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Brownian diffusion of particles with hydrodynamic interaction

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The classical theory of Brownian motion applies to suspensions which are so dilute that each particle is effectively alone in infinite fluid. We consider here the modifications to the theory that are needed when rigid spherical particles are close enough to interact hydrodynamically. It is first shown that Brownian motion is a diffusion process of the conventional kind provided that the particle configuration does not change significantly during a viscous relaxation time. The original argument due to Einstein, which invokes an equilibrium situation, is generalized to show that the particle flux in probability space due to Brownian motion is the same as that which would be produced by the application of a certain 'thermodynamic' force to each particle. We then use this prescription to deduce the Brownian diffusivities in two different types of situation. The first concerns a dilute homogeneous suspension which is being deformed, and the relative translational diffusivity of two rigid spherical particles with a given separation is calculated from the properties of the low-Reynolds-number flow due to two spheres moving under equal and opposite forces. The second concerns a suspension in which there is a gradient of concentration of particles. The thermodynamic force on each particle in this case is shown to be equal to the gradient of the chemical potential of the particles, which brings considerations of the multi-particle excluded volume into the problem. Determination of the particle flux due to the action of this force is equivalent to determination of the sedimentation velocity of particles falling through fluid under gravity, for which a theoretical result correct to the first order in volume fraction of the particles is available. The diffusivity of the particles is found to increase slowly as the concentration rises from zero. These results are generalized to the case of a (dilute) inhomogeneous suspension of several different species of spherical particle, and expressions are obtained for the diagonal and off-diagonal elements of the diffusivity matrix. Numerical values of all the relevant hydrodynamic functions are given for the case of spheres of uniform size.

1. Introduction

The classical theory of Brownian diffusion developed by Einstein (1905, 1906) and many later workers is concerned with random migration of isolated colloidal particles or large solute molecules due to interaction with molecules of the suspending fluid. The results of this theory are applicable to very dilute solutions or suspensions in which the particles on average are far apart from each other. When the suspension is not extremely dilute, the interaction of particles will affect their migration. We shall consider here the effects of two basic types of interaction, both of which depend on the ratio of the particle size to the average particle spacing. Both the particles and the suspending fluid will be assumed to be incompressible, so that there is no change of volume accompanying diffusion. We shall assume the particles to be large enough for the suspending fluid to be regarded as a continuum.

One type of interaction, that due to inter-particle forces, has been studied intensively by physical chemists, and the dependence of the thermodynamic quantities describing the state of a statistically homogeneous suspension or solution on the concentration of particles is known, in the form of 'virial expansions', for various functional forms of the interaction potential. For simplicity we shall assume the particles to be rigid spheres with interparticle forces which have the purely geometrical effect of preventing particles from overlapping, but it should be possible to generalize the results to suit other forms of the interaction potential. The other type of interaction to be considered is hydrodynamic, and results from the fact that movement of one particle through the fluid generates a velocity field which affects the motion of neighbouring particles. The first type of interaction is relevant to systems in equilibrium, and both are relevant to diffusive transport of particles in non-equilibrium systems.

Other papers published recently which have been concerned with the Brownian diffusion of particles with hydrodynamic interaction are by Deutch & Oppenheim (1971), Murphy & Aguirre (1972), and Aguirre & Murphy (1973). The investigations by these two groups of workers were based on consideration of the dynamics of particles moving under the action of the fluctuating force exerted by the surrounding medium. Here we use an alternative and much simpler method for the statistical mechanics part of the investigation which is a generalization of the argument used by Einstein and which gives the asymptotic or long-time statistical properties of the displacement of particles in terms of the thermal energy of the medium. The result is an indirect but general prescription of multi-particle Brownian diffusive flux which tells us that the flux is the same as if certain steady forces were acting on the particles. The calculation of the diffusive flux in particular cases is then a hydrodynamic problem involving two or more particles moving under the action of given forces. This kind of hydrodynamic problem also arises in the sedimentation of particles, and some recent progress with the calculation of interaction effects in the sedimentation of particles in a dilute suspension is used in §6 to determine the rate at which particles diffuse down a concentration gradient.

As a preliminary we show in §2 that multi-particle displacements due to Brownian motion have statistics of Gaussian form and that the joint probability density functions describing particle displacements satisfy a diffusion equation with a diffusivity which rapidly approaches a constant value.

2. Multi-particle Brownian motion as a diffusion process

Suppose that the position of the centre of volume of a particle subject to Brownian motion is given at some initial instant, and that the displacement and velocity of the centre of volume after a time t are denoted by $\mathbf{X}(t)$ and $\mathbf{v}(t)$, where

$$\mathbf{X}(t) = \int_0^t \mathbf{v}(t')\,dt'. \tag{2.1}$$

In circumstances such that the velocity $\mathbf{v}$ is a *stationary* random function of time, it follows from the central limit theorem that the probability distribution of $\mathbf{X}$ tends to the normal or Gaussian form as $t \to \infty$. We may see this formally by dividing the range of integration t into a number of equal intervals Δt, whence $\mathbf{X}(t)$ becomes the sum of a series of terms with equal means and equal variances. If now we choose Δt to be sufficiently large for the coefficient of correlation of two adjacent terms in the series to be small, and then let $t/\Delta t \to \infty$, the conditions for application of the central limit theorem are satisfied.

A Gaussian form for the probability density function $P(\mathbf{X})$ satisfies the diffusion equation

$$\frac{\partial P}{\partial t} = \nabla.\left(\frac{1}{2}\frac{d\langle\mathbf{XX}\rangle}{dt}.\nabla P\right),$$

and the tensor coefficient

$$\frac{1}{2}\frac{d\langle\mathbf{XX}\rangle}{dt} = \int_0^t \mathbf{R}(\xi)\,d\xi \tag{2.2}$$

is termed the diffusivity, where $\mathbf{R}(\xi) = \langle\mathbf{v}(t)\,\mathbf{v}(t+\xi)\rangle$ and the angle brackets denote an ensemble average. Provided that the integral in (2.2) converges as $t \to \infty$, the diffusivity attains the asymptotic value

$$\mathbf{D} = \int_0^\infty \mathbf{R}(\xi)\,d\xi \tag{2.3}$$

after a time of order τ, where

$$\tau = \int_0^\infty |\mathbf{R}(\xi)|\,d\xi/|\mathbf{R}(0)| \tag{2.4}$$

and $|\mathbf{R}|$ denotes the trace of $\mathbf{R}$. The asymptotic value (2.3) is usually the only relevant value of the diffusivity in practical diffusion problems since τ is a very small time. We note that since the principle of equipartition of energy gives

$$|\mathbf{R}(0)| = 3kT/m$$

for a particle of mass m in an equilibrium situation, the relaxation time τ is equal to $m|\mathbf{D}|/3kT$.

These familiar results hold when the particle velocity $\mathbf{v}$ is a stationary random function of t. That is certainly true if the particle is free from interactions with other particles and if any external force acting on it is constant. But when there are interactions between particles which depend on the relative positions of the particles, the statistical properties of the velocity of one particle might change slowly with time simply as a consequence of change of the spatial configuration of particles. For instance, two particles which are very close have an inhibited relative Brownian motion and respond to thermal forces with approximately the mass and hydrodynamic resistance of a rigidly joined pair, whereas after some time when the particles have wandered far apart each has the Brownian motion of an isolated particle. It is conceivable that a theory which takes full account of the effect of change of the particle configuration on the Brownian movement could be devised, but here we shall evade the difficulties by supposing that the change in the particle configuration during the relaxation time τ is negligibly small. In these circumstances the velocities of a number of interacting particles are approximately stationary random functions of time over a time interval of order τ (which if necessary is redefined as the largest of any different values obtained for the various particles); and a simple generalization of the argument above to multi-particle statistics shows that the joint probability distribution of the displacement vectors of N interacting particles tends to the Gaussian form and that the corresponding tensor diffusion coefficients of the form

$$\frac{1}{2}\frac{d\langle \mathbf{X}_i \mathbf{X}_j \rangle}{dt}, \tag{2.5}$$

where i and j refer to two different particles, tend to constant values like (2.3) which now are functions of the particle configuration.

The essence of our assumption is that the particle configuration is effectively constant during the time τ that characterizes the diffusion process. If for estimation purposes we suppose that each particle migrates with the scalar diffusivity $\tau kT/m$ (and that any other motion-producing agency changes the particle configuration more slowly), the change in the distance between two particles in time τ is of order $\tau(kT/m)^{\frac{1}{2}}$, or $(mkT)^{\frac{1}{2}}/6\pi\eta a$ in the case of rigid spheres of radius a where η is the fluid viscosity. Expressed as a fraction of a particle radius, this relative displacement of two spheres in time τ is

$$(mkT)^{\frac{1}{2}}/6\pi\eta a^2, \tag{2.6}$$

which is less than 10^{-3} in the case of spheres of radius 10^{-3} mm in water at normal temperature and so is normally negligible. If two particles are very close together, and ϵ is the minimum distance between the two surfaces, it would be more logical to compare the relative displacement of the two particles during time τ with ϵ; but then the relative diffusivity differs from that just assumed by a factor of order ϵ/a (as will be seen later), and (2.6) is *again* an estimate of the change in the distance between the two centres in time τ expressed as a fraction of the relevant configuration length which now is ϵ. It appears that our assumption of a constant configuration during the time interval τ that characterizes the diffusion process will be accurate in common circumstances.

Both Deutch & Oppenheim (1971) and Murphy & Aguirre (1972) also find it necessary, in their different treatments of the problem, to assume that the change in the particle configuration during the relaxation time τ is small.

3. A formal prescription for the diffusive flux in a multi-particle system

The classical argument for the diffusion of independent particles

The argument used by Einstein (1905) to determine the Brownian diffusivity of an isolated particle suspended in fluid is ingenious and simple, and involves an appeal to a hypothetical equilibrium system. Einstein considered a situation in which a steady external force derivable from a potential $\Phi(\mathbf{x})$ acts on the particle and drives it toward an impermeable boundary in opposition to random movement away from the boundary due to thermal agitation. In this state of thermodynamic equilibrium involving the suspended particle and the fluid molecules at temperature T, the probability density function for the position of the particle is given by the Boltzman distribution as

$$P(\mathbf{x}) = P_0 \exp(-\Phi/kT), \tag{3.1}$$

where P_0 is a constant determined by the normalization condition $\int P(\mathbf{x})\,d\mathbf{x} = 1$. Alternatively, we can follow Einstein (1905) more closely† and use the fact that, in a system with variable composition, uniformity of the chemical potential of each component (the components in this case being the particle and the suspending fluid), as well as of the temperature, is a necessary condition for thermodynamic equilibrium (Landau & Lifschitz 1968, §86). In a dilute suspension of non-interacting particles with number density $P(\mathbf{x})$ the local chemical potential of the particles in the presence of the applied force is approximately

$$kT \log P + \Phi + \text{const.},$$

whence (3.1) is recovered.

Now in this equilibrium system the mean particle flux due to movement under the action of the applied force balances that due to Brownian diffusion down the probability gradient. Provided the particle is so small that the fluid flow about it is governed by the linear low-Reynolds-number equation of motion, the velocity imparted to the particle by a steady force $\mathbf{F}$ is $\mathbf{b}\,.\,\mathbf{F}$, where the second-rank tensor $\mathbf{b}$ is the particle mobility. Hence the local flux balance in the equilibrium state is represented by

$$-P\mathbf{b}\,.\,\nabla\Phi - \mathbf{D}\,.\,\nabla P = 0. \tag{3.2}$$

Substitution for P from (3.1) then shows that the diffusivity due to Brownian motion has the uniform value

$$\mathbf{D} = kT\mathbf{b}. \tag{3.3}$$

For a rigid spherical particle of radius a the mobility tensor is isotropic and may be obtained from the Stokes resistance law, giving the classical formula

$$\mathbf{D} = \frac{kT}{6\pi\eta a}\mathbf{I}, \tag{3.4}$$

where $\mathbf{I}$ is the unit isotropic tensor and η is the viscosity of the suspending fluid.

This expression for $\mathbf{D}$ has been derived for the postulated equilibrium situation; but since the Brownian agitation and the steady applied force lead to independent and superposable movements of the particle in a linear low-Reynolds-number

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† Although not identically; Einstein's argument was in terms of the osmotic pressure of the suspension, which is related to the chemical potentials of the components.

system, the expression for the diffusive flux is equally valid in the absence of the applied force. And in a dilute suspension containing many identical non-interacting particles, the particles diffuse independently and the diffusive particle flux density is $-\mathbf{D}.\nabla n$, where n is the local mean number density.

It should be noted for future reference that the particle flux due to Brownian migration is the same here as if a certain steady force acted on the particles (this force being equal and opposite to the external force $-\nabla\Phi$ that, in the equilibrium situation, produces a convective flux which *balances* the diffusive flux); that is, in view of (3.1), the same as if a steady force

$$\mathbf{F} = -kT\nabla \log P(\mathbf{x}) \tag{3.5}$$

acted on the particle. It is of course not to be supposed that the interaction of a particle with the molecules of the surrounding medium is literally equivalent to the exertion of a steady force on the particle. When the probability density of the particle position is non-uniform, the mean Brownian velocity of a particle, *conditional upon it being near a point* $\mathbf{x}$, is non-zero simply as a consequence of the fact that the particle is more likely to have come from a direction in which the probability density increases than from one in which it decreases; and it is this bias in the statistics of particle velocities at $\mathbf{x}$ (which is quite consistent with zero mean of the Brownian velocity of a given particle in the absence of an applied force) that is equivalent, so far as its effect on the diffusive flux is concerned, to the action of the steady force (3.5) on the particle. The equivalent steady force (3.5) is sometimes termed the thermodynamic force.

This classical argument has been reproduced because it is the basis of our investigation of the effect of particle interaction. We shall show that, even when the suspension is not so dilute that particles may be regarded as independent, the diffusive flux is the same as that which would be generated by the application of a certain steady force to the particles. The way in which we shall do this depends on whether the suspension is homogeneous or inhomogeneous. In the case of a statistically homogeneous suspension the problem at issue is the *relative* diffusion of groups of interacting particles (on account of its bearing on the rheological properties of dilute suspensions). And in the case of an inhomogeneous suspension there is the additional and important possibility of diffusive transport of particles in space. Both cases may be treated by suitable generalizations of the Einstein argument.

Relative diffusion in a homogeneous suspension

Consider a group of m particles in a homogeneous suspension (where $m > 1$ but is not large) which are within a few particle radii of each other and so are close enough to interact hydrodynamically. The chance of another particle being close to the group is small, in a dilute suspension, and we may therefore regard the group as isolated from other particles. We now hypothesize an equilibrium situation in which a steady external interactive force with mutual potential energy $\Phi(\mathbf{x}_1, \ldots, \mathbf{x}_m)$ is applied to the particles of the group (say by joining particles with elastic strings), where Φ depends only on the relative position vectors $\mathbf{x}_2 - \mathbf{x}_1, \ldots, \mathbf{x}_m - \mathbf{x}_1$ and not on the location of the group in space. There is in addition the interactive force with mutual potential energy $U(\mathbf{x}_1, \ldots, \mathbf{x}_m)$ which in the case of our hard spheres is infinite if any two particles overlap and zero otherwise. Since the group of particles is independent of other particles in the suspension we again have the Boltzmann form

$$P(\mathbf{x}_1, \ldots, \mathbf{x}_m) = P_0 \exp\left(\frac{-\Phi - U}{kT}\right) \tag{3.6}$$

for the joint probability distribution of the position vectors of the m particles.

The diffusive flux of one particle relative to others in this equilibrium situation is equal and opposite to the convective flux produced by the steady applied force. Provided the two fluxes are independent, as may be assumed in view of linearity of the hydrodynamic equations for the motion due to particles acted on by external forces, it follows that when the external force is suddenly removed there is a flux due to diffusion which is the same as if each particle were acted on by a steady force equal and opposite to that derived from Φ, where Φ is given by (3.6), that is, the same as if the k particle were acted on by the steady force

$$\mathbf{F}_k = -kT\frac{\partial \log P(\mathbf{x}_1, \ldots, \mathbf{x}_m)}{\partial \mathbf{x}_k} \quad (k = 1, \ldots, m). \tag{3.7}$$

(Values of $\mathbf{x}_k$ such that the k particle is touching another particle must be excluded since $P(\mathbf{x}_1, \ldots, \mathbf{x}_m)$ may be discontinuous there.) Thus when the probability density function for the particle configuration is known, the relative diffusive flux can be calculated. Such a calculation involves a consideration of the hydrodynamic resistance to relative motion of neighbouring particles under the action of the forces (3.7), and we take it up in §5 for the case of a group of two particles.

Gradient diffusion in an inhomogeneous suspension

We consider now the diffusive flux of particles down a spatial gradient of concentration. Suppose that the particles are identical, and that the mean number density is $n(\mathbf{x})$ in some hypothetical equilibrium situation in which the steady external force $-\nabla\Phi(\mathbf{x})$ acts on each particle. We seek the relation between $\nabla\Phi$ and ∇n in this equilibrium system, since this will give us the effective or thermodynamic force on a particle, which balances the external force $-\nabla\Phi$, in terms of the concentration gradient ∇n. The Boltzmann distribution for the positions of a large number of particles in a closed volume of suspension does not seem to be suitable for this purpose, and we use instead the alternative version of the Einstein argument based on the fact that in equilibrium both the chemical potential of the particles and the temperature must be uniform.

Those who are more at home in fluid mechanics than thermodynamics may welcome the reminder that for a statistically homogeneous system containing N particles in suspension the chemical potential per particle μ is defined as the derivative, with respect to N, of one of the thermodynamic energy functions, the most useful for the present purpose being

$$\mu = (\partial G/\partial N)_{N_0, p, T}, \tag{3.8}$$

where N_0 denotes the number of molecules of fluid in the system and the Gibbs free energy of the system is defined, with conventional notation, as

$$G = E + PV - TS$$

in the absence of any external forces. G is a homogeneous function of the first order in N and N_0, and so μ is a function of the ratio N/N_0, or, more conveniently, of the particle number density

$$n = N/(N_0 v_0 + Nv), \tag{3.9}$$

where v and v_0 are the volumes of a particle and a fluid molecule respectively; μ is also a function of p and T. If now an external force with potential energy Φ per particle acts, there is an additional term $N\Phi$ in the expression for the Gibbs free energy, and the chemical potential per particle is

$$\mu(n, p, T) + \Phi, \tag{3.10}$$

where $\mu(n, p, T)$ is the function of n, p and T that represents the chemical potential in the absence of the external force.

The above quantities have been defined for a homogeneous system, and in the case of a statistically inhomogeneous system they may be defined as local quantities, with n, p and Φ being functions of position. The requirement of uniformity of the particle chemical potential in equilibrium then shows that the external force $-\nabla\Phi$ applied to a particle is balanced (statistically) by a 'thermodynamic' force

$$\mathbf{F} = -\nabla\mu(n, p, T)$$

which evidently represents the effect of diffusion. And since the Brownian motion of a particle and that due to the external force $-\nabla\Phi$ are superposable, the diffusive flux will be specified by this thermodynamic force in the absence of the external force, that is, in a non-equilibrium situation. Bearing in mind the definition of the chemical potential as the change in the Gibbs free energy due to the introduction of an additional particle at constant pressure and temperature, it is understandable that when the chemical potential varies with position the diffusive driving force on a particle should be of the form $-\nabla\mu$. The idea of the gradient of chemical potential as a diffusive driving force on particles has been familiar to physical chemists for many years, but it appears to have played little part in theoretical studies of Brownian diffusion hitherto.

Note that, in the hypothetical equilibrium system with an external force acting on the particles, both n and p vary with position, the variation of the latter being given by the force-balance relation

$$\nabla p = -n\nabla\Phi; \tag{3.11}$$

and so in this case

$$\nabla\mu = \left(\frac{\partial\mu}{\partial n}\right)_{p,T} \nabla n + \left(\frac{\partial\mu}{\partial p}\right)_{n,T} \nabla p.$$

But, when diffusion is taking place in the absence of an external force acting on either the particles or the suspending fluid, both p and T are uniform in the suspension and the thermodynamic driving force on a particle becomes

$$\mathbf{F} = -\left(\frac{\partial\mu}{\partial n}\right)_{p,T} \nabla n. \tag{3.12}$$

There is a corresponding thermodynamic force $\mathbf{F}_0 = -\nabla\mu_0$ on each fluid molecule, where $\mu_0(n, p, T)$ is the chemical potential per fluid molecule. In the hypothetical equilibrium situation in which an external force acts only on the particles, $\nabla\mu_0$ is zero, as may be seen explicitly by use of the thermodynanic relations

$$n_0\frac{\partial\mu_0}{\partial n}+n\frac{\partial\mu}{\partial n} = 0 \quad\text{and}\quad \left(\frac{\partial\mu}{\partial p}\right)_{n,T} = v, \quad \left(\frac{\partial\mu_0}{\partial p}\right)_{n,T} = v_0,$$

where n_0 is the (local) number density of the fluid molecules. And when diffusion is taking place in the absence of external forces, p and T are uniform and

$$\mathbf{F}_0 = -\left(\frac{\partial\mu_0}{\partial n}\right)_{p,T}\nabla n = -\frac{n}{n_0}\mathbf{F}, \tag{3.13}$$

the resultant thermodynamic force on the particles and fluid molecules in unit volume then being zero as expected. The existence of a diffusive driving force on the fluid molecules as well as on the particles has implications for the relative diffusive flux of particles and fluid. For the moment we simply note that, since a uniform body force $-\mathbf{F}_0/v_0$ per unit volume acting on particles and fluid alike produces no relative motion of particles and fluid, the relative diffusive flux of particles and fluid is the same as if each particle were acted on by a modified force

$$\mathbf{F}^* = \mathbf{F}\left(1+\frac{nv}{n_0v_0}\right) = \frac{\mathbf{F}}{1-\phi} \tag{3.14}$$

and the fluid molecules were force free, where $\mathbf{F}$ is given by (3.12) and $\phi = nv$ is the volume fraction of the particles. When $\phi \ll 1$ and only the first approximation to the diffusive flux of particles is required, as in Einstein's work, the effect of the diffusive driving force on the fluid molecules can be ignored.

In view of the simplicity and power of the result (3.14) (with (3.12)) for the particle force that gives the same flux as Brownian motion, it may be helpful to see it also as a consequence of the following argument from non-equilibrium statistical mechanics. Consider a large volume V of a suspension in which the pressure, temperature and particle number density are uniform with values p, T, n_0. The minimum amount of work (corresponding to a reversible change) which must be done in order to change the number of particles in a part of this suspension initially of volume τ from m_0 to m, where $(m-m_0)/m_0$ is small but finite, under conditions of constant pressure and temperature is

$$\Delta G-(m-m_0)\,\mu(n_0,p,T),$$

where ΔG is the change in the Gibbs free energy of that part of the suspension (see Landau & Lifshitz 1968, §§98,117). By expanding ΔG in powers of $m-m_0$, and remembering the definition (3.8), we see that the minimum total amount of work needed to bring about such changes in all parts of V is approximately

$$\begin{aligned} W &= \int\frac{\frac{1}{2}(m-m_0)^2}{\tau}\left\{\left(\frac{\partial\mu}{\partial m}\right)_{p,T}\right\}_{m=m_0}dV, \\ &= \frac{1}{1-\phi_0}\left\{\left(\frac{\partial\mu}{\partial n}\right)_{p,T}\right\}_{n=n_0}\int\tfrac{1}{2}(n-n_0)^2\,dV \end{aligned}$$

with use of (3.9) (N being replaced there by m), where ϕ_0 is the volume fraction of the particles in the uniform state. This quantity W is also equal to $kT(S_0-S)$, where S_0 is the total entropy of the uniform system and S that of the changed system. If we now allow the suspension to relax back to the equilibrium state by diffusion, with a local particle flux density $\mathbf{f}$, the rate of change of W and S, regarded as parameters of the system at any instant, are given by

$$\begin{aligned}\frac{dW}{dt} = -kT\frac{dS}{dt} &= -\frac{1}{1-\phi_0}\left\{\left(\frac{\partial\mu}{\partial n}\right)_{T,p}\right\}_{n=n_0}\int (n-n_0)\nabla.\mathbf{f}\,dV,\\ &= \frac{1}{1-\phi_0}\left\{\left(\frac{\partial\mu}{\partial n}\right)_{T,p}\right\}_{n=n_0}\int (\nabla n).\mathbf{f}\,dV \qquad (3.15)\end{aligned}$$

provided there is no particle flux across the boundary of V. We expect $-dW/dt$ to be equal to the rate of working in the suspension by the 'dissipative' driving force on particles representing the effect of diffusion, and we see that the right-hand side of (3.15) does indeed allow this interpretation if the driving force has the modified value (3.14).

In the case of a suspension which is so dilute that the particles do not interact, μ is approximately equal to const. $+kT\log n$, and $n(\mathbf{x})$ and $P(\mathbf{x})$ are proportional, so that we recover (3.5) from (3.12). At larger particle concentrations this expression for μ must be supplemented by a 'virial' expansion in powers of nv ($=\phi$, the volume fraction of the particles), the form of which is known for hard spheres and will be described later. This virial expansion for μ represents the dependence on n of the part of the suspension volume that is free or accessible to particles; the larger is n, the smaller is the space available for the introduction of more particles, and $n\,\partial\mu/\partial n$ is an increasing function of n.

In more general circumstances there may be s different species of particle in an inhomogeneous suspension. For each species i, with properties given by μ_i, n_i, v_i, ϕ_i (where μ_i depends on $n_1, n_2, \ldots$, and not on n_i alone) we introduce an external force with potential energy $\Phi_i(\mathbf{x})$ per particle. The chemical potential per particle of species i is then $\mu_i + \Phi_i$, and since this must be uniform in the resulting equilibrium system we see that the effective or thermodynamic force on a particle of this species is $-\nabla\mu_i$. This will also represent the effect of diffusion in a non-equilibrium system; and when such a system is free from external forces p and T are uniform, in which case the diffusive driving force acting on each particle of species i is

$$\mathbf{F}_i = -\sum_{j=1}^{s}\left(\frac{\partial\mu_i}{\partial n_j}\right)_{p,T}\nabla n_j \quad (i = 1, 2, \ldots, s). \qquad (3.16)$$

There is a corresponding thermodynamic force

$$\mathbf{F}_0 = -\sum_{j=1}^{s}\left(\frac{\partial\mu_0}{\partial n_j}\right)_{p,T}\nabla n_j = -\frac{1}{n_0}\sum_{i=1}^{s} n_i\mathbf{F}_i \qquad (3.17)$$

on each fluid molecule, and so the relative diffusion of particles and fluid is the same as if each particle of species i were acted on by the modified force

$$\mathbf{F}_i^* = \mathbf{F}_i - \frac{v_i}{v_0}\mathbf{F}_0 = \mathbf{F}_i + \frac{v_i}{1-\phi}\sum_{j=1}^{s} n_j\mathbf{F}_j \qquad (3.18)$$

and the fluid molecules were force free, where $\phi = 1 - n_0v_0$ and $\mathbf{F}_i$ is given by (3.16).

We remark finally that there is no neglect, here or elsewhere in the paper, of the effect of Brownian couples on the translational diffusion of particles. It is true that, through hydrodynamic interaction, rotation of one particle does cause translational displacement of a neighbouring particle, but there is no need to take explicit account of Brownian couples. All such effects are incorporated implicitly in the above expressions for the steady thermodynamic force on particles that gives the same translational flux as the diffusion, provided that the particles moving under the action of the thermodynamic force are regarded as couple-free. And in the case of spherical particles there is of course no need to take account of the angular displacements.

This completes the statistical mechanical part of the investigation. We have shown that in several different circumstances the diffusive flux due to Brownian motion can be identified with the flux due to the action of certain 'thermodynamic' forces applied to the particles. Determination of the flux which would be produced by these external forces is a multi-particle hydrodynamical problem which will now be considered. The thermodynamic driving forces are linear in the probability or concentration gradients, and so, bearing in mind the linearity of the hydrodynamical equations, we expect to be able to obtain expressions for the diffusion coefficients from the hydrodynamical investigations.

4. The relevant hydrodynamic functions for two spherical particles

The above description of diffusive flux indicates that we shall need to know how a particle moves, under the influence of an applied force, through fluid containing other moving particles. It is convenient to specify the relevant hydrodynamic functions here, for the particular case of two spherical particles, as a preliminary to their use in the discussion of Brownian diffusion in subsequent sections of this paper.

Suppose that a sphere of radius a_1 with centre at $\mathbf{x}_1$ acted on by an external force $\mathbf{F}_1$ and a sphere of radius a_2 with centre at $\mathbf{x}_2$ acted on by an external force $\mathbf{F}_2$ are otherwise alone in fluid which is at rest at infinity. There is zero applied couple on each sphere. We wish to find the instantaneous velocities of the two sphere centres, $\mathbf{U}_1$ and $\mathbf{U}_2$. Provided the inertia forces on both fluid and spheres are negligible we have the linear relations

$$\mathbf{U}_1 = \mathbf{b}_{11}.\mathbf{F}_1+\mathbf{b}_{12}.\mathbf{F}_2, \quad \mathbf{U}_2 = \mathbf{b}_{21}.\mathbf{F}_1+\mathbf{b}_{22}.\mathbf{F}_2, \tag{4.1}$$

where the mobility tensors $\mathbf{b}_{11}$, etc., are inversely proportional to the fluid viscosity η and also depend on the geometry of the two spheres, that is, on $\mathbf{r} = \mathbf{x}_2-\mathbf{x}_1$. Since the sphere configuration is symmetrical about the direction of $\mathbf{r}$ we may write

$$\mathbf{b}_{ij}(\mathbf{r}) = \frac{1}{3\pi\eta(a_i+a_j)}\left\{A_{ij}(r)\frac{\mathbf{rr}}{r^2}+B_{ij}(r)\left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right)\right\} \tag{4.2}$$

($i,j = 1$ or 2; no summation convention here) where $r = |\mathbf{r}|$. The non-dimensional coefficients A_{ij} and B_{ij} depend on r, a_1, and a_2, and will be given here as functions of the two non-dimensional variables

$$\rho = \frac{2r}{a_1+a_2}, \quad \lambda = \frac{a_2}{a_1}. \tag{4.3}$$

By comparing the two flow systems obtained by choosing $\mathbf{F}_1 = \mathbf{F}, \mathbf{F}_2 = 0$ and $\mathbf{F}_1 = 0$, $\mathbf{F}_2 = \mathbf{F}$, we find

$$A_{11}(\rho,\lambda) = A_{22}(\rho,\lambda^{-1}), \quad B_{11}(\rho,\lambda) = B_{22}(\rho,\lambda^{-1}) \tag{4.4}$$

and

$$A_{12}(\rho,\lambda) = A_{21}(\rho,\lambda^{-1}), \quad B_{12}(\rho,\lambda) = B_{21}(\rho,\lambda^{-1}).$$

Also, the reciprocal theorem of Lorentz (1906) tells us that A_{12} and A_{21}, and B_{12} and B_{21}, are identical functions. Hence

$$\left.\begin{aligned} A_{12}(\rho,\lambda) = A_{21}(\rho,\lambda) = A_{12}(\rho,\lambda^{-1}) = A_{21}(\rho,\lambda^{-1}),\\ B_{12}(\rho,\lambda) = B_{21}(\rho,\lambda) = B_{12}(\rho,\lambda^{-1}) = B_{21}(\rho,\lambda^{-1}).\end{aligned}\right\} \tag{4.5}$$

This reduces the enquiry to a consideration of the functions of $A_{11}(\rho,\lambda)$, $B_{11}(\rho,\lambda)$ over the range $0 \leqslant \lambda < \infty$ and the functions $A_{12}(\rho,\lambda)$, $B_{12}(\rho,\lambda)$ over the range $1 \leqslant \lambda < \infty$, with $2 \leqslant \rho < \infty$ in all four cases. The choice of non-dimensionalizing factors made in (4.2) ensures that these functions are finite at all values of λ.

Asymptotic forms for $\rho \gg 1$ can be worked out by simple methods, and it will be worthwhile to give them here – for the case of rigid spheres – so that we shall know whether certain integrals which arise later are convergent. Consider a case for which $\mathbf{F}_1 = \mathbf{F}$, $\mathbf{F}_2 = 0$. When $\rho \gg 1$ the velocity of sphere 1 is approximately that of an isolated sphere, viz. $\mathbf{F}/6\pi\eta a_1$. The error is due to the fact that the movement of sphere 1 generates in the surrounding fluid a velocity gradient which is of order r^{-2} at distance r and this velocity gradient makes sphere 2 act as a force dipole which then generates a velocity of order r^{-4} at the position of sphere 1. The velocity at position $\mathbf{r}$ in the fluid relative to the centre of sphere 1 when it moves in isolation is

$$\mathbf{u}(\mathbf{r}) = \mathbf{U}_0 . \left\{\mathbf{I}\left(\frac{3a_1}{4r}+\frac{a_1^3}{4r^3}\right)+\frac{\mathbf{rr}}{r^2}\left(\frac{3a_1}{4r}-\frac{3a_1^3}{4r^3}\right)\right\}, \quad r \geqslant a_1, \tag{4.6}$$

where $\mathbf{U}_0 = \mathbf{F}/6\pi\eta a_1$, and the corresponding rate-of-strain tensor is

$$\mathbf{e}(\mathbf{r}) = \frac{3a_1}{4r^3}\left(\mathbf{I}-\frac{3\mathbf{rr}}{r^2}\right)\mathbf{r}.\mathbf{U}_0$$

to leading order; and then the resulting additional velocity of sphere 1 due to the induced-dipole action of sphere 2 is found by familiar relations (see Batchelor & Green 1972*a*) to be asymptotically

$$\frac{5}{2}\frac{a_2^3}{r^3}\mathbf{r}\frac{\mathbf{r}.\mathbf{e}.\mathbf{r}}{r^2}, \quad = -\frac{15}{4}\frac{a_1 a_2^3}{r^6}\mathbf{rr}.\mathbf{U}_0.$$

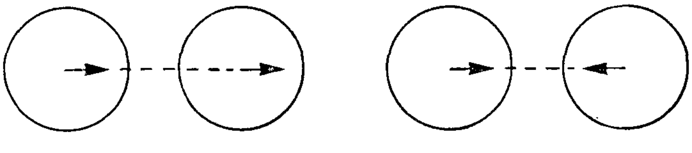
Thus the asymptotic forms of A_{11} and B_{11} are

$$A_{11} = 1-\frac{60\lambda^3}{(1+\lambda)^4\rho^4}+O(\rho^{-6}), \quad B_{11} = 1+O(\rho^{-6}), \tag{4.7}$$

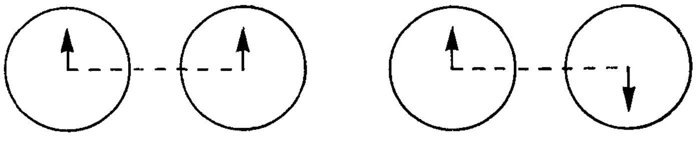
the magnitude of the error terms being evident from a qualitative extension of the argument.

Now consider the velocity of the force-free sphere 2. The 'environment' velocity at the position of sphere 2 is that due to the sphere 1 regarded as moving in isolation, so by Faxen's theorem (see Batchelor 1972) the velocity of sphere 2 is approximately

$$\mathbf{u}(\mathbf{r})+\tfrac{1}{6}a_2^2\nabla^2\mathbf{u}(\mathbf{r}),$$



(i) $U=(A_{11}+A_{12})F$ (ii) $U=(A_{11}-A_{12})F$



(iii) $U=(B_{11}+B_{12})F$ (iv) $U=(B_{11}-B_{12})F$

FIGURE 1. Four particular flow fields involving two equal couple-free spheres moving under the action of applied forces of equal magnitude F through fluid at rest at infinity. The arrows show the directions of both the applied forces and the velocities of the sphere centres. Determination of the sphere speed U in each case gives the value of the quantity shown in brackets (see (4.1) and (4.2)).

where $\mathbf{u}(\mathbf{r})$ is given by (4.6). Hence

$$\mathbf{U}_2 \approx \mathbf{U}_0 . \left\{ \mathbf{I} \left(\frac{3a_1}{4r} + \frac{a_1^3}{4r^3} + \frac{a_1 a_2^2}{4r^3} \right) + \frac{\mathbf{rr}}{r^2} \left(\frac{3a_1}{4r} - \frac{3a_1^3}{4r^3} - \frac{3a_1 a_2^2}{4r^3} \right) \right\},$$

and since the presence of sphere 2 gives sphere 1 an additional dipole strength of order r^{-5} the error in this expression for $\mathbf{U}_2$ is of order r^{-7}. It follows that

$$\left.\begin{aligned} A_{12} &= \frac{3}{2\rho} - \frac{2(1+\lambda^2)}{(1+\lambda)^2 \rho^3} + O(\rho^{-7}), \\ B_{12} &= \frac{3}{4\rho} + \frac{1+\lambda^2}{(1+\lambda)^2 \rho^3} + O(\rho^{-7}). \end{aligned}\right\} \qquad (4.8)$$

Several authors have given series of this kind, usually for the resistance tensors (the inverses of the mobility tensors), but I do not know of any which improve on the results (4.7) and (4.8) for arbitrary values of λ.

Many particular problems of low-Reynolds-number flow due to two moving spheres have been investigated and described in the literature, and by appropriate interpretation of the available data it is possible with some trouble to assemble a fairly complete numerical description of the two-sphere functions A_{11}, A_{12}, B_{11}, B_{12}. I give here the fruits of a search of the literature only for the important case of two rigid spheres of the same size ($\lambda = 1$). Figure 1 shows four particular configurations of the spheres and applied forces of equal magnitude, and derivation of the velocities of the spheres in each case provides a value of a certain linear combination of the four functions for each value of the distance between the spheres.

$\rho\left(=\dfrac{r}{a}\right)$	$A_{11}+A_{12}$ (Cooley & O'Neill)	$A_{11}-A_{12}$ (O'Neill)	A_{11}, A_{12}	A_{12}, A_{21}
2·0	1·5500	0	0·7750	0·7750
2·01	1·5487	0·0187	0·7837	0·7650
2·05	1·5431	0·0787	0·8109	0·7322
2·10	1·5363	0·1349	0·8356	0·7007
2·25	1·5167	0·2478	0·8823	0·6345
2·50	1·4861	0·3607	0·9234	0·5627
2·75	1·4580	0·4352	0·9466	0·5114
3·0	1·4320	0·4905	0·9613	0·4708
3·5	1·3861	0·5702	0·9782	0·4080
4·0	1·3472	0·6263	0·9868	0·3605
5·0	1·2866	0·7021	0·9944	0·2923
7·0	1·2100	0·7871	0·9986	0·2115
∞			1·0	0

TABLE 1. Values of the scalar mobility functions for forces parallel to the line of centres and two equal-sized rigid spheres ($\lambda = 1$). $G(\rho) = A_{11}-A_{12}$ when $\lambda = 1$

	$\rho\left(=\dfrac{r}{a}\right)$	$B_{11}+B_{12}$	$B_{11}-B_{12}$	B_{11}, B_{22}	B_{12}, B_{21}
Nir & Acrivos	2·0	1·381	0·401	0·891	0·490
O'Neill & Majumdar	2·001	1·4004	0·4670	0·9337	0·4667
	2·005	1·4027	0·4834	0·9431	0·4597
	2·01	1·4032	0·4935	0·9484	0·4549
	2·1	1·3918	0·5564	0·9741	0·4177
	3·0	1·2668	0·7297	0·9983	0·2686
	7·0	1·1086	0·8913	1·000	0·1087
	∞			1·0	0

TABLE 2. Values of the scalar mobility functions for forces normal to the line of centres and two equal-sized rigid spheres ($\lambda = 1$). $H(\rho) = B_{11}-B_{12}$ when $\lambda = 1$

Problem (i) has been solved exactly by Stimson & Jeffery (1926) in terms of bispherical coordinates, and the resulting values of $A_{11}+A_{12}$ have been computed by Cooley & O'Neill (1969*a*–see their table 2) and are reproduced in table 1. (In common with many other authors, Cooley & O'Neill state their results in terms of resistance coefficients for the two spheres, but for the particular configurations sketched in figure 1 the mobility coefficients are simply reciprocals of the resistance coefficients.) Brenner (1961) has given a formula for the sphere velocities in problem (ii), and the results of computations of this formula for several values of λ have been given (see Cooley & O'Neill 1969*b*). Strangely the published data does not include the case $\lambda = 1$, but Dr O'Neill has kindly extended his calculation to this case and provided me with the values of $A_{11}-A_{12}$ shown in table 1. The table also shows the corresponding values of A_{11} and A_{12} obtained from these two sets of data.

The more difficult problem (iii) in which the couple-free spheres rotate with an angular velocity proportional to F has been investigated by Goldman, Cox & Brenner (1966) with the aid of bispherical coordinates, and their computed

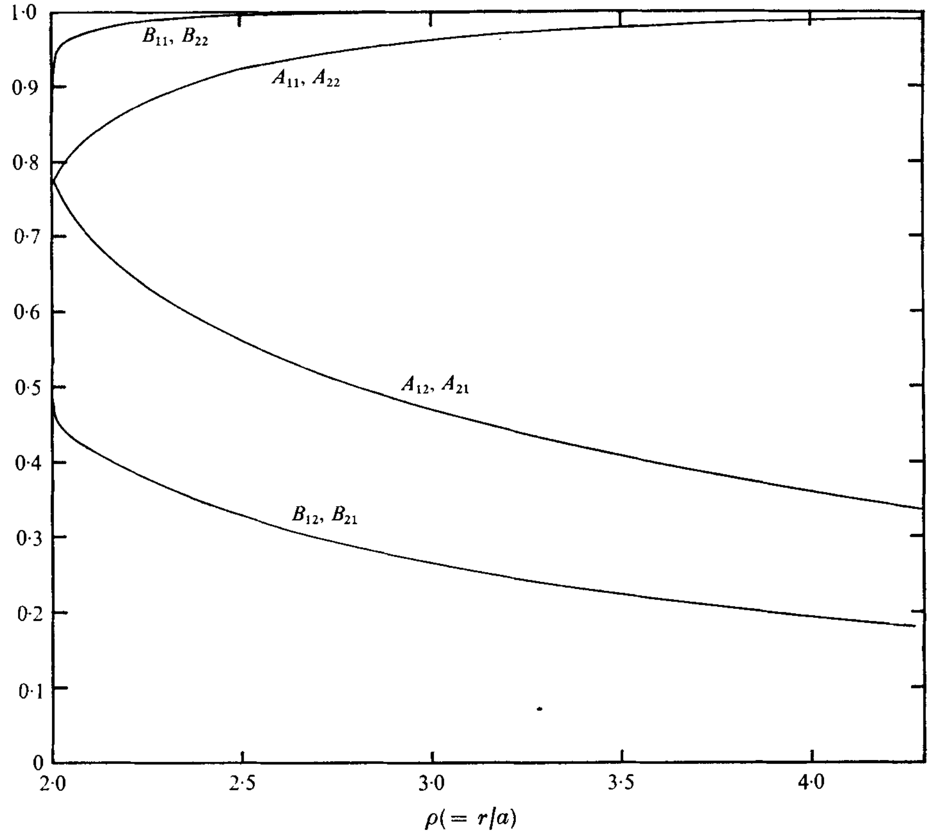


FIGURE 2. The scalar mobility functions (defined in (4.1) and (4.2)) for two rigid spheres of equal radii ($\lambda = 1$).

values of $B_{11}+B_{12}$ are given in their table 11A under the heading $\theta = 0$. (This same table also gives values of $A_{11}+A_{12}$, under the heading $\theta = 90°$, for the same set of values of r/a, recomputed from the Stimson & Jeffrey solution.) O'Neill & Majumdar (1970) have made a similar but more general investigation of the flow due to two spheres moving under the action of applied forces normal to the line of centres, and by combining appropriately the functions given in their table 1 it is possible to calculate values of both $B_{11}+B_{12}$ and $B_{11}-B_{12}$. These are shown in table 2, together with the corresponding values of B_{11} and B_{12}. The functions B_{11} and B_{12} are known to vary rapidly when $\log(\rho-2)^{-1} \gg 1$, probably with behaviour like

$$\text{const.}+\frac{\text{const.}}{\log(\rho-2)^{-1}}$$

(whereas A_{11} and A_{12} are regular), and the exact solutions used by Goldman *et al.* (1966) and by O'Neill & Majumdar (1970) are not convenient for determination of the values of B_{11} and B_{12} very near the end point $\rho = 2$. However, Nir & Acrivos (1973) have recently given a different exact solution for the flow due to two touching spheres on which a given external force and couple act, and by recasting the data in the appendix to their paper we obtain the values of B_{11} and B_{12} shown in table 2 in the row labelled $\rho = 2{\cdot}0$.

A_{11}, A_{12}, B_{11} and B_{12} are also shown as functions of ρ in figure 2 for this case $\lambda = 1$.

5. Relative diffusion of two particles in a dilute homogeneous suspension

In the case of a statistically homogeneous suspension of particles which is being deformed, a non-uniform probability distribution of the relative positions of particles may be produced by the bulk flow. The effect of Brownian motion of the particles is then to tend to restore the uniformity. Since the rheological properties of the suspension depend on the statistics of the relative positions of particles, it is desirable to have detailed information about this relative diffusion of particles due to Brownian motion.

When the suspension is dilute, the chance of a particle having m neighbours within a few diameters at any instant is of order ϕ^m, where $\phi (\ll 1)$ is the volume fraction of the particles, and in rheological calculations which are correct only to within a certain order in ϕ it is normally sufficient to consider finite groups of neighbouring interacting particles. We shall consider here the relative diffusion of an effectively isolated pair of spherical particles with a given vector separation, this being the case that is of interest in current investigations of the stress system in a dilute homogeneous suspension correct to the order ϕ^2 (Batchelor & Green 1972*b*). For a homogeneous suspension the joint probability density function of the positions of a sphere of type one of radius a_1 and of a sphere of type two of radius a_2 is of the form

$$P(\mathbf{x}_1, \mathbf{x}_2) = n_1 n_2 p(\mathbf{r}), \tag{5.1}$$

where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$ and n_1, n_2 are the (uniform) number densities of the two types of sphere. The pair-distribution function $p(\mathbf{r})$ will satisfy the condition

$$p(\mathbf{r}) \to 1 \quad \text{as} \quad r \to \infty$$

in the absence of long-range order in the suspension.

According to the results of §3, the relative diffusive flux due to Brownian motion is the same as if spheres one and two moved under the action of steady applied forces $\mathbf{F}_1$ and $\mathbf{F}_2$ respectively, where, in view of (3.7),

$$\left.\begin{aligned} \mathbf{F}_1 &= -kT\frac{\partial \log P(\mathbf{x}_1, \mathbf{x}_2)}{\partial \mathbf{x}_1} = kT\nabla \log p(\mathbf{r}), \\ \mathbf{F}_2 &= -kT\frac{\partial \log P(\mathbf{x}_1, \mathbf{x}_2)}{\partial \mathbf{x}_2} = -kT\nabla \log p(\mathbf{r}). \end{aligned}\right\} \tag{5.2}$$

Now when two couple-free spheres are acted on by external forces $\mathbf{F}_1$ and $\mathbf{F}_2$ in fluid which is at rest at infinity, they acquire velocities $\mathbf{U}_1$ and $\mathbf{U}_2$ given by (4.1). The diffusive flux of sphere 2 relative to sphere 1 is then

$$(\mathbf{U}_2 - \mathbf{U}_1) P(\mathbf{x}_1, \mathbf{x}_2) = -kT(\mathbf{b}_{11} + \mathbf{b}_{22} - \mathbf{b}_{12} - \mathbf{b}_{21}) . \nabla(n_1 n_2 p), \tag{5.3}$$

and we may define the relative diffusivity of two spheres with separation vector $\mathbf{r}$ as

$$\mathbf{D}(\mathbf{r}) = kT(\mathbf{b}_{11} + \mathbf{b}_{22} - \mathbf{b}_{12} - \mathbf{b}_{21}). \tag{5.4}$$

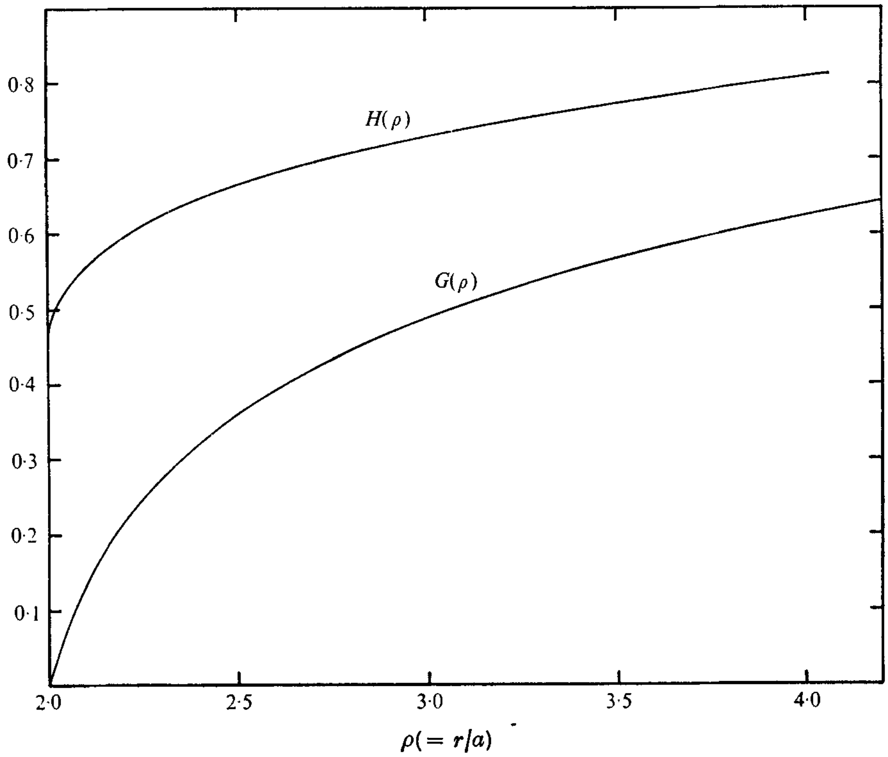


FIGURE 3. The scalar relative-diffusion functions (defined in (5.5) and (5.7)) for two rigid spheres of equal radii ($\lambda = 1$).

This is the diffusivity that is needed in an investigation of the pair-distribution function in a dilute homogeneous suspension of spheres subjected to a bulk deforming motion.

On substituting the expressions for the mobility tensors given in (4.2) we find

$$\mathbf{D}(\mathbf{r}) = D_0\left\{G(r)\frac{\mathbf{rr}}{r^2}+H(r)\left(\mathbf{I}-\frac{\mathbf{rr}}{r^2}\right)\right\}, \tag{5.5}$$

where
$$D_0 = \frac{kT}{6\pi\mu}\left(\frac{1}{a_1}+\frac{1}{a_2}\right), \tag{5.6}$$

$$\left.\begin{aligned} G(\rho,\lambda) &= \frac{\lambda A_{11}+A_{22}}{1+\lambda}-\frac{4\lambda A_{12}}{(1+\lambda)^2},\\ H(\rho,\lambda) &= \frac{\lambda B_{11}+B_{22}}{1+\lambda}-\frac{4\lambda B_{12}}{(1+\lambda)^2},\end{aligned}\right\} \tag{5.7}$$

and $\rho = 2r/(a_1+a_2)$, $\lambda = a_2/a_1$. We note from the inversion relations (4.4) and (4.5) that

$$G(\rho,\lambda) = G(\rho,\lambda^{-1}), \quad H(\rho,\lambda) = H(\rho,\lambda^{-1}). \tag{5.8}$$

When the two spheres are far apart they move independently, corresponding to

$$G\to 1, \quad H\to 1 \quad \text{and} \quad \mathbf{D}\to D_0\mathbf{I}$$

as $\rho\to\infty$. The asymptotic developments of G and H as $\rho\to\infty$ can be found from (4.7) and (4.8) correct to the order of ρ^{-5}.

For two spheres of equal radii ($\lambda = 1$), (5.7) reduces to

$$G(\rho) = A_{11} - A_{12}, \quad H(\rho) = B_{11} - B_{12}, \tag{5.9}$$

and the numerical values of G and H for this case have already been given in tables 1 and 2 respectively. These values of G and H are also shown in figure 3.

Deutch & Oppenheim (1971) also define a relative diffusion tensor for two (equal) spheres with vector separation $\mathbf{r}$, and derive an expression for it from the (coupled) equations of motion of two particles acted on by random thermal forces. Their expression is consistent with (5.4). For the functions $G(r)$ and $H(r)$ they give only the asymptotic forms correct to the order of a/r when $a/r \ll 1$. Murphy & Aguirre (1972, 1973) did not consider relative diffusion of particles.

Similar arguments may be applicable to the relative diffusion of three or more particles in a suspension, but determination of the hydrodynamic functions occurring in the expressions for the mobility of one particle in the presence of two other particles would be a formidable task.

6. Diffusion of identical particles down a concentration gradient

We consider here the diffusion of identical spherical particles down a concentration gradient, the more general case of simultaneous diffusion of several different kinds of particle being left for §7. As before we denote the mean number density of particles by n and the corresponding volume fraction of the particles by $\phi(=nv$, where v is the volume of a particle), both of which are functions of position $\mathbf{x}$. The starting point for the hydrodynamic problem is the result of §3 that the local diffusive flux is the same as that produced by the application of a steady force $\mathbf{F}^*$ to each particle and zero force on the fluid, where

$$\mathbf{F}^* = -\frac{1}{1-\phi}\left(\frac{\partial \mu}{\partial n}\right)_{p,T} \nabla n = -\frac{1}{1-\phi}\left(\frac{\partial \mu}{\partial \phi}\right)_{p,T} \nabla \phi \tag{6.1}$$

and μ is the local chemical potential per particle.

In order to be able to make any progress with the calculation of the flux produced by forces applied to all the particles, we shall need to restrict attention to the case of a concentration gradient for which $L|\nabla \log n|$ is small and approximately constant over a volume of the suspension with linear dimensions L which contains a large number of particles (N say). The point of this restriction, which is common in calculations of diffusivities, is that the thermodynamic driving force is then approximately the same for all the particles in a large volume of the suspension. The flux of particles is now the same as that in a suspension of identical particles which are falling out under gravity, the force $\mathbf{F}^*$ given by (6.1) being identified with $(\rho-\rho_0)\,v\mathbf{g}$, where ρ is the density of the sedimenting particles and ρ_0 that of the suspending fluid. Moreover since n is approximately constant over the suspension containing the diffusing particles, the suspension containing the sedimenting particles can be regarded as *homogeneous*.

In this sense the diffusion of identical particles down a concentration gradient is related to the problem of sedimentation of a homogeneous suspension of particles. A connection of some kind has been surmised in the literature for many years; see for instance Sadron (1953).

The velocities of the N particles in the suspension moving under the action of identical steady forces will not all be the same and will depend on the geometrical configuration represented by the instantaneous particle position vectors $\mathbf{x}_1$, $\mathbf{x}_2, \ldots, \mathbf{x}_N$. We are interested in the particle velocity averaged over a large number of particles, or, equivalently, in the velocity of a particle acted on by a steady force $\mathbf{F}^*$ averaged over all positions of the surrounding particles, each of which is acted on by the same steady force. Let $\langle \mathbf{U} \rangle$ denote this average particle velocity, relative to the chosen frame of reference. There is need for a careful specification of the appropriate reference velocity, because there is no general meaning to the term 'velocity of a particle relative to the surrounding fluid' when particles are close enough to interact hydrodynamically. The significant reference velocity in an incompressible two-phase medium in which the two phases have different velocities is the average velocity at a point, regardless of whether it is embedded in solid or in fluid material, to be denoted by $\langle \mathbf{u} \rangle$. The required average particle velocity, relative to axes such that there is zero average flux of material volume, is therefore $\langle \mathbf{U} \rangle - \langle \mathbf{u} \rangle$. This is of course the average particle velocity relative to the walls of a vessel containing a statistically homogeneous suspension. One could also describe $\langle \mathbf{U} \rangle - \langle \mathbf{u} \rangle$ as the average velocity of particles relative to the velocity that they would have if they were acted on by zero force.

The average particle velocity relative to zero-volume-flux axes is necessarily a linear function of the uniform force that acts on the particles, so we have

$$\langle \mathbf{U} \rangle - \langle \mathbf{u} \rangle = \frac{\mathbf{F}^* . \mathbf{K}(\phi)}{6\pi\eta a}, \tag{6.2}$$

where a is a length characteristic of the particles and the mobility coefficient $\mathbf{K}$ is a tensor function of particle shape and concentration and the statistical properties of the configuration of the particles. When the particles are spheres and the particle configuration is isotropic, the average velocity of particles is in the same direction as the applied force and

$$\mathbf{K}(\phi) = K(\phi)\,\mathbf{I}. \tag{6.3}$$

For the Brownian motion problem, in which the uniform force $\mathbf{F}^*$ has the value (6.1), we now have

$$\begin{aligned} \text{particle flux density} &= n\{\langle \mathbf{U} \rangle - \langle \mathbf{u} \rangle\} \\ &= -\frac{K(\phi)}{6\pi\eta a}\frac{\phi}{1-\phi}\left(\frac{\partial \mu}{\partial \phi}\right)_{p,T} \nabla n. \end{aligned} \tag{6.4}$$

The diffusivity representing the effect of Brownian motion is thus given as a function of ϕ by

$$\mathbf{D} = \frac{K(\phi)}{6\pi\eta a}\frac{\phi}{1-\phi}\left(\frac{\partial \mu}{\partial \phi}\right)_{p,T} \mathbf{I}. \tag{6.5}$$

Values of the coefficient $K(\phi)$ are provided in principle by theory or observation concerning sedimentation of the particles. However we must remember that a requirement for identity of the two problems is that the probability distribution of relative particle positions should be the same in the two problems and hence that there should be uniform probability of all accessible sphere configurations in the sedimentation problem. Whether a real suspension of sedimenting spheres has this property is not known. The other undetermined quantity on the right-hand side of (6.5) is $\partial\mu/\partial\phi$, which may be obtained from observations or calculations of the chemical potential of the particles in a stationary suspension in equilibrium.

No restrictions on the concentration of the particles have been made in the argument leading to (6.5). If now we assume that $\phi \ll 1$ we can take the calculation further. Both $\phi\,\partial\mu/\partial\phi$ and $K(\phi)$ are unity in the limit $\phi \rightarrow 0$, and the departures from unity can be expressed as series in integral powers of ϕ for sufficiently small values of ϕ. In both series terms of order ϕ^m represent the effect of interactions between groups of $m+1$ particles, the interactions being by interparticle force in the case of $\phi\,\partial\mu/\partial\phi$ and by hydrodynamic influence in the case of $K(\phi)$. We consider each series in turn.

According to the statistical mechanical theory of dilute (non-electrolyte) solutions (described by Hill 1960, chap. 19, and Landau & Lifshitz 1968, chap. 9) the Gibbs free energy of volume V of a solution containing N identical particles each of volume v and N_0 solvent molecules of volume v_0 may be written as

$$\begin{aligned} G &= N_0 G_0(p,T) + N G_1(p,T) - kT\log\left(V^N Q_N / v^N N!\right) \\ &= N_0 G_0 + N(G_1 + kT\log\phi/e) - kT\log Q_N. \end{aligned} \tag{6.6}$$

Here N has been assumed to be so large that Stirling's formula may be used, G_0 is the free energy per molecule of solvent in the pure state, and $N(G_1 + kT\log\phi/e)$ represents the effect of interaction of the solvent with independent and identical particles. The effect of interaction between particles is represented by $-kT\log Q_N$, where Q_N is the so-called configuration integral, or configurational partition function, given by

$$Q_N = \frac{1}{V^N}\int\cdots\int \exp\frac{-U_0(\mathbf{x}_1,\ldots,\mathbf{x}_N)}{kT}\,d\mathbf{x}_1\ldots d\mathbf{x}_N, \tag{6.7}$$

where $U(\mathbf{x}_1,\ldots,\mathbf{x}_N)$ is the potential energy of interaction between the N particles at positions $\mathbf{x}_1,\ldots,\mathbf{x}_N$ in the volume V. The last two terms of (6.6) have the same form as for a volume V of a gas containing N molecules essentially because when the particle positions are given there is only one way of distributing the (identical) solvent molecules to fill up the remaining space in V. When N is large Q_N may be expanded (Fisher 1964, chap. 2) in the form

$$Q_N^{1/N} = \exp\left\{\sum_{j=1}^{\infty}\frac{\beta_j}{j+1}\phi^j\right\},$$

where the coefficient β_j depends on the interaction of a group of j particles. The series for the chemical potential of the particles is then obtained by differentiation (remembering that $\phi = Nv/(N_0 v_0 + Nv)$):

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{N_0,p,T} = G_1 + kT(\log\phi - \phi) - kT\sum_{j=1}^{\infty}\beta_j\left(\phi^j - \frac{j}{j+1}\phi^{j+1}\right). \tag{6.8}$$

The corresponding series for the chemical potential per molecule of solvent is

$$\mu_0 = \left(\frac{\partial G}{\partial N_0}\right)_{N,p,T} = G_0 + kT\frac{v_0}{v}\left(-\phi + \sum_{j=1}^{\infty}\frac{j}{j+1}\beta_j\phi^{j+1}\right),$$

which may be shown to agree, at least as far as the term of order ϕ^2, with the series in powers of N/N_0 given by Hill (1960, § 19.3 – *not* § 19.1, which is concerned with the dependence of μ on ϕ under conditions of constant μ_0).

Hence from (6.8) we have

$$\phi \left(\frac{\partial \mu}{\partial \phi}\right)_{p,\,T} = kT\,(1-\phi)\left(1-\sum_{j=1}^{\infty} j\beta_j \phi^j\right). \tag{6.9}$$

In the case of hard spheres the exponential factor in (6.7) vanishes for values of $\mathbf{x}_1, \ldots, \mathbf{x}_N$ such that any two spheres overlap and is unity otherwise, and Q_N is independent of pressure and temperature. The standard method of evaluating the multiple integral gives for this case

$$\beta_1 = -8, \quad \beta_2 = -15. \tag{6.10}$$

(The first of these results is evident from the fact that the fraction of V that is accessible to a particle when there are already m particles in V is approximately $1-(8mv/V)$, whence $Q_N^{1/N}$ is equal to $1-4\phi$ to the first order in ϕ.) The effect of interparticle forces, which in this case of hard spheres is simply an excluded volume effect, is to increase the diffusivity relative to its value for $\phi = 0$, as we see from the negative sign of β_1, essentially because there are more free sites available for a migrating particle in a region where the particle number density is lower.

The available theoretical result for the sedimentation velocity in a dilute suspension (Batchelor 1972) is that for rigid spherical particles, and uniform probability of all accessible sphere configurations (which is the pair distribution that is relevant to the problem of Brownian diffusion),

$$K(\phi) = 1 - 6{\cdot}55\phi + O(\phi^2). \tag{6.11}$$

The negative sign of the term linear in ϕ, corresponding to a decrease in the settling rate, is due mainly to the return flow that balances the 'downward' volume flux of the particles and the fluid dragged with them. The derivation of this result is not straight forward, because a simple summation of the changes in the velocity of a particle due to hydrodynamic pairwise interaction with each one of the other particles in the suspension yields a non-convergent integral. The argument needed to overcome this difficulty is described in the appendix in preparation for the generalization made in the next section.

On putting together the results (6.5), (6.9) and (6.11) we find that the diffusivity due to Brownian motion in a dilute suspension of rigid spheres is

$$\mathbf{D} = \{1-(\beta_1 + 6{\cdot}55)\phi\}\frac{kT}{6\pi\eta a}\mathbf{I} = (1+1{\cdot}45\phi)\frac{kT}{6\pi\eta a}\mathbf{I} \tag{6.12}$$

correct to the order of ϕ. It appears that the enhancement of the diffusivity due to the greater availability of particle sites in regions of lower concentration is a little greater than the reduction due to hydrodynamic hindrance to the movement of particles.

There does not appear to be any previous theoretical work with which the above results can be compared. Deutch & Oppenheim (1971) did not consider gradient diffusion of particles. Murphy & Aguirre (1972, 1973) did consider gradient diffusion, and attempted to find the approximate value of the diffusivity that takes account of pairwise hydrodynamic interactions but were blocked by the non-convergent integrals that turn up except in the case of diffusion of 'tracer' particles surrounded by other particles with larger number density (see the footnote to the next section). The excluded volume effect that gives rise to the series in (6.9) and which makes the effective driving force on particles different from $-\nabla \log n$ is absent from Murphy & Aguirre's analysis; and it is difficult to see, how, even in principle, it should be included in a consideration of the dynamical equations for the random motion of particular particles.

So far as I am aware, observations of the diffusivity of colloidal particles have not led to an agreed empirical formula for the dependence on concentration for particles which might be expected to behave as hard spheres.

7. Simultaneous Brownian diffusion of different species of particle in a dilute suspension

Situations in which two or more kinds of particle are each diffusing down a concentration gradient in the same body of fluid are not uncommon in physical chemistry and colloid science, and are possibly of more practical interest than the corresponding problem of sedimentation of a mixture of different kinds of particle. When interactions are taken into account the driving forces and motions of different types of particle are coupled, and expressions for the diffusivities which are generalizations of (6.5) become rather cumbersome. In this section we shall derive the approximate formulae corresponding to (6.12) for diffusivities of several different sizes of particle in a dilute suspension.

The different types of particle, all of which are rigid spheres, will be distinguished by the suffix i, and the defining properties of particles of type i are the radius a_i (or volume v_i) and the number density n_i. The number density of each type of particle will be assumed to vary by only a small fraction over a volume V containing many particles, and although in practice the gradient vectors ∇n_i will often be parallel there is no additional difficulty in allowing for different directions. The modified force $\mathbf{F}_i^*$ that acts on each particle of type i is then given by equation (3.18). We shall assume that the total volume fraction of the particles $\phi\,(=\sum_i \phi_i)$ is small, and seek expressions for the fluxes of the different kinds of particle which take account of pair interactions only.

The first step is to calculate the driving force $\mathbf{F}_i$ from (3.16) approximately, and and for this we need a virial expansion corresponding to (6.9) for a mixture of particles. For a suspension containing N particles, of which N_i are identical particles of type i, the appropriate expression for the free energy, in place of (6.6), appears to be

$$G = N_0 G_0(p,T) + \sum_i N_i G_i(p,T) - kT \log \left(\frac{V^N Q_N}{\prod_i v_i^N N_i\,!} \right)$$

$$= N_0 G_0 + \sum_i N_i (G_i + kT \log Q_i/e) - kT \log Q_N, \tag{7.1}$$

and the configuration integral Q_N is again given by (6.7). When differentiating G with respect to N_i it must be remembered that $\phi_i = N_i v_i / V$ and $V = N_0 v_0 + \sum_i N_i v_i$.

The change in the value of $\log Q_N$ due to an increase in the number of particles of type i by one may be seen (by carrying out the integration with respect to the position of this additional particle before the other N integrations in (6.7)) to be

$$-\sum_j \left(\frac{a_i}{a_j}+1\right)^3 \phi_j$$

correct to the order of the first power of the small quantities $\phi_1, \phi_2, \ldots$. The chemical potential per particle of type i is thus

$$\mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{p,\,T} = G_i + kT(\log\phi_i - nv_i) + kT\sum_j \left(\frac{a_i}{a_j}+1\right)^3 \phi_j \qquad (7.2)$$

approximately, where $n = \sum_i n_i$. Then on substituting in (3.16) and (3.18) we find with consistent approximation that

$$\mathbf{F}_i^* = -kT\nabla\log n_i - kT\,v_i\sum_j\left(1+\frac{a_j}{a_i}\right)^3\nabla n_j. \qquad (7.3)$$

The second step is to calculate the mean velocity of particles of type i relative to axes such that there is zero mean flux of material volume in the suspension, given that particles of type j are acted on by the external force $\mathbf{F}_j^*$. This mean velocity $\langle\mathbf{U}_i\rangle - \langle\mathbf{u}\rangle$ must be evaluated by means of relations like those given in the appendix for a suspension of identical particles. The required generalization is evident in most places, although it is necessary to make the notation a little more elaborate in order to keep track of the properties of the different types of particle involved in an interaction.

Corresponding to (A 5) there is the exact expression for the mean velocity of a particle of type i with centre at $\mathbf{x}$:

$$\begin{aligned}\langle\mathbf{U}_i\rangle - \langle\mathbf{u}\rangle = \mathbf{U}_{i0} - \langle\mathbf{u}\rangle + \langle\{\mathbf{v}_i(\mathbf{y},\mathbf{x}) + \tfrac{1}{6}a_i^2\nabla_{\mathbf{y}}^2\mathbf{v}_i(\mathbf{y},\mathbf{x})\}_{\mathbf{y}=\mathbf{x}}\rangle \\ -\tfrac{1}{6}a_i^2\langle\nabla^2\mathbf{u}\rangle^{(f)} - \frac{a_i^2}{6\eta}\sum_j n_j\langle\mathbf{R}_j\rangle + \langle\mathbf{W}_i\rangle, \qquad (7.4)\end{aligned}$$

with notation which will be obvious. This is in a suitable form for the approximate evaluation of the averages as integrals over the position of just one sphere in the neighbourhood of the point $\mathbf{x}$. This one sphere may be of any type, and on summing over the different types, each with its own probability density, we find, corresponding to (A 7), that

$$\begin{aligned}\langle\mathbf{U}_i\rangle - \langle\mathbf{u}\rangle = \mathbf{U}_{i0} - \sum_j\left(1-\tfrac{1}{2}\frac{a_i^2}{a_j^2}\right)\phi_j\,\mathbf{U}_{j0} \\ -\sum_j\int_{r\geqslant a_j}\{\mathbf{u}(\mathbf{x}|\mathbf{x}',a_j) + \tfrac{1}{6}a_i^2\nabla_{\mathbf{x}}^2\mathbf{u}(\mathbf{x}|\mathbf{x}',a_j)\}\{P(\mathbf{x}',a_j) - P(\mathbf{x}',a_j|\mathbf{x},a_i)\}\,d\mathbf{x}' \\ +\sum_j\int\mathbf{W}(\mathbf{x},a_i|\mathbf{x}',a_j)\,P(\mathbf{x}',a_j|\mathbf{x},a_i)\,d\mathbf{x}' \qquad (7.5)\end{aligned}$$

correct to order ϕ; here the combination $\mathbf{x}$, a_i indicates that there is a sphere of radius a_i at $\mathbf{x}$ and similarly for $\mathbf{x}'$, a_j.

Again we may assume, to a consistent approximation, that all realizable configurations of pairs of spheres are equally probable, in which case

$$P(\mathbf{x}',a_j|\mathbf{x},a_i) = n_j \quad \text{for} \quad r \geqslant a_i + a_j \quad \text{and} \quad 0 \quad \text{otherwise.}$$

For the velocity $u(\mathbf{x}|\mathbf{x}', a_j)$ at point $\mathbf{x}$ due to the presence of a sphere of radius a_j at $\mathbf{x}'$ we may again use the expression (4.6), with $\mathbf{x}'-\mathbf{x}$ and a_j replacing $\mathbf{r}$ and a there, and the first integral in (7.5) is then found to be equal to

$$\left(\frac{3a_i^2}{2a_j^2}+\frac{3a_i}{a_j}\right)\phi_j\mathbf{U}_{j0}.$$

The function $\mathbf{W}(\mathbf{x}, a_i|\mathbf{x}', a_j)$ can be expressed in terms of two-sphere mobility functions by rewriting (A 9), the two spheres now being of different radii, and the final approximate formula, corresponding to (A 10), is

$$\begin{aligned}\langle\mathbf{U}_i\rangle-\langle\mathbf{u}\rangle = \mathbf{U}_{i0}-\mathbf{U}_{i0}\sum_j\phi_j\left(\frac{1+\lambda}{2\lambda}\right)^3C(\lambda)\\ -\sum_j\mathbf{U}_{j0}\phi_j\left\{1+\frac{3}{\lambda}+\frac{1}{\lambda^2}+\left(\frac{1+\lambda}{2\lambda}\right)^2D(\lambda)\right\},\end{aligned}\qquad(7.6)$$

where

$$\left.\begin{aligned}C(\lambda) &= \int_2^\infty\{3-A_{11}(\rho,\lambda)-2B_{11}(\rho,\lambda)\}\rho^2d\rho,\\ D(\lambda) &= \int_2^\infty\left\{\frac{3}{\rho}-A_{12}(\rho,\lambda)-2B_{12}(\rho,\lambda)\right\}\rho^2d\rho,\end{aligned}\right\}\qquad(7.7)$$

and $\rho = 2r/(a_1+a_2)$, $\lambda = a_2/a_1 = a_j/a_i$. We note from (4.7) and (4.8) that when $\rho \gg 1$

$$\{3-A_{11}(\rho,\lambda)-2B_{11}(\rho,\lambda)\}\rho^2 = \frac{60\lambda^3}{(1+\lambda)^4}\rho^{-2}+O(\rho^{-4}),$$

$$\left\{\frac{3}{\rho}-A_{12}(\rho,\lambda)-2B_{12}(\rho,\lambda)\right\}\rho^2 = O(\rho^{-5}),$$

which shows that the integrals in (7.7) are convergent.

The flux of number of spheres of type i relative to zero-volume-flux axes then follows from (7.3) and (7.6) (recall that $\mathbf{U}_{i0} = \mathbf{F}_i^*/6\pi\eta a_i$) as

$$\begin{aligned}n_i(\langle\mathbf{U}_i\rangle-\langle\mathbf{u}\rangle) = -D_{i0}\left\{1-\sum_j\phi_j\left(\frac{1+\lambda}{2\lambda}\right)^3C(\lambda)\right\}\nabla n_i\\ -D_{i0}\phi_i\sum_j\{\lambda^3+2\lambda^2-\tfrac{1}{4}(1+\lambda)^2D(\lambda)\}\nabla n_j,\end{aligned}\qquad(7.8)$$

where $D_{i0} = kT/6\pi\eta a_i$ is the scalar diffusion coefficient for isolated particles of type i and $\lambda = a_j/a_i$. This expression for the flux of i-type particles may also be written as

$$-\sum_j\mathbf{D}_{ij}.\nabla n_j.$$

The diagonal element of the diffusivity matrix is

$$\mathbf{D}_{ii} = D_{i0}\left\{1+1{\cdot}45\phi_i-\sum_{j(\neq i)}\phi_j\left(\frac{1+\lambda}{2\lambda}\right)^3C(\lambda)\right\}\mathbf{I},\qquad(7.9)$$

in which we have used the result $C(1)+D(1) = 1{\cdot}55$, and the off-diagonal element is

$$\underset{(i\neq j)}{\mathbf{D}_{ij}} = D_{i0}\phi_i\{\lambda^3+2\lambda^2-\tfrac{1}{4}(1+\lambda)^2D(\lambda)\}\mathbf{I}.\qquad(7.10)$$

The off-diagonal contribution to the flux of particles of type i due to a gradient of concentration of particles of type j is essentially a consequence of (*a*) the movement of i-type particles to regions of lower j-type concentration where more sites are available and (*b*) the back-flow in the medium which is needed to compensate for the volume flux associated with the movement of j-type particles down their concentration gradient. The flux of number of spheres of all types, obtained by summing (7.8) over all values of i, may readily be seen to be consistent with (6.12) when all the spheres are of the same size.

Since the rate of increase of entropy per unit volume of the medium is proportional to the product of $\mathbf{F}_i^*$ and the flux of number of i-type particles, summed over all values of i, the Onsager relations (or the princple of symmetry of kinetic coefficients) demand that the coefficient of $\mathbf{F}_j^*$ in (7.6), the relevant part of which is

$$a_j^2\{1+3\lambda^{-1}+\lambda^{-2}+\tfrac{1}{4}(1+\lambda^{-1})^2 D(\lambda)\},$$

be unchanged when a_i and λ are replaced by a_j and λ^{-1}. The inversion relations for the functions A_{12} and B_{12} given in (4.5) show that $D(\lambda) = D(\lambda^{-1})$ so that this is indeed so.

The values of the integrals $C(\lambda)$ and $D(\lambda)$ defined by (7.7) have been calculated for $\lambda = 1$ from the data given in tables 1 and 2, the accuracy of the numerical integration being increased in the case of $C(1)$ by first subtracting from the integrand its asymptotic form as given by (4.7). The results are

$$C(1) = 1{\cdot}83, \quad D(1) = -0{\cdot}28.$$

The second decimal place is unreliable as a consequence of values of both B_{11} and B_{12} being available for only a few values of ρ.

Several interesting special cases may be recovered from the general formulae (7.9) and (7.10), one of which will be mentioned in view of its relevance to many experimental systems. If we put

$$i = 1, \quad j = 2, \quad \phi_1 \ll \phi_2,$$

in (7.9) and (7.10), we find that the flux of 'tracer' particles of radius a_1 in a suspension which contains many more particles of radius a_2 per unit volume (while remaining dilute) is obtained from the diffusivities

$$\mathbf{D}_{11} \approx \mathbf{I}D_{10}\left\{1-\phi_2\left(\frac{1+\lambda}{2\lambda}\right)^3 C(\lambda)\right\}, \quad \mathbf{D}_{12} \approx 0.$$

And if $a_2 = a_1$, the factor within braces becomes $(1-1{\cdot}83\phi_2)$. The numerous particles of type 2 are acting here solely as passive obstacles to the migration of particles of type 1, and the factor $(1-1{\cdot}83\phi_2)$ represents the reduction in the rate of change of mean-square displacement of a particle of type 1 due to the presence of type 2 particles. No convergence difficulties arise in this special case of diffusion of tracer particles because there is no summation of induced velocities due to neighbouring particles acted on by an external force, and it is also made simpler by the absence of excluded-volume effects; the expression for the diffusivity

$\mathbf{D}_{11}$ can consequently be obtained by straightforward methods, as Aguirre & Murphy (1973) have shown.†

The origin of this work was a perceptive suggestion from Professor J. D. Goddard of the University of Michigan that the new techniques for handling apparently divergent interactions between particles might be useful in Brownian motion theory. I am grateful also to my colleague Dr E. J. Hinch for his valuable comments and advice, and to Mr J. R. Aldabe and Dr M. E. O'Neill for their help with the numerical data on the mobility functions.

Appendix. An explicit formula for the sedimentation velocity in a dilute suspension of identical spheres

Here we show how to determine the average particle velocity relative to zero-volume-flux axes (denoted above by $\langle\mathbf{U}\rangle-\langle\mathbf{u}\rangle$) correct to order ϕ for a dilute homogeneous suspension of identical spheres on which the same force $\mathbf{F}^*$ acts. The argument to be given is an abbreviated and improved form of that already published (Batchelor 1972).

The quantity $\langle\mathbf{U}\rangle$ is the velocity of a sphere with centre at, say, the point $\mathbf{x}$ averaged over all configurations relative to $\mathbf{x}$ of the other spheres in the suspension. And $\langle\mathbf{u}\rangle$ is the velocity at a point, again taken as $\mathbf{x}$ for convenience, averaged over all configurations of spheres relative to $\mathbf{x}$ regardless of whether $\mathbf{x}$ lies within fluid or within a sphere. In the limit $\phi \rightarrow 0$, a sphere is effectively alone in infinite fluid, $\langle\mathbf{u}\rangle$ is the uniform velocity of the ambient fluid for the motion of this isolated sphere, and

$$\langle\mathbf{U}\rangle-\langle\mathbf{u}\rangle = \mathbf{U}_0 = \frac{\mathbf{F}^*}{6\pi\eta a} \tag{A 1}$$

for rigid spheres of radius a. But, when there are hydrodynamic interactions between spheres, the environment in which the sphere at $\mathbf{x}$ has been placed is not one with uniform velocity and (A 1) needs correction. We introduce the 'environment' velocity $\mathbf{v}(\mathbf{y},\mathbf{x})$ which may be defined precisely as the velocity at point $\mathbf{y}$ if the material of the sphere at $\mathbf{x}$ were suddenly converted to fluid of viscosity η without change of other spheres in the suspension, and use the well-known expression for the velocity of a sphere of radius a in a non-uniform environment (another use of Faxen's theorem) to obtain

$$\langle\mathbf{U}\rangle-\langle\mathbf{u}\rangle = \mathbf{U}_0+\langle\{(\mathbf{v}+\tfrac{1}{6}a^2\nabla_y^2\mathbf{v})_{\mathbf{y}=\mathbf{x}}+\mathbf{W}(\mathbf{x})\}\rangle-\langle\mathbf{u}\rangle. \tag{A 2}$$

Here $\mathbf{W}(\mathbf{x})$ is a remainder term which arises from image systems, in the boundaries of all other spheres, of the forces exerted on the fluid at the surface of the sphere

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† They concluded, on the basis of some lengthy algebra, that convergence difficulties disappear only for spherical particles, but consideration of the asymptotic form of the hydrodynamic interaction of a tracer particle with a zero-force type 2 particle shows that the same is true for any shape of particle. And the number 2·625 (or 21/8) given in their equation (23) should be 15/8, this being what one obtains (for $\lambda = 1$) instead of the accurate value 1·83 if only the asymptotic forms of A_{11} and B_{11} correct to order $(a/r)^4$ are used in the evaluation of the integral in the expression (7.7) for $C(1)$.

at $\mathbf{x}$ and which is of order a^4/r^4 when there is just one other sphere at distance r from $\mathbf{x}$.

Now when ϕ is small the probability of one sphere being found within a distance of several sphere radii from a given point (the distance within which particle interactions are significant) is of order ϕ, and the probability of two spheres being found simultaneously within this distance is of order ϕ^2. We therefore seek an approximation to $\langle\mathbf{U}\rangle - \langle\mathbf{u}\rangle$, correct to the order of ϕ, by supposing that the values of $\mathbf{U}$ and $\mathbf{u}$ at point $\mathbf{x}$ are influenced by the presence of only one of the surrounding spheres, with centre at $\mathbf{x}'$. This leads to a representation of the averages in (A 2) as integrals over the position of this one sphere at $\mathbf{x}'$, with appropriate weighting of the different positions, whence the right-hand side becomes

$$\mathbf{U}_0 + \int [-\mathbf{u}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}') + \{\mathbf{v}(\mathbf{y},\mathbf{x}|\mathbf{x}') + \tfrac{1}{6}a^2\nabla^2_{\mathbf{y}}\mathbf{v}(\mathbf{y},\mathbf{x}|\mathbf{x}')\}_{\mathbf{y}=\mathbf{x}}P(\mathbf{x}'|\mathbf{x})]\,d\mathbf{x}' \\ + \int \mathbf{W}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}'|\mathbf{x})\,d\mathbf{x}', \qquad \text{(A 3)}$$

where the integration is over all values of $\mathbf{x}'$, $P(\mathbf{x}')$ is the probability density of a sphere centre being at $\mathbf{x}'$, $P(\mathbf{x}'|\mathbf{x})$ is the corresponding probability density conditional on there being a sphere centre at $\mathbf{x}$, and the addition of $|\mathbf{x}'$ to the arguments of $\mathbf{u}(\mathbf{x})$, $\mathbf{v}(\mathbf{y},\mathbf{x})$ and $\mathbf{W}(\mathbf{x})$ shows explicitly the location of the one neighbouring sphere on which these functions depend. However, this is a meaningless approximation, because the first integral in (A 3) is not absolutely convergent; both $\mathbf{u}$ and $\mathbf{v}$ are of order $a/|\mathbf{x}'-\mathbf{x}|$ when $|\mathbf{x}'|$ is large, and although these large terms cancel trouble comes from the term $\nabla^2\mathbf{v}$ which is of order $a^3/|\mathbf{x}'-\mathbf{x}|^3$. The idea of expansion in powers of ϕ is not necessarily invalid but (A 3) is not a proper expression of the mean particle velocity correct to the order ϕ.

A simple remedy is to modify the expression (A 2), without approximation, in such a way that an absolutely convergent integral is obtained when the averages are represented as integrals over the position of only one sphere of the configuration about $\mathbf{x}$. This may be done by noting that, since the deviatoric part of the stress tensor, $\mathbf{d}$ say ($\mathbf{d}$ being equal to 2μ times the rate-of-strain tensor, in the fluid part of the medium), is a stationary random function in a statistically homogeneous suspension, we have

$$\eta\langle\nabla^2\mathbf{u}\rangle^{(f)} = -\langle\nabla\,.\,\mathbf{d}\rangle^{(s)} = -n\langle\mathbf{R}\rangle, \qquad \text{(A 4)}$$

where the superscripts (f) and (s) indicate that the average is taken over the fluid and solid parts of the medium respectively, n is the number density of spheres, and $\mathbf{R}$ is the resultant force on a sphere due to the deviatoric stress exerted by the fluid at the sphere surface. We now rewrite (A 2), without approximation, as

$$\langle\mathbf{U}\rangle - \langle\mathbf{u}\rangle = \mathbf{U}_0 - \langle\mathbf{u}\rangle + \langle(\mathbf{v} + \tfrac{1}{6}a^2\nabla^2_{\mathbf{y}}\mathbf{v})_{\mathbf{y}=\mathbf{x}}\rangle - \tfrac{1}{6}a^2\langle\nabla^2\mathbf{u}\rangle^{(f)} \\ - \frac{na^2}{6\eta}\langle\mathbf{R}\rangle + \langle\mathbf{W}\rangle, \qquad \text{(A 5)}$$

which does have the desired form.

A valid approximation, correct to the order ϕ and involving only absolutely convergent integrals, is then obtained from (A 5) as

$$\langle\mathbf{U}\rangle - \langle\mathbf{u}\rangle = \mathbf{U}_0 - \int_{r\leqslant a}\mathbf{u}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}')\,d\mathbf{x}' + \int_{r\geqslant a}[-\mathbf{u}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}') \\ + \{\mathbf{v}(\mathbf{y},\mathbf{x}|\mathbf{x}') + \tfrac{1}{6}a^2\nabla^2_{\mathbf{y}}\mathbf{v}(\mathbf{y},\mathbf{x}|\mathbf{x}')\}_{\mathbf{y}=\mathbf{x}}P(\mathbf{x}'|\mathbf{x}) - \tfrac{1}{6}a^2\nabla^2_{\mathbf{x}}\mathbf{u}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}')]\,d\mathbf{x}' \\ + \tfrac{1}{2}\phi\mathbf{U}_0 + \int \mathbf{W}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}'|\mathbf{x})\,d\mathbf{x}', \qquad \text{(A 6)}$$

where $r = |\mathbf{x}'-\mathbf{x}|$ and $\mathbf{R}$ has been approximated as $4\pi\eta a\mathbf{U}_0$. Now the unconditional probability density $P(\mathbf{x}')$ is equal to n, whence the first integral in (A 6) is equal to $\phi\mathbf{U}_0$ with a consistent approximation. In the second integral the functions $\mathbf{u}(\mathbf{y}|\mathbf{x}')$ and $\mathbf{v}(\mathbf{y},\mathbf{x}|\mathbf{x}')$ both represent the velocity at $\mathbf{y}$ due to the presence at $\mathbf{x}'$ of a sphere on which the force $\mathbf{F}^*$ acts (and were previously distinguished notationally to indicate that different probability weighting functions were required when averaging), so that (A 6) becomes

$$\langle\mathbf{U}\rangle-\langle\mathbf{u}\rangle = \mathbf{U}_0-\tfrac{1}{2}\phi\mathbf{U}_0-\int_{r\geqslant a}\{\mathbf{u}(\mathbf{x}|\mathbf{x}')+\tfrac{1}{6}a^2\nabla_{\mathbf{x}}^2\mathbf{u}(\mathbf{x}|\mathbf{x}')\}\{P(\mathbf{x}')-P(\mathbf{x}'|\mathbf{x})\}\,d\mathbf{x}' + \int\mathbf{W}(\mathbf{x}|\mathbf{x}')\,P(\mathbf{x}'|\mathbf{x})\,d\mathbf{x}'. \qquad \text{(A 7)}$$

We now consider the forms of the various functions appearing in (A 7). In the Brownian diffusion problem the effect of Brownian motion is to make equally probable all realizable relative configurations of a large number of neighbouring spheres, and although this does not imply that the pair distribution function is uniform it is evident – and well known in the theory of the liquid state – that the departure from uniformity (which arises from the fact that the volume from which the centres of other spheres in the suspension are excluded varies with the separation of the pair) vanishes with ϕ and so is negligible for the present purpose. Hence

$$\left.\begin{aligned} P(\mathbf{x}'|\mathbf{x}) &= n \quad \text{for} \quad r \geqslant 2a,\\ &= 0 \quad \text{for} \quad r < 2a.\end{aligned}\right\} \qquad \text{(A 8)}$$

This form of the pair distribution function was also adopted in the sedimentation problem (Batchelor 1972).

The fluid velocity $\mathbf{u}(\mathbf{x}|\mathbf{x}')$ at position $\mathbf{x}$ due to an isolated sphere with centre at $\mathbf{x}'$ acted on by a force is given by (4.6), with $\mathbf{x}'-\mathbf{x}$ replacing $\mathbf{r}$ there, and the value of the first integral in (A 7) is thus found to be $6\pi a^3 n\mathbf{U}_0$, that is, $\tfrac{9}{2}\phi\mathbf{U}_0$.

It will be recalled that $\mathbf{W}(\mathbf{x}|\mathbf{x}')$ is the additional velocity of a sphere at $\mathbf{x}$ due to the presence of a second sphere at $\mathbf{x}'$, on which the same force $\mathbf{F}^*$ acts, minus $\{\mathbf{u}(\mathbf{x}|\mathbf{x}')+\tfrac{1}{6}a^2\nabla_{\mathbf{x}}^2\mathbf{u}(\mathbf{x}|\mathbf{x}')\}$. The two-sphere mobility tensors defined by (4.1) may be used here to express $\mathbf{W}$ as

$$\mathbf{W}(\mathbf{x}|\mathbf{x}') = (\mathbf{b}_{11}+\mathbf{b}_{12})\,.\,\mathbf{F}^*-\mathbf{U}_0-\mathbf{u}(\mathbf{x}|\mathbf{x}')-\tfrac{1}{6}a^2\nabla_{\mathbf{x}}^2\mathbf{u}(\mathbf{x}|\mathbf{x}'), \qquad \text{(A 9)}$$

where $\mathbf{F}^* = 6\pi\eta a\mathbf{U}_0$. The dependence of the mobility tensors on the direction of $\mathbf{x}'-\mathbf{x}$ is given by (4.2), in which $a_i = a_j = a$, and for $\mathbf{u}(\mathbf{x}|\mathbf{x}')$ we have the explicit expression (4.6). The integration of $\mathbf{W}$ over all directions of $\mathbf{x}'-\mathbf{x}$ may be carried out, and the final expression for the average particle velocity is

$$\langle\mathbf{U}\rangle-\langle\mathbf{u}\rangle = \mathbf{U}_0\{1-\phi(5+C+D)+o(\phi)\}, \qquad \text{(A 10)}$$

where

$$C = \int_2^\infty \{3-A_{11}(\rho)-2B_{11}(\rho)\}_{\lambda=1}\rho^2\,d\rho, \quad D = \int_2^\infty \left\{\frac{3}{\rho}-A_{12}(\rho)-2B_{12}(\rho)\right\}_{\lambda=1}\rho^2\,d\rho,$$

and $\rho = r/a$. The sum of these two integrals involves the combinations $A_{11}+A_{12}$ and $B_{11}+B_{12}$, which have been calculated by Goldman *et al.* (1966) for a common set of values of r/a and are shown in their table 11 A under the headings $\theta = 90°$

and $\theta = 0°$ respectively as already mentioned. The numerical integration reported in the previous paper (Batchelor 1972) gave the result $C+D = 1{\cdot}55$, from which the quoted result (6.11) follows after comparison of (6.2) and (A 10).

Reference should be made to the original publication for the hydrodynamical interpretation of the various contributions to the coefficient of ϕ in the expression for $\langle \mathbf{U} \rangle - \langle \mathbf{u} \rangle$.

Note added in proof. My attention has just been drawn to some recent publications in which the expression (6.5) for the diffusivity of identical particles with non-uniform concentration is regarded as being a direct consequence of arguments commonly used in non-equilibrium thermodynamics (see chap. 13 of *Dynamic Light Scattering*, by B. J. Berne & R. Pecora, Wiley 1976). So far as I can tell, the reasoning I have used in this paper is essentially equivalent. The result (6.5) will thus not be new for some physical chemists. It appears also that the particular result (6.12) for a dilute suspension of uncharged hard spheres has recently been found to agree well with diffusion data obtained for monodisperse DNA molecules by the new technique of intensity fluctuation spectroscopy by Newman, Swinney, Berkowitz & Day (*Biochemistry*, **13**, 1974, 4832).

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