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The effect of particle interactions on dynamic light scattering from a dilute suspension

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The calculation of dynamic laser-light scattering by dilute suspensions of Brownian particles is reviewed. It is shown that present theories of diffusion can provide approximations for the autocorrelation of the intensity of the scattered light that are only uniformly accurate for correlation times up to order $(D_0 k^2)^{-1}$ where D_0 is the diffusivity of a single particle and $\boldsymbol{k}$ is the scattering wave vector. The meanings of, and connections between, down-gradient, self- and tracer diffusion for both short and long times are established and it is shown how these may be inferred from light-scattering experiments for optically monodisperse and polydisperse systems.

For dilute systems, equations giving the time evolution of the intermediate and self-intermediate scattering functions, $F(\boldsymbol{k}, t)$ and $F_s(\boldsymbol{k}, t)$, accurate to first order in the volume concentration of particles are constructed, and are solved for suspensions of hard spheres with and without hydrodynamic interaction. For short and long times (semi-) analytic solutions are given; for intermediate times numerical results are presented. The formal correspondence of the limiting values of the time-dependent solutions with the results of Batchelor (1976, 1983) and others for steady sedimentation in polydisperse systems is established.

1. Introduction

The technique of scattering laser light from quiescent solutions of macromolecules is widely used as a method of determining the translational and rotational diffusivity of isolated molecules and thereby extracting information about their size (molecular weight) and shape. As the particles of the solution or suspension move under the influence of Brownian impacts from solvent molecules, so the instantaneous scattered light changes. By monitoring the autocorrelation function of the electric field or the intensity of the scattered light, it is possible to infer the motion of the particles and thus their diffusivities. The optics of the scattering is well understood (Berne & Pecora 1976), and the principal theoretical difficulty in the analysis of experimental data is the calculation of the rates of diffusion. For dilute suspensions, where each particle is unaffected by its neighbours, the calculation is straightforward, but for more concentrated dispersions, considerable complications arise. It is clear that the particle diffusion and hence the scattered light are affected by particle interactions and hence in principle it should be possible to infer some features of the forces between particles by suitable interpretation of the scattering data. We seek in this paper to analyse the problem for the simplest case in which interactions are important, namely when the concentration ϕ is sufficiently small for pairwise interactions to be the dominant effect.

The problem of including the effects of two-particle interactions has received a good deal of attention. Table 1 gives a partial list of relevant papers. A detailed explanation of the symbols used is given in §2. The papers fall into two categories. Those influenced by suspension mechanical work on steady transport phenomena in two-phase flow have tended to use exact hydrodynamic data (which is an important ingredient of the problem), but have provided results appropriate only to special limiting cases of the light-scattering problem. Papers in the second category have attempted (more) complete solutions of the problem but have used approximate hydrodynamic data. For many papers in both categories it is not always clear to which regime in wavenumber and time the result applies, nor the extent of its accuracy and validity. In this account we seek to combine the better features of both approaches, to use exact hydrodynamics whenever possible, and to provide both a physical explanation for, and a mathematical proof of, the correspondence between the various results which provide partial solutions to the full problem. The difference between 'exact' and 'approximate' hydrodynamics should be amplified since the term exact is intended to convey more than mere accuracy. The solution of two- and many-body problems in hydrodynamics can in general be achieved only numerically, and in consequence the final results are subject to rounding and cut off errors (e.g. see table 2). On the other hand, the analytic expressions given *are* exact, and can exhibit *qualitative* differences from results obtained using 'approximate' data (see for example the discussion of §3.2). In §2 we delineate the various timescales of interest, and in §3 provide a full mathematical formulation for the dilute limit. In §§4 and 5 we solve the equations in two cases, first for an 'excluded-annulus' model where hydrodynamic interactions are neglected and where analytic progress is possible, and second a numerical solution for the case of hard spheres with hydrodynamic interactions. The term 'excluded annulus' is intended to convey the physical picture of a very small particle surrounded by a much larger region in which the repulsive interparticle force (modelling, say, a thick diffusive charge double layer) is high, but which cuts off suddenly at a shell radius where hydrodynamic interactions have become negligible. (In that case, ϕ is the volume concentration given by the outer radius of an annulus, not that of the particle.) Our results for the excluded annulus are mathematically identical to those of Ackerson & Fleishman (1982) (though our interpretation differs somewhat). Our results which include hydrodynamic interactions are largely new.

2. The connection between particle diffusivity and light scattering

Since the term 'particle diffusivity' has several possible meanings, we start by defining the regimes in which its use is appropriate.

2.1. *Timescales of interest*

The shortest time of possible interest for the dynamic light-scattering experiment is that over which the velocity of an individual particle relaxes after a Brownian impact. At this level, the important physical ingredients are the inertia of the particle (and associated fluid) and friction, giving an inertial relaxation time t_{I} of order $m/6\pi\mu a$, where m is the mass of the particle, a its linear dimension, and μ the viscosity of the fluid. To discuss the dynamics at these short times it is necessary to use a Langevin equation (or to work in phase space), and this leads to a prediction of the 'long-time tail' (i.e. long when time is scaled with t_{I}) for the velocity autocorrelation function (e.g. Hinch 1975).

Author(s)	Calculation	Domain of applicability	Hydrodynamics	Remarks
Altenberger & Deutsch (1973)	$F(k, t)$	All ka, all t	Oseen	Incorrect pair statistics
Pusey (1975)	$\dot{F}(k, 0)$	All ka	None	—
Batchelor (1976)	D^{c}	$ka \rightarrow 0$	Exact	—
	D_0^{s}	$ka \rightarrow 0$	Exact	Supposed incorrectly to be D_∞^{s}
Batchelor (1983)	D_∞^{s}	$ka \rightarrow 0$	Exact	—
Ackerson (1976)	$\dot{F}(k, 0)$, $\ddot{F}(k, 0)$	All ka	None	—
Hess & Klein (1976)	$F(k, t)$	All ka, all t	Oseen	Incorrect treatment of hard spheres
Felderhof (1978)	D_0^{s}	$ka \rightarrow 0$	Oseen	—
Altenberger (1979)	$\dot{F}(k, 0)$, $\dot{F}_s(k, 0)$	All ka	Oseen	—
Hanna *et al.* (1981)	$\ddot{F}_s(k, t)$	$ka \rightarrow 0$	None	Via velocity and force autocorrelations
Phillies & Wills (1981)	$\ddot{F}(k, 0)$	All ka	Modified for finite boundaries	Langevin approach; incorrect hydrodynamics
Russel & Glendinning (1981)	$\dot{F}(k, 0)$	All ka	Exact	—
Wills (1981)	$\dot{F}(k, 0)$, $\dot{F}_s(k, 0)$	All ka	Oseen	—
Fijnaut (1981)	$\dot{F}(k, 0)$	All ka	Oseen	—
Pusey & Tough (1982)	$\dot{F}, \ddot{F}, \dddot{F}$ at $t = 0$	All ka	None	—
Ackerson & Fleishman (1982)	$F(k, t)$, $F_s(k, t)$	All ka, all t	None	—
Hanna *et al.* (1982)	D_∞^{s}	$ka \rightarrow 0$, $t \rightarrow \infty$	None/Oseen	—
	$F_s(k, t)$	All ka, all t		
Jones & Burfield (1982)	D_∞^{s}	$ka \rightarrow 0$	Oseen	—
Felderhof & Jones (1983)	$F(k, t)$, $F_s(k, t)$	All ka, all t	None	—
Pusey & Tough (1983)	$\frac{d\langle r\rangle}{dt}$, $\frac{d^2\langle r^2\rangle}{dt^2}$ at $t = 0$	$ka \rightarrow 0$	None/semi-exact	Langevin approach; incorrect treatment of hard spheres
	$\dot{F}_s(k, 0)$	All ka		
Lekkerkerker & Dhont (1984)	D_∞^{s}	$ka \rightarrow 0$	None	By dynamic and steady methods
Present work	$F(k, t)$, $F_s(k, t)$	All ka, $D_0 k^2 t \lesssim 1$	None/exact	

TABLE 1. Summary of relevant literature for hard-sphere suspensions

Note that we use 'Oseen' as a shorthand for approaches where the hydrodynamics are approximated by one or more terms of a reflections expansion, and 'exact' where accurate numerical data has been used.

	D^c/D_0	D_0^s/D_0	D_∞^s/D_0	$\left.\frac{a^2}{D_0^2}\frac{d^2\langle r^2\rangle}{dt^2}\right\rvert_{t=0}$
Without HI	$1+8\phi$	1	$1-2\phi$	$-\infty\phi$
With accurate HI	$1+1.47\phi$	$1-1.81\phi$	$1-2.06\phi$	-2.22ϕ
Batchelor (1976, 1983)	$1+1.45\phi$	$1-1.83\phi$	$1-2.10\phi$	

TABLE 2. Summary of numerical and analytic results

In this paper we shall be concerned only with times much longer than t_I so that many uncorrelated impacts of solvent molecules have occurred and the corresponding momenta have relaxed. In this regime it is appropriate to describe the coupled-particle motions by a diffusion equation in physical rather than phase space. The short-lived inertial features do not then enter the calculation at all. The characteristic diffusivity of a single particle is given by the Stokes–Einstein relation as $D_0 = kT/6\pi\mu a$ with k Boltzmann's constant and T the absolute temperature. The timescale for diffusive motions depends on the length over which the particles are required to diffuse and, in a light-scattering context, this is the wavelength $2\pi/k$ of the scattering vector, which may in principle be varied *ad lib*. It is only when the particles have diffused over the wavelength of the scattered light that intensity autocorrelations can be changed significantly. Thus the timescale of importance in experiments is $t_k = (D_0 k^2)^{-1}$. In practice it is difficult (at the present time) to achieve reliable experimental results for the autocorrelation function once $t \gtrsim 3t_k$.

There are, in addition, further natural lengthscales associated with the suspension itself rather than the light, and these give rise to further diffusion timescales. In particular $t_a = a^2/D_0$ is the time taken for a particle to diffuse across its own diameter, and $t_\phi = a^2\phi^{-\frac{2}{3}}/D_0$ is the time taken to diffuse across a typical particle separation distance, $a\phi^{-\frac{1}{3}}$. The significance of this timescale was suggested in this context by Pusey (1975). He (and others) have used the term 'cage' to describe the lengthscale determined by mean neighbours of a test particle. For a dilute suspension $\phi \ll 1$, and so $t_\phi \gg t_a$.

2.2. *The meaning of diffusivity*

There are (at least) two meanings which may naturally be attached to the term 'particle diffusivity'. First, an experiment may be imagined in which a steady small concentration gradient $\nabla\phi$ of particles is maintained and in which the resulting flux $\boldsymbol{F}$ of particles down the gradient is measured. The constant of proportionality $D^c(\phi)$ is called the *collective* or *down-gradient* diffusivity so that

$$\boldsymbol{F} = -D^c(\phi)\,\nabla\phi.$$

Second, a quiescent suspension (in equilibrium) may be considered and the mean-square displacement of a given particle starting at the origin monitored as a function of time t. Taking an ensemble average over all other particle motions, the test particle 'sees' for short times an isotropic cage surrounding it (which affects its motion only in modifying its hydrodynamic resistance), and thus its motion is diffusive in character with $\langle r^2\rangle \propto t$. This purely diffusive motion can persist for as long as the configuration of particles surrounding the test particle is not influenced significantly by the motion of the test particle, for thereafter its velocity ceases to be a *stationary* random function of time. This was first noted in a related context by Ermak and Yeh (1974) and has subsequently been developed by Pusey (1975) for light scattering and by Batchelor (1976) for diffusion (see also the careful discussion in Pusey & Tough 1982). At first sight it may be thought (Pusey 1975, 1978; Batchelor 1983) that the purely diffusive motion persists until the test particle has diffused to its mean nearest neighbour (i.e. t_ϕ). This conclusion is wrong, however, since when a test particle has diffused only over its own length (in a time t_a) there is already an $O(\phi)$ probability that it will have collided (or interacted significantly) with a second particle, and in consequence there will be an $O(\phi)$ modification to its motion. Thus for non-zero ϕ, the purely diffusive character of the motion persists only for $t \lesssim t_a$ and there is thus a *short-time self-diffusivity* $D_0^s(\phi)$ such that

$$\langle r^2 \rangle \sim 6D_0^s t \quad \text{for} \quad t_I \ll t \ll t_a.$$

Thus the concept of a 'cage' whose size depends on concentration, though intuitively appealing, can give incorrect quantitative estimates of the important timescales in the diffusion problem. For t comparable with t_a a test particle interacts with its neighbours (which presumably slow it down) and its motion cannot be described by a pure diffusion process, i.e. $\langle r^2 \rangle / t \neq$ constant, and the probability density for r is no longer Gaussian. But for long times $t \gg t_a$ the test particle will have had many (uncorrelated) encounters with other particles and the sum of these random steps is again a diffusion process with a *long-time self-diffusivity* $D_\infty^s(\phi)$ such that

$$\langle r^2 \rangle \sim 6D_\infty^s t \quad \text{for} \quad t \gg t_a.$$

It may be worth mentioning at this point a conceptual issue which is the source of some confusion. By restricting attention to times $t \gg t_I$ we are able to neglect inertia and so velocity autocorrelations do not appear as such in our analysis – only positional correlations (for the particles; the individual solvent molecules do not appear directly in the calculations at all). It is equally legitimate, however, to consider the particles as if they themselves constituted the molecules of a new 'fluid' (even though these motions are governed by a Smolochowski equation rather than a Langevin equation). In that case it is natural to speak in terms of velocity autocorrelations for the particles (see e.g. Hanna, Hess & Klein 1981) and, in this framework, D_∞^s is the integral of the velocity autocorrelation over times *long compared with* t_a. In other words t_a from this perspective plays the role of t_I from ours, even though the physics for $t \lesssim t_a$ (particle-pair distribution coming to equilibrium) is entirely different from that for $t \lesssim t_I$ (viscous decay of Brownian impulse).

One further type of diffusivity should be mentioned here where *two* species of particle are present: a relatively numerous quiescent species with concentration ϕ, and a labelled ('tracer') species otherwise identical to the first whose concentration ϕ_{tr} is very low ($\phi_{tr} \ll \phi$) but in which there is a gradient $\nabla \phi_{tr}$ and hence a flux F_{tr}.

It is perhaps conceptually easiest to imagine a quiescent suspension of a single species in which at some initial instant ($t = 0$) a very few tracer particles are suddenly labelled in such a way that a small gradient of tracers exist. (This might seem a difficult experiment to set up, but it is, in essence, what the optically polydisperse light-scattering experiment achieves.)

Since any given labelled particle interacts only with unlabelled particles (neglecting effects of order ϕ_{tr}/ϕ), its motion is unaffected by the small concentration gradient, so that its mean drift is zero and its r.m.s. displacement $\langle r^2 \rangle$ is identical at all times with that for the monodisperse suspension discussed above. This tracer situation is therefore formally identical with the down-gradient diffusion of an infinitely dilute

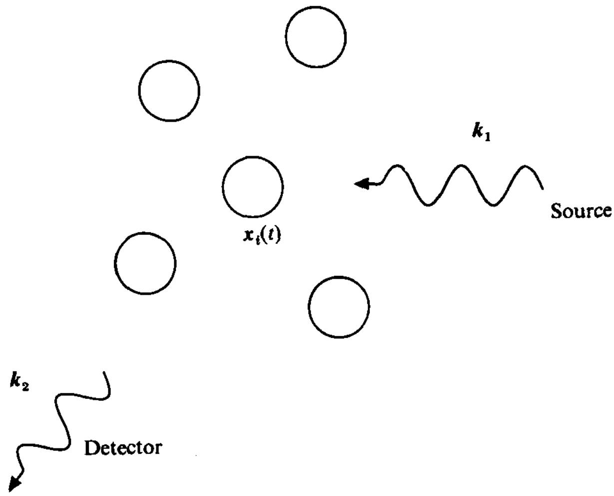

FIGURE 1. Schematic sketch of the light-scattering apparatus.

single species whose diffusivity varies in time in a prescribed manner. The instantaneous tracer flux is therefore

$$F_{tr} = -D^{tr}(\phi, t)\,\nabla\phi_{tr}$$

and $D^{tr}(\phi, t) = \frac{1}{2}(d/dt)\langle r^2\rangle$. We supply a formal proof of this assertion in Appendix A. In the particular limits $t\to 0$ and $t\to\infty$, $\langle r^2\rangle \propto t$ as above, and then

$$D^{tr}(\phi, 0) = D^s_0(\phi), \quad D^{tr}(\phi, \infty) = D^s_\infty(\phi),$$

so that self-diffusivities may alternatively be regarded as tracer diffusivities.

At zero concentration, all the diffusivities above are equal (to D_0). For non-zero ϕ they differ however, e.g. for rigid spheres with hydrodynamic interaction, Batchelor (1976, 1983) gives the following results correct to $O(\phi)$:

$$D^c(\phi) = D_0(1+1.45\phi), \tag{2.1}$$

$$D^s_0(\phi) = D_0(1-1.83\phi), \tag{2.2}$$

$$D^s_\infty(\phi) = D_0(1-2.10\phi). \tag{2.3}$$

2.3. *Interpretation of light-scattering results*

The question arises as to which of the diffusivities (if any) is measured by light scattering. Our discussion here is an amplified version of that of Fijnaut (1981). In the experiment shown schematically in figure 1, an incident monochromatic plane wave generated by a laser with wave vector $\boldsymbol{k}_1$ is scattered by each particle of the suspension (whose positions are $\boldsymbol{x}_i(t)$ $(i = 1, \ldots, \mathcal{N})$), and the scattered light is measured in a direction which is specified by an outgoing wave vector $\boldsymbol{k}_2$ (and $|\boldsymbol{k}_2| = |\boldsymbol{k}_1|$). Then, neglecting multiple scattering, the electric field of the scattered light at $\boldsymbol{x}$ is proportional to

$$\sum_{i=1}^{\mathcal{N}} a_i \frac{e^{i\boldsymbol{k}_2\cdot(\boldsymbol{x}-\boldsymbol{x}_i)}}{|\boldsymbol{x}-\boldsymbol{x}_i|}\, e^{i(\boldsymbol{k}_1\cdot\boldsymbol{x}_i-\omega t)},$$

where a_i is the amplitude of the scattering by particle i. Thus the phase shift by particle i is $e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i(t)}$ where $\boldsymbol{k} = \boldsymbol{k}_1 - \boldsymbol{k}_2$ is the *scattering vector*. It follows that the autocorrelation function of the scattered light at a time delay t is proportional to (the ensemble average of)

$$\sum_{i,j=1}^{\mathcal{N}} a_i a_j \, e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_i(t)-\boldsymbol{x}_j(0))}.$$

(This result is established above only for the *electric field* of the scattered light; it is often more convenient in experiments to measure the *intensity* of the scattered light, but it may be shown (Berne & Pecora 1976) that provided $\mathcal{N} \gg 1$ the same averaged quantity is involved.)

There are two forms of the light-scattering experiment. The conceptually simpler uses optical polydispersity so that the scattering amplitudes a_i vanish (or are comparatively small) except for a subset of $\mathcal{N}_1 (\gg 1$ but $\ll \mathcal{N})$ tracer particles for which $a_i = 1$. In that case the scattered light is proportional to

$$F_s(k, t) = \frac{1}{\mathcal{N}_1}\left\langle \sum_{i=1}^{\mathcal{N}_1} e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_i(t)-\boldsymbol{x}_i(0))}\right\rangle. \tag{2.4}$$

F_s is called the *self-intermediate scattering function*. In the second experiment, all the particles scatter light equally, $a_i = 1$ for all i, and then the autocorrelation is proportional to the *intermediate scattering function* $F(k, t)$ where

$$F(k, t) = \frac{1}{\mathcal{N}}\left\langle \sum_{i,j=1}^{\mathcal{N}} e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_i(t)-\boldsymbol{x}_j(0))}\right\rangle. \tag{2.5}$$

In each case the angle brackets denote an ensemble average.

For dilute systems, correlations between different particles are negligible and thus $F = F_s$. Equation (2.4) shows that F_s is then just the Fourier transform of the displacement of a single particle which is a Gaussian distribution. It follows that $F = F_s = e^{-k^2 D_0 t}$. But for non-dilute suspensions $F \neq F_s$ and, as noted in §2.2, the statistics are no longer Gaussian so that a purely exponential decay of F and F_s cannot in general be expected. We discuss the interpretation of the two experiments below.

The tracer experiment

It is natural to guess that, for the extreme times $t \ll t_a$, $t \gg t_a$ discussed earlier when pure diffusion obtains, the autocorrelation will again be exponential with diffusivities D_0^s and D_∞^s respectively. For short times this conclusion is correct, but surprisingly it is not necessarily correct for the long-time limit as the following model calculation demonstrates.

Consider a very dilute suspension containing particles of two species both of which scatter light (equally, say), whose diffusivities are D_1, $D_2 (< D_1)$ and for which $\phi_2 \ll \phi_1 \ll 1$. Then the probability distribution for a particle chosen at random that starts at the origin is

$$P(r, t) = \left(1 - \frac{\phi_2}{\phi_1}\right) e^{-r^2/2D_1 t} + \frac{\phi_2}{\phi_1} e^{-r^2/2D_2 t}.$$

This distribution gives a mean-square displacement at time t

$$\begin{aligned}\langle r^2\rangle &= \left(1 - \frac{\phi_2}{\phi_1}\right) 6D_1 t + \frac{\phi_2}{\phi_1} 6D_2 t \\ &\approx 6D_1 t,\end{aligned}$$

with relative error of order ϕ_2/ϕ_1 at all times. In other words, the particles of species 2 are so rare that the mean long-time diffusivity of a particle chosen at random is D_1 as expected. On the other hand (either form of) the light-scattering experiment measures the spatial Fourier transform of P, viz.

$$\tilde{P}(k,t) = \left(1-\frac{\phi_2}{\phi_1}\right)\mathrm{e}^{-D_1k^2t}+\frac{\phi_2}{\phi_1}\mathrm{e}^{-D_2k^2t},$$

and thus for sufficiently long times, however small ϕ_2/ϕ_1 is, the second term dominates, so

$$F \approx \frac{\phi_2}{\phi_1}\mathrm{e}^{-D_2k^2t},$$

and so the diffusivity measured is D_2 not D_1. This model calculation demonstrates that at large times (i.e. large values of Dk^2t) the most significant contribution to the autocorrelation function comes from the structures in the suspension with a smaller diffusivity, rather than the long-time behaviour of the most common particles. (Since $D \sim kT/6\pi\mu a$, the structures with smaller diffusivities are the larger ones.)

In any suspension that is not at infinite dilution, groups of two or more particles always exist in close proximity, albeit transiently, and, in a fairly dilute system, progressively larger groups will occur with decreasing probability. The measured $\tilde{P}(k,t)$ will therefore be a complicated sum of small terms (for $t \gg t_k$) whose total is not expected to be a single exponential, and whose instantaneous slope does not necessarily represent D^{s}_{∞}. From a theoretical point of view, this also means that a small-ϕ expansion is bound to fail in the limit $t \gg t_k$ since groups of particles give ϕ^2, ϕ^3, ..., contributions which are neglected at the outset. Thus the limit $t \gg t_k$ lies outside the scope of the analysis of this paper, is not expected to be a single exponential, and is difficult to obtain experimentally too.

The D^{s}_{∞} diffusivity may nevertheless be measured if *both* the criteria $t \gg t_a$ and $t \lesssim t_k$ are satisfied. These are simultaneously possible only if $ka \ll 1$. In this case there is an intermediate time regime in which a particle can diffuse through many particle diameters before diffusing through a wavelength. Further, in this long-wavelength limit the identification of 'tracer' and 'self' properties may be made for *all* times t (not just $t \gg t_a$) as shown in Appendix A. Hence the mean-square particle displacement can be identified as

$$\langle r^2\rangle = -\frac{6}{k^2}\log F_{\mathrm{s}} \quad \text{as} \quad ka \to 0.$$

Validity of the two-particle expansion

In calculating the lowest-order effect of particle interactions on *steady* suspension transport properties (the $O(\phi)$ term here) it is generally appropriate to examine pairwise interactions between particles. We have noted above that this procedure will produce non-uniform approximations in time whenever $t \gg t_k$. The timescale t_k depends, of course, on the experiment and not the suspension, and so the question arises as to whether other non-uniformities of approximation can occur owing in particular to repeated collisions between particles if only pairwise interactions are considered (and $t \gg t_a$).

It is certainly the case that if a pair of test particles is chosen, and the pair diffuses apart, then if $t \gg t_a$ the specific pair ceases to represent the pair-distribution function for test particles in the suspension as a whole. But if for a given test particle *all* possible neighbours are considered (whatever their initial position may have been), then the pair-distribution function is representative at all times, and the only error in dealing with pairwise interactions alone is the neglect of occasional three-particle collisions.

So far as the steady diffusivities are concerned, these three-particle effects undoubtedly generate $O(\phi^2)$ corrections which we neglect here. In regard to the time-dependent behaviour they introduce contributions which become significant only when $t \sim t_k$.

In summary, then, for times $t \lesssim t_k$ a uniformly valid approximation at $O(\phi)$ may be obtained by considering just pairs of particles, provided that all possible neighbours of a test particle are included.

The monodisperse experiment

On noting that $e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i(t)}$ is the Fourier transform of $\delta(\boldsymbol{x}-\boldsymbol{x}_i(t))$, and that the number density of particles is given by

$$n(\boldsymbol{x}, t) = \sum_{i=1}^{\mathcal{N}} \delta(\boldsymbol{x}-\boldsymbol{x}_i(t)),$$

(2.5) shows that

$$F(\boldsymbol{k}, t) = \frac{1}{\mathcal{N}}\langle \tilde{n}(\boldsymbol{k}, t)\, \tilde{n}^*(\boldsymbol{k}, 0)\rangle,$$

where ˜ denotes a Fourier transform and * is a complex-conjugate. As the constant background level of n is irrelevant, $F(\boldsymbol{k}, t)$ may be regarded as measuring the autocorrelation of *fluctuations* in number density $\tilde{n}'(\boldsymbol{k}, t)$ at wavenumber $\boldsymbol{k}$.

This interpretation is helpful in understanding three limiting circumstances. First, at the initial instant, if the particles were *independent* then $\tilde{n}'(\boldsymbol{k}, 0)$ (as the sum of $\mathcal{N}$ random variables, $e^{i\boldsymbol{k}\cdot\boldsymbol{x}_i}$ with mean 0 and variance 1) would have mean 0 and variance $\mathcal{N}^{\frac{1}{2}}$, giving the static structure function $F(\boldsymbol{k}, 0) = 1$. But, by virtue of interparticle forces, the particle positions are *not* independent even at $t = 0$ and the departure of $F(\boldsymbol{k}, 0)$ from unity therefore provides a measure of the equilibrium pair-distribution function at wavenumber $\boldsymbol{k}$ (see §3.2).

Second, if $ka \ll 1$ the scale of the number-density fluctuation to be considered is much greater than the size of an individual particle. It follows that the flux of particles down the gradient is the same as if the gradient persisted everywhere, i.e. $-D^c\nabla n'$. Thus the fluctuation decays exponentially at a rate $-D^c k^2$. Further, the pair-distribution function varies on a lengthscale a, so $F(\boldsymbol{k}, 0) \sim 1$, and hence $F(\boldsymbol{k}, t) \sim e^{-D^c k^2 t}$ as $ka \to 0$.

Third, if $ka \gg 1$ then the relevant scale of number-density fluctuations is *small* compared with the size of an individual particle. Hence it is only the motion of a single tracer particle which matters. If further $t \lesssim t_k$ then $t \ll t_a$ so that the structure of the pair-distribution function is still isotropic and therefore $\tilde{n}'$ decays by a purely diffusive mechanism and the relevant diffusivity is D_0^s. On this timescale the structure function F is unchanged from its static value and so

$$D_0^s = -\frac{\dot{F}(\boldsymbol{k}, 0)}{k^2 F(\boldsymbol{k}, 0)}.$$

In summary, the steady particle diffusivities may be identified in dynamic light-scattering experiments in the following limiting circumstances:

$$D^{c} = -\frac{\dot{F}}{k^2 F} \quad \text{for } ka \to 0 \quad \text{and} \quad t \lesssim t_k\,,$$

$$D_0^{s} = \begin{cases} -\dfrac{\dot{F}_s}{k^2 F_s} & \text{for } t \ll t_a, \\[2ex] -\dfrac{\dot{F}}{k^2 F} & \text{for } ka \to \infty \quad \text{and} \quad t \ll t_a, \end{cases}$$

$$D_\infty^{s} = -\frac{\dot{F}_s}{k^2 F_s} \quad \text{for } t_a \ll t \ll t_k \quad \text{if} \quad ka \ll 1.$$

We now turn to a mathematical formulation of these ideas.

3. The governing equations

3.1. *Formulation of the problem*

We consider a suspension of $\mathcal{N} \gg 1$ spherical particles, identical except, perhaps, for their optical properties, which occupy a large volume $\mathcal{V}$. We suppose that the particles may be regarded as point scatters of light (at their centres) and that the optical contrast between particles and solvent is sufficiently small that multiple scattering may be neglected.

Suppose first that the particles are optically monodisperse. Then the intermediate scattering function $F(\boldsymbol{k}, t)$ is given by (2.5) as

$$F(\boldsymbol{k}, t) = \left\langle \frac{1}{\mathcal{N}} \sum_{i,j=1}^{\mathcal{N}} \mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{x}_i(t)-\boldsymbol{x}_j(0))} \right\rangle .$$

A similar expression, (2.4), gives $F_s(\boldsymbol{k}, t)$ for the polydisperse case. Here the angle brackets represent an ensemble average over all possible initial configurations of the suspension, and over all configurations at time t which started from that at $t = 0$. Thus if $P_0(\boldsymbol{x}_i(0))$ is the probability density for the set of positions at $t = 0$, and $P(\boldsymbol{x}_i(t)|\boldsymbol{x}_j(0))$ is that for the set of positions $\boldsymbol{x}_i$ at time t, given that the particles occupied positions $\boldsymbol{x}_j(0)$ at $t = 0$, then

$$\langle \cdot \rangle \equiv \int_{\mathcal{V}^{2\mathcal{N}}} \cdot\, P(\boldsymbol{x}_i(t)|\boldsymbol{x}_j(0))\, P_0(\boldsymbol{x}_j(0))\, \mathrm{d}^{3\mathcal{N}} x_i(t)\; \mathrm{d}^{3\mathcal{N}} x_j(0). \tag{3.1}$$

We assume that the suspension is at thermodynamic equilibrium, and that (direct) interactive forces between the particles may be described by a potential given (in terms of a dimensionless function) as $\ell T V(\boldsymbol{x}_i)$. Then at time $t = 0$ the probability distribution for the particle positions is Maxwell–Boltzmann with

$$P_0(\boldsymbol{x}_i(0)) = \frac{1}{Z}\, \mathrm{e}^{-V(\boldsymbol{x}_i(0))}, \tag{3.2}$$

where Z is a normalization factor given by

$$Z = \int_{\mathcal{V}^{\mathcal{N}}} \mathrm{e}^{-V(\boldsymbol{x}_i)}\; \mathrm{d}^{3\mathcal{N}} x_i.$$

We now specify the way in which the structure of the suspension changes in time. On the assumption that $t \gg t_I$, the evolution of P may be described by a diffusion process, and furthermore the hydrodynamic interaction between particles i and j is described by the mobility tensor $(1/kT)\boldsymbol{D}_{ij}$, which depends on all the instantaneous particle positions $\boldsymbol{x}_k(t)$. P then satisfies the $\mathcal{N}$-particle Smolochowski equation

$$\frac{\partial P}{\partial t} = \boldsymbol{\nabla}_i \cdot \boldsymbol{D}_{ij} \cdot (\boldsymbol{\nabla}_j P + P \boldsymbol{\nabla}_j V) \quad (i, j \text{ summed from 1 to } \mathcal{N}), \tag{3.3}$$

with the initial condition

$$P = \prod_{i=1}^{\mathcal{N}} \delta(\boldsymbol{x}_i(t) - \boldsymbol{x}_i(0)) \tag{3.4}$$

and the boundary condition that the flux of P through the walls of $\mathcal{V}^{\mathcal{N}}$ is zero.

Two (exact) simplifications may now be made. First, we may exploit the fact that the scattering particles are identical to choose any one as representative and thus (2.4) becomes

$$F_s(k, t) = \langle e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_1(t) - \boldsymbol{x}_1(0))} \rangle,$$

and similarly (2.5) may be written

$$F(k, t) = F_s(k, t) + (\mathcal{N} - 1) \langle e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_2(t) - \boldsymbol{x}_1(0))} \rangle.$$

Second, the ensemble average over the initial values $\boldsymbol{x}_i(0)$ may be performed analytically by the following device. Define

$$\hat{P}(\boldsymbol{x}_i, t; \boldsymbol{k}) \equiv \frac{1}{Z} \int_{\mathcal{V}^{\mathcal{N}}} P(\boldsymbol{x}_i(t) | \boldsymbol{x}_j(0))\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_1(0) - V(\boldsymbol{x}_j(0))}\, d^{3\mathcal{N}} x_j(0).$$

Then from (3.4), $\hat{P}$ satisfies the initial condition

$$\hat{P}(\boldsymbol{x}_i, 0; \boldsymbol{k}) = \frac{1}{Z} e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_1 - V(\boldsymbol{x}_i)}. \tag{3.5}$$

Further, since in the evolution equation (3.3) for P the initial values $\boldsymbol{x}_j(0)$ do not occur explicitly, $\hat{P}$ also satisfies equation (3.3). Finally, the expressions for the ensemble averages may be simplified to

$$F_s(k, t) = \int_{\mathcal{V}^{\mathcal{N}}} e^{i\boldsymbol{k}\cdot\boldsymbol{x}_1} \hat{P}(\boldsymbol{x}_i, t; \boldsymbol{k})\, d^{3\mathcal{N}} x_i, \tag{3.6}$$

and

$$F(k, t) = F_s(k, t) + (\mathcal{N} - 1) \int_{\mathcal{V}^{\mathcal{N}}} e^{i\boldsymbol{k}\cdot\boldsymbol{x}_2} \hat{P}(\boldsymbol{x}_i, t; \boldsymbol{k})\, d^{3\mathcal{N}} x_i. \tag{3.7}$$

3.2. *Initial values of F and* dF/dt

We can now use the initial condition (3.5) for $\hat{P}$ to obtain the static values $F(\boldsymbol{k}, 0)$, $F_s(\boldsymbol{k}, 0)$. For F we have

$$F(\boldsymbol{k}, 0) = \frac{1}{Z} \int_{\mathcal{V}^{\mathcal{N}}} [1 + (\mathcal{N} - 1)\, e^{i\boldsymbol{k}\cdot(\boldsymbol{x}_2 - \boldsymbol{x}_1)}]\, e^{-V}\, d^{3\mathcal{N}} x_i.$$

Defining the structure function $g(r)$ (with $\boldsymbol{r} = \boldsymbol{x}_2 - \boldsymbol{x}_1$) as

$$g(r) = \frac{\mathcal{N}(\mathcal{N} - 1)}{n^2} \frac{1}{Z} \int_{\mathcal{V}^{\mathcal{N}-2}} e^{-V(\boldsymbol{x}_i)}\, d^3 x_3 \ldots d^3 x_{\mathcal{N}},$$

where $n = \mathcal{N}/\mathcal{V}$ is the (uniform) particle number density, and taking the thermodynamic limit $\mathcal{N} \to \infty$, $\mathcal{V} \to \infty$ with $\mathcal{N}/\mathcal{V}$ constant, F may be written

$$F(k, 0) = 1 + \mathcal{N}\delta(\boldsymbol{k}) + n \int (g(r) - 1)\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\, d^3 r, \tag{3.8}$$

with the integral taken over all $\boldsymbol{r}$-space since $g \to 1$ rapidly as $|\boldsymbol{r}|/a \to \infty$. $F(k, 0)$, often written $S(k)$, is called the *static-structure function*. The δ-function contribution (the Fourier transform of the large scattering volume $\mathscr{V}$) is independent of time and so irrelevant to our subsequent discussion and will be ignored.

The analogous result for F_s is simply

$$F_s(k, 0) = 1.$$

To obtain the initial slopes $\dot{F}(k, 0)$, $\dot{F}_s(k, 0)$, we substitute the initial value of $\partial \hat{P}/\partial t$ obtained from the Smolochowski equation (3.3) and integrate by parts to give

$$\dot{F}(k, 0) = -\frac{1}{Z}\int_{\mathscr{V}^{\mathscr{N}}} [\boldsymbol{k}\cdot\boldsymbol{D}_{11}\cdot\boldsymbol{k} + (\mathscr{N}-1)\,\boldsymbol{k}\cdot\boldsymbol{D}_{12}\cdot\boldsymbol{k}\; \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}_2-\boldsymbol{x}_1)}]\,\mathrm{e}^{-V}n\,\mathrm{d}^{3\mathscr{N}}x_i.$$

This expression admits an especially simple physical interpretation. Regarding the diffusivities as mobilities, $-\dot{F}(k, 0)/k^2$ is the rate of sedimentation of a test particle when a modulated 'gravitational' force $\hat{\boldsymbol{k}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot(\boldsymbol{x}_2-\boldsymbol{x}_1)}$ is applied to every particle in a suspension at thermodynamic equilibrium. Russel & Glendinning (1981) have used this interpretation to exploit Batchelor's (1972) work on sedimentation and derive $\dot{F}(k, 0)$ for arbitrary values of ka for dilute suspensions with accurate hydrodynamics. If ka is small, then the modulation is slight so that the same force $\hat{\boldsymbol{k}}$ acts on every suspended particle, and then $-\dot{F}/k^2F$ is just the collective diffusivity D^{c} as discussed in §2.3 (cf. Batchelor 1976). The expression above is ill-suited for computation of D^{c} because in the limit $\mathscr{V} \to \infty$ the integral diverges due to the long-range $1/r$ behaviour of $\boldsymbol{D}_{12}$. In §3.4 we give (for dilute suspensions) a more suitable convergent expression. The equation above for $\dot{F}(k, 0)$ has been obtained in related contexts by many authors (see e.g. Akcasu & Gurol 1976 for polymers).

The corresponding result for F_s is

$$\dot{F}_s(k, 0) = -\frac{1}{Z}\int_{\mathscr{V}^{\mathscr{N}}} \boldsymbol{k}\cdot\boldsymbol{D}_{12}\cdot\boldsymbol{k}\;\mathrm{e}^{-V}\,\mathrm{d}^{3\mathscr{N}}\,x_i,$$

and hence (for all values of ka) $-\dot{F}_s(k, 0)/k^2$ is the sedimentation rate of a tracer particle (the other particles being force-free), and so $-\dot{F}_s/k^2F_s$ is the tracer or self-diffusivity D_0^{s}.

The question arises as to whether we can use the Smolochowski equation (3.3) to continue this process and obtain $\ddot{F}(k, 0)$ and higher derivatives (i.e. second, third and higher cumulants in the sense of Koppel 1972). The answer depends on the degree of differentiability of $\hat{P}$ at $t = 0$, and this in turn on the (spatial) analyticity properties of $\boldsymbol{D}_{ij}$ and V. We show later (§§4.1, 4.2) that, for hard spheres without hydrodynamic interactions, $\ddot{F}(k, 0)$ does not exist, whereas for hard spheres *with* hydrodynamic interactions $\ddot{F}(k, 0)$ exists but $\dddot{F}(k, 0)$ does not. Calculation of cumulants must therefore be conducted with care.

To make further progress we now restrict attention to the case where the particle concentration is small.

3.3. *Dilute approximation*

The aim of our calculation is to compute F and F_s correct to $O(\phi)$ for $t \lesssim t_k$. It is convenient for this purpose to define probability densities $\hat{P}_q$ for groups of q test particles chosen at random as

$$\hat{P}_q(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_q, t; \boldsymbol{k}) \equiv \frac{\mathscr{N}!}{(\mathscr{N}-q)!}\int_{\mathscr{V}^{\mathscr{N}-q}} \hat{P}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{\mathscr{N}}, t; \boldsymbol{k})\,\mathrm{d}^3x_{q+1}\ldots\mathrm{d}^3x_{\mathscr{N}}.$$

It follows that $\hat{P}_q$ is of order n^q as $n \to 0$ for $q \ll \mathcal{N}$. Without approximation we may then write

$$F_s(\boldsymbol{k}, t) = \frac{1}{\mathcal{N}} \int_{\mathscr{V}} e^{i\boldsymbol{k}\cdot\boldsymbol{x}_1} \hat{P}_1 \, d^3x_1$$

and

$$F(\boldsymbol{k}, t) = F_s(\boldsymbol{k}, t) + \frac{1}{\mathcal{N}} \int_{\mathscr{V}^2} e^{i\boldsymbol{k}\cdot\boldsymbol{x}_2}(\hat{P}_2 - n\hat{P}_1) \, d^3x_1 \, d^3x_2.$$

It follows that, in order to achieve the desired accuracy in F and F_s, it will suffice to obtain $\hat{P}_1$ correct to $O(\phi)$, and $\hat{P}_2$ correct only to $O(1)$. Furthermore, it is clear that to achieve an accuracy of $O(\phi^2)$, the diffusivities $\boldsymbol{D}_{ij}$ must be calculated for sets of three interacting particles. No universally valid results (numerical or analytic) for the associated mobilities are available at present. It should be emphasized that although the result

$$\hat{P}_1 = \frac{1}{\mathcal{N}-1} \int_{\mathscr{V}} \hat{P}_2 \, d^3x_2$$

is *exact*, an $O(1)$ estimate for $\hat{P}_2$ used in this equation will not produce a sufficiently accurate value for $\hat{P}_1$. In addition, since $\hat{P}$ involves an average over all possible initial configurations, $\hat{P}_2$ gives the pair-distribution function to sufficient accuracy at all times t (see the discussion at the end of §2.3).

Now Felderhof (1978) has shown that correct to $O(1)$, $\hat{P}_2$ may be determined by solving a two-particle Smolochowski equation

$$\frac{\partial \hat{P}_2}{\partial t} = \nabla_i \cdot \boldsymbol{D}_{ij} \cdot (\nabla_j \hat{P}_2 + \hat{P}_2 \nabla_j V) \quad (\text{sum over } i, j = 2), \tag{3.9}$$

in which the isolated two-particle values are used for $\boldsymbol{D}_{ij}$ and V. In Felderhof's derivation, the assumptions are made that hydrodynamic interactions and potential forces are pairwise additive. We demonstrate in Appendix B that the assumptions are in fact unnecessary, and show further that an $O(\phi)$-accurate equation for $\hat{P}_1$ is

$$\frac{\partial \hat{P}_1}{\partial t} = D_0 \nabla_1^2 \hat{P}_1 + \nabla_1 \cdot \int_{\mathscr{V}} [(\boldsymbol{D}_{11} - D_0 \boldsymbol{I}) \cdot \nabla_1 \hat{P}_2 + \boldsymbol{D}_{12} \cdot \nabla_2 \hat{P}_2 + \hat{P}_2(\boldsymbol{D}_{11} \cdot \nabla_1 V + \boldsymbol{D}_{12} \cdot \nabla_2 V)] \, d^3x_2. \tag{3.10}$$

At the same level of approximation, we have as initial conditions

$$\hat{P}_1 = n \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_1}, \quad \hat{P}_2 = n^2 \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_2 - V}.$$

Now at present $\hat{P}_2$ depends on the six spatial variables $\boldsymbol{x}_1$, $\boldsymbol{x}_2$, but the problem may be further reduced by noting that $\hat{P}_1$ and $\hat{P}_2$ take the following forms:

$$\hat{P}_1(\boldsymbol{x}_1, t) = n \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_1} f_1(t),$$
$$\hat{P}_2(\boldsymbol{x}_1, \boldsymbol{x}_2, t) = n^2 \, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}_1 - \frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2(\boldsymbol{r}, t) \quad \text{with} \quad \boldsymbol{r} = \boldsymbol{x}_2 - \boldsymbol{x}_1.$$

It is then straightforward to show that

$$\frac{\partial f_2}{\partial t} = -\boldsymbol{k} \cdot \boldsymbol{D}_t \cdot \boldsymbol{k} f_2 + \nabla \cdot \boldsymbol{D}_r \cdot (\nabla f_2 + f_2 \nabla V), \tag{3.11}$$

$$\frac{df_1}{dt} = -k^2 D_0 f_1 + i\boldsymbol{k} \cdot \int [(\boldsymbol{D}_t - \tfrac{1}{2} D_0 \boldsymbol{I}) \cdot i\boldsymbol{k} f_2 + (\tfrac{1}{2}\boldsymbol{D}_r - D_0 \boldsymbol{I}) \cdot \nabla f_2 + f_2 \tfrac{1}{2}\boldsymbol{D}_r \cdot \nabla V] \, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} n \, d^3r, \tag{3.12}$$

where now $\nabla \equiv \partial/\partial \boldsymbol{r}$, $\boldsymbol{D}_t = \frac{1}{2}(\boldsymbol{D}_{11} + \boldsymbol{D}_{12})$ and $\boldsymbol{D}_r = 2(\boldsymbol{D}_{11} - \boldsymbol{D}_{12})$ and the integral may be extended to the whole of $\boldsymbol{r}$-space. $\boldsymbol{D}_t$ and $\boldsymbol{D}_r$ are the diffusivities for centre-of-mass translation and for relative motion of two particles respectively.

The initial conditions become

$$f_1 = 1, \quad f_2 = e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}-V} \quad \text{at} \quad t = 0.$$

The boundary condition as $r \to \infty$ is that $\hat{P}_2 \propto e^{i\boldsymbol{k}\cdot\boldsymbol{x}_1}$ so that $f_2 \sim e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}-D_0k^2t}$. The scattering functions become

$$F(k,t) = f_1(t) + \int (f_2 - e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}-k^2D_0t})\, e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} n\, d^3r,$$

$$F_s(k,t) = f_1(t).$$

A final manipulation which is useful for subsequent calculation is to differentiate the above expressions for F and F_s above with respect to time, use the results for df_1/dt and $\partial f_2/\partial t$ and integrate by parts to obtain

$$\frac{dF}{dt} = -k^2D_0F - \int [\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}\ \ 2\cos\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r} + (\nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k}) - \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V)\sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}] f_2 n\, d^3r, \quad (3.13)$$

$$\frac{dF_s}{dt} = -k^2D_0F_s - \int [\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k} + \nabla\cdot(\tfrac{1}{2}\boldsymbol{D}_r\cdot\boldsymbol{k}) - \tfrac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V]\, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2 n\, d^3r. \quad (3.14)$$

Associated with these are the initial values $F(\boldsymbol{k}, 0)$ and $F_s(\boldsymbol{k}, 0)$ obtained in §3.2 which at this level of approximation may be written

$$F(\boldsymbol{k},0) = 1 + n\int (e^{-V(r)}-1)\, e^{i\boldsymbol{k}\cdot\boldsymbol{r}} d^3r; \quad F_s(\boldsymbol{k},0) = 1. \quad (3.15)$$

So far we have considered a fully general potential interaction $V(r)$ between the particles. It is now convenient to specialise to the case where the particles are rigid spheres of radius a, possibly with other 'soft' interactive forces at separations greater than $2a$. We therefore suppose that V can be decomposed as

$$V = V^h + V^s$$

where $V^h \to \infty$ as $r \to 2a$, and V^s (and also $\boldsymbol{D}$) are defined only for $r > 2a$. Then f_2 varies rapidly in a boundary layer near $r = 2a$, and, as shown in Appendix C, (3.13) and (3.14) become

$$\frac{dF}{dt} = -D_0k^2F - \int_{r=2a} \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}}\sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r} f_2 n\, d^2r - \int_{r>2a} [\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}\ \ 2\cos\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r} + (\nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k}) - \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V^s)\sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}] f_2 n\, d^3r, \quad (3.16)$$

$$\frac{dF_s}{dt} = -D_0k^2F_s - \int_{r=2a} \tfrac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}}\, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2 n\, d^2r - \int_{r>2a} [\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k} + \nabla\cdot(\tfrac{1}{2}\boldsymbol{D}_r\cdot i\boldsymbol{k}) - \tfrac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V^s]\, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2 n\, d^3r. \quad (3.17)$$

The function $f_2(\boldsymbol{r}, t)$ is now governed by

$$\frac{\partial f_2}{\partial t} = -\boldsymbol{k}\cdot\boldsymbol{D}_t\cdot\boldsymbol{k} f_2 + \nabla\cdot\boldsymbol{D}_r\cdot(\nabla f_2 + f_2\nabla V^s) \quad \text{for} \quad r > 2a \quad (3.18)$$

and subject to the boundary condition that the flux of f_2 through $r = 2a$ is zero

$$\hat{\boldsymbol{r}}\cdot\boldsymbol{D}_r\cdot(\nabla f_2+f_2\nabla V^{\mathrm{s}}) = 0 \quad \text{at} \quad r = 2a, \tag{3.19}$$

the condition at infinity $f_2 \sim \mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}-D_0k^2t}$; and the initial condition

$$f_2 = \begin{cases} \mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}-V^{\mathrm{s}}} & \text{for} \quad r \geqslant 2a \quad \text{at} \quad t=0, \\ 0 & \quad r < 2a. \end{cases} \tag{3.20}$$

At this point we have constructed governing equations for a dilute suspension valid correct to $O(\phi)$ for arbitrary ka, and for all times t such that $t_{\mathrm{I}} \ll t \lesssim t_k$. In §§4 and 5 we provide analytic and numerical solutions. First, however, we discuss the simpler cases introduced in §2 where purely exponential behaviour of F and F_{s} is expected.

3.4. *Short-time behaviour* $t \ll t_a$

This is the same limit as that discussed in §3.2 for arbitrary concentrations and provides a check on the manipulations performed here so far. Using the initial condition (3.20) for f_2 and substituting in (3.16) we obtain (using symmetry)

$$\dot{F}(\boldsymbol{k},0) = -k^2D_0F(\boldsymbol{k},0)-\frac{1}{2\mathrm{i}}\int_{r=2a}\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}-V^{\mathrm{s}}}n\,\mathrm{d}^2r$$
$$-\int_{r>2a}[\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}\,(1+\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}})+\frac{1}{2\mathrm{i}}(\nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k})-\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V^{\mathrm{s}})\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}]\,\mathrm{e}^{-V^{\mathrm{s}}}n\,\mathrm{d}^3r.$$

Now, on noting that

$$\nabla\cdot\boldsymbol{D}_r = \nabla\cdot(\boldsymbol{D}_r-\boldsymbol{D}_r^{\infty}), \quad \nabla\cdot\boldsymbol{D}_{12} = \nabla\cdot(\boldsymbol{D}_{12}-\boldsymbol{D}_{12}^{\infty}),$$

where $\boldsymbol{D}_r^{\infty}$ is defined to be the far-field terms of order $1/r$ and $1/r^3$ in $\boldsymbol{D}_r$ (whose divergences exactly vanish), and $\boldsymbol{D}_{12}^{\infty}$ is similarly defined from $\boldsymbol{D}_{12}$, an integration by parts gives

$$\dot{F}(\boldsymbol{k},0) = -k^2D_0F(\boldsymbol{k},0) + \int_{r=2a}\mathrm{i}\boldsymbol{k}\cdot(\tfrac{1}{2}\boldsymbol{D}_r^{\infty}-D_0\boldsymbol{I})\cdot\hat{\boldsymbol{r}}\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}n\,\mathrm{d}^2r$$
$$-\int_{r>2a}[\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}\,\mathrm{e}^{-V^{\mathrm{s}}}+(\boldsymbol{k}\cdot\boldsymbol{D}_{12}\cdot\boldsymbol{k}\,\mathrm{e}^{-V^{\mathrm{s}}}-\boldsymbol{k}\cdot\boldsymbol{D}_{12}^{\infty}\cdot\boldsymbol{k})\,\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}]\,n\,\mathrm{d}^3r. \tag{3.21}$$

This expression is indeed the renormalised dilute form for the modulated sedimentation problem discussed in §3.2. It is noteworthy that the divergence difficulties due to long-range $O(1/r)$ interactions which bedevil suspension mechanical problems (Batchelor 1972) are avoided, since it is $\nabla\cdot\boldsymbol{D}_r$ rather than $\boldsymbol{D}_r$ itself which appears in (3.16). The above theory therefore provides a formal justification for 'subtracting off' the divergent terms as suggested by Batchelor (1972), and for the analogous methods of Ackerson (1976) and Felderhof (1978).

The corresponding result for $\dot{F}_{\mathrm{s}}(\boldsymbol{k},0)$ is

$$\dot{F}_{\mathrm{s}}(\boldsymbol{k},0) = -k^2D_0 - \int_{r>2a}\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}\,\mathrm{e}^{-V^{\mathrm{s}}}n\,\mathrm{d}^3r, \tag{3.22}$$

in agreement with §3.2, for which no divergence difficulties arise.

In the case where $V^{\mathrm{s}} = 0$, and for exact hydrodynamic interactions, the evaluation of the integrals in (3.21) has been performed for general ka by Russel & Glendinning (1981), and for the particular case $ka \ll 1$ (in which all the particles experience the same 'gravitational' force) by Batchelor (1976) to give the results (2.1), (2.2); and for the case $ka \ll 1$ and a general form of V^{s} by Batchelor (1983).

3.5. *Long-time behaviour* $ka \ll 1$, $t_a \ll t \lesssim t_k$

As noted in §2.3, the long-time behaviour $t \gg t_a$ is amenable to interpretation (and experiment) only if $t \lesssim t_k$, which requires $ka \ll 1$. Some analytic progress is possible in that case as follows.

In the limit $ka \ll 1$, (3.18) becomes

$$\frac{\partial f_2}{\partial t} = \nabla \cdot (\boldsymbol{D}_r \cdot (\nabla f_2 + f_2 \nabla V^s)) + O(k^2 a^2) \quad \text{for} \quad r > 2a,$$

with initial condition (3.20)

$$f_2 = e^{-V^s}(1 + \tfrac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r} + O(k^2a^2)) \quad \text{for} \quad r \text{ of order } a.$$

Furthermore, on a timescale for which $t \ll t_k$ (as may be established in detail by a two-timing analysis, Rallison & Leal 1981) f_2 achieves an equilibrium in which the initial value is unchanged as $r/a \to \infty$.

Writing $f_2 = e^{-V^s}(1 + \frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r} - ip(r))$, we find p is determined by the equations

$$\nabla \cdot (e^{-V^s}\boldsymbol{D}_r \cdot \nabla p) = \nabla \cdot (e^{-V^s}\boldsymbol{D}_r \cdot \tfrac{1}{2}\boldsymbol{k}), \tag{3.23}$$

$$p \to 0 \quad \text{as} \quad r/a \to \infty, \tag{3.24}$$

and

$$\hat{\boldsymbol{r}}\cdot\boldsymbol{D}_r \cdot \nabla p = \tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}} \quad \text{on} \quad r = 2a. \tag{3.25}$$

Furthermore on this timescale we may write

$$F_s = 1 - D^s_\infty k^2 t,$$

and it follows from (3.17) that

$$D^s_\infty = D_0 + \frac{1}{2}\frac{n}{k^2}\int_{r=2a} \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}}\,p\,\mathrm{d}^2r$$
$$+\frac{n}{k^2}\int_{r>2a} [\boldsymbol{k}\cdot(\boldsymbol{D}_{11} - D_0\boldsymbol{I})\cdot\boldsymbol{k} + \tfrac{1}{2}p\nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k}) - \tfrac{1}{2}p\boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V^s]\,e^{-V^s}\,\mathrm{d}^3r. \tag{3.26}$$

Now this calculation may be compared with that of Batchelor (1982) for the (long-time) sedimentation rate of tracer particles ($\lambda = 1, \gamma = 0$ in his notation) in the low-Péclet-number limit. The quantity $p(r)$ defined here proves to satisfy the same equations as his $p^{(1)}(r)$ (see in particular his equation (4.26)), and D^s_∞ is the sedimentation rate (when $\boldsymbol{k}$ is identified with gravity) at long times. Using exact hydrodynamics, $\boldsymbol{D}_r = 0$ when $r = 2a$ and so the first integral in (3.26) vanishes. The remaining integral contains three contributions which are identified by Batchelor as the additional sedimentation fluxes arising from: first, the modified mobility of a test particle due to its neighbours (his equation (6.10)); second, the additional Brownian flux due to non-uniformity of the pair-distribution function (his (6.12) but with a sign error corrected later – see corrigendum 1983); and third, the interparticle potential (his (6.11)). For $V^s = 0$, Batchelor & Wen (1982) have given the result (2.3) for D^s_∞, and have also displayed D^s_∞ for other simple choices of V^s.

3.6. *Discussion*

The $O(\phi)$ light-scattering problem has now been reduced to the solution of a three-dimensional diffusion equation (3.18) together with the evaluation of two integrals (3.16), (3.17). Further analytic progress is difficult since the fluid-dynamical diffusivities $\boldsymbol{D}_{ij}(\boldsymbol{r})$ are themselves determined by solving the Stokes equations for two spheres and are known only numerically for general values of $\boldsymbol{r}$. In §5, therefore, we generate a numerical solution of the full problem, but first, in order to develop greater physical understanding and to provide a check on the numerical accuracy, we treat a simpler case where the hydrodynamics have been artificially simplified.

4. The excluded-annulus model

We consider a model problem in which (i) hydrodynamic interactions between particles are neglected so that $\boldsymbol{D}_t = \frac{1}{2}D_0\boldsymbol{I}$ and $\boldsymbol{D}_r = 2D_0\boldsymbol{I}$ are both constant; and (ii) the particles interact only via a hard-sphere repulsion at $r = 2a$ so that $V^s = 0$.

The problem to be solved can then be written

$$\frac{1}{D_0}\frac{\partial f_2}{\partial t} = -\tfrac{1}{2}k^2 f_2 + 2\nabla^2 f_2 \quad (r \geqslant 2a), \tag{4.1}$$

with boundary conditions

$$\left.\begin{aligned} \frac{\partial f_2}{\partial r} &= 0 \quad \text{at} \quad r = 2a, \quad t > 0, \\ f_2 &\sim e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r} - D_0 k^2 t} \quad \text{as} \quad r \to \infty, \quad t > 0, \end{aligned}\right\} \tag{4.2}$$

and initial condition

$$f_2 = e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} \quad \text{at} \quad t = 0. \tag{4.3}$$

The scattering functions are given by

$$\dot{F} = -k^2 D_0 F - 2D_0 n \int_{r=2a} \boldsymbol{k}\cdot\hat{\boldsymbol{r}} \sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}\, f_2 \, d^2 r, \tag{4.4}$$

$$\dot{F}_s = -k^2 D_0 F_s - D_0 n \int_{r=2a} i\boldsymbol{k}\cdot\hat{\boldsymbol{r}}\, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2 \, d^2 r, \tag{4.5}$$

with initial conditions, from (3.15),

$$\left.\begin{aligned} F(\boldsymbol{k}, 0) &= 1 + \frac{8\pi n a}{k^2}\left(\cos 2ka - \frac{\sin 2ka}{2ka}\right) = 1 - \frac{12\phi}{ka} j_1(2ka), \\ F_s(\boldsymbol{k}, 0) &= 1, \end{aligned}\right\} \tag{4.6}$$

where j_n is a spherical Bessel function of the first kind. The result for the static structure function $F(\boldsymbol{k}, 0)$ is well known, and gives the asymptotic limits

$$F(\boldsymbol{k}, 0) \to \begin{cases} 1 - 8\phi & \text{as} \quad ka \to 0, \\ 1 & \text{as} \quad ka \to \infty. \end{cases}$$

In the first of these, pair correlations are important only in generating an excluded volume ($\frac{4}{3}\pi(2a)^3$ for pairs of spheres); in the second, the lengthscale of interest k^{-1} is so short that, as noted in §2.3, pair correlations are altogether negligible.

4.1. *Solutions of the equations*

We seek a solution to (4.1) by expanding f_2 as a far field together with a disturbance written as a sum of spherical harmonics, i.e. taking $\theta = 0$ parallel to $\boldsymbol{k}$,

$$f_2 = e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r} - D_0 k^2 t} + \sum_{n=0}^{\infty} f_{(n)}(r, t)\, P_n(\cos\theta),$$

with $f_{(n)} \to 0$ as $r \to \infty$. By orthogonality we obtain an evolution equation for each harmonic in the form

$$\frac{1}{D_0}\frac{\partial f_{(n)}}{\partial t} = -\tfrac{1}{2}k^2 f_{(n)} + 2\frac{\partial^2 f_{(n)}}{\partial r^2} + \frac{4}{r}\frac{\partial f_{(n)}}{\partial r}.$$

Now, noting the identity

$$e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} = \sum_{n=0}^{\infty} (2n+1)\, i^n j_n(\tfrac{1}{2}kr)\, P_n(\cos\theta),$$

the boundary condition (4.2) gives

$$\frac{\partial f_{(n)}}{\partial r} = -(2n+1)\, i^n \tfrac{1}{2}k j_n'(ka)\, e^{-D_0 k^2 t} \quad \text{at} \quad r = 2a.$$

On taking Laplace transforms which we denote by $\tilde{}$, and with p the variable conjugate to t, we may solve for $\tilde{f}_{(n)}$ to obtain

$$\tilde{f}_n(r,p) = -(2n+1)\, i^n \tfrac{1}{2}ka\, j_n'(ka)\frac{1}{p^2 + D_0 k}\frac{k_n(\lambda r/a)}{\lambda k_n'(2\lambda)},$$

in which

$$\lambda = a\left(\frac{p}{2D_0} + \tfrac{1}{4}k^2\right)^{\frac{1}{2}},$$

and k_n is a modified spherical Bessel function of the third kind. This expression for $\tilde{f}_2$ may now be substituted in (4.4), (4.5) to give, finally, for the Laplace transforms of F and F_s

$$\tilde{F} = \frac{1}{p + D_0 k^2}\left\{1 + \frac{12\phi}{ka} j_0'(2ka)\left[1 + \frac{D_0 k^2}{p + D_0 k^2}\right] - \frac{24\phi D_0 k^2}{p + D_0 k^2}\sum_{n,\,\text{even}=0}^{\infty} (2n+1)\,(j_n'(ka))^2 \frac{k_n(2\lambda)}{2\lambda k_n'(2\lambda)}\right\}, \quad (4.7)$$

$$\tilde{F}_s = \frac{1}{p + D_0 k^2}\left\{1 - \frac{12\phi D_0 k^2}{p + D_0 k^2}\sum_{n=0}^{\infty} (2n+1)\,(j_n'(ka))^2 \frac{k_n(2\lambda)}{2\lambda k_n'(2\lambda)}\right\}. \quad (4.8)$$

It is not possible to invert these Laplace transforms in general, but some special cases can be examined. The results have been derived independently by Ackerson & Fleishman (1982), Hanna *et al.* (1981), Jones & Burfield (1982) and Felderhof & Jones (1983), and thereby confirm the formal correctness of the manipulations of §3. The interpretation of the results which follows differs somewhat from theirs.

4.2. *Short-time behaviour* $t_I \ll t \ll t_a$

The limiting behaviour for $t \to 0$ can be obtained by examining the limit $p \to \infty$. As $p \to \infty$, so $\lambda \to \infty$ and

$$\frac{k_n(2\lambda)}{2\lambda k_n'(2\lambda)} \sim -\frac{1}{2\lambda} + \frac{1}{4\lambda^2} + \dots \quad \text{for all } n.$$

Then, using the identities

$$\sum_{n=0}^{\infty} (2n+1)\,(j_n'(ka))^2 = \tfrac{1}{3}, \qquad \sum_{n=0}^{\infty} (-)^n (2n+1)\,(j_n'(ka))^2 = -j_1'(2ka),$$

we obtain the short-time asymptotes

$$F = 1-\tau+\tfrac{1}{2}\tau^2+12\phi\frac{j_0'(2ka)}{ka}[1-\tfrac{1}{2}\tau^2]+\phi(\tfrac{2}{3}-2j_1'(2ka))\left[\frac{8}{(2\pi)^{\frac{1}{2}}}\frac{\tau^{\frac{3}{2}}}{ka}-\frac{3}{2}\frac{\tau^2}{(ka)^2}+\dots\right], \quad (4.9)$$

$$F_s = 1-\tau+\tfrac{1}{2}\tau^2+\phi\tfrac{4}{3}\left[\frac{4}{(2\pi)^{\frac{1}{2}}}\frac{\tau^{\frac{3}{2}}}{ka}-\frac{3}{2}\frac{\tau^2}{(ka)^2}+\dots\right], \quad (4.10)$$

in which we have set $\tau = D_0 k^2 t$. In particular this gives $\dot{F}(k,0) = \dot{F}_s(k,0) = -D_0 k^2$ in agreement with §3.4 when hydrodynamic interactions are neglected. What is more surprising is the appearance of the $\tau^{\frac{3}{2}}$ terms, which imply that $\ddot{F}(\boldsymbol{k},0)$ and $\ddot{F}_s(\boldsymbol{k},0)$ do not exist in this case. These non-analytic terms arise from a diffusive layer of thickness $(D_0 t)^{\frac{1}{2}}$ near the boundary $r = 2a$, in which the failure of the initial conditions (4.3) to satisfy the boundary condition (4.2) is rapidly corrected. Pusey & Tough (1982) have also shown that the second cumulant $\ddot{F}$ is infinite at short times, and in the $ka \ll 1$ limit Hanna *et al.* (1981) have demonstrated that $\ddot{F}_s \propto (D_0 t/a^2)^{-\frac{1}{2}}$ as $t \to 0$ by an alternative method.

4.3. *Very long times $t \gg t_k$*

The limit of very long times, $t \gg t_k$ is not physically important for the reasons given in §2.3, but we include it here both for completeness, and as a check on the numerical results in §5. The limiting behaviour as $t\to\infty$ is dominated by the singularity in $\tilde{F}$ and $\tilde{F}_s$ with the largest real part in the complex p-plane. This is a branch point (overlooked by Ackerson & Fleishman 1982 and by Felderhof & Jones 1983) at $\lambda = 0$, i.e. $p = -\frac{1}{2}D_0 k^2$. As $\lambda \to 0$ the expansion of $k_n(2\lambda)/2\lambda k_n'(2\lambda)$ has a first non-zero odd power in λ of order λ^{2n+1}. (The even powers are irrelevant as they do not involve a branch point singularity.) The dominant term in the infinite sums in (4.7), (4.8) is thus $n = 0$, and

$$\frac{k_0(2\lambda)}{2\lambda k_0'(2\lambda)} \sim -1+2\lambda-4\lambda^2+\dots \quad \text{as} \quad \lambda\to 0.$$

This gives the (very) long-time asymptotes

$$F = e^{-\tau}+\phi\frac{96}{(2\pi)^{\frac{1}{2}}}(j_0'(ka))^2\, ka\frac{e^{-\frac{1}{2}\tau}}{\tau^{\frac{3}{2}}}, \quad (4.11)$$

and

$$F_s = e^{-\tau}+\phi\frac{48}{(2\pi)^{\frac{1}{2}}}(j_0'(ka))^2\, ka\frac{e^{-\frac{1}{2}\tau}}{\tau^{\frac{3}{2}}}, \quad (4.12)$$

in which we have again used $\tau = D_0 k^2 t$.

The surprising appearance of the second term in these equations (which dominates the first as $t\to\infty$ however small ϕ is) arises as follows. The exponential factor comes from the *translational* diffusion of a pair of particles through distances of order k^{-1} which is *slower* than that for a single particle (cf. the example of §2.3). The $t^{-\frac{3}{2}}$ term comes from the *relative* diffusion of a pair which has the character of a diffusion 'source'. It should again be emphasized that neither of these results is a uniformly valid approximation to the solution of the full problem as $t\to\infty$ (i.e. the $O(\phi^2)$ errors cannot be ignored at very large times $t \gg t_k$).

4.4. *The long-wavelength limit $ka \ll 1$*

Analytic progress is possible for the case where $ka \ll 1$ for the 'long' time for which $t \gg t_a$ but $t \ll t_k$. In that case, $\lambda \ll 1$, so that $k_n(2\lambda)/2\lambda k_n'(2\lambda) \sim 1/n+1$ but p is large so that $(p+D_0 k^2)^{-1} \sim p^{-1}-D_0 k^2/p^2$. Expanding (4.7) and (4.8) accordingly, and noting that

$$j_0'(ka) = -\tfrac{1}{3}ka+\tfrac{1}{30}(ka)^3+\dots; \quad j_1'(ka) = \tfrac{1}{3}-\tfrac{1}{10}(ka)^2+\dots;$$

$$j_2'(ka) = \tfrac{2}{15}ka+\dots; \quad j_n'(ka) = O((ka)^{n-1}) \quad \text{as} \quad ka \to 0 \quad n \geqslant 1;$$

we have

$$F \sim 1-\tau+\tfrac{1}{2}\tau^2+\phi[-8(1-\tfrac{2}{5}(ka)^2)+\tfrac{152}{45}(ka)^2\tau+4(1-\tfrac{34}{45}(ka)^2)\,\tau^2+\dots], \tag{4.13}$$

$$F_s \sim 1-\tau+\tfrac{1}{2}\tau^2+\dots+\phi[2(1+\tfrac{56}{45}(ka)^2)\,\tau-2\tau^2+\dots], \tag{4.14}$$

and hence in particular that $-\dot{F}_s/k^2F_s \sim D_0(1-2\phi)$ on this timescale. As noted in §2.3 this value is the long-time self-diffusivity D^s_∞. This value has also been obtained by Hanna, Hess & Klein (1982) and by Ackerson & Fleishman (1982).

The same result can be obtained more succinctly by the method of §3.5. In the case of our excluded-annulus model, the governing equations (3.24)–(3.26) can be written

$$\nabla^2 p = 0 \quad (r \geqslant 2a)$$

$$\hat{\boldsymbol{r}}\cdot\boldsymbol{\nabla}p = \tfrac{1}{2}\boldsymbol{k}\cdot\hat{\boldsymbol{r}} \quad (r = 2a)$$

$$p \to 0 \quad \text{as} \quad r \to \infty$$

with solution

$$p = -\frac{4a^3\boldsymbol{k}\cdot\boldsymbol{r}}{r^3}.$$

Then, by (3.27),

$$D^s_\infty = D_0-\frac{1}{2}\frac{nD_0}{k^2}\int_{r=2a}\frac{\boldsymbol{k}\cdot\hat{\boldsymbol{r}}\,4a^3\boldsymbol{k}\cdot\hat{\boldsymbol{r}}}{r^2}\,\mathrm{d}^2r$$

$$= D_0(1-2\phi) \tag{4.15}$$

as above.

This result has been derived also by Lekkerkerker & Dhont (1984) using a 'steady' method. Hanna *et al.* (1982) and Jones & Burfield (1982) have gone further and shown that the velocity autocorrelation function for a tracer particle described in §2.2 is proportional to $(D_0 t/a^2)^{-\frac{5}{2}}$. It follows that the asymptotic approach to the diffusivity $D^s_\infty = D_0(1-2\phi)$ involves a decaying term proportional to $(D_0 t/a^2)^{-\frac{3}{2}}$.

The analogous result for the dominant term in F shows that $-\dot{F}/k^2F$ differs only by terms of order $O((ka)^2)$ from its initial value, as anticipated in §2.3, i.e. $D^c = D_0(1+8\phi)$ *either* from the initial value (4.6) in the limit $ka \to 0$, *or* from the equation above.

4.5. *The short-wavelength limit $ka \gg 1$*

Again analytic progress is possible here but now in the case when $t \gg t_k$ and $t \ll t_a$. The first restriction means that this limit is inapplicable to the interpretation of light-scattering experiments, but we include it in brief for completeness.

Extracting the asymptotic form from the harmonic expressions (4.7) and (4.8) is difficult because the contribution from all harmonics are comparable. It is easier to perform a boundary-layer analysis for the original problem for $\tilde{f}_2$. Near $r = 2a$ we find

$$\tilde{f}_2(r,\theta,p) \sim \frac{\mathrm{e}^{\mathrm{i}ka\cos\theta}}{p+D_0k^2}\left[\mathrm{e}^{\frac{1}{2}\mathrm{i}k(r-2a)\cos\theta}+\tfrac{1}{2}\mathrm{i}k\cos\theta\frac{\mathrm{e}^{-q(r-a)}}{q}\right],$$

where

$$q = \left[\frac{p}{2D_0}+\tfrac{1}{4}k^2(1+\sin^2\theta)\right]^{\frac{1}{2}}.$$

This then gives a long-time behaviour

$$F \sim F_s \sim e^{-\tau} + \frac{48}{(2\pi)^{\frac{1}{2}}} \frac{\phi}{ka} \frac{e^{-\frac{1}{2}\tau}}{\tau^{\frac{3}{2}}}. \tag{4.16}$$

4.6. *Numerical results*

These are discussed in detail as a special case of the problem with full hydrodynamic interactions in §5.

5. Suspension of hard spheres, with hydrodynamic interactions

We turn finally to a more physically plausible system of hard spheres with hydrodynamic interactions. In what follows we neglect interactive potentials and take $V^s = 0$. The problem to be solved is

$$\frac{\partial f_2}{\partial t} = -\boldsymbol{k}\cdot\boldsymbol{D}_t\cdot\boldsymbol{k} f_2 + \nabla\cdot(\boldsymbol{D}_r\cdot\nabla f_2) \quad (r > 2a), \tag{5.1}$$

with boundary condition

$$(r-2a)\frac{\partial f_2}{\partial r} \to 0 \quad \text{as} \quad r \to 2a, \tag{5.2}$$

and initial condition

$$f_2 = e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} \quad \text{at} \quad t = 0. \tag{5.3}$$

The scattering functions are given by

$$\dot{F} = -D_0 k^2 F - \int_{r>2a} [2\boldsymbol{k}\cdot(\boldsymbol{D}_{11} - D_0\boldsymbol{I})\cdot\boldsymbol{k}\cos\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r} + \nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k})\sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}] f_2 n \, d^3r, \tag{5.4}$$

$$\dot{F}_s = -D_0 k^2 F_s - \int_{r>2a} [\boldsymbol{k}\cdot(\boldsymbol{D}_{11} - D_0\boldsymbol{I})\cdot\boldsymbol{k} + \nabla\cdot(\tfrac{1}{2}\boldsymbol{D}_r\cdot i\boldsymbol{k})] \, e^{-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} f_2 \, n \, d^3r, \tag{5.5}$$

in which we have used the fact that $\boldsymbol{D}_r \propto (r-2a)$ when $r \to 2a$. Finally, the initial conditions for F and F_s are the same as those for the hard-shell model of §4, namely

$$F(\boldsymbol{k}, 0) = 1 + \frac{12\phi}{ka} j_0'(2ka); \quad F_s(\boldsymbol{k}, 0) = 1. \tag{5.6}$$

For general values of t these equations must be solved numerically, but for special values some analytic progress is possible as suggested by §4.

5.1. *Short times* $t_I \ll t \ll t_a$

In §3.4 we have produced results for $\dot{F}(\boldsymbol{k}, 0)$ and $\dot{F}_s(\boldsymbol{k}, 0)$ valid in the dilute limit for all values of ka, and general potentials V^s. In §4.2 we found that for an excluded-annulus model $\ddot{F}$ is unbounded at $t = 0$. The question arises as to whether a second cumulant (Pusey & Tough 1983) can be defined here, and if so to determine its value. As in §4, we first Laplace transform the governing equations (5.1)–(5.6) and then examine the limit $p \to \infty$. Equations (5.1) and (5.3) give

$$\tilde{f}_2 = \frac{1}{p} e^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}} + \frac{1}{p}\mathscr{L}\tilde{f}_2$$

in which

$$\mathscr{L}\tilde{f}_2 \equiv -\boldsymbol{k}\cdot\boldsymbol{D}_t\cdot\boldsymbol{k}\tilde{f}_2 + \nabla\cdot(\boldsymbol{D}_r\cdot\nabla\tilde{f}_2) \quad (r > 2a)$$

and by (5.2)

$$(r-2a)\frac{\partial \tilde{f}_2}{\partial r} \to 0 \quad \text{as} \quad r \to 2a. \tag{5.7}$$

Now suppose that $\tilde{f}_2$ is expanded in inverse powers of p. This suggests

$$\tilde{f}_2 \sim \frac{1}{p}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\frac{1}{p^2}\,\mathscr{L}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\frac{1}{p^3}\,\mathscr{L}^2\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\ldots,$$

provided that each term satisfies the boundary condition (5.7). But using lubrication methods Jeffrey & Onishi (1984) have shown that near $r = 2a$ (in fact *very* near: $2a < r < 2.01a$)

$$\|\boldsymbol{D}_r\| \sim A_1(r-2a)+A_2(r-2a)^2\log(r-2a)+\ldots$$

where A_1 and A_2 are non-zero constants. It follows that

$$\mathscr{L}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \sim (r-2a)\log(r-2a)\times(\text{regular function of } r) \quad \text{near } r = 2a,$$

which satisfies the boundary condition, but that

$$\mathscr{L}^2\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \sim \log(r-2a)\times(\text{regular function of } r) \quad \text{near } r = 2a,$$

which does not. Hence we try an alternative expansion for $p\rightarrow\infty$ in the form

$$\tilde{f}_2 = \frac{1}{p}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\frac{1}{p^2}\,\mathscr{L}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\frac{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}{p^3}\,g(r,p)\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+O\left(\frac{1}{p^3}\right),$$

where g is forced by the above irregular logarithmic term. Writing $x = r-2a$, we find that near $r = 2a$ g satisfies

$$g-\frac{1}{p}\frac{\partial}{\partial x}\left(x\frac{\partial g}{\partial x}\right) = \log x\times(\text{regular function of } x),$$

with

$$x\frac{\partial g}{\partial x}\rightarrow 0 \quad \text{as} \quad x\rightarrow 0.$$

Putting $\xi = px$, this gives for $p\rightarrow\infty$

$$\xi\frac{\partial^2 g}{\partial\xi^2}+\frac{\partial g}{\partial\xi}-g = \log\left(\frac{\xi}{p}\right).$$

Thus $g \propto \log p$ as $p\rightarrow\infty$, and so

$$\tilde{f}_2 = \frac{1}{p}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+\frac{1}{p^2}\,\mathscr{L}\,\mathrm{e}^{\frac{1}{2}\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}+O\left(\frac{\log p}{p^3}\right) \quad \text{as} \quad p\rightarrow\infty.$$

Now (5.5) and (5.6) give

$$\tilde{F}_\mathrm{s} = \frac{1}{p+D_0k^2}-\frac{n}{p+D_0k^2}\int_{r>2a}[\boldsymbol{k}\cdot(\boldsymbol{D}_{11}-D_0\boldsymbol{I})\cdot\boldsymbol{k}+\tfrac{1}{2}\nabla\cdot(\boldsymbol{D}_r\cdot\mathrm{i}\boldsymbol{k})]\tilde{f}_2\,\mathrm{d}^3r,$$

and similarly for F. Hence

$$\begin{pmatrix}F\\F_\mathrm{s}\end{pmatrix} = \begin{pmatrix}F(\boldsymbol{k},0)\\1\end{pmatrix}(1-\tau+\tfrac{1}{2}\tau^2)+\phi\begin{pmatrix}\alpha\\\alpha_\mathrm{s}\end{pmatrix}\tau(1-\tfrac{1}{2}\tau)+\tfrac{1}{2}\phi\begin{pmatrix}\beta\\\beta_\mathrm{s}\end{pmatrix}\tau^2+O(\tau^3\log\tau).$$

This demonstrates that the first and second cumulants at $t = 0$ are both finite, but that $\dddot{F}$ and $\dddot{F}_\mathrm{s}$ are unbounded at $t = 0$.

To determine the constants α, β it only remains to substitute the expression above for $\tilde{f}_2$ into the integrals for $\tilde{F}$ and $\tilde{F}_\mathrm{s}$ and to identify the coefficients of $1/p^2$ and $1/p^3$. If the diffusivities $\boldsymbol{D}_{ij}(\boldsymbol{r})$ are written in the (general) form

$$\boldsymbol{D}_{ij}(\boldsymbol{r}) = D_0\left[B_{ij}\left(\frac{r}{a}\right)\boldsymbol{I}+\left(A_{ij}\left(\frac{r}{a}\right)-B_{ij}\left(\frac{r}{a}\right)\right)\frac{\boldsymbol{rr}}{r^2}\right],$$

where A_{ij} and B_{ij} are dimensionless functions of r, and A_r and B_r are defined similarly with reference to $\boldsymbol{D}_r$, then we have

$$\nabla \cdot \boldsymbol{D}_r = 2D_0 C(r)\frac{\boldsymbol{r}}{r},$$

where

$$C(r) = \frac{1}{2}\left(A_r' + \frac{2}{r}(A_r - B_r)\right).$$

The angular integrals in the expressions above may then be performed analytically to give, after some algebra,

$$\alpha_s = -\int_2^\infty (A_{11} + 2B_{11} - 3)\, r^2 \,\mathrm{d}r,$$

$$\beta_s = \int_2^\infty \left[\tfrac{1}{5}(3A_{11}^2 + 4A_{11}B_{11} + 8B_{11}^2) - A_{11} - 2B_{11} + \frac{1}{(ka)^2}C^2\right] r^2 \,\mathrm{d}r,$$

and

$$\alpha = \alpha_s - 3\int_2^\infty \left\{(A_{11}-1)j_0 - \frac{2}{kar}(A_{11}-B_{11})j_1 + \frac{1}{ka}Cj_1\right\} r^2 \,\mathrm{d}r,$$

$$\beta = \beta_s + 3\int_2^\infty \left\{A_{11}^2 j_0 - \frac{4}{kar}(A_{11}-B_{11})A_{11}j_1 - \frac{8}{(kar)^2}(A_{11}-B_{11})^2\left(j_0 - \frac{3}{kar}j_1\right)\right.$$
$$- A_{11}j_0 + \frac{2}{kar}(A_{11}-B_{11})j_1 + \frac{1}{(ka)^2}C^2\left(j_0 - \frac{2}{kar}j_1\right) - \frac{1}{ka}Cj_1$$
$$\left. + \frac{2}{ka}\left[B_{11}Cj_1 + (A_{11}-B_{11})C\left(\frac{2}{kar}j_0 + \left(1 - \frac{6}{(kar)^2}\right)j_1\right)\right]\right\} r^2 \,\mathrm{d}r,$$

in which

$$j_0 = \frac{\sin kar}{kar}, \quad j_1 = \frac{\sin kar}{(kar)^2} - \frac{\cos kar}{kar}.$$

Finally, using (A 2) from Appendix A, the mean-square displacement of a particle may be identified as

$$\begin{aligned}\langle r^2 \rangle &= -\operatorname*{Limit}_{ka\to 0} \frac{6}{k^2}\log F_s \\ &= 6(1-\phi\alpha_s)D_0 t - 3\operatorname*{Limit}_{ka\to 0}(1 - \phi\alpha_s + \phi\beta_s + (\phi\alpha_s - 1)^2)D_0^2 k^2 t^2 \\ &= 6D_0 t - \phi\left[6\alpha_s D_0 t + \frac{3D_0^2 t^2}{a^2}\int_2^\infty r^2 C^2 \,\mathrm{d}r + O(t^3 \ln t)\right].\end{aligned}$$

The result for α_s (which is independent of ka) is given also by (3.21) and has been found by several authors (e.g. Batchelor 1976; Pusey & Tough 1983). A numerical evaluation with Jeffrey and Onishi's (1984) hydrodynamic data gives $\alpha_s = -1.81$. The small discrepancy from Batchelor's result (2.2) arises from numerical rounding and cutoff errors.

The expression for α, which does depend on ka, is equivalent to (3.20) and so is the same as the result of Russel & Glendinning (1981) for the modulated sedimentation problem discussed in §3.4. The variation of α with ka is sketched in figure 2.

The results for β and β_s and the quadratic term in $\langle r^2 \rangle$ are new for hard spheres with hydrodynamic interactions. Pusey & Tough (1983) have derived expressions for β_s and $\langle r^2 \rangle$ which are similar in structure to those above but which differ from them. Their approach starts from a Langevin rather than a Smolochowski equation, but

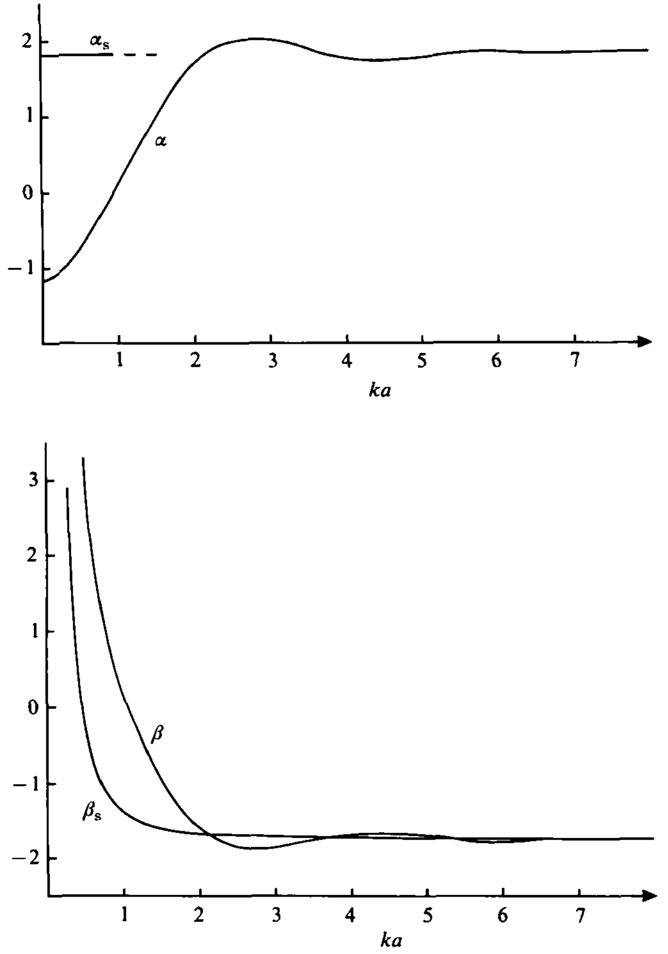

FIGURE 2. The first and second cumulants.

the discrepancy between the two results appears to arise from their treatment of the singular potential near $r = 2a$ for hard spheres. Specifically, in evaluating expressions of the form (their equation (2.31)),

$$\int e^{-V^h} \frac{d^2 V^h}{dr^2} (A_{11} - A_{12})^2 \, dr,$$

the second derivative has the character of a generalized function and although $A_{11} - A_{12}$ vanishes at $r = 2a$, a non-zero contribution results.

A remarkable feature of the expression above for $\langle r^2 \rangle$ is that whatever the form of the diffusivity $\boldsymbol{D}_{ij}(\boldsymbol{r})$, the first correction of the mean-square particle displacement from linearity in time is always negative, i.e. other particles always act to *hinder* the diffusion of a test particle. On evaluating the integrals we find

$$\langle r^2 \rangle = 6D_0(1-1.81\phi)\,t - 1.11\phi\left(\frac{D_0 t}{a}\right)^2 + O\left(\phi a\left(\frac{D_0 t}{a}\right)^3 \ln\left(\frac{D_0 t}{a^2}\right)\right).$$

The sign of the second term differs from that of Pusey & Tough (1984) but accords with their intuitive physical expectation.

The cumulant expansion derived in this section will only be valid for very short times, times so short that it is unlikely that they can be resolved in an experiment. While the relative diffusivity D_r vanishes at $r = 2a$, it does so only within the lubrication region $2a < r < 2.01a$: outside this region the diffusivity appears to tend to a non-zero constant as r approaches $2a$. Hence while two particles diffuse over the separation $0.01a$, we can expect to see the cumulant expansion. But at later times, $t > 10^{-4}\, a^2/D_0$, we would expect to see the $t^{\frac{3}{2}}$ behaviour of the excluded-annulus model which had $D_r \neq 0$ at $r = 2a$.

5.2. *The long-wavelength limit* $ka \ll 1$

As shown in §3.4, D^{s}_{∞} may be evaluated from the long-wavelength result by steady-state methods. Batchelor (1983), has shown that

$$D^{\mathrm{s}}_{\infty} = D_0(1-2.10\phi),$$

and we, using more accurate hydrodynamic data, obtain -2.06.

The other wavenumber-independent property which emerges from the $ka \ll 1$ limit is the full time-evolution of $\langle r^2 \rangle$ as noted in Appendix A. Equation (A 2) relates $\langle r^2 \rangle$ to F_{s}, and thus we can write

$$\langle r^2 \rangle = 6D_0 t\left[1-\phi f\left(\frac{D_0 t}{a^2}\right)\right],$$

$$f(\xi) \sim \begin{cases} 1.81+0.18\xi & \text{as} \quad \xi \rightarrow 0, \\ 2.06 & \text{as} \quad \xi \rightarrow \infty. \end{cases}$$

Anticipating slightly the discussion of the next section we can then determine f from the numerical solution. A graph of f together with these asymptotes is plotted in figure 3. It is notable that the timescale of variation of f is indeed t_a as predicted in §2.2 rather than the (longer) time t_{ϕ}.

5.3. *The short wavelength limit* $ka \gg 1$

In this limit, the Fourier wave is decaying in a medium whose diffusivity varies on a lengthscale large compared with the wavelength. Thus to leading order

$$f_2 \sim \mathrm{e}^{\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}-\boldsymbol{k}\cdot\boldsymbol{D}_{11}(\boldsymbol{r})\cdot\boldsymbol{k}t}. \tag{5.8}$$

The assumption that the spatial variation in the diffusivity is smaller than that in the phase factor yields a restriction $\tau = D_0 k^2 t \ll ka$. Note that, unlike the case with no hydrodynamics, there is at leading order no effect of a boundary layer at $r = 2a$, because $D_r \rightarrow 0$ as $r \rightarrow 2a$.

5.4. *Numerical calculations*

The equations for f_2, F and F_{s} including the full hydrodynamic interactions and a hard-sphere repulsion at touching $r = 2a$ have been solved numerically. The diffusion equation for f_2 was solved having first subtracted off everywhere the far field $\exp(-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r}-\boldsymbol{k}^2 D_0 t)$, the remaining disturbance field being limited to $r \lesssim (4D_0 t)^{\frac{1}{2}}$. Forward time-stepping and central space-differencing was employed on the interior of an equispaced (r, θ)-grid. Attention was restricted to $0 \leqslant \theta \leqslant \frac{1}{2}\pi$ using the symmetry of f_2 about $\theta = \frac{1}{2}\pi$ (real part even, imaginary part odd). The condition that the disturbance decayed at large r was applied in the crude form

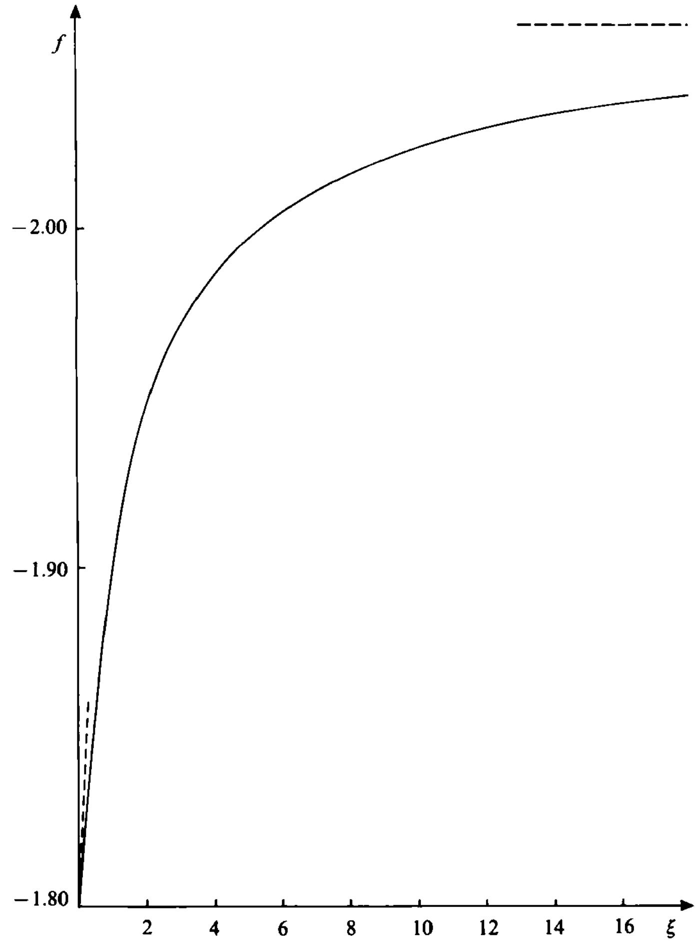

FIGURE 3. The time-dependent factor $f(D_0 t/a^2)$ in the mean-square displacement of a random walk.

$f_2 \equiv \exp(-\frac{1}{2}i\boldsymbol{k}\cdot\boldsymbol{r} - k^2 D_0 t)$ at $r = r_\infty$. The boundary condition was applied to second-order accuracy using values of the diffusivity (which varies rapidly near to touching) extrapolated from values at the interior grid points. The diffusivities were evaluated from expressions accurate to $O(r^{-15})$ supplied by Dr D. J. Jeffrey, which gave the diffusivities everywhere accurate to within 1 %. The volume and area integrals for $\dot{F}$ and $\dot{F}_S$ were performed to second-order spatial accuracy. It was found necessary to apply a correction to the volume integral of $kD_0 c \frac{45}{4}(a/r_\infty)\, e^{-k^2 D_0 t}$ for the far-field part of f_2 beyond r_∞. A numerical accuracy within 1 % could normally be obtained with numerical parameters $\delta r = \frac{1}{3}a$, $\delta\theta = \pi/18$, $k^2 D_0 \delta t = 10^{-2}$ and $r_\infty = 12a$; with a finer spatial resolution being necessary when $ka > 3$, and with greater values of r_∞ being necessary when $a^2 D_0 t > 60$.

The program was tested against some simpler but cruder schemes, for internal consistency in the behaviour of the rounding errors, for the initial values and initial slopes which could be calculated analytically, and against the long-time asymptote found in the previous section for the excluded-annulus model (diffusivities all set to D_0).

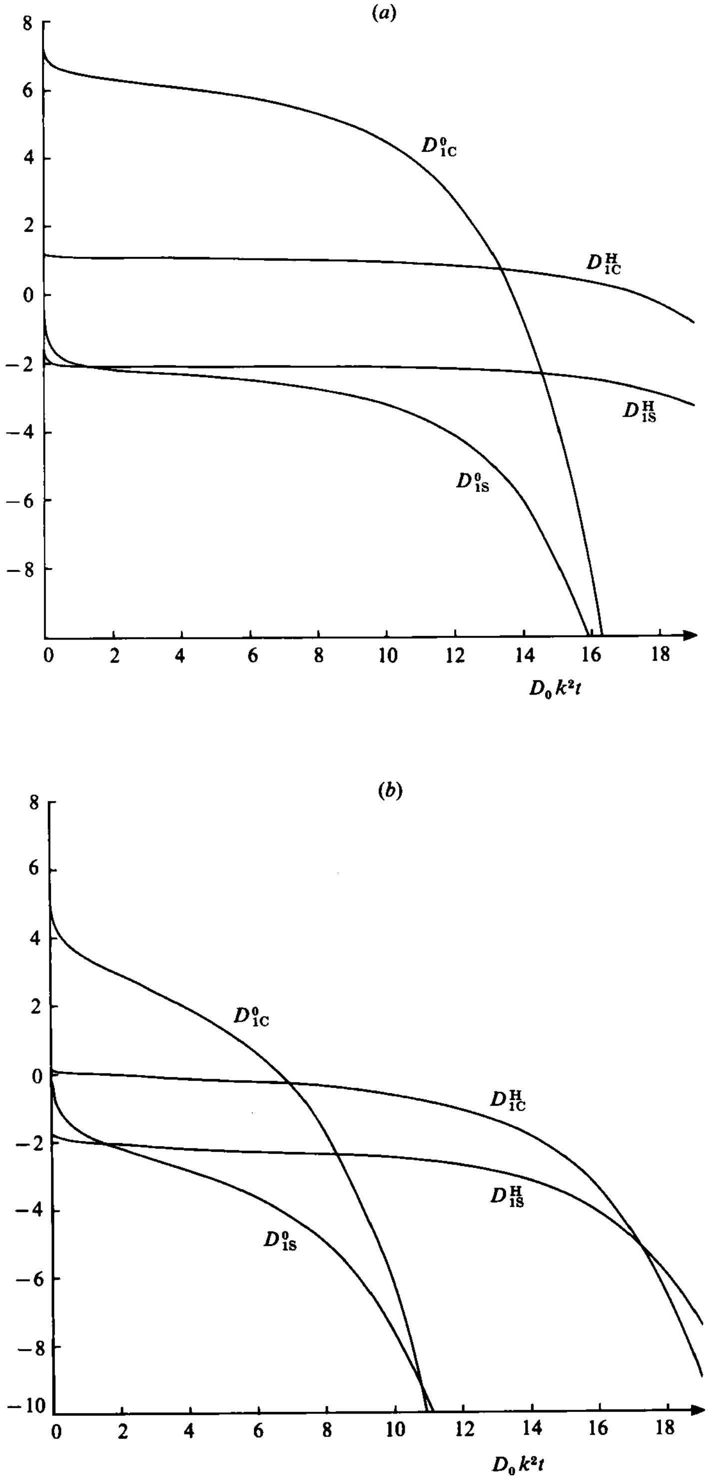

FIGURE 4 (*a*, *b*). For caption see next page.

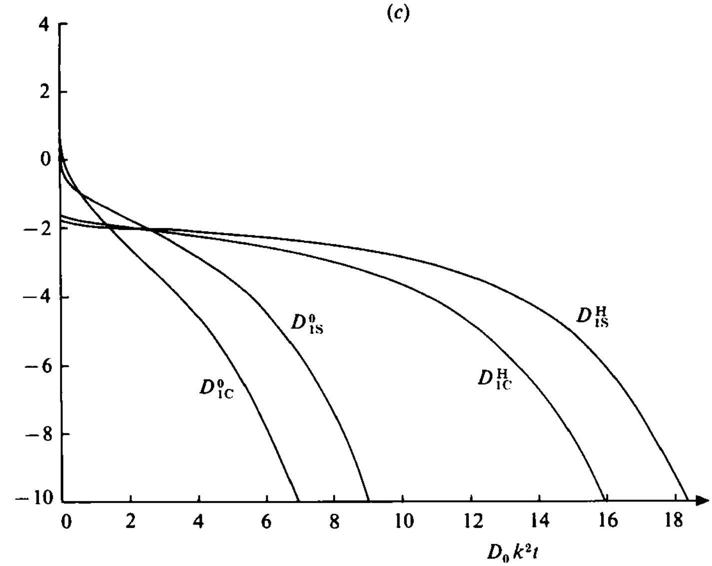

FIGURE 4. Numerical results for the $O(\phi)$ term in the time-dependent light-scattering diffusivity at (*a*) $ka = \frac{1}{2}$, (*b*) 1 and (*c*) 2. The superscripts H and 0 denote the cases with and without hydrodynamic interactions. The subscripts C and S denote the full and the self-light-scattering functions respectively.

The numerical results are presented in figures 4–9 in the form of the $O(\phi)$ term for the time-dependent diffusivity, defined as

$$D(k, t; \phi) = -\frac{\dot{F}(k, t; \phi)}{D_0 k^2 F}$$

$$= 1 + \phi D_1(k, t) + O(\phi^2).$$

Superscripts H and 0 are used to denote results with and without hydrodynamic interactions respectively in the excluded-annulus model. The second subscripts C and S are used to denote the full and the self-scattering functions.

Figure 4 gives the results for $ka = \frac{1}{2}$, 1 and 2. After a short initial adjustment, the diffusivity is fairly level before finally growing exponentially to $-\infty$. When hydrodynamic interactions are included the initial adjustment is smaller and the level period is more nearly constant. Remembering that experimental observations are restricted to $\tau = D_0 k^2 t < 7$ (because $e^{-7} < 10^{-3}$), we speculate that this level period accounts for the ease in measuring a 'long-time' diffusivity in an experiment. We must emphasize, however, that the light-scattering experiment does not describe a simple diffusion process, so that there is no true 'long-time' diffusivity (at least within our $O(\phi)$ theory). The reason that there is no asymptotic diffusion process at long-times is that the microstructure described by f_2 does not tend to a quasi-equilibrium but instead, on the timescale of interest, t_k is always evolving. Finally, we note in figure 4 that the difference between the full and the self-scattering diffusivities decreases as the wavelength becomes shorter.

The short-time behaviour for the excluded-annulus model, (4.9) and (4.10), gives a $\tau^{\frac{1}{2}}$ term in the light-scattering diffusivity. This behaviour is brought out in figure 5 by plotting the results of the numerical calculation (at $ka = 1$) against $\tau^{\frac{1}{2}}$. It is seen that the asymptotic result up to $\tau^{\frac{1}{2}}$ provides a 10%-accurate estimate only in

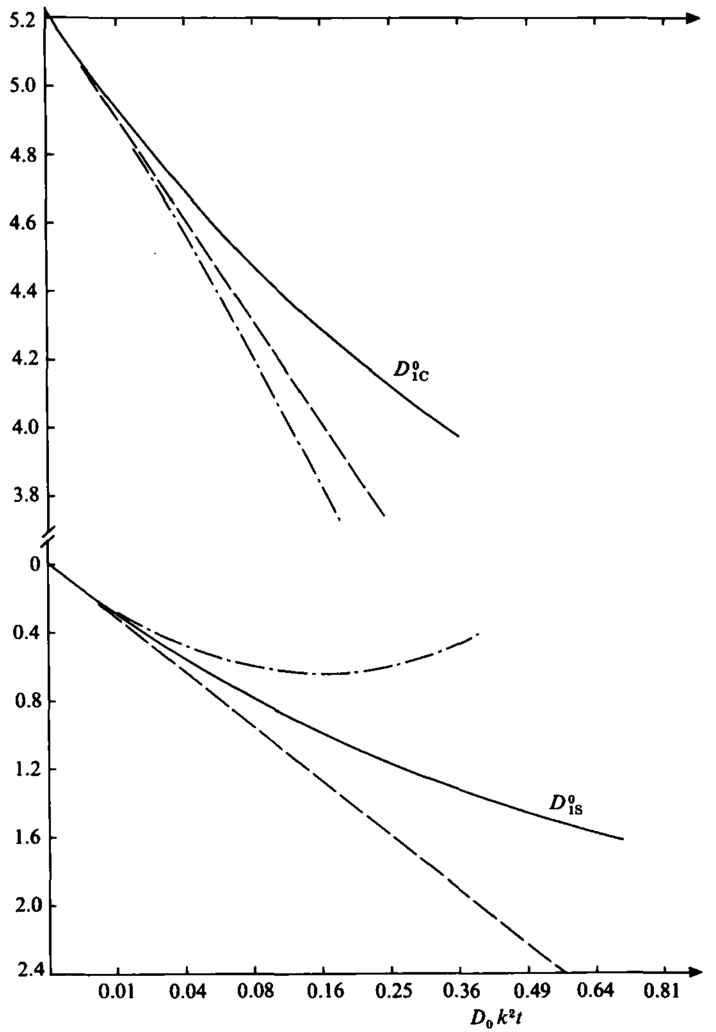

FIGURE 5. The short-time behaviour for the $O(\phi)$ term in the time-dependent light-scattering diffusivity: ——, numerical results for the excluded-annulus model at $ka = 1$; ---, the asymptotic results (4.9) and (4.10) up to the $\tau^{\frac{1}{2}}$ terms; –·–·, include the next τ-terms.

$\tau = D_0 k^2 t < 0.2$. Adding the next τ-term does not improve the estimate. For the case of hydrodynamic interactions, the short-time behaviour lasts for too short a time to be of interest.

The long-time behaviour for the excluded-annulus model, (4.11) and (4.12), predicts an $\exp \frac{1}{2}\tau/\tau^{\frac{3}{2}}$ form of the light-scattering diffusivity. This behaviour is brought out in figure 6 by plotting the results of the numerical calculation (at $ka = 1$) on log–linear paper. It is seen that the asymptotic result for the full scattering function provides a 10%-accurate estimate when $\tau = D_0 k^2 t > 13$, while the similar result for the self-scattering is not within 10% until $\tau = D_0 k^2 t > 23$. For the case of hydrodynamic interactions, the long-time behaviour also seems from the numerical calculations to be exponential. We have been unable, however, to construct an asymptotic theory owing to difficulties associated with the slow r^{-1} decay in D_r.

At long wavelengths it is possible to diffuse over many particle radii, and for the

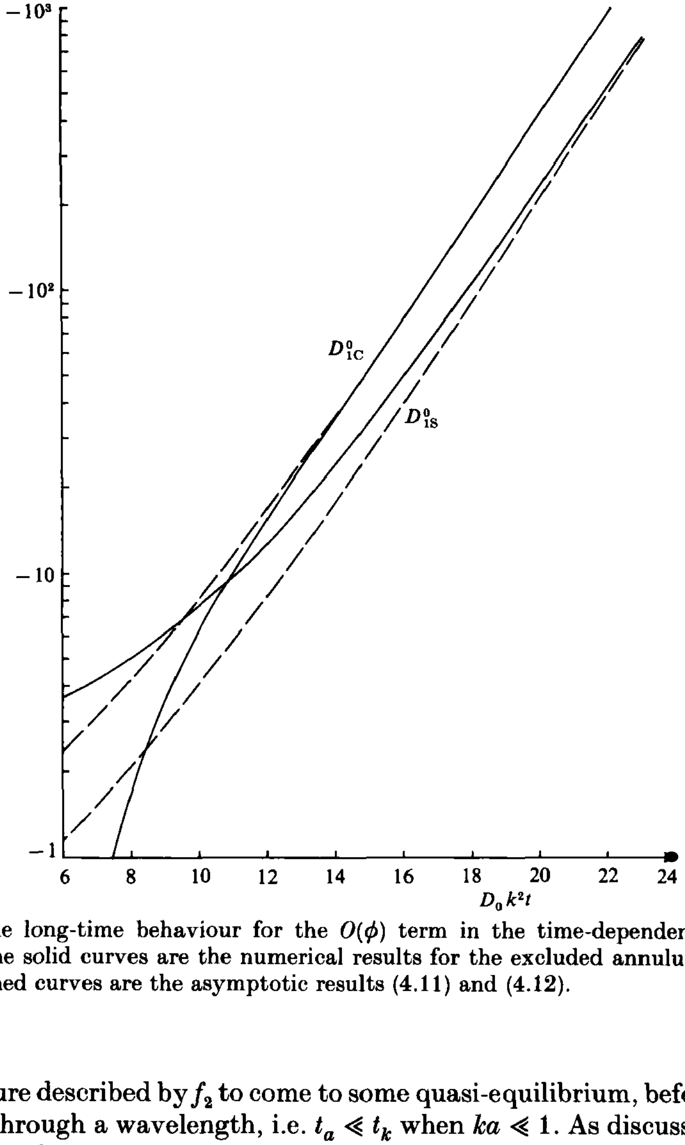

FIGURE 6. The long-time behaviour for the $O(\phi)$ term in the time-dependent light-scattering diffusivity. The solid curves are the numerical results for the excluded annulus model at $ka = 1$ while the dashed curves are the asymptotic results (4.11) and (4.12).

microstructure described by f_2 to come to some quasi-equilibrium, before the particles can diffuse through a wavelength, i.e. $t_a \ll t_k$ when $ka \ll 1$. As discussed in §§3.6 and 5.2, for $t \ll t_k$ the full light-scattering function F is described by a diffusivity D_{1C} which hardly changes from its initial value. This is confirmed by the numerical calculations, e.g. D^H_{1C} changes by less than 0.2% from $\tau = 0$ to $\tau = 10$ when $ka = 0.1$. The self-diffusivity D^H_{1S} on the other hand changes on the timescale t_a from its initial value to a plateau value which it holds for $8t_a \leqslant t \ll t_k$. Figure 7 shows this behaviour for the case with hydrodynamic interactions for $ka = 1, \frac{1}{2}, \frac{1}{4}$ and $\frac{1}{10}$. Referring back to figure 4(*a*), we see that the plateau effectively extends to $t = 16t_k$.

While the plateau value of D_{1S} for hydrodynamic interactions is -2.06 and without hydrodynamics is -2.00, there are circumstances in which the value of the plateau can lie outside this narrow band. We have made some calculations for particles with a hard potential which only acts to exclude particles becoming closer than $r = 2a$, but we have allowed the hydrodynamic radius of the particles to be smaller at R_H ($\leqslant a$). Note that the results are normalized on the excluded-volume radius. The results for the plateau value of D^H_{1S} on the timescale $t_a \ll t \ll t_k$ are given in figure 8.

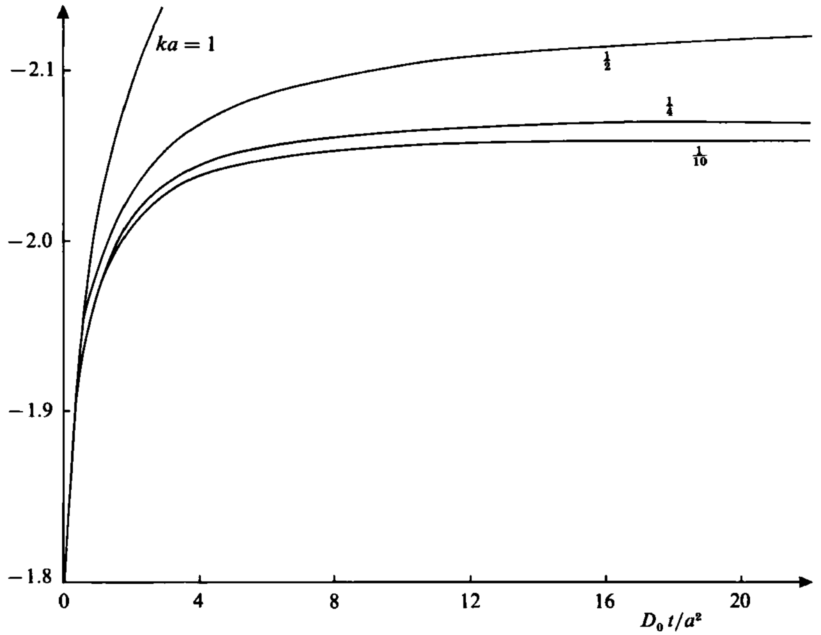

FIGURE 7. The long-wavelength behaviour of $D^{\rm H}_{\rm 1S}$ showing a plateau on timescale $t_a \ll t \ll t_k$.

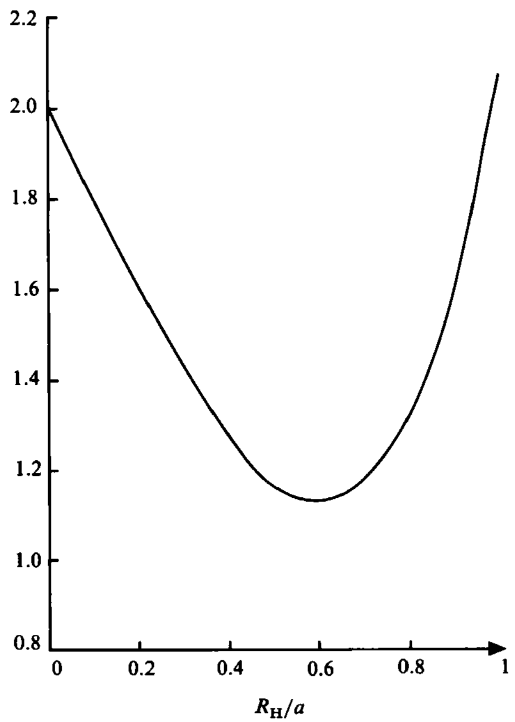

FIGURE 8. The dependence of the plateau value of $D^{\rm H}_{\rm 1S}$ on the ratio of the hydrodynamic radius $R_{\rm H}$ and the excluded-volume radius a of the particle.

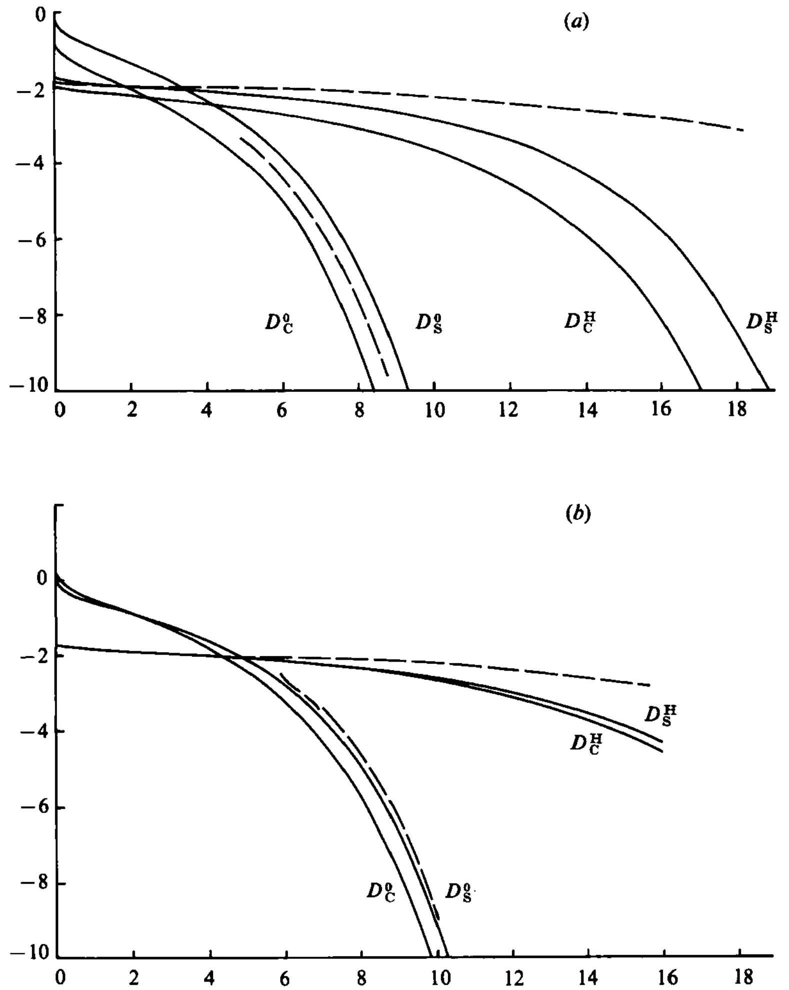

FIGURE 9. The short-wavelength behaviour at (a) $ka = 3$ and (b) 5. The broken curves are the asymptotic results corresponding to (4.16) and (5.8).

There is a non-monotonic variation in R_H/a, with a minimum value of 1.12 at $R_H = 0.58a$.

The short-wavelength behaviour is represented in figure 9 by the results for $ka = 3$ and 5. The results show that the values of the full and the self-diffusivities approach one another while $\tau \ll (ka)^2$ (i.e. $t \ll t_a$) as $ka \to \infty$. Also plotted in the figure are the asymptotic results corresponding to (4.16) and (5.8). These asymptotic results are seen to apply when $\tau \leqslant 2ka$.

6. Discussion

We draw together in this section the principal conclusions of the paper.

First, we note in regard to the suspension itself, that at non-zero particle concentration the motion of an individual particle in the suspension is not purely diffusive because of its interactions with neighbours except for very long and very short times. This result is now well known, but more surprisingly we assert that the time at which the asymptotic diffusivity becomes established is *independent* of the concentration (in the dilute limit) and is simply that taken for a particle to diffuse across its own length (i.e. it does not have to cross the 'cage' to its nearest neighbour).

Second, in regard to the scattering we observe that no exact theory (including this one) for a dilute suspension applies when $D_0 k^2 t \gg 1$. This does not preclude the possibility that such a theory could be constructed, but indicates at such long times multiple interactions are bound to be as significant as pair interactions.

Third, we have demonstrated that the analysis of experimental data by short-time cumulants is difficult, when the interactions between particles is via hard rather than soft interparticle potentials. The first cumulant is always defined, but second and higher cumulants may be infinite for hard systems.

Fourth, for general times we have shown that in general both F and F_s are non-exponential functions of time.

The authors would like to thank Dr P. N. Pusey for his helpful comments.

Appendix A. The relation between down-gradient tracer diffusion and self-diffusion

The purpose of this Appendix is to establish the formal identity of tracer diffusion and of self-diffusion as defined in §2.

Analogous results have been known in the literature of simple liquids for some time (Rahman, Singwi & Sjölander 1962; Boon & Yip 1980). In the context of Brownian hydrodynamics, Hess & Klein (1983) quote some of the results below (in particular a version of (A 2)) and establish them by means of a propagator formalism. Here we prefer to use more simple-minded probabilistic ideas to generate the less-sophisticated results we need in the body of the paper.

When the processes are *purely* diffusive, so that the movement of a test particle is given as a sum of random displacements whose statistics are stationary in time, then the probability density for particle position is Gaussian. This is indeed the case for dilute systems, and for both the long- and short-time asymptotes for concentrated systems (see §2.2). In such circumstances it is well known that the constant of proportionality for the tracer flux can be identified with the self-diffusivity. But for concentrated systems, the spatial probability density is *not* Gaussian for intermediate times when a test particle is interacting with its neighbours, and it is no longer obvious how the 'self' and 'tracer' statistics are related.

Consider first a monodisperse suspension (of arbitrary concentration) and suppose that the probability distribution at time t for the ensemble-averaged displacement $\boldsymbol{r}$ of a test particle which starts at the origin at $t = 0$ is $p(\boldsymbol{r}, t)$. Depending on the concentration of the particles and the interactions between them, p may not be Gaussian or even isotropic. Let p be normalized so that

$$\int p(\boldsymbol{r}, t)\, \mathrm{d}^3 r = 1.$$

The mean-square displacement of the particle in the x-direction at time t is then

$$\langle x^2 \rangle = \int x^2 p(\boldsymbol{r}, t)\, \mathrm{d}^3 r.$$

Alternatively, consider the down-gradient tracer flux of particles (for the same particle species) discussed in §2.2 for which we anticipate that

$$\boldsymbol{F}^{\mathrm{tr}} = -\boldsymbol{D}^{\mathrm{tr}}(\phi, t)\cdot\nabla\phi^{\mathrm{tr}}.$$

We seek to show that

$$D_{11}^{\mathrm{tr}} = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle.$$

Suppose that, without loss of generality, $\nabla\phi^{\mathrm{tr}}$ is in the x-direction and that the gradient is *small* in the sense $|a\nabla\phi^{\mathrm{tr}}| \ll \phi^{\mathrm{tr}}$. Then define

$P(X, t) =$ Probability [particle initially at the origin lies in the region $x > X$ at time t].

$$= \iint_{-\infty}^{\infty}\int_X^{\infty} p(\boldsymbol{r}, t)\,\mathrm{d}^3r.$$

Now the number of particles which lie in the region $x > 0$ at time t, $N(t)$, can be written

$$N(t) = \int_{-\infty}^{\infty}\mathrm{d}x\ \text{(Number density of particles starting at } x) \times \text{Prob. [particle starting at } x \text{ is in } x > 0 \text{ at time } t]$$

$$= \frac{\mathrm{d}\phi^{\mathrm{tr}}}{\mathrm{d}x}\int_{-\infty}^{\infty} xP(-x, t)\,\mathrm{d}x,$$

because the constant concentration ϕ^{tr} generates no flux, and $\nabla\phi^{\mathrm{tr}}$ is assumed sufficiently small that second and higher derivatives are negligible. Hence the flux across unit area of the plane $x = 0$ is

$$F_1^{\mathrm{tr}} = \frac{\mathrm{d}N}{\mathrm{d}t} = \frac{\mathrm{d}\phi^{\mathrm{tr}}}{\mathrm{d}x}\int_{-\infty}^{\infty} x\frac{\partial}{\partial t}P(-x, t)\,\mathrm{d}x,$$

which proves the linearity of $\boldsymbol{F}^{\mathrm{tr}}$ in $\nabla\phi^{\mathrm{tr}}$ anticipated above. Finally,

$$D_{11}^{\mathrm{tr}}(\phi, t) = \frac{\partial}{\partial t}\int_{-\infty}^{\infty} xP(-x, t)\,\mathrm{d}x$$

$$= -\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\tfrac{1}{2}x^2\frac{\mathrm{d}P}{\mathrm{d}x}\,\mathrm{d}x = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle$$

as required.

Further, integrating this relationship for the isotropic case, we have

$$\langle r^2\rangle = 6\int_0^t D^{\mathrm{tr}}\,\mathrm{d}t. \qquad \text{(A 1)}$$

This formula can be used to infer $\langle r^2\rangle$ from tracer light-scattering data as follows. If $ka \ll 1$, then the gradient of the tracer species is indeed small since $a\nabla\phi^{\mathrm{tr}}/\phi^{\mathrm{tr}} = O(ka)$. In consequence the analysis above is valid and

$$\frac{\partial\phi^{\mathrm{tr}}}{\partial t} = -\nabla\cdot\boldsymbol{F}^{\mathrm{tr}} = D^{\mathrm{tr}}\nabla^2\phi^{\mathrm{tr}}.$$

Now for the tracer light-scattering problem (2.4) shows that F_{s} may be identified as the Fourier transform of ϕ^{tr} and so

$$\frac{\partial F_{\mathrm{s}}}{\partial t} = -D^{\mathrm{tr}}k^2F_{\mathrm{s}}$$

and hence

$$\langle r^2 \rangle = -\frac{6}{k^2} \log F_s \tag{A 2}$$

in the limit $ka \to 0$.

Appendix B. The approximation of diluteness for the Smolochowski equation

We suppose that the concentration of particles $\phi \ll 1$, and seek to find a simplified approximate form of the Smolochowski equation valid as $\phi \to 0$ and appropriate for small sets of interacting particles.

We start from the full equation (3.3) for $\mathcal{N}$ particles

$$\frac{\partial P}{\partial t} = \nabla_i \cdot \boldsymbol{D}_{ij} \cdot (\nabla_j P + P \nabla_j V)$$

and define diffusivities $\boldsymbol{D}_{ij}^{(q)}$ and potentials $V^{(q)}$ for sets of just q interacting (and otherwise isolated) particles as

$$V^{(q)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_q) = \underset{\boldsymbol{x}_{q+1}, \ldots, \boldsymbol{x}_{\mathcal{N}} \to \infty}{\text{Limit}} \; V,$$

$$\boldsymbol{D}_{ij}^{(q)}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_q) = \underset{\boldsymbol{x}_{q+1}, \ldots, \boldsymbol{x}_{\mathcal{N}} \to \infty}{\text{Limit}} \; \boldsymbol{D}_{ij}.$$

Note that the superscript (q) is needed only in the appendix; $q = 2$ is to be understood throughout the body of the paper. The probability density P_q for sets of q particles is given by

$$P_q(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_q; t) = \frac{\mathcal{N}!}{(\mathcal{N}-q)!} \int_{\mathscr{V}^{\mathcal{N}-q}} P(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_{\mathcal{N}}; t) \, \mathrm{d}^3x_{q+1} \ldots \mathrm{d}^3x_{\mathcal{N}}.$$

On integrating the $\mathcal{N}$-particle equation we have therefore

$$\frac{\partial P_q}{\partial t} = \frac{\mathcal{N}!}{(\mathcal{N}-q)!} \nabla_i \cdot \int_{\mathscr{V}^{\mathcal{N}-q}} \boldsymbol{D}_{ij} \cdot (\nabla_j P + P \nabla_j V) \, \mathrm{d}^3x_{q+1} \ldots \mathrm{d}^3x_{\mathcal{N}},$$

in which j runs from 1 to $\mathcal{N}$. Since the flux of P through the walls of $\mathscr{V}^{\mathcal{N}}$ is zero, the summation on i runs only from 1 to q. The above equation may be rewritten in a form suitable for approximation as

$$\begin{aligned}
\frac{\partial P_q}{\partial t} = \mathscr{L}^{(q)} P_q &+ \frac{\mathcal{N}!}{(\mathcal{N}-q)!} \nabla_i \cdot \int (\boldsymbol{D}_{ij} - \boldsymbol{D}_{ij}^{(q)}) \cdot (P \nabla_j V + \nabla_j P) \, \mathrm{d}^3x_{q+1} \ldots \mathrm{d}^3x_{\mathcal{N}} \\
&+ \frac{\mathcal{N}!}{(\mathcal{N}-q)!} \nabla_i \cdot \int \boldsymbol{D}_{ij}^{(q)} \cdot (P \nabla_j V - P \nabla_j V^{(q)}) \, \mathrm{d}^3x_{q+1} \ldots \mathrm{d}^3x_{\mathcal{N}} \\
&+ \frac{\mathcal{N}!}{(\mathcal{N}-q)!} \nabla_i \cdot \int \boldsymbol{D}_{ik} \cdot (P \nabla_k V + \nabla_k P) \, \mathrm{d}^3x_{q+1} \ldots \mathrm{d}^3x_{\mathcal{N}},
\end{aligned}$$

in which

$$\mathscr{L}^{(q)} P_q \equiv \nabla_i \cdot \boldsymbol{D}_{ij}^{(q)} \cdot (P_q \nabla_j V^{(q)} + \nabla_j P_q) \tag{B 1}$$

and in which both i and j now run from 1 to q and k runs from $q+1$ to $\mathcal{N}$.

Now, $\boldsymbol{D}_{ij} - \boldsymbol{D}_{ij}^{(q)}$ and $V - V^{(q)}$ are non-zero only when one of $\boldsymbol{x}_{q+1}, \ldots, \boldsymbol{x}_{\mathcal{N}}$ lies within a distance of $O(a)$ of one of $\boldsymbol{x}_1, \ldots, \boldsymbol{x}_q$. It follows that the second and third terms on the right-hand side of (B 1) are both $O(\phi)$. The final term is the flux of particle i due to gradients of particles $k = q+1, \ldots, \mathcal{N}$ (which would vanish in the absence of hydrodynamic interactions). Hence it too is at most $O(\phi)$, as $\phi \to 0$. Thus, correct to $O(1)$, P_q satisfies the q-particle Smolochowski equation

$$\frac{\partial P_q}{\partial t} = \mathscr{L}^{(q)} P_q. \tag{B 2}$$

The $O(\phi)$ correction for P_1

In the body of the paper we require P_1 correct to $O(\phi)$ and hence a more accurate approximation than (B 2) is needed. Taking $q = 1$, and noting that $V^{(1)} = 0$ and $\boldsymbol{D}^{(1)} = D_0 \boldsymbol{I}$, (B 1) becomes

$$\frac{\partial P_1}{\partial t} = D_0 \nabla_1^2 P_1 + \nabla_1 \cdot \boldsymbol{j},$$

with

$$\boldsymbol{j} = \mathscr{N} \int (\boldsymbol{D}_{11} - D_0 \boldsymbol{I}) \cdot (P \nabla_1 V + \nabla_1 P)\, \mathrm{d}^3x_2 \ldots \mathrm{d}^3x_{\mathscr{N}}$$

$$+ \mathscr{N} \int D_0 P \nabla_1 V\, \mathrm{d}^3x_2 \ldots \mathrm{d}^3x_{\mathscr{N}}$$

$$+ \mathscr{N} \int \boldsymbol{D}_{ik} \cdot (P \nabla_k V + \nabla_k P)\, \mathrm{d}^3x_2 \ldots \mathrm{d}^3x_{\mathscr{N}} \quad (k = 2, \ldots, \mathscr{N}).$$

Now

$$\boldsymbol{D}_{11} - D_0 \boldsymbol{I} = \left[\boldsymbol{D} - \sum_{k=2}^{\mathscr{N}} (\boldsymbol{D}_{11}^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_k) - D_0 \boldsymbol{I}) - D_0 \boldsymbol{I}\right] + \sum_{k=2}^{\mathscr{N}} (\boldsymbol{D}_{11}^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_k) - D_0 \boldsymbol{I}).$$

The square-bracketed term vanishes unless at least two of $\boldsymbol{x}_2, \ldots, \boldsymbol{x}_{\mathscr{N}}$ lie within an $O(a)$ distance of $\boldsymbol{x}_1$, i.e. it will generate an $O(\phi^2)$ contribution. It is similarly possible to write

$$V = \left[V - \sum_{k=2}^{\mathscr{N}} V^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_k)\right] + \sum_{k=2}^{\mathscr{N}} V^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_k).$$

Then, on substituting these results in the expansion for $\boldsymbol{j}$, and using the fact that the particles are identical, we have for the first term of $\boldsymbol{j}$

$$\mathscr{N} \sum_{k=2}^{\mathscr{N}} \int (\boldsymbol{D}_{11}^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_k) - D_0 \boldsymbol{I}) \cdot (P \nabla_1 V + \nabla_1 P)\, \mathrm{d}^3x_2 \ldots \mathrm{d}^3x_{\mathscr{N}} + O(\phi^2)$$

$$= \mathscr{N}(\mathscr{N}-1) \int (\boldsymbol{D}_{11}^{(2)}(\boldsymbol{x}_1, \boldsymbol{x}_2) - D_0 \boldsymbol{I}) \cdot (P \nabla_1 V + \nabla_1 P)\, \mathrm{d}^3x_2 \ldots \mathrm{d}^3x_{\mathscr{N}} + O(\phi^2)$$

$$= \int (\boldsymbol{D}_{11}^{(2)} - D_0 \boldsymbol{I}) \cdot (P_2 \nabla_1 V^{(2)} + \nabla_1 P_2)\, \mathrm{d}^3x_2 + O(\phi^2).$$

The remaining terms can be simplified similarly to yield, correct to $O(\phi)$,

$$\frac{\partial P_1}{\partial t} = D_0 \nabla^2 P_1 + \nabla_1 \cdot \int (\boldsymbol{D}_{11}^{(2)} - D_0 \boldsymbol{I}) \cdot (P_2 \nabla_1 V^{(2)} + \nabla_1 P_2)\, \mathrm{d}^3x_2$$

$$+ \nabla_1 \cdot \int D_0 P_2 \nabla_1 V^{(2)} + \nabla_1 \cdot \int \boldsymbol{D}_{12}^{(2)} \cdot (P_2 \nabla_2 V^{(2)} + \nabla_2 P_2)\, \mathrm{d}^3x_2,$$

as used in the body of the paper (3.10).

Appendix C. Hard-sphere repulsion: the boundary layer at $r = 2a$

We suppose that for pairs of hard spheres a repulsive potential V^{h} exists in a thin layer outside $r = 2a$ such that

$$e^{-V^{\mathrm{h}}(r)} = \begin{cases} 0 & (r \leqslant 2a) \\ 1 & (r > 2a), \quad \text{'outside' the layer.} \end{cases}$$

Thus f_2 rises from zero for $r < 2a$ (an overlap impossible) to a value f_2^+ (which depends on angular position θ, ϕ) just outside $r = 2a$. Within the layer, the distribution of f_2 is approximately Maxwell–Boltzmann and thus

$$f_2(r, \theta, \phi) = f_2^+(\theta, \phi)\, e^{-V^{\mathrm{h}}(r)}.$$

The equation (3.13) for F then gives

$$\dot{F} = -D_0 k^2 F - \int_{r \geqslant 2a} [\boldsymbol{k}\cdot(\boldsymbol{D}_{11} - D_0 \boldsymbol{I})\cdot\boldsymbol{k}\; 2\cos\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}$$
$$+ (\nabla\cdot(\boldsymbol{D}_r\cdot\boldsymbol{k}) - \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla(V^{\mathrm{h}} + V^{\mathrm{s}}))\sin\tfrac{1}{2}(\boldsymbol{k}\cdot\boldsymbol{r})]\, f_2 n\, \mathrm{d}^3 r.$$

The contribution to the integral from V^{h} and the boundary layer is negligible, except for the term

$$\int_{r \geqslant 2a} \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\nabla V^{\mathrm{h}} \sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}\, f_2 n\, \mathrm{d}^3 r$$
$$= \int_{r = 2a} \boldsymbol{k}\cdot\boldsymbol{D}_r \sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}\, f_2^+ n\, \mathrm{d}^2 r\cdot\hat{\boldsymbol{r}} \int_{\text{boundary layer}} \frac{\partial V^{\mathrm{h}}}{\partial r} e^{-V^{\mathrm{h}}}\, \mathrm{d}r$$
$$= -\int_{r = 2a} \boldsymbol{k}\cdot\boldsymbol{D}_r\cdot\hat{\boldsymbol{r}} \sin\tfrac{1}{2}\boldsymbol{k}\cdot\boldsymbol{r}\, f_2^+ n\, \mathrm{d}^2 r.$$

This is the 'extra' term in (3.16). The result (3.17) for F_{s} may be derived similarly.

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