steady-state non-equilibrium pair-distribution function as particles move down a spatial gradient of concentration. However, this is a misreading of my assumption. As stated explicitly in my paper, I assumed only that the particle configuration does not change significantly during the Brownian relaxation time $(m/6\pi\eta a)$ – a condition which is in fact easily satisfied for particles even as small as 10^{-3} μm in radius in water.

have zero relative velocity and the Péclet number for their relative motion is zero. There is no reason on the other hand to expect the three-sphere distribution function, which is relevant at larger concentrations, to have the equilibrium form.

Appendix. The pair-distribution function in a sedimenting system at small Péclet number

The pair probability density function $n_j p_{ij}(\boldsymbol{r})$ is defined as the probability that the centre of a sphere of species j lies within unit volume at position $\boldsymbol{r}$ relative to the centre of a sphere of species i. For a dilute system at zero Péclet number $p_{ij}(\boldsymbol{r})$ has the equilibrium or Maxwell–Boltzmann form $\exp(-\Phi_{ij}/kT)$. The perturbed-equilibrium form at small Péclet number was shown (Batchelor 1982) to be

$$p_{ij}(\boldsymbol{r}) = \exp\left(-\frac{\Phi_{ij}}{kT}\right)\left\{1 + \mathbb{P}_{ij}\frac{\boldsymbol{r}\cdot(\boldsymbol{U}_i^{(0)}Q' + \boldsymbol{U}_j^{(0)}\lambda_{ij}^{-2}Q'')}{r\,|\boldsymbol{U}_j^{(0)} - \boldsymbol{U}_i^{(0)}|} + O(\mathbb{P}_{ij}^2)\right\},$$

where the Péclet number $\mathbb{P}_{ij}$ is defined as in (3.2), $\boldsymbol{U}_i^{(0)}$ and $\boldsymbol{U}_j^{(0)}$ are the velocities of isolated i and j particles to which the forces $\boldsymbol{F}_i^{(0)}$ and $\boldsymbol{F}_j^{(0)}$ are applied, and Q', Q'' are functions of $s(=2r/(a_i+a_j))$ and $\lambda_{ij}(=a_j/a_i)$ only. This is equivalent to

$$p_{ij}(\boldsymbol{r}) = \exp\left(-\frac{\Phi_{ij}}{kT}\right)\left\{1 + \frac{\boldsymbol{r}\cdot(\boldsymbol{F}_i^{(0)}a_j Q' + \boldsymbol{F}_j^{(0)}a_i Q'')}{2rkT} + O(\mathbb{P}_{ij}^2)\right\}.$$

Note that the perturbation term is not spherically symmetric.

$p_{ij}(\boldsymbol{r})$ satisfies a conservation equation containing convection (due to the applied and interactive forces) and diffusion terms, and this equation determines Q' and Q''. In the paper on sedimentation (Batchelor 1982) the combination $Q' + \gamma_{ij}Q''$ was employed, where γ_{ij} is the ratio of the reduced densities of the i and j spheres, but an equivalent formulation of the equations for Q' and Q'' which makes no reference to particle densities and gravity (and does not involve any assumption of parallelism of the applied forces) is

$$\frac{\mathrm{d}}{\mathrm{d}s}\left(sG\frac{\mathrm{d}Q^{','' }}{\mathrm{d}s}\right) - \frac{\mathrm{d}(\Phi_{ij}/kT)}{\mathrm{d}s}s^2 G\frac{\mathrm{d}Q^{',''}}{\mathrm{d}s} - 2HQ^{',''} = s^2 W^{',''} - \frac{\mathrm{d}(\Phi_{ij}/kT)}{\mathrm{d}s}s^2 L^{',''},$$

where $G(s)$ and $H(s)$ are the longitudinal and lateral relative diffusivity functions and L', L'' and W', W'' bear the same relation to the functions L and W defined in the paper as Q', Q'' bear to $Q(=(Q'+\gamma_{ij}Q'')/(\gamma_{ij}\lambda_{ij}^2-1))$. G, H, L', L'', W' and W'' are known functions of $s(=2r/(a_i+a_j))$ and λ_{ij}. The boundary conditions satisfied by Q' and Q'' are $G\,\mathrm{d}Q^{',''}/\mathrm{d}s = 0$ at $s = 2$ and $Q^{',''} \to 0$ as $s \to \infty$. Numerical values of the functions $Q'(s)\,(=-(Q)_{\gamma_{ij}=0})$ and $(Q'+Q'')/(\lambda_{ij}^2-1)\,(=(Q)_{\gamma_{ij}=1})$ for various values of λ_{ij} are given by Batchelor & Wen (1982).

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