

## Self-diffusion in sheared suspensions

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(Received 20 June 1995 and in revised form 20 October 1995)

Self-diffusion in a suspension of spherical particles in steady linear shear flow is investigated by following the time evolution of the correlation of number density fluctuations. Expressions are presented for the evaluation of the self-diffusivity in a suspension which is either macroscopically quiescent or in linear flow at arbitrary Péclet number  $Pe = \dot{\gamma}a^2/2D$ , where  $\dot{\gamma}$  is the shear rate,  $a$  is the particle radius, and  $D = k_B T/6\pi\eta a$  is the diffusion coefficient of an isolated particle. Here,  $k_B$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $\eta$  is the viscosity of the suspending fluid. The short-time self-diffusion tensor is given by  $k_B T$  times the microstructural average of the hydrodynamic mobility of a particle, and depends on the volume fraction  $\phi = \frac{4}{3}\pi a^3 n$  and  $Pe$  only when hydrodynamic interactions are considered. As a tagged particle moves through the suspension, it perturbs the average microstructure, and the long-time self-diffusion tensor,  $\mathbf{D}_\infty^s$ , is given by the sum of  $\mathbf{D}_0^s$  and the correlation of the flux of a tagged particle with this perturbation. In a flowing suspension both  $\mathbf{D}_0^s$  and  $\mathbf{D}_\infty^s$  are anisotropic, in general, with the anisotropy of  $\mathbf{D}_0^s$  due solely to that of the steady microstructure. The influence of flow upon  $\mathbf{D}_\infty^s$  is more involved, having three parts: the first is due to the non-equilibrium microstructure, the second is due to the perturbation to the microstructure caused by the motion of a tagged particle, and the third is by providing a mechanism for diffusion that is absent in a quiescent suspension through correlation of hydrodynamic velocity fluctuations.

The self-diffusivity in a simply sheared suspension of identical hard spheres is determined to  $O(\phi Pe^{3/2})$  for  $Pe \ll 1$  and  $\phi \ll 1$ , both with and without hydrodynamic interactions between the particles. The leading dependence upon flow of  $\mathbf{D}_0^s$  is  $0.22D\phi Pe\hat{\mathbf{E}}$ , where  $\hat{\mathbf{E}}$  is the rate-of-strain tensor made dimensionless with  $\dot{\gamma}$ . Regardless of whether or not the particles interact hydrodynamically, flow influences  $\mathbf{D}_\infty^s$  at  $O(\phi Pe)$  and  $O(\phi Pe^{3/2})$ . In the absence of hydrodynamics, the leading correction is proportional to  $\phi Pe D\hat{\mathbf{E}}$ . The correction of  $O(\phi Pe^{3/2})$ , which results from a singular advection-diffusion problem, is proportional, in the absence of hydrodynamic interactions, to  $\phi Pe^{3/2} D\mathbf{I}$ ; when hydrodynamics are included, the correction is given by two terms, one proportional to  $\hat{\mathbf{E}}$ , and the second a non-isotropic tensor.

At high  $\phi$  a scaling theory based on the approach of Brady (1994) is used to approximate  $\mathbf{D}_\infty^s$ . For weak flows the long-time self-diffusivity factors into the product of the long-time self-diffusivity in the absence of flow and a non-dimensional function of  $\bar{Pe} = \dot{\gamma}a^2/2D_0^s(\phi)$ . At small  $\bar{Pe}$  the dependence on  $\bar{Pe}$  is the same as at low  $\phi$ .

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## 1. Introduction

This work addresses the problem of calculating the self-diffusivity in a suspension undergoing steady shear at small Reynolds number. Self-diffusion is one of the most basic transport processes occurring in a suspension, and self-diffusivity in a quiescent system is among the most intensely studied properties in colloid and polymer science. The limited theoretical study of the diffusivity in a sheared suspension has followed a different course from that taken in the study of quiescent suspensions. This difference proves unnecessary and aspects of the problem that are common to both quiescent and flowing suspensions are emphasized as we develop a methodology for determining the self-diffusivity in a linear flow.

In a suspension, the trajectory of a particle is typically unpredictable whether the particle moves as the result of Brownian motion, because of a bulk flow, or through the influence of both factors. In a quiescent suspension, it has been established in numerous studies (see the review by Pusey 1991) that the variance in position of a particle subject to Brownian forces grows linearly on two separate time scales, and the Brownian diffusivity of a quiescent suspension is thus characterized by both a short-time and long-time diffusion coefficient. Successful theory, based upon the experimental technique of dynamic light scattering (Berne & Pecora 1976), has been developed to calculate these coefficients (Russel & Glendinning 1981; Jones & Burfield 1982; Rallison & Hinch 1986; Brady 1994). The technique is based upon observation of the temporal decay of correlation in number density fluctuations, which may be related to the diffusivity because decorrelation of the scattered light arises from the uncorrelated, and hence over appropriate time scales diffusive, motions of the particles. The relationship between the rate at which number density fluctuations decay and the self- and collective-diffusivities lies at the centre of the analytical theory of diffusivity in quiescent suspensions and is shown in this investigation to have the same role in the theory of self-diffusion in a sheared suspension.

Alternative analytical methods for the investigation of dispersion in flowing suspensions have been presented. Frankel & Brenner (1991) considered an isolated particle with internal degrees of freedom in unbounded linear flows, using a transformation of the time coordinate to remove the bulk linear motion. It may be possible to extend this method to multi-particle systems, but the complexity of the analysis for an isolated particle indicates that this would be an extremely difficult task. Acrivos *et al.* (1992) studied the self-diffusivity of hydrodynamically interacting hard spheres in simple-shear flow in the absence of Brownian motion and determined the  $O(\phi)$  coefficient of  $\dot{\gamma}a^2$  in the flow direction by a trajectory calculation, where  $\dot{\gamma}$  is the shear rate and  $a$  is the sphere radius. A similar trajectory calculation (Wang, Mauri & Acrivos 1996) has determined the  $O(\phi^2)$  coefficient in the velocity-gradient direction. (The symmetry of the relative motion of two identical particles in Stokes flow necessitates that three-particle interactions be included to determine the self-diffusivity in the velocity-gradient direction.) These trajectory methods appear to be restricted to small particle fractions, and it is unclear how to formulate the trajectory calculation in a system with Brownian motion.

Evaluation of the self-diffusivity requires determining the microstructure at some initial time, which we choose as the steady microstructure at the conditions of interest, as well as the microstructural perturbation caused by a given particle as it moves through a suspension (Rallison & Hinch 1986; Brady 1994), which we denote by the function  $f_N$ . The equation governing the pair microstructure in a suspension at low particle Reynolds number was studied for weak straining flow by Batchelor (1977).

The bulk of the analytical effort of this study is thus devoted to development of the governing equation for  $f_N$  and determination of the steady small- $k$  solution of the pair-perturbation function,  $f$ , obtained by reduction of  $f_N$ ; only the steady small- $k$  solution for  $f$  is needed for the evaluation of self-diffusion.

In contrast to what one might expect from prior work on generalized Taylor dispersion (Frankel & Brenner 1991), which gives a first correction of  $O(Pe^2)$ , the first effects of weak shear on the self-diffusivity are  $O(Pe)$ . Here,  $Pe = \dot{\gamma}a^2/2D$ , where  $D = k_B T/6\pi\eta a$  is the diffusivity of an isolated particle with thermal energy  $k_B T$  in a fluid of viscosity  $\eta$ . The  $O(Pe)$  distortion of the pair-distribution function  $g$  (Batchelor 1977) leads to a correction to the short-time self-diffusion tensor,  $\mathbf{D}_0^s$ , proportional to  $\phi Pe D \hat{\mathbf{E}}$ , where  $\hat{\mathbf{E}}$  is the dimensionless rate-of-strain tensor. The  $O(\phi Pe)$  correction to the long-time self-diffusion tensor,  $\mathbf{D}_\infty^s$ , from its value of  $D_0^s(\phi)I$  in the quiescent suspension is also proportional to  $\hat{\mathbf{E}}$  for general linear flows, regardless of whether or not hydrodynamics are included. In simple-shear flow the  $O(\phi Pe)$  correction does not contribute to the long-time self-diffusivity in the velocity-gradient direction, and to capture the leading correction in all directions, we must go to the next order in the perturbation. The effect of weak advection is singular, with a balance of advection and diffusion at large separations  $r/a \sim O(Pe^{-1/2})$ , and the next correction is  $O(\phi Pe^{3/2})$ , with the tensor form dependent upon whether or not hydrodynamics are included.

In closely related work, Leal (1973) studied the effective thermal conductivity in a dilute suspension of spherical drops or rigid particles in weak simple-shear flow. The influence of a single particle or drop upon the temperature and velocity fields was determined and the first dependence upon  $Pe$  of the thermal conductivity in the direction of the velocity gradient was shown to be  $O(\phi Pe^{3/2})$ , as it is in the corresponding component of  $\mathbf{D}_\infty^s$  under weak-flow conditions. This correspondence is reflective of the similarity in the problems governing the temperature disturbance and  $f$  of the present problem in the case of hydrodynamically interacting particles. The essential difference is that the relative diffusivity of suspended particles depends upon their separation. Because the present method identifies all elements of the diffusivity tensor, it is clear that an  $O(\phi Pe)$  contribution to the thermal conductivity proportional to  $\hat{\mathbf{E}}$  also exists. The approach used by Leal is not able to determine the conductivity in any direction other than the velocity gradient.

Experimental data on the diffusivity in suspensions at conditions corresponding to those of this work are not presently available. Qiu *et al.* (1988) have measured the long-time self-diffusivity in a simple-shear flow for a suspension of polystyrene particles at  $\phi \approx 0.003$ . Their particles were electrostatically repulsive, and their effective radii could be varied by changing the ionic strength of the suspending fluid. The self-diffusivity was shown to have an expected strong dependence upon the effective radius. Unfortunately, the Péclet number based upon the effective radius of these particles was of  $O(10)$ , and our results are not directly applicable. We are not aware of any other experimental study at small Péclet number.

At the other extreme of large Péclet number, there have been a number of studies of shear-induced self-diffusion, for example by Eckstein, Bailey & Shapiro (1977) and Leighton & Acrivos (1987). These studies showed that hydrodynamic dispersion occurs with the self-diffusivity scaling as  $\dot{\gamma}a^2$  (or as  $Pe$  in dimensionless form). Although the results we have obtained for weak shear flow do not apply at large Péclet number, the Fourier-transform method remains applicable. In a forthcoming publication (Morris & Brady 1996) the effects of strong shear upon

the microstructure of a suspension, and the implications for the rheology and self-diffusivity, are addressed. In particular, we show that the methodology developed in this paper can be applied at high Péclet numbers and use it to predict the  $O(\dot{\gamma}a^2)$  long-time self-diffusivity in a general linear flow as  $Pe \rightarrow \infty$ .

Simulations by Stokesian Dynamics of hydrodynamically interacting suspensions in shear flow (Phung, Brady & Bossis 1996; Phung 1993) have shown that  $\mathbf{D}_\infty^s$  is generally non-isotropic in the plane perpendicular to the mean flow; as in an experiment, the diagonal component of  $\mathbf{D}_\infty^s$  in the direction of the mean flow is not readily determined owing to the nonlinear temporal growth of the variance dominating the dispersion. The complete particle mobility tensor, and thus the complete short-time self-diffusivity for the simulated conditions, is also available from these simulations (Phung 1993). Simulations of the shear flow of a monolayer suspension of identical particles by Bossis & Brady (1987) demonstrated that residual Brownian motion may have a profound influence upon the correlation time and the self-diffusivity at large Péclet number.

We begin, in §2, by introducing the Fourier-transform method in the context of the problem of an isolated Brownian particle immersed in linear flow. In §3, a framework for the description of self-diffusivity valid for a quiescent or linearly flowing suspension at arbitrary Péclet number is presented, with application of the theory to a weakly sheared and dilute suspension of hard spheres presented in §4. To obtain predictions of the self-diffusivity at large particle fraction, we have applied the scaling ideas of Brady (1994) to a weakly sheared suspension near maximum packing, and the results are presented in §4.4. We conclude with a summary and discussion.

## 2. Advection and diffusion of an isolated particle

Self-diffusivity in a macroscopically quiescent suspension is directly related to the rate at which the variance in a particle's position grows with time:

$$\langle \mathbf{x}\mathbf{x} \rangle \sim 2DIt,$$

where  $D$  is the magnitude of the isotropic diffusion tensor, and we have presumed that sufficient time has elapsed to achieve the long-time asymptotic limit. A suspension in linear flow presents a different and richer situation, as the variance in position does not necessarily grow linearly in time owing to the position-dependent velocity field, and therefore the variance in the particle position is not so readily related to the diffusivity. An extreme example occurs in pure straining motion where the variance grows exponentially in time (Foister & van de Ven 1980). In simple shear there is a balance of straining and rotation, and the coupled effects of advection and diffusion lead to a variance in particle position proportional to  $t^3$  in the flow direction.

To understand how we may determine the diffusivity in shearing flows, consider the equation governing the probability distribution of a Brownian sphere released into a linear flow, which is mathematically identical to the equation describing the evolution of an impulse of dye or heat released into the same flow:

$$\frac{\partial G}{\partial t} + \dot{\mathbf{I}} \cdot \mathbf{x} \cdot \nabla G + \mathbf{U} \cdot \nabla G - D\nabla^2 G = 0, \quad (1)$$

where  $\dot{\mathbf{I}}$  is the constant velocity-gradient tensor,  $\mathbf{U}$  is a uniform velocity, and  $D$  is the diffusion coefficient. We assume that the particle (or dye) is released at the origin so

that  $G(\mathbf{x}, t)$  satisfies the initial condition

$$G(\mathbf{x}, 0) = \delta(\mathbf{x}).$$

The spatial Fourier transform of (1) is

$$\frac{\partial F_s}{\partial t} - \mathbf{k} \cdot \dot{\Gamma} \cdot \nabla_{\mathbf{k}} F_s - i\mathbf{k} \cdot \mathbf{U} F_s + k^2 D F_s = 0, \quad (2)$$

while the initial condition transforms to

$$F_s(\mathbf{k}, 0) = 1,$$

where  $\mathbf{k}$  is the Fourier-space position vector (wavevector), and the Fourier transform of  $G$  is given by

$$F_s(\mathbf{k}, t) = \int G(\mathbf{x}, t) e^{i\mathbf{k} \cdot \mathbf{x}} d\mathbf{x}.$$

We use this notation for the transform of  $G$  because it is equivalent to the self-intermediate scattering function of dynamic light scattering (Berne & Pecora 1976).

In the absence of flow, it is well-known that the self-diffusivity is related to the scattering function by

$$D^s = -\frac{\dot{F}_s}{k^2 F_s}, \quad (3)$$

for time scales over which the right-hand side is a constant. Here, the overdot denotes differentiation with respect to time. Equation (3) suggests that the self-diffusivity is given by the coefficient of  $k^2$  in  $\partial \ln F_s / \partial t$  under any flow conditions. That this definition is correct may be appreciated by observing that in (2) diffusive variation of  $F_s$  is  $O(k^2)$ , while linear and uniform flow cause rates of variation which are independent of  $k$  and  $O(k)$ , respectively. The governing equation for the probability distribution of a tagged particle in a suspension is the many-particle generalization of (1), and the equation for  $F_s$  for a suspension retains the essential structure exhibited by (2). It is thus conceptually simple to identify the self-diffusivity of a suspension in linear flow. Although the diffusion coefficient is simply identifiable in (2), this does not imply that the variance in particle position necessarily grows linearly in time in a flowing suspension.

For  $\mathbf{U} = 0$ , Batchelor (1979) generalized the solutions of (1) determined by Novikov (1958) and Elrick (1962) for the case of simple-shear flow to show that the solution to (2) could be written for any linear flow as

$$F_s(\mathbf{k}, t) = \exp(-Dk_i k_j B_{ij}), \quad (4)$$

where  $\mathbf{B}(t)$  is a symmetric tensor satisfying

$$\frac{\partial B_{ij}}{\partial t} = \delta_{ij} + \dot{\Gamma}_{il} B_{jl} + \dot{\Gamma}_{jl} B_{il}, \quad \text{with } B_{ij} \sim \delta_{ij} t, \quad \text{as } t \rightarrow 0.$$

The physical space solution obtained by transforming (4) is

$$G(\mathbf{x}, t) = \frac{1}{(4\pi D)^{3/2} \Delta^{1/2}} \exp\left(\frac{-x_i x_j b_{ij}}{4D\Delta}\right), \quad (5)$$

where  $\Delta(t)$  is the determinant of the matrix  $\mathbf{B}$ , and  $b_{ij}(t)$  is the cofactor of the  $ij$  element of  $\mathbf{B}$ . The solution (5) can be straightforwardly generalized for a tensorial diffusion coefficient.

In simple-shear flow  $u_x = \dot{\gamma}y$ , denoting  $\mathbf{x} = (x_1, x_2, x_3)$  as  $(x, y, z)$ , the non-zero components of  $\mathbf{B}$  are

$$B_{11} = t(1 + \frac{1}{3}\dot{\gamma}^2 t^2), \quad B_{22} = t, \quad B_{33} = t, \quad B_{12} = \frac{1}{2}\dot{\gamma}t^2,$$

and the determinant  $\Delta$  is

$$\Delta = t^3(1 + \frac{1}{12}\dot{\gamma}^2 t^2).$$

For reference, note that when  $\dot{\gamma} = 0$  the diffusive solution with  $\mathbf{B} = \mathbf{I}t$  is obtained. The  $t^3$  dependence of  $B_{11}$  in simple shear indicates that advectively enhanced, or Taylor, dispersion with nonlinear temporal growth in the variance is contained directly in (5).

Other treatments of diffusion in sheared systems (Duffy 1984; san Miguel & Sancho 1979; Frankel & Brenner 1991) have not used the Fourier-transform approach, but rather have transformed to a coordinate system moving with the shearing motion to remove the linear shear flow from the governing equation (1). While such an approach is possible, it unnecessarily complicates the analysis. Seeking a solution in the form of a Fourier transform places the analysis of quiescent and flowing suspensions on the same footing with an easy identification of the diffusivity.

It is worthwhile to consider the time scale over which a long-time diffusion in a sheared suspension may be expected to occur. While not an issue for the isolated particle problem discussed here, the motion of a particle in a quiescent suspension is, in general, diffusive only on time scales that are alternately much shorter and much longer than the time required for a particle to wander a distance comparable to its own size,  $t \ll a^2/D$  and  $t \gg a^2/D$ , respectively. At intermediate times correlated interaction of a particle with neighbouring particles renders its motion non-diffusive (for a discussion of the physical significance of the short- and long-time self-diffusivities in quiescent suspensions, see Rallison & Hinch 1986). The same time scales apply to a weakly sheared suspension, while at large Péclet number long-time diffusion in a shear flow may be expected to occur on time scales  $t \gg \dot{\gamma}^{-1}$ , although some caution should be exercised in making a definitive statement about this time scale. For diffusion to occur, a particle must make a large number of essentially uncorrelated motions, and for large Péclet number motions are generated predominantly by configuration-dependent hydrodynamic interactions (perhaps also by non-hydrodynamic interparticle forces). Hence, to move diffusively, a particle must experience a large number of configurations, with the rate at which new configurations are encountered proportional to the shear rate. While the estimate of  $t \gg \dot{\gamma}^{-1}$  is therefore reasonable, the correlation time can be extremely large in shear flow of a suspension at low Reynolds number (Bossis & Brady 1987), and the time scale at which diffusion will be observed for general conditions remains unknown, but will depend upon concentration, residual Brownian motion, and non-hydrodynamic interparticle forces.

### 3. Theoretical development

#### 3.1. The self-intermediate scattering function

We consider  $N$  spherical particles of radius  $a$  immersed in a Newtonian fluid at small Reynolds number. The  $N$ -particle configuration is denoted  $\mathbf{x}^N$ , while the centre of particle  $\alpha$  is located at  $\mathbf{x}_\alpha$ . The number density at any point  $\mathbf{x}$  is

$$n(\mathbf{x}, t) = \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{x}_\alpha),$$

with Fourier transform given by

$$\tilde{n}(\mathbf{k}, t) = \int e^{i\mathbf{k}\cdot\mathbf{x}} \sum_{\alpha=1}^N \delta(\mathbf{x} - \mathbf{x}_{\alpha}) d\mathbf{x} = \sum_{\alpha=1}^N e^{i\mathbf{k}\cdot\mathbf{x}_{\alpha}}.$$

In dynamic light scattering, the intermediate scattering function  $F(\mathbf{k}, t)$  (also known as the dynamic structure factor) is related to the autocorrelation in number density (Berne & Pecora 1976):

$$F(\mathbf{k}, t) = \frac{1}{N} \langle \tilde{n}(\mathbf{k}, t) \tilde{n}^*(\mathbf{k}, 0) \rangle = \sum_{\alpha=1}^N \sum_{\beta=1}^N \langle e^{i\mathbf{k}\cdot(\mathbf{x}_{\alpha}(t) - \mathbf{x}_{\beta}(0))} \rangle,$$

where \* indicates a complex conjugate and the second equality follows from the fact that  $n(\mathbf{x}, t)$  is real. The indistinguishability of particles allows  $F$  to be expressed as

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

in which the first term on the right-hand side is the self-intermediate scattering function,

$$F_s(\mathbf{k}, t) = \langle e^{i\mathbf{k}\cdot(\mathbf{x}_1(t) - \mathbf{x}_1(0))} \rangle; \tag{6}$$

in this investigation of the self-diffusivity we are concerned only with  $F_s$  and hereafter the remainder of  $F$  will not be considered. The temporal behaviour of the complete scattering function can be related to the collective-diffusivity (Pusey 1991).

### 3.2. Probability distributions and the ensemble average

In (6) and the preceding equations, the angle brackets  $\langle \rangle$  denote an ensemble average taken with respect to both the initial,  $\mathbf{x}^N(0)$ , and present,  $\mathbf{x}^N(t)$ , configurations of the particles. We denote the distribution function for the initial configuration  $\mathbf{x}^N(0)$  as  $P_N^0(\mathbf{x}^N(0))$ , while the conditional probability of the configuration  $\mathbf{x}^N(t)$  given that the configuration was initially  $\mathbf{x}^N(0)$  is denoted  $P_N(\mathbf{x}^N(t)|\mathbf{x}^N(0))$ . Thus,  $F_s$  may be written as

$$F_s(\mathbf{k}, t) = \int \int e^{i\mathbf{k}\cdot(\mathbf{x}_1(t) - \mathbf{x}_1(0))} P_N(\mathbf{x}^N(t)|\mathbf{x}^N(0)) P_N^0(\mathbf{x}^N(0)) d\mathbf{x}^N(t) d\mathbf{x}^N(0). \tag{7}$$

In this work,  $P_N^0$  denotes the steady initial distribution for the conditions of interest (cf. (28)). The transition probability is governed by the conservation equation

$$\frac{\partial P_N}{\partial t} + \sum_{\alpha=1}^N \nabla_{\alpha} \cdot \mathbf{j}_{\alpha} = 0, \tag{8}$$

and satisfies the initial condition

$$P_N(t = 0) = \delta(\mathbf{x}^N - \mathbf{x}^N(0)). \tag{9}$$

In (8),  $\mathbf{j}_{\alpha}$  is the probability flux associated with particle  $\alpha$ , given by

$$\mathbf{j}_{\alpha} = U_{\alpha} P_N - \sum_{\beta=1}^N \mathbf{D}_{\alpha\beta} P_N \cdot \nabla_{\beta} (\ln P_N + V), \tag{10}$$

where  $\mathbf{D}_{\alpha\beta} = k_B T \mathbf{M}_{\alpha\beta}$ , with  $\mathbf{M}_{\alpha\beta}$  the hydrodynamic mobility of particle  $\alpha$  to a force on particle  $\beta$ , and  $V$  is the interparticle potential energy made dimensionless by  $k_B T$ . In the absence of Brownian motion and interparticle forces, particle  $\alpha$  moves with

the hydrodynamic velocity  $U_\alpha$ , which may include the influence of a buoyancy or external force acting upon the particles.

We write  $U_\alpha$  as

$$\begin{aligned} U_\alpha &= U^\infty(\mathbf{x}_0) + \dot{\Gamma} \cdot (\mathbf{x}_\alpha - \mathbf{x}_0) + U'_\alpha(\mathbf{x}_N) \\ &= U^*(\mathbf{x}_0) + \dot{\Gamma} \cdot \mathbf{x}_\alpha + U'_\alpha(\mathbf{x}_N), \end{aligned} \quad (11)$$

where  $U^\infty(\mathbf{x}_0)$  is the bulk average velocity measured at an arbitrary field point,  $\mathbf{x}_0$ , from which the bulk shear velocity is referenced,  $U^*(\mathbf{x}_0)$  is given by

$$U^*(\mathbf{x}_0) = U^\infty(\mathbf{x}_0) - \dot{\Gamma} \cdot \mathbf{x}_0,$$

and  $U'_\alpha$  is the configuration-dependent velocity fluctuation from  $U^* + \dot{\Gamma} \cdot \mathbf{x}_\alpha$ . The bulk flow is divergence-free, thus satisfying  $\dot{\Gamma}_{ii} = 0$ .

Inserting (10) to (8) yields the Smoluchowski equation governing  $P_N$ ,

$$\frac{\partial P_N}{\partial t} + \sum_{\alpha=1}^N \nabla_\alpha \cdot \left[ U_\alpha P_N - \sum_{\beta=1}^N \nabla_\alpha \cdot \{ \mathbf{D}_{\alpha\beta} P_N \cdot \nabla_\beta (\ln P_N + V) \} \right] = 0. \quad (12)$$

Following Rallison & Hinch (1986), we integrate over the initial coordinates  $\mathbf{x}^N(0)$ , defining

$$\hat{P}_N(\mathbf{x}^N, t; \mathbf{k}) \equiv \int P_N(\mathbf{x}^N | \mathbf{x}^N(0)) P_N^0(\mathbf{x}^N(0)) e^{-i\mathbf{k} \cdot \mathbf{x}_1(0)} d\mathbf{x}^N(0). \quad (13)$$

The operator in (12) depends only on present variables, and thus replacing  $P_N$  with  $\hat{P}_N$  in (12) yields the governing equation for  $\hat{P}_N$ , which satisfies the initial condition

$$\hat{P}_N(\mathbf{x}^N, 0; \mathbf{k}) = P_N^0(\mathbf{x}^N) e^{-i\mathbf{k} \cdot \mathbf{x}_1}. \quad (14)$$

In terms of  $\hat{P}_N$ , the scattering function is

$$F_s(\mathbf{k}, t) = \int \hat{P}_N e^{i\mathbf{k} \cdot \mathbf{x}_1} d\mathbf{x}^N.$$

Reduced forms of  $\hat{P}_N$  are given by

$$\hat{P}_M(\mathbf{x}_1, \dots, \mathbf{x}_M, t; \mathbf{k}) = \frac{N!}{(N-M)!} \int \hat{P}_N d\mathbf{x}_{M+1} \cdots d\mathbf{x}_N \quad \text{for } M < N,$$

which when used for  $\hat{P}_1$  yields

$$F_s(\mathbf{k}, t) = \frac{1}{N} \int \hat{P}_1 e^{i\mathbf{k} \cdot \mathbf{x}_1} d\mathbf{x}_1. \quad (15)$$

As discussed in §2, the self-diffusivity is the coefficient – in general, a non-isotropic tensor – of the  $O(k^2)$  term in  $\partial \ln F_s / \partial t$ . Making use of the divergence theorem and the requirement that the probability flux from the system is zero, we find

$$\frac{\partial F_s}{\partial t}(\mathbf{k}, t) = \int e^{i\mathbf{k} \cdot \mathbf{x}_1} \frac{\partial \hat{P}_N}{\partial t} d\mathbf{x}^N = i\mathbf{k} \cdot \int \hat{\mathbf{j}}_1 e^{i\mathbf{k} \cdot \mathbf{x}_1} d\mathbf{x}^N, \quad (16)$$

Upon inserting  $\hat{\mathbf{j}}_1$ , given by (10) with  $\hat{P}_N$  replacing  $P_N$ , into (16), we obtain

$$\begin{aligned} (\ln F_s)(\mathbf{k}, t) &= \mathbf{k} \cdot \dot{\Gamma} \cdot \nabla_k \ln F_s + i\mathbf{k} \cdot \mathbf{U}^* \\ &\quad + \frac{i\mathbf{k}}{F_s} \cdot \int [U'_1 \hat{P}_N - \sum_{\alpha=1}^N \mathbf{D}_{1\alpha} \hat{P}_N \cdot \nabla_\alpha (\ln \hat{P}_N + V)] e^{i\mathbf{k} \cdot \mathbf{x}_1} d\mathbf{x}^N, \end{aligned} \quad (17)$$

where the notation

$$\frac{\partial \ln F_s}{\partial t} = \langle \ln \dot{F}_s \rangle$$

is employed.

3.3. Initial value of  $\langle \ln \dot{F}_s \rangle$ : short-time self-diffusivity and mean velocity

Using the known initial value of  $\hat{P}_N$  given by (14), we find

$$\langle \ln \dot{F}_s \rangle(\mathbf{k}, 0) = \mathbf{k} \cdot \dot{\mathbf{T}} \cdot \nabla_{\mathbf{k}} \ln F_s + i\mathbf{k} \cdot \langle \mathbf{U}_1 \rangle^0 - \mathbf{k} \cdot \langle \mathbf{D}_{11} \rangle^0 \cdot \mathbf{k}, \quad (18)$$

where  $\langle \rangle^0$  denotes the unconditional average with respect to the initial distribution  $P_N^0$ . Recalling that  $\mathbf{D}_{11} = k_B T \mathbf{M}_{11}$ , where  $\mathbf{M}_{11}$  is the mobility of particle 1 due to a force exerted upon it, we see that the short-time self-diffusion tensor, in a quiescent or a flowing suspension, is

$$\mathbf{D}_0^s = \langle \mathbf{D}_{11} \rangle^0 = k_B T \langle \mathbf{M}_{11} \rangle^0. \quad (19)$$

The short-time self-diffusivity will generally be non-isotropic in a non-equilibrium suspension, and the full tensor  $\mathbf{D}_{11}$  must be retained in (18).

The  $O(\mathbf{k})$  term in (18),  $\langle \mathbf{U}_1 \rangle^0$ , is the average velocity of the tagged particle:

$$\langle \mathbf{U}_1 \rangle^0 = \mathbf{U}^* + \langle \mathbf{U}'_1 \rangle^0 - \int \sum_{\alpha=1}^N \mathbf{D}_{1\alpha} \cdot \nabla_{\mathbf{x}} (\ln P_N^0 + V) P_N^0 d\mathbf{x}_N. \quad (20)$$

In (20)  $\langle \mathbf{U}'_1 \rangle^0$  is the average velocity of a particle due to hydrodynamic interactions or due to an external force acting on the particle. For the linear flow considered here,  $\langle \mathbf{U}'_1 \rangle^0 = 0$ . The last term on the right-hand side of (20) is the mean velocity of particle 1 arising from the initial distribution and would vanish identically if the initial distribution were the equilibrium Boltzmann distribution, i.e.  $P_N^0 = P_N^{eq} \sim e^{-V}$ . However, there is no need in general, and particularly at high Péclet number, to choose the initial distribution to be the equilibrium one, and the final term in (20) may contribute to the mean velocity of a tagged particle. In the linear flow considered here the last term in (20) is also zero as may be seen from symmetry arguments: the mean velocity of a particle must be proportional to  $\dot{\mathbf{T}}$  and there is no vector with which to contract  $\dot{\mathbf{T}}$  to form a vector, so this velocity is zero.

3.4. Perturbation function

To evaluate the rate of decay of number density correlation at arbitrary times requires a solution for  $\hat{P}_N$ . Noting that  $\mathbf{x}_1$  is a coordinate that plays a special role due to the initial condition (14), we write  $\hat{P}_N$  as†

$$\hat{P}_N = \frac{1}{N} \hat{P}_1 P_{(N-1)|1}^0 [1 + f_N], \quad (22)$$

thus defining a perturbation function  $f_N$ . The function  $P_{(N-1)|1}^0$  is the conditional probability for  $N - 1$  particles given particle 1 fixed at the initial time. The coordinate

† The form of  $\hat{P}_N$  given by (22) is in the same spirit as

$$\hat{P}_N = P_N^0 e^{-i\mathbf{k} \cdot \mathbf{x}_1} F_s [1 + f_N], \quad (21)$$

which was used by Brady (1994). Employing (22) in place of (21) for a quiescent suspension,  $f_N$  and its reduced forms satisfy the governing equations found by Brady (1994). However, application of  $f_N$  as defined by (21) for a suspension in linear flow fails to generate the linear-velocity convective derivative of  $F_s$  in Fourier space, i.e.  $-\mathbf{k} \cdot \dot{\mathbf{T}} \cdot \nabla_{\mathbf{k}} F_s$ , which as is known from (2) should appear, and thus results in more complicated analysis for  $f_N$ .

dependences are given explicitly by

$$\hat{P}_N(\mathbf{x}_1, \mathbf{r}^N, t), \quad \hat{P}_1(\mathbf{x}_1, t), \quad P_{(N-1)1}^0(\mathbf{r}^N), \quad \text{and} \quad f_N(\mathbf{r}^N, t),$$

indicating a change of coordinates to

$$\mathbf{x}_1 \quad \text{and} \quad \mathbf{r}^N \equiv (\mathbf{r}_2, \dots, \mathbf{r}_N),$$

related to the original coordinates, which we denote using a superscript prime, by

$$\mathbf{x}_1 = \mathbf{x}'_1 \quad \text{and} \quad \mathbf{r}_\alpha = \mathbf{x}'_\alpha - \mathbf{x}'_1 \quad \text{for} \quad 2 \leq \alpha \leq N.$$

We consider an interparticle potential  $V(\mathbf{r}^N)$  which is independent of absolute position. The effect of an external force derivable from a potential can be included directly into  $U_\alpha$ . Thus, the flux is given by

$$\hat{\mathbf{j}}_\alpha = U_\alpha \hat{P}_N - \mathbf{D}_{\alpha 1} \cdot \nabla_1 \hat{P}_N - \sum_{\beta=2}^N (\mathbf{D}_{\alpha\beta} - \mathbf{D}_{\alpha 1}) \hat{P}_N \cdot \nabla_\beta (\ln \hat{P}_N + V), \quad 1 \leq \alpha \leq N, \quad (23)$$

and the Smoluchowski equation for  $\hat{P}_N(\mathbf{x}_1, \mathbf{r}^N)$  is

$$\begin{aligned} \frac{\partial \hat{P}_N}{\partial t} + \nabla_1 \cdot U_1 \hat{P}_N - \mathbf{D}_{11} : \nabla_1 \nabla_1 \hat{P}_N - \sum_{\alpha=2}^N \nabla_1 \cdot (\mathbf{D}_{1\alpha} - \mathbf{D}_{11}) \hat{P}_N \cdot \nabla_\alpha (\ln \hat{P}_N + V) \\ + \sum_{\alpha=2}^N \nabla_\alpha \cdot [U'_\alpha \hat{P}_N - (\mathbf{D}_{\alpha 1} - \mathbf{D}_{11}) \cdot \nabla_1 \hat{P}_N] - \sum_{\alpha,\beta=2}^N \nabla_\alpha \cdot \mathbf{D}'_{\alpha\beta} \hat{P}_N \cdot \nabla_\beta (\ln \hat{P}_N + V) = 0 \end{aligned} \quad (24)$$

where we have defined

$$U'_\alpha \equiv U_\alpha - U_1, \quad \text{and} \quad \mathbf{D}'_{\alpha\beta} \equiv \mathbf{D}_{\alpha\beta} - \mathbf{D}_{\alpha 1} - \mathbf{D}_{1\beta} + \mathbf{D}_{11}.$$

The temporal variation of  $F_s$  in terms of  $f_N$  is found by substituting (22) into (17). Making the necessary alterations for the change of coordinates and performing the integration with respect to  $\mathbf{x}_1$ , we obtain

$$\begin{aligned} (\ln \dot{F}_s) = \mathbf{k} \cdot \dot{\Gamma} \cdot \nabla_k \ln F_s + i\mathbf{k} \cdot \langle U_1 \rangle^0 - \mathbf{k} \cdot \langle \mathbf{D}_{11} \rangle^0 \cdot \mathbf{k} \\ - \mathbf{k} \cdot \int (\mathbf{D}_{11} - \langle \mathbf{D}_{11} \rangle^0) \cdot \mathbf{k} f_N P^0 d\mathbf{r}^N \\ + i\mathbf{k} \cdot \int (U_1 - \dot{\Gamma} \cdot \mathbf{x}_1 - \langle U_1 \rangle^0) f_N P^0 d\mathbf{r}^N \\ - i\mathbf{k} \cdot \int \sum_{\alpha=2}^N [(\mathbf{D}_{1\alpha} - \mathbf{D}_{11}) \cdot \nabla_\alpha f_N + (\mathbf{D}_{1\alpha} - \mathbf{D}_{11}) f_N \cdot \nabla_\alpha \bar{V}] P^0 d\mathbf{r}^N, \end{aligned} \quad (25)$$

where we denote  $P_{(N-1)1}^0$  as  $P^0$  and define

$$\bar{V} \equiv \ln P^0 + V$$

to simplify notation. In obtaining (25) we have made use of the fact that, since both  $\hat{P}_N$  and  $P_N^0$  are normalized,

$$\int f_N P_{(N-1)1}^0 d\mathbf{r}^N = \int f_N P^0 d\mathbf{r}^N = 0.$$

3.5. Equation governing the perturbation function  $f_N$ 

The equation governing  $f_N$  is obtained by inserting (22) into (24), multiplying the equation by  $e^{ik \cdot x_1}$ , and integrating over  $x_1$ . We then make use of (25) for  $(\ln F_s)$  to write the equation as

$$\begin{aligned}
P^0 \frac{\partial f_N}{\partial t} + P^0 \sum_{\alpha=2}^N [U_\alpha^r - \sum_{\beta=2}^N \mathbf{D}_{\alpha\beta}^r \cdot \nabla_\beta \bar{V}] \cdot \nabla_\alpha f_N - \sum_{\alpha,\beta=2}^N \nabla_\alpha \cdot \mathbf{D}_{\alpha\beta}^r P^0 \cdot \nabla_\beta f_N \\
= -Q [\mathbf{i}k \cdot (\mathbf{U}_1 - \dot{\Gamma} \cdot \mathbf{x}_1 - \langle \mathbf{U}_1 \rangle^0) + \mathbf{k} \cdot (\mathbf{D}_{11} - \langle \mathbf{D}_{11} \rangle^0) \cdot \mathbf{k}] \\
+ \mathbf{i}k \cdot \sum_{\alpha=2}^N \{ \nabla_\alpha \cdot [(\mathbf{D}_{\alpha 1} - \mathbf{D}_{11})Q] + (\mathbf{D}_{1\alpha} - \mathbf{D}_{11})Q \cdot \nabla_\alpha (\ln Q + V) \} \\
- Q \left[ \mathbf{i}k \cdot \int (\mathbf{U}_1 - \dot{\Gamma} \cdot \mathbf{x}_1 - \langle \mathbf{U}_1 \rangle^0) f_N P^0 d\mathbf{r}^N \right. \\
- \mathbf{k} \cdot \int (\mathbf{D}_{11} - \langle \mathbf{D}_{11} \rangle^0) \cdot \mathbf{k} f_N P^0 d\mathbf{r}^N \\
\left. - \mathbf{i}k \cdot \int \sum_{\alpha=2}^N [(\mathbf{D}_{1\alpha} - \mathbf{D}_{11}) \cdot \nabla_\alpha f_N + (\mathbf{D}_{1\alpha} - \mathbf{D}_{11}) f_N \cdot \nabla_\alpha \bar{V}] P^0 d\mathbf{r}^N \right], \quad (26)
\end{aligned}$$

where we write  $Q = P^0[1 + f_N]$  to simplify notation. The initial condition for  $f_N$  is

$$f_N(\mathbf{r}^N, t = 0) = 0. \quad (27)$$

In writing (26) we have made use of the fact that the initial distribution satisfies the steady equation

$$\sum_{\alpha=2}^N \nabla_\alpha \cdot \left[ U_\alpha^r P^0 - \sum_{\beta=2}^N \mathbf{D}_{\alpha\beta}^r P^0 \cdot \nabla_\beta [\ln P^0 + V] \right] = 0. \quad (28)$$

In the absence of flow, the initial distribution reduces to the equilibrium Boltzmann distribution,  $P_N^{eq} \sim e^{-V}$ . Note that we could have used a time-dependent initial distribution by including  $\partial P / \partial t$  in (28) with no change to the subsequent equations.

Equation (26) is a nonlinear integro-differential equation for  $f_N$ , showing that departures from the initial distribution are driven by fluctuations in velocity and diffusivity; this equation is valid for all times and for all linear flows, regardless of the value of the Péclet number. Used in conjunction with (25) the diffusivity can be determined at any time and for any lengthscale (i.e. any  $\mathbf{k}$ ) of perturbation.

To determine the long-time self-diffusivity, the small- $k$  (long-wavelength) form of (26) is sufficient. Because  $P^0$  is the steady non-equilibrium probability distribution, examination of (26) shows that  $f_N$  is  $O(k)$ . Thus, keeping terms to  $O(k)$  only on the right-hand side of (26) we have

$$P^0 \frac{\partial f_N}{\partial t} + P^0 \sum_{\alpha=2}^N [U_\alpha^r - \sum_{\beta=2}^N \mathbf{D}_{\alpha\beta}^r \cdot \nabla_\beta \bar{V}] \cdot \nabla_\alpha f_N - \sum_{\alpha,\beta=2}^N \nabla_\alpha \cdot \mathbf{D}_{\alpha\beta}^r P^0 \cdot \nabla_\beta f_N$$

$$\begin{aligned}
&= \mathbf{i}\mathbf{k} \cdot \left( P^0(\mathbf{U}_1 - \dot{\mathbf{I}} \cdot \mathbf{x}_1 - \langle \mathbf{U}_1 \rangle^0) \right. \\
&\quad \left. - \sum_{\alpha=2}^N \{ \nabla_{\alpha} \cdot [(\mathbf{D}_{\alpha 1} - \mathbf{D}_{11})P^0] - (\mathbf{D}_{1\alpha} - \mathbf{D}_{11})P^0 \cdot \nabla_{\alpha} \bar{V} \} \right) + o(k). \quad (29)
\end{aligned}$$

### 3.6. The pair problem

To make analytical progress we define the pair-perturbation function,

$$f(\mathbf{r}_2) = \int P_{N-2|2}^0(\mathbf{r}_3, \dots, \mathbf{r}_N | \mathbf{r}_2) f_N(\mathbf{r}^N) d\mathbf{r}_3 \cdots d\mathbf{r}_N. \quad (30)$$

Hereafter, we write  $\mathbf{r}$  and  $\nabla$  in place of  $\mathbf{r}_2$  and  $\nabla_2$ , respectively. Also, we write

$$\mathbf{U}_r = \mathbf{U}_2 - \mathbf{U}_1, \quad \text{and} \quad \mathbf{D}_r = \mathbf{D}_{22} - \mathbf{D}_{21} - \mathbf{D}_{12} + \mathbf{D}_{11}.$$

Quantities are scaled as

$$r \sim a, \quad U \sim \dot{\gamma}a, \quad k \sim a^{-1}, \quad \mathbf{D}_r \sim 2D, \quad \text{and} \quad t \sim \frac{a^2}{D},$$

and the Péclet number is defined as

$$Pe \equiv \frac{\dot{\gamma}a^2}{2D},$$

where  $U$  indicates velocities in general,  $\dot{\gamma} \equiv (\dot{\mathbf{I}}:\dot{\mathbf{I}})^{1/2}$ , and  $D$  is the diffusion coefficient of an isolated particle. In this non-dimensionalization,  $\mathbf{D}_r \sim \mathbf{I}$  as  $r \rightarrow \infty$ . As we do not employ alternative symbols to denote dimensionless quantities, it should be borne in mind that all quantities are dimensionless unless noted otherwise in the following.

Integrating (29) with respect to  $N-2$  of the relative coordinates, we find the dimensionless governing equation for  $f$  in the limit of small  $k$ ,

$$\begin{aligned}
&\frac{1}{2}g \frac{\partial f}{\partial t} + Pe g \langle \mathbf{U}_r \cdot \nabla f_N \rangle_2^0 - g \langle \mathbf{D}_r \cdot \nabla \bar{V} \cdot \nabla f_N \rangle_2^0 \\
&\quad - \nabla \cdot g \langle \mathbf{D}_r \cdot \nabla f_N \rangle_2^0 - \nabla \cdot g \int P_{3|2}^0 \langle \mathbf{D}_{23}^r \cdot f_N \rangle_3^0 d\mathbf{r}_3 \\
&= \frac{1}{2} \mathbf{i}\mathbf{k} \cdot \{ -Pe g \langle \mathbf{U}'_r \rangle_2^0 + \nabla \cdot g \langle \mathbf{D}_r \rangle_2^0 + g \langle \mathbf{D}_r \cdot \nabla \bar{V} \rangle_2^0 \} + o(k), \quad (31)
\end{aligned}$$

where the steady pair-distribution function  $g(\mathbf{r})$  is defined by  $P_{1|1}^0 = ng(\mathbf{r})$ , and  $\langle \rangle_2^0$  stands for the conditional average over the initial distribution with two particles fixed as in (30). The boundary condition at the pair level is obtained by requiring the relative flux  $\hat{\mathbf{j}}_2 - \hat{\mathbf{j}}_1$  to vanish at particle contact,

$$\begin{aligned}
&\hat{\mathbf{r}} \cdot [ - \langle \mathbf{D}_r \cdot \nabla f_N \rangle_2^0 - \langle [\mathbf{D}_r \cdot \nabla \bar{V}] f_N \rangle_2^0 - \int \langle \mathbf{D}_{23}^r \cdot \nabla_3 f_N \rangle_3^0 P_{3|2}^0 d\mathbf{r}_3 + Pe \langle \mathbf{U}_r f_N \rangle_2^0 ] \\
&= \frac{1}{2} \hat{\mathbf{r}} \cdot \langle \mathbf{D}_r \rangle_2^0 \cdot \mathbf{i}\mathbf{k} \quad \text{at} \quad r = 2. \quad (32)
\end{aligned}$$

Here,  $\hat{\mathbf{r}}$  is a unit vector from particle 1 to 2. At large separation the perturbation vanishes,

$$f \sim 0 \quad \text{as} \quad r \rightarrow \infty, \quad (33)$$

and the initial condition is unchanged,

$$f = 0 \quad \text{at} \quad t = 0. \quad (34)$$

A similar reduction of the expression for  $\langle \ln F_s \rangle$  is performed by integrating over  $N - 2$  of the relative coordinates in (25). Since  $\langle \ln F_s \rangle$  pertains to a single particle, we scale the diffusivities by  $D$  rather than  $2D$  to obtain

$$\langle \ln F_s \rangle = 2Pe(\mathbf{k} \cdot \dot{\Gamma} \cdot \nabla_{\mathbf{k}} \ln F_s + i\mathbf{k} \cdot \langle \mathbf{U}_1 \rangle^0) - \mathbf{k} \cdot \mathbf{D}_0^s \cdot \mathbf{k} + \phi \frac{3}{4\pi} i\mathbf{k} \cdot \int \{ \{ [-2Pe \mathbf{U}'_r + \mathbf{D}_r \cdot \nabla \bar{V}] f_N \}_2^0 + \langle \mathbf{D}_r \cdot \nabla f_N \rangle_2^0 \} g(\mathbf{r}) d\mathbf{r} + O(k^3), \quad (35)$$

where  $\mathbf{U}'_r = \mathbf{U}'_2 - \dot{\Gamma} \cdot \mathbf{r}$  and we have introduced the volume fraction  $\phi = \frac{4}{3}\pi a^3 n$ , with  $n$  the number density of particles. Note that  $\mathbf{D}_r = 2(\mathbf{D}_{11} - \mathbf{D}_{21})$  and  $\mathbf{U}'_r = -2(\mathbf{U}_1 - \dot{\Gamma} \cdot \mathbf{x}_1 - \langle \mathbf{U}_1 \rangle^0)$  for identical particles; the first term on the right-hand side has a factor of 2 because  $Pe$  has been defined relative to  $2D$ .

#### 4. Diffusivity in a weakly sheared suspension

The expressions derived in the preceding section, which are valid for all shear rates, are applied to the determination of self-diffusivity in a sheared suspension at small Péclet number. To obtain a rigorous solution we assume the particle fraction to be dilute and consider the dual limit of  $Pe \ll 1$  and  $\phi \ll 1$ . Diluteness allows us to neglect nonlinear averages of fluctuational quantities as well as third-particle effects to obtain a closed equation for  $f$ .

We first determine, in §4.2, the pair-perturbation function and the self-diffusivities in the absence of hydrodynamic interactions. In §4.3 we complete the determination of the diffusivities with hydrodynamic interactions included. Finally, because the assumption of diluteness restricts the results to small  $\phi$ , we remedy this by applying the scaling ideas of Brady (1994) to estimate the effects of weak flow on the self-diffusivity near maximum packing, with the results presented in §4.4. Except where necessary to make a point about correlations, angle brackets will be omitted, with all quantities implicitly assumed to have their average value conditioned on the separation of a pair of particles.

##### 4.1. Steady microstructure and the short-time self-diffusivity in a dilute suspension

The steady pair-distribution function is expanded as

$$g(\mathbf{r}) = g^{eq}(\mathbf{r})[1 + Pe p(\mathbf{r}) + O(Pe^2)], \quad (36)$$

where  $g^{eq}(\mathbf{r})$  is the equilibrium radial-distribution function, assumed for small volume fraction to be uniform, i.e.  $g^{eq}(\mathbf{r}) = 1$  for all  $\mathbf{r}$ . The problem for  $p$  was first solved for hydrodynamically interacting particles by Batchelor (1977), who showed that, because the problem is forced by the straining motion,

$$p(\mathbf{r}) = -\hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}} q(\mathbf{r}),$$

where  $\hat{E}_{ij} = (\dot{\Gamma}_{ij} + \dot{\Gamma}_{ji})/2\dot{\gamma}$  is the rate-of-strain tensor made dimensionless with  $\dot{\gamma}$ . The quadrupolar solution  $q(\mathbf{r})$  decays as  $r^{-3}$  for large  $r$ .

In the absence of hydrodynamic interactions,  $p$  satisfies

$$\nabla^2 p = 0, \quad \text{with} \quad \hat{\mathbf{r}} \cdot \nabla p = 2\hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}} \quad \text{at} \quad r = 2, \quad (37)$$

and  $p \rightarrow 0$  for large  $r$ . Note that in the absence of hydrodynamic interactions neither  $\mathbf{U}_r$  nor  $\mathbf{D}_r$  vanish at contact, and the boundary condition at contact is modified accordingly. The solution of (37) is simply

$$p = -\frac{32}{3} \frac{1}{r^3} \hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}. \quad (38)$$

In the absence of hydrodynamic interactions, the short-time self-diffusivity is unaffected by the microstructure and remains the constant  $D = k_B T / 6\pi\eta a$  in dimensional form. However, the steady perturbation to the suspension microstructure influences the short-time self-diffusivity of hydrodynamically-interacting particles as, from (19),  $D_0^s$  is  $k_B T$  times the average mobility of a particle in the steady microstructure. With the diffusivities non-dimensionalized by  $D$  we have

$$\begin{aligned} D_0^s &= I + \phi \frac{3}{4\pi} \int \mathbf{D}_{11} g(\mathbf{r}) d\mathbf{r} \\ &= I + \phi \frac{3}{4\pi} \int \mathbf{D}_{11} g^{eq}(\mathbf{r})(1 + Pe p(\mathbf{r})) d\mathbf{r}. \end{aligned} \quad (39)$$

The integral over  $g^{eq}$  produces an isotropic  $O(\phi)$  correction to the diffusivity, first determined by Batchelor (1983). We denote this equilibrium correction by  $D_0^s(\phi)$ :

$$D_0^s(\phi) = (1 - 1.83\phi). \quad (40)$$

The  $O(Pe)$  disturbance to the structure gives

$$\begin{aligned} \phi \frac{3}{4\pi} Pe \int \mathbf{D}_{11}(\mathbf{r}) p(\mathbf{r}) d\mathbf{r} &= -\frac{2}{5} \phi Pe \hat{\mathbf{E}} \int_2^\infty (x_{11}^a(s) - y_{11}^a(s)) q(s) s^2 ds \\ &= 0.22 \phi Pe D \hat{\mathbf{E}}, \end{aligned}$$

where  $x_{11}^a(s)$  and  $y_{11}^a(s)$  are mobility functions defined in Kim & Karrila (1991). Thus, we find

$$D_0^s = D_0^s(\phi) I + 0.22 \phi Pe \hat{\mathbf{E}} + O(\phi^2, Pe^2), \quad (41)$$

with  $D_0^s$  given by (40); the  $O(\phi Pe)$  correction has been available since the work of Batchelor (1977) to evaluate the microstructural distortion by a weak straining flow.

#### 4.2. The long-time self-diffusivity in a dilute suspension: no hydrodynamics

To determine the long-time self-diffusivity we need the limit as  $t \rightarrow \infty$ , or only the steady solution, for  $f_N$ . The analysis is simplest if we consider separately the cases with and without hydrodynamic interactions. In the absence of hydrodynamics the analytical analysis is considerably simplified, although the general features are the same in the two cases. Here, the case without hydrodynamic interactions is studied; hydrodynamic interactions are treated in §4.3. A suspension without hydrodynamic interactions can be realized with particles interacting through a long-range repulsive force. If the repulsive force is hard-sphere-like, with characteristic length  $b \gg a$ , then the following analysis will apply with all lengths scaled by  $b$  instead of  $a$ , except in the isolated particle diffusivity;  $D$  remains  $k_B T / 6\pi\eta a$  because it is the hydrodynamic radius  $a$  that sets the single-particle diffusivity.

##### 4.2.1. Closure for $f$

For small particle fraction, we assume  $g^{eq} = 1$  and the nonlinear averages appearing in (31) are approximated as

$$\begin{aligned} \langle \mathbf{U}_r \cdot \nabla f_N \rangle_2^0 &\approx \dot{\mathbf{I}} \cdot \mathbf{r} \cdot \nabla f, \\ \langle \mathbf{D}_r \cdot \nabla \bar{V} \cdot \nabla f_N \rangle_2^0 &\approx \nabla(\ln g + \langle V \rangle_2^0) \cdot \nabla f = Pe \nabla p \cdot \nabla f, \\ \langle \mathbf{D}_r \cdot \nabla f_N \rangle_2^0 &\approx \nabla f, \end{aligned}$$

with an error of  $O(\phi)$  in each case; a similar small error is incurred by neglecting the integral over  $r_3$ . With averaging again implicit, the steady form of (31) and associated

boundary conditions are given by

$$\nabla \cdot (1 + Pe p) \nabla f - Pe (\dot{\mathbf{I}} \cdot \mathbf{r} - \nabla p) \cdot \nabla f = -Pe \mathbf{i} \mathbf{k} \cdot \nabla p + O(Pe^2), \quad (42a)$$

$$\hat{\mathbf{r}} \cdot \nabla f = -\frac{1}{2} \hat{\mathbf{r}} \cdot \mathbf{i} \mathbf{k} + O(Pe^2) \quad \text{at } r = 2, \quad (42b)$$

$$f \rightarrow 0 \quad \text{as } r \rightarrow \infty. \quad (42c)$$

#### 4.2.2. Asymptotic expansion of $f$

The condition of  $Pe \ll 1$  indicates that advection is weak on the lengthscale of the particle. However, as is usual in problems involving a balance of diffusion with weak advection, it is not a uniformly valid approximation to neglect the flow in the entire domain. In this case of a linear flow, advection balances diffusion for  $r \sim Pe^{-1/2}$ , and we construct  $f$  by matched asymptotic expansions, a method now standard for problems of this type (Proudman & Pearson 1957; Acrivos & Taylor 1962; Leal 1992).

The governing equation for  $f$  is forced by a term linear in  $\mathbf{i} \mathbf{k}$ , and thus we write

$$f = \mathbf{i} \mathbf{k} \cdot \mathbf{b}(r). \quad (43)$$

This defines the wavevector-independent field  $\mathbf{b}$ , which is analogous to the so-called 'B-field' introduced by Brenner (1980). We now write  $\mathbf{b}$  in two separate regions as

$$\mathbf{b} = \mathbf{b}(r), \quad r = O(1),$$

and

$$\mathbf{b} = \mathbf{B}(\mathbf{R}), \quad \mathbf{R} \equiv Pe^{1/2} \mathbf{r} = O(1),$$

which are to be matched in the domain of mutual validity. Both  $\mathbf{b}$  and  $\mathbf{B}$  are expressed as series in  $Pe$ , i.e.

$$\mathbf{b}(r) = \sum_{n=0}^{\infty} h_n(Pe) \mathbf{b}_n(r), \quad \text{and} \quad \mathbf{B}(\mathbf{R}) = \sum_{n=0}^{\infty} H_n(Pe) \mathbf{B}_n(\mathbf{R}).$$

The first three  $h_n$  and  $H_0$  will be seen to be

$$h_0 = 1, \quad h_1 = Pe, \quad h_2 = Pe^{3/2}, \quad \text{and} \quad H_0 = Pe. \quad (44)$$

The leading term of the inner expansion is governed by

$$\nabla^2 \mathbf{b}_0 = 0, \quad \text{and} \quad \hat{\mathbf{r}} \cdot \nabla \mathbf{b}_0 = -\frac{1}{2} \hat{\mathbf{r}} \quad \text{at } r = 2. \quad (45)$$

With  $h_1 = Pe$ , the governing equations at  $O(Pe)$  are

$$\nabla^2 \mathbf{b}_1 = (\dot{\mathbf{I}} \cdot \mathbf{r} - 2\nabla p) \cdot \nabla \mathbf{b}_0 - \nabla p, \quad \text{and} \quad \hat{\mathbf{r}} \cdot \nabla \mathbf{b}_1 = 0 \quad \text{at } r = 2. \quad (46)$$

The far-field conditions on  $\mathbf{b}_0$  and  $\mathbf{b}_1$  are those of matching with the outer solution. Here, and at many later points, it is more convenient to maintain the analysis in terms of a general  $\dot{\mathbf{I}}$ ; when it is necessary to be specific, the dimensionless velocity gradient will be for simple-shear flow  $\dot{\mathbf{I}}_{ij} = \delta_{i1} \delta_{j2}$ .

The solution to (45) is

$$\mathbf{b}_0 = \frac{2\hat{\mathbf{r}}}{r^2}, \quad (47)$$

where a constant (in  $r$ ) vector solution is set to zero to agree with the known solution for  $Pe \equiv 0$ . Inserting  $\mathbf{b}_0$  and  $p$  into (46) yields

$$\nabla^2 \mathbf{b}_1 = 2\hat{\mathbf{\Omega}} \cdot \hat{\mathbf{r}} r^{-2} + \hat{\mathbf{E}} \cdot \hat{\mathbf{r}} \left( 2r^{-2} + \frac{64}{3} r^{-4} + \frac{256}{3} r^{-7} \right)$$

$$+ \hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}} \hat{\mathbf{r}} \left( -6r^{-2} - \frac{160}{3}r^{-4} + \frac{512}{3}r^{-7} \right),$$

which has the particular solution

$$b_{1,k}^p = -\hat{\Omega}_{kj} \hat{\mathbf{r}}_j + \hat{\mathbf{r}}_i \hat{E}_{ij} \hat{\mathbf{r}}_j \hat{\mathbf{r}}_k \left( \frac{1}{2} + \frac{16}{3r^2} + \frac{64}{3r^5} \right),$$

where  $\hat{\Omega}_{ij} = (\Gamma_{ij} - \Gamma_{ji})/2\dot{\gamma}$  is the dimensionless vorticity tensor. The harmonic homogeneous solution is determined by application of the boundary condition at  $r = 2$  to yield the complete  $\mathbf{b}_1$ ,

$$b_{1,k} = \hat{\mathbf{r}}_i \hat{E}_{ij} \hat{\mathbf{r}}_j \hat{\mathbf{r}}_k \left( \frac{1}{2} + \frac{16}{3}r^{-2} - 24r^{-4} + \frac{64}{3}r^{-5} \right) + \hat{E}_{kj} \hat{\mathbf{r}}_j \left( -\frac{36}{5}r^{-2} + \frac{72}{5}r^{-4} \right) - \hat{\Omega}_{jk} \hat{\mathbf{r}}_j. \tag{48}$$

Proceeding to a consideration of the outer expansion, the choice of  $H_0 = Pe$  is now clear, because  $\mathbf{b}_0$  and part of  $Pe\mathbf{b}_1$  are  $O(Pe)$  for  $r = O(Pe^{-1/2})$ . The leading term in the outer expansion satisfies

$$\bar{\nabla}^2 \mathbf{B}_0 - Y \frac{\partial \mathbf{B}_0}{\partial X} = 0, \quad \text{and} \quad \mathbf{B}_0 \rightarrow 0 \quad \text{as} \quad R \rightarrow \infty, \tag{49}$$

where  $\bar{\nabla}$  denotes the gradient with respect to  $\mathbf{R} = (X, Y, Z)$ ;  $\mathbf{B}_0$  must match the inner solution as  $R \rightarrow 0$ . We construct  $\mathbf{B}_0$  using the solution for an instantaneous point source in the simple shear flow, which satisfies

$$\frac{\partial G}{\partial t} - \bar{\nabla}^2 G + Y \frac{\partial G}{\partial X} = 4\pi\delta(\mathbf{R})\delta(t), \tag{50}$$

and was given by Elrick (1962) as

$$G(\mathbf{R}, t) = \frac{1}{2\pi^{1/2} t^{3/2} (1 + t^2/12)^{1/2}} \exp \left[ -\frac{(X - Yt/2)^2}{4t(1 + t^2/12)} - \frac{(Y^2 + Z^2)}{4t} \right]. \tag{51}$$

The inner solution to be matched is a  $Y$ -directed dipole, requiring that

$$\begin{aligned} \mathbf{B}_0(\mathbf{R}) &= -\alpha_d \int_0^\infty \left( \bar{\nabla} + t\mathbf{1}_Y \frac{\partial}{\partial X} \right) G(\mathbf{R}, t) dt \\ &= -\frac{\alpha_d}{2\pi^{1/2}} \int_0^\infty V(\mathbf{R}, t) \frac{e^{-R^2/4t} e^{\mathcal{E}}}{t^{3/2} (1 + t^2/12)^{1/2}} dt, \end{aligned} \tag{52}$$

where  $\alpha_d$  denotes the coefficient of the  $r^{-2}$  dependence of the inner solution (i.e. the dipole strength) and  $\mathcal{E}$  is given by

$$\mathcal{E}(X, Y, t) = \frac{(X^2 - 3Y^2)t/12 + XY}{4(1 + t^2/12)}. \tag{53}$$

The components of  $V(\mathbf{R}, t)$  are

$$V_X = -\frac{X}{2t} + \frac{Y + Xt/6}{4(1 + t^2/12)}, \quad V_Y = -\frac{Y}{2t} + \frac{-X + Yt/2}{4(1 + t^2/12)}, \quad \text{and} \quad V_Z = -\frac{Z}{2t}.$$

The solution (52) agrees with the dipole solution of Blawdziewicz & Szamel (1993), who have given the solution to the steady advection-diffusion equation for simple shear flow and general dipolar forcing. The operator

$$\bar{\nabla} + t\mathbf{1}_Y \partial / \partial X,$$

which is the gradient in the frame following the deformation of the material, commutes with the operator on the left-hand side of (50).

We see from the inner solution that  $\alpha_d = 2$ , and thus the asymptotic form of  $\mathbf{B}_0$  as  $R \rightarrow 0$  needed for matching to the inner solution is given by

$$\mathbf{B}_0 \sim \mathbf{R}(2R^{-3} + A_1) - \hat{\boldsymbol{\Omega}} \cdot \mathbf{R}(R^{-1} + A_2) + \frac{1}{2}R^{-3}\mathbf{R} \cdot \hat{\mathbf{E}} \cdot \mathbf{R}\mathbf{R} + O(R^2), \quad (54)$$

where

$$A_1 = \frac{1}{2\pi^{1/2}} \int_0^\infty \frac{1 - (1 + t^2/12)^{1/2}}{t^{5/2}(1 + t^2/12)^{1/2}} dt = -\frac{0.192}{2\pi^{1/2}}, \quad (55)$$

and

$$A_2 = \frac{1}{2\pi^{1/2}} \int_0^\infty \frac{1 - (1 + t^2/12)^{1/2}}{t^{3/2}(1 + t^2/12)^{3/2}} dt = -\frac{1.37}{2\pi^{1/2}}. \quad (56)$$

In inner variables, terms of (54) which are linear in  $R$  generate terms in  $H_0\mathbf{B}_0$  proportional to  $rPe^{3/2}$  which cannot be matched by  $h_0\mathbf{b}_0 + h_1\mathbf{b}_1$ . Thus,  $h_2 = Pe^{3/2}$ , and the governing equation and boundary condition for  $\mathbf{b}_2$  are homogeneous:

$$\nabla^2 \mathbf{b}_2 = 0, \quad \text{and} \quad \hat{\mathbf{r}} \cdot \nabla \mathbf{b}_2 = 0 \quad \text{at} \quad r = 2. \quad (57)$$

From the matching condition, we deduce that  $\mathbf{b}_2$  is a combination of harmonic solutions linear in  $r$ :

$$\mathbf{b}_2 = \mathbf{r}(a_1 + a_3r^{-3}) + \hat{\boldsymbol{\Omega}} \cdot \mathbf{r}(a_2 + a_4r^{-3}).$$

Application of the matching and boundary conditions yields

$$a_1 = A_1, \quad a_2 = A_2, \quad a_3 = 4A_1, \quad \text{and} \quad a_4 = 4A_2.$$

This completes the solution of  $\mathbf{b}$  to  $O(Pe^{3/2})$  in the absence of hydrodynamic interactions.

#### 4.2.3. Evaluation of the long-time self-diffusivity

Consistent with the closure of the equation for  $f$ , for small  $\phi$  we neglect correlations in (35). Inserting  $f = i\mathbf{k} \cdot \mathbf{b}$  and rearranging, we obtain

$$\begin{aligned} (\ln F_s) &= 2Pe(\mathbf{k} \cdot \hat{\Gamma} \cdot \nabla_k \ln F_s + i\mathbf{k} \cdot \langle U_1 \rangle^0) - \mathbf{k} \cdot \mathbf{D}_0^s \cdot \mathbf{k} \\ &\quad - \phi \frac{3}{4\pi} \mathbf{k}\mathbf{k} : \int (\nabla \mathbf{b} + Pe\mathbf{b}\nabla p)g(\mathbf{r})d\mathbf{r} + O(k^3, Pe^2). \end{aligned} \quad (58)$$

Thus, to  $O(Pe^2)$  the long-time self-diffusivity in the dilute limit is given by

$$\begin{aligned} \mathbf{D}_\infty^s &= \mathbf{D}_0^s + \phi \frac{3}{4\pi} \int (\nabla \mathbf{b} + Pe\mathbf{b}\nabla p)g(\mathbf{r})d\mathbf{r}, \\ &= \mathbf{D}_0^s + \phi \frac{3}{4\pi} \int \nabla[(1 + Pe p)\mathbf{b}]d\mathbf{r}, \end{aligned}$$

where we have made use of the perturbation to the steady microstructure. Integrating by parts and inserting the expansion for  $\mathbf{b}$  to  $O(Pe^{3/2})$  we have

$$\mathbf{D}_\infty^s = \mathbf{D}_0^s - \phi \frac{3}{\pi} \left[ \oint_{r=2} \hat{\mathbf{r}}\mathbf{b}_0 d\Omega + Pe \oint_{r=2} \hat{\mathbf{r}}(\mathbf{b}_0 p + \mathbf{b}_1) d\Omega + Pe^{3/2} \oint_{r=2} \hat{\mathbf{r}}\mathbf{b}_2 d\Omega \right], \quad (59)$$

where  $d\Omega$  is the element of solid angle.

From the solutions for  $\mathbf{b}$  we have

$$\begin{aligned}\oint_{r=2} \hat{\mathbf{r}} \mathbf{b}_0 d\Omega &= \frac{2\pi}{3} \mathbf{I}, \\ \oint_{r=2} \hat{\mathbf{r}} (\mathbf{b}_0 p + \mathbf{b}_1) d\Omega &= \frac{16\pi}{45} \hat{\mathbf{E}} + \frac{2\pi}{3} \hat{\mathbf{E}}, \\ \oint_{r=2} \hat{\mathbf{r}} \mathbf{b}_2 d\Omega &= -\frac{12\pi}{3} A_1 \mathbf{I},\end{aligned}$$

giving a long-time self-diffusivity in dimensional form of

$$\mathbf{D}_\infty^s = D[(1 - 2\phi)\mathbf{I} + \frac{46}{15}\phi Pe \hat{\mathbf{E}} + 0.65\phi Pe^{3/2}\mathbf{I}] + O(\phi^2, Pe^2), \quad (60)$$

using the numerical value  $A_1 \approx -0.054$ . The  $O(Pe^{3/2})$  term is valid only for simple-shear flow, while the  $O(Pe)$  term is valid for a general linear flow.

In integrating by parts to obtain (59) we have neglected the surface integral at infinity. Since the dipolar solution  $\mathbf{b}_0$  decays as  $r^{-2}$ , neglecting this surface integral needs to be justified. That it is proper to discard this integral can be seen by noting that the small- $k$  expansion of the governing equation for  $f_N$ , (29), is not valid when  $r \sim k^{-1}$ . There is an outer region where the  $O(k^2)$  term,  $\mathbf{i}\mathbf{k} \cdot \nabla f_N$ , from the right-hand side of (26) cannot be neglected. Here  $\mathbf{i}\mathbf{k}$  acts like a uniform velocity and, as is common in all problems of diffusion and weak uniform advection, this outer region changes the decay from being algebraic to exponential, thus justifying the neglect of the surface integral at large  $r$ .

#### 4.3. The long-time self-diffusivity in a dilute suspension: hydrodynamics

We now turn to the problem for the long-time self-diffusivity with hydrodynamic interactions. The analysis proceeds much as before. The only qualitatively new feature is the presence of hydrodynamic velocity fluctuations as a source of diffusive behaviour.

##### 4.3.1. Closure for $f$

With hydrodynamic interactions the nonlinear averages appearing in (31) are approximated as

$$\begin{aligned}\langle \mathbf{U}_r \cdot \nabla f_N \rangle_2^0 &\approx \langle \mathbf{U}_r \rangle_2^0 \cdot \nabla f, \\ \langle \mathbf{D}_r \cdot \nabla \bar{V} \cdot \nabla f_N \rangle_2^0 &\approx \langle \mathbf{D}_r \rangle_2^0 \cdot \nabla (\ln g + \langle V \rangle_2^0) \cdot \nabla f = Pe \langle \mathbf{D}_r \rangle_2^0 : \nabla p \nabla f, \\ \langle \mathbf{D}_r \cdot \nabla f_N \rangle_2^0 &\approx \langle \mathbf{D}_r \rangle_2^0 \cdot \nabla f,\end{aligned}$$

with the same  $O(\phi)$  errors as before. The steady form of (31) and associated boundary conditions are now given by

$$\begin{aligned}\nabla \cdot [\mathbf{D}_r (1 + Pe p) \cdot \nabla f] - Pe (\mathbf{U}_r - \mathbf{D}_r \cdot \nabla p) \cdot \nabla f \\ = \frac{1}{2} \mathbf{i}\mathbf{k} \cdot [Pe (\mathbf{U}_r' - 2\mathbf{D}_r \cdot \nabla p) - (1 + Pe p) \nabla \cdot \mathbf{D}_r] + O(Pe^2),\end{aligned} \quad (61a)$$

$$\hat{\mathbf{r}} \cdot \mathbf{D}_r \cdot \nabla f = 0 \quad \text{at } r = 2 \quad (61b)$$

$$f \rightarrow 0 \quad \text{as } r \rightarrow \infty. \quad (61c)$$

##### 4.3.2. Asymptotic expansion of $f$

The asymptotic expansion of  $f = \mathbf{i}\mathbf{k} \cdot \mathbf{b}$  with hydrodynamic interactions proceeds as before with the same inner and outer regions and the same scale functions (44). In

the inner region, the leading-order governing equations are

$$\nabla \cdot (\mathbf{D}_r \cdot \nabla \mathbf{b}_0) = -\frac{1}{2} \nabla \cdot \mathbf{D}_r, \quad \text{and} \quad \hat{\mathbf{r}} \cdot \mathbf{D}_r \cdot \nabla \mathbf{b}_0 = 0 \quad \text{at} \quad r = 2. \quad (62)$$

At  $O(Pe)$ ,  $\mathbf{b}_1$  is governed by

$$\nabla \cdot (\mathbf{D}_r \cdot \nabla \mathbf{b}_1) = (U_r - 2\mathbf{D}_r \cdot \nabla p) \cdot \nabla \mathbf{b}_0 + \frac{1}{2} U'_r - \mathbf{D}_r \cdot \nabla p, \quad (63a)$$

$$\text{and} \quad \hat{\mathbf{r}} \cdot \mathbf{D}_r \cdot \nabla \mathbf{b}_1 = 0 \quad \text{at} \quad r = 2. \quad (63b)$$

Because the relative diffusivity varies spatially and the relative velocity deviates from  $\hat{\mathbf{r}} \cdot \mathbf{r}$ , solutions are not available in closed form and in the inner region must be determined numerically. However, the basic findings with regard to the influence of shear upon the long-time self-diffusivity for hydrodynamically non-interacting particles are unchanged by hydrodynamics: the leading influence of the flow upon the diffusion tensor is  $O(\phi Pe)$  and mirrors the geometry of the rate of strain; the next dependence is  $O(\phi Pe^{3/2})$ .

At large  $r$ ,  $\mathbf{D}_r \sim \mathbf{I}$  and  $\nabla_r \cdot \mathbf{D}_r$  scales as  $r^{-5}$ , so that the particular solution to (63) is proportional to  $r^{-3}$ , while the homogeneous solution is dipolar and thus proportional to  $r^{-2}$ . Including the first variation of  $\mathbf{D}$  at large  $r$ ,

$$G = 1 - \frac{3}{2}r^{-1} + O(r^{-3}) \quad \text{and} \quad H = 1 - \frac{3}{4}r^{-1} + O(r^{-3}),$$

where  $G$  and  $H$  are known functions of  $r$  defined by (Batchelor 1976)

$$\mathbf{D}_r = G(r)\hat{\mathbf{r}}\hat{\mathbf{r}} + H(r)(\mathbf{I} - \hat{\mathbf{r}}\hat{\mathbf{r}}),$$

we find

$$\mathbf{b}_0 = \hat{\mathbf{r}}b_0(r) \sim \hat{\mathbf{r}} \left( \frac{\alpha_d}{r^2} + \frac{9\alpha_d - 15}{8r^3} \right), \quad (64)$$

which satisfies (62) to terms in  $r^{-5}$ . The coefficient  $\alpha_d$  (recall that  $\alpha_d$  denotes the strength of the dipole created by the pair interaction) must be chosen so that a logarithmically divergent term in the general solution at  $r = 2$  vanishes; the appropriate value is found by trial to be  $\alpha_d = 1.07$ , which differs from the value of 2 for the coefficient of  $r^{-2}$  in the equivalent problem without hydrodynamics. The solution for  $b_0(r)$  is presented in figure 1. This combined asymptotic and numerical procedure, which was outlined by Batchelor (1977) for the determination of the microstructural distortion  $p$  defined by (36) of the present work, is used also for the solution of the other problems in the inner region.

The homogeneous outer solution  $\mathbf{B}_0^h$  satisfies the same governing equation as in the absence of hydrodynamics, and the solution differs only through the magnitude of the induced dipole. The fluctuation velocity  $U'_r$  caused by the force dipoles (stresslets) of the particles is proportional to  $r^{-2}$  and thus the leading-order outer problem is inhomogeneous,

$$-\bar{\nabla}^2 \mathbf{B}_0 + Y \frac{\partial \mathbf{B}_0}{\partial X} = -\frac{1}{2} U'_r(\mathbf{R}); \quad (65)$$

it is only the dominant portion of  $U'_r$  that enters the outer problem at leading order in  $Pe$ , i.e. (Batchelor & Green 1972)

$$U'_r \sim -5\hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}\hat{\mathbf{r}}^{-2} = -5Pe\hat{\mathbf{R}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{R}}\hat{\mathbf{R}}^{-2}. \quad (66)$$

The particular solution to (65) is constructed by weighting the Green's function for

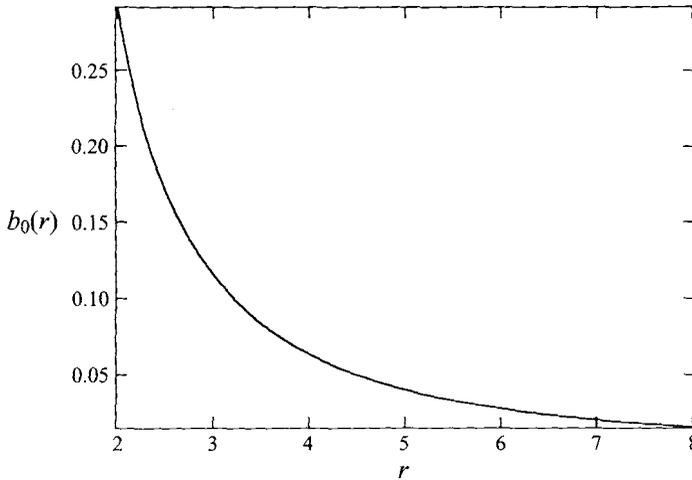


FIGURE 1. The function  $b_0(r)$  specifying the radial dependence of  $\mathbf{b}_0$ .

the problem, given by (51) integrated over  $t$ , by  $U'_r/2$  to yield

$$\mathbf{B}_0^p(\mathbf{R}) = -\frac{1}{2} \frac{1}{4\pi} \int U'_r(\mathbf{S}) \int_0^\infty G(\mathbf{R} - \mathbf{S}, t) dt d\mathbf{S}. \tag{67}$$

To completely determine the solution in the inner region up to and including terms of  $O(Pe^{3/2})$ , we insert  $G$  (given by (51)) and the leading term of  $U'_r$  into (67), and expand for small  $R$  to obtain

$$\begin{aligned} B_i^p(\mathbf{R}) &\sim \frac{5}{16\pi^{3/2}} E_{jk} \int \frac{S_i S_j S_k}{S^5} d\mathbf{S} \int_0^\infty t^{-3/2} e^{-R-S^2/4t} dt + O(R^2) \\ &\sim \frac{5}{8\pi} E_{jk} \int \frac{S_i S_j S_k}{S^5 |\mathbf{R} - \mathbf{S}|} d\mathbf{S} + O(R^2). \end{aligned} \tag{68}$$

The integral of (68) may be evaluated by observing that it is of the form

$$\int \frac{y_i y_j y_k}{y^5 |\mathbf{x} - \mathbf{y}|} d\mathbf{y} = C_1 (\delta_{ij} \hat{\mathbf{x}}_k + \delta_{ik} \hat{\mathbf{x}}_j + \delta_{jk} \hat{\mathbf{x}}_i) + C_2 \hat{\mathbf{x}}_i \hat{\mathbf{x}}_j \hat{\mathbf{x}}_k.$$

Contracting the integral with  $\hat{\mathbf{i}}\hat{\mathbf{x}}$  and  $\hat{\mathbf{x}}\hat{\mathbf{x}}\hat{\mathbf{x}}$  yields two equations which may be solved to find  $C_1 = C_2 = \pi/3$ .

The homogeneous  $\mathbf{B}_0^h$  is obtained by multiplying  $\mathbf{B}_0$  determined in the absence of hydrodynamics, given in asymptotic form for small  $R$  by (54), by  $\alpha_d/2$  to account for the different dipole strength in the problem with hydrodynamic interactions. Thus, the complete outer solution asymptotes to

$$\begin{aligned} \mathbf{B}_0 &\sim \frac{\alpha_d}{2} \mathbf{R} (2R^{-3} + A_1) - \frac{\alpha_d}{2} \hat{\boldsymbol{\Omega}} \cdot \mathbf{R} (R^{-1} + A_2) \\ &\quad + \left( \frac{\alpha_d}{4} + \frac{5}{24} \right) R^{-3} \mathbf{R} \cdot \hat{\mathbf{E}} \cdot \mathbf{R} \mathbf{R} + \frac{5}{12} R^{-1} \hat{\mathbf{E}} \cdot \mathbf{R} + O(R^2), \end{aligned} \tag{69}$$

where  $A_1$  and  $A_2$  are given by (55) and (56), respectively. Because the remainder in (68) is  $O(R^2)$ , the  $O(Pe^{3/2})$  inner solution  $h_2 \mathbf{b}_2$  will match only with terms from the homogeneous outer solution, and is identical in functional form to, but differs in magnitude from, the corresponding solution found when hydrodynamic interactions are neglected.

Consideration of the forcing of (63) indicates that  $\mathbf{b}_1$  may be written

$$\mathbf{b}_1 = M_1(r)\hat{\mathbf{r}} \cdot \hat{\mathbf{E}} \cdot \hat{\mathbf{r}}\hat{\mathbf{r}} + M_2(r)\hat{\mathbf{E}} \cdot \hat{\mathbf{r}} + M_3(r)\hat{\mathbf{\Omega}} \cdot \hat{\mathbf{r}}, \quad (70)$$

with the  $M_i(r)$  satisfying

$$\begin{aligned} \frac{d}{dr} \left( r^2 G \frac{dM_1}{dr} \right) - 12HM_1 &= r^2 L_1(r), \\ \frac{d}{dr} \left( r^2 G \frac{dM_2}{dr} \right) - 2HM_2 &= r^2 L_2(r) - 4H(r)M_1, \\ \frac{d}{dr} \left( r^2 G \frac{dM_3}{dr} \right) - 2HM_3 &= r^2 b_0(r), \end{aligned}$$

where

$$\begin{aligned} L_1 = -(1-B)b_0 + (1+B-A)rb'_0 + \frac{(B-A)r}{2} \\ + 2[Gb'_0q' - \frac{2Hb_0q}{r^2}] + Gq' - \frac{2Hq}{r}, \end{aligned}$$

and

$$L_2 = \left[ 1 - B + \frac{2Hq}{r^2} \right] b_0 - \frac{Br}{2} + \frac{2Hq}{r}.$$

At large  $r$ , we find the asymptotic solutions

$$\begin{aligned} M_1(r) &\sim \frac{\alpha_d}{4} + \frac{5}{24} + \frac{18\alpha_d - 25}{32r}, \\ M_2(r) &\sim \frac{5}{12} + \frac{3\alpha_d}{16r}, \\ M_3(r) &\sim -\frac{\alpha_d}{2} + \frac{15}{16r}(1 - \alpha), \end{aligned}$$

whose constant portions match with the small- $R$  asymptote (69) of the outer solution  $\mathbf{B}_0$ . Starting at large  $r$  ( $r = 10$ ) and integrating back to  $r = 2$  yields a complete solution for  $\mathbf{b}_1$ ; small additive corrections to the asymptotic solutions determined by trial were sufficient to determine the solution which satisfies the boundary condition at contact. The solution curves for  $M_1$ ,  $M_2$ , and  $M_3$  are presented in figure 2(a-c), respectively.

The equation and boundary condition for  $\mathbf{b}_2$  are homogeneous,

$$\nabla \cdot (\mathbf{D}_r \cdot \nabla \mathbf{b}_2) = 0, \quad \text{and} \quad \hat{\mathbf{r}} \cdot \mathbf{D}_r \cdot \nabla \mathbf{b}_2 = 0 \quad \text{at} \quad r = 2. \quad (71)$$

Because  $\mathbf{b}_2$  matches with terms of (69) which are linear in  $R$ , it may be written

$$\mathbf{b}_2 = N_1(r)\hat{\mathbf{r}} + N_2(r)\hat{\mathbf{\Omega}} \cdot \hat{\mathbf{r}}, \quad (72)$$

where, as  $r \rightarrow \infty$ ,

$$N_1 \sim \frac{\alpha_d}{2} a_1 r, \quad \text{and} \quad N_2 \sim \frac{\alpha_d}{2} a_3 r,$$

with the next terms constant in  $r$ . This asymptotic solution was used as an estimate of the solution to start integration of the equation toward  $r = 2$  from large  $r$ . Small additive corrections found by trial were sufficient to satisfy the boundary condition at contact. The solutions determined for  $N_1$  and  $N_2$  are presented in figure 3(a-b).

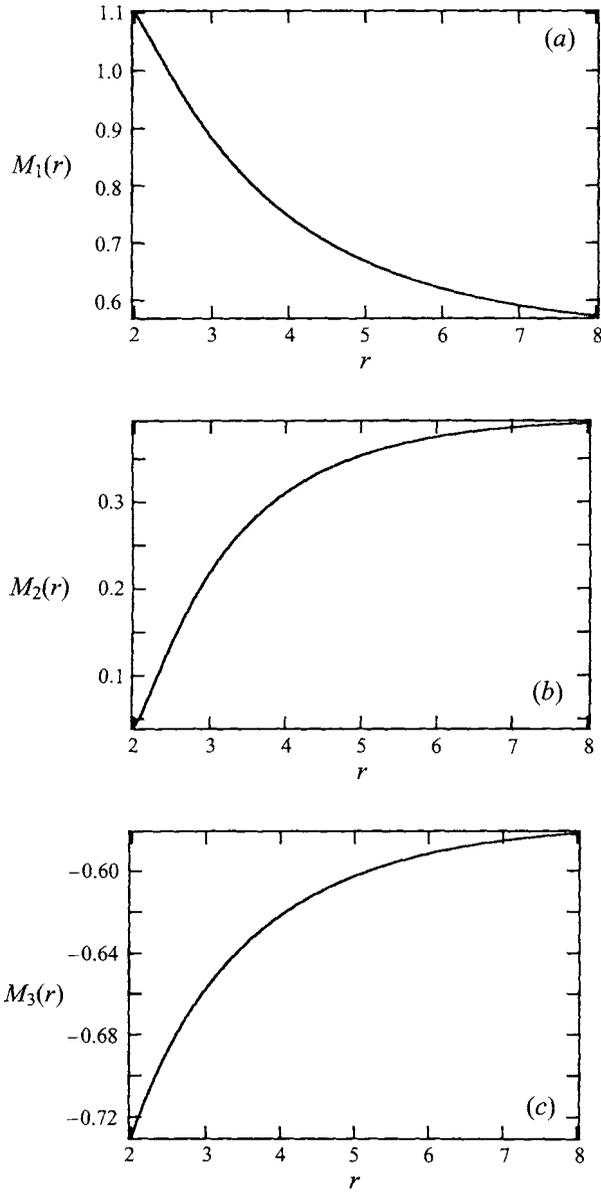


FIGURE 2. The functions (a)  $M_1(r)$ , (b)  $M_2(r)$ , and (c)  $M_3(r)$  specifying the radial dependence of  $\mathbf{b}_1$ .

4.3.3. *Evaluation of the long-time self-diffusivity*

Including hydrodynamic interactions and taking  $g^{eq} = 1$ , the equation to determine the long-time self-diffusivity, (35), becomes

$$\begin{aligned}
 (\ln F_s) &= 2Pe(\mathbf{k} \cdot \dot{\Gamma} \cdot \nabla_{\mathbf{k}} \ln F_s + i\mathbf{k} \cdot \langle U_1 \rangle^0) - \mathbf{k} \cdot \mathbf{D}_0^s \cdot \mathbf{k} \\
 &+ \phi \frac{3}{4\pi} \mathbf{k} \mathbf{k} : \int \mathbf{D}_r \cdot \nabla \mathbf{b} \, d\mathbf{r} + \phi \frac{3}{4\pi} Pe \mathbf{k} \mathbf{k} : \int \nabla \cdot [\mathbf{D}_r, p \mathbf{b}] \, d\mathbf{r} \\
 &- \phi \frac{3}{4\pi} Pe \mathbf{k} \mathbf{k} : \int [2U'_r + p \nabla \cdot \mathbf{D}_r] \mathbf{b} \, d\mathbf{r} + O(k^3, Pe^2).
 \end{aligned}
 \tag{73}$$

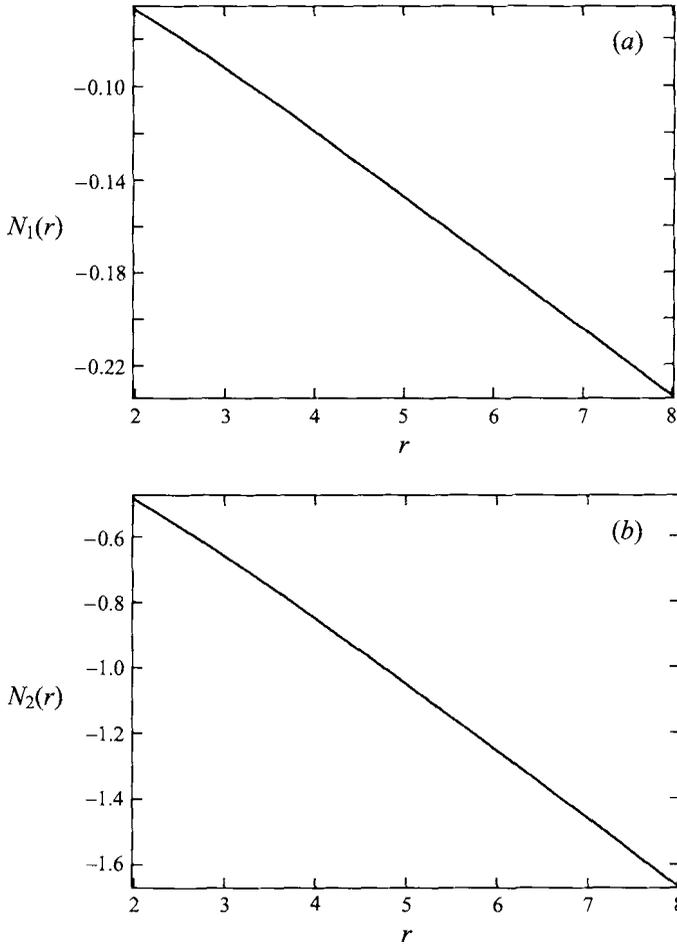


FIGURE 3. The functions (a)  $N_1(r)$ , and (b)  $N_2(r)$  specifying the radial dependence of  $\mathbf{b}_2$ .

Hence, the long-time self-diffusivity with hydrodynamic interactions is given by

$$\begin{aligned} \mathbf{D}_\infty^s = & \mathbf{D}_0^s + \phi \frac{3}{4\pi} \int \mathbf{D}_r \cdot \nabla \mathbf{b} \, d\mathbf{r} + \phi \frac{3}{4\pi} Pe \int \nabla \cdot [\mathbf{D}_r, p \mathbf{b}] \, d\mathbf{r} \\ & - \phi \frac{3}{4\pi} Pe \int [2U'_r + p \nabla \cdot \mathbf{D}_r] \mathbf{b} \, d\mathbf{r}. \end{aligned}$$

The first two integrals on the right-hand side can be integrated by the divergence theorem. The surface integral at infinity is discarded as discussed before, and since with hydrodynamic interactions  $\hat{\mathbf{r}} \cdot \mathbf{D}_r = 0$  at contact, the contact contribution is zero. Thus, the long-time self-diffusivity reduces to

$$\mathbf{D}_\infty^s = \mathbf{D}_0^s - \phi \frac{3}{4\pi} \int (1 + Pe p) \mathbf{b} \nabla \cdot \mathbf{D}_r \, d\mathbf{r} - \phi \frac{3}{2\pi} Pe \int U'_r \mathbf{b} \, d\mathbf{r}. \quad (74)$$

We first consider the particle-fraction dependence of  $\mathbf{D}_\infty^s$  for  $Pe \equiv 0$ , which requires knowledge of  $\mathbf{b}_0$  only. Batchelor (1976, 1982) found  $\mathbf{D}_\infty^s = (1 - 2.10\phi)\mathbf{I}$ , for  $\phi \ll 1$ . Rallison & Hinch (1986) obtained  $\mathbf{D}_\infty^s = (1 - 2.06\phi)\mathbf{I}$  using improved hydrodynamic functions (Jeffrey & Onishi 1984). Here, it is determined as the correlation of  $\mathbf{b}_0$ , the

$\mathbf{b}$ -field at  $Pe = 0$ , with the divergence of  $\mathbf{D}_r$ ,

$$\nabla \cdot \mathbf{D} \equiv \hat{r} Z(r), \quad \text{where} \quad Z(r) = G'(r) + 2 \frac{G(r) - H(r)}{r},$$

and is calculated as

$$\phi \frac{3}{4\pi} \int \mathbf{b}_0(\mathbf{r}) \hat{r} Z(r) d\mathbf{r} = -0.24\phi \mathbf{I}.$$

This result sums with  $\mathbf{D}_0^s$  given by (40) to yield in dimensional form

$$\mathbf{D}_\infty^s = D(1 - 2.07\phi)\mathbf{I}, \tag{75}$$

a result sufficiently close to previous findings to provide confidence in the accuracy of the hydrodynamic data employed.

The first advective effects on the diffusivity arise from the correlation of  $\mathbf{b}$  with  $\nabla \cdot \mathbf{D}_r$  in (74):

$$\begin{aligned} -\phi \frac{3}{4\pi} Pe \int Z(r) p(r) \hat{r} \mathbf{b}_0(\mathbf{r}) d\mathbf{r} &= \frac{2}{5} \phi Pe \hat{\mathbf{E}} \int_2^\infty Z(s) q(s) b_0(s) s^2 ds \\ &= 0.09\phi Pe \hat{\mathbf{E}}; \end{aligned} \tag{76}$$

$$\begin{aligned} -\phi \frac{3}{4\pi} Pe \int Z(r) \hat{r} \mathbf{b}_1(\mathbf{r}) d\mathbf{r} &= -\phi Pe \hat{\mathbf{E}} \int_2^\infty Z(s) \left[ \frac{2}{5} M_1(s) + M_2(s) \right] s^2 ds \\ &= -0.75\phi Pe \hat{\mathbf{E}}; \end{aligned} \tag{77}$$

and

$$\begin{aligned} -\phi \frac{3}{4\pi} Pe^{3/2} \int Z(r) \hat{r} \mathbf{b}_2(\mathbf{r}) d\mathbf{r} &= -\phi Pe^{3/2} \mathbf{I} \int_2^\infty Z(s) N_1(s) s^2 ds \\ &= 0.13\phi Pe^{3/2} \mathbf{I}. \end{aligned} \tag{78}$$

At large  $s$ ,  $\mathbf{b}_1(s)$  and  $\mathbf{b}_2(s)$  are constant and linear in  $s$ , respectively, while  $Z(s) \sim 15s^{-5}$ ; thus, the integrals converge.

Contributions to  $\mathbf{D}_\infty^s$  from the velocity fluctuation correlation integral,

$$-\phi \frac{3}{2\pi} Pe \int U'_r \mathbf{b} d\mathbf{r},$$

are present only when hydrodynamic interactions are considered. We calculate these contributions to  $O(Pe^{3/2})$ . The first is from the integral over the inner region, yielding

$$\begin{aligned} -\phi \frac{3}{2\pi} Pe \int U'_r(\mathbf{r}) \mathbf{b}_0(\mathbf{r}) d\mathbf{r} &= \frac{1}{5} \phi Pe D_0^s \int [2A(s) + 3B(s)] b_0(s) s^3 ds \\ &= 0.96\phi Pe \hat{\mathbf{E}}, \end{aligned} \tag{79}$$

where  $A(s)$  and  $B(s)$  are relative velocity functions defined in Batchelor & Green (1972).

There is also an  $O(\phi Pe^{3/2})$  contribution from integration of  $U' \mathbf{b}$  over the *outer* region. In terms of outer variables, the correlation integral is

$$-Pe \int U'_r(\mathbf{r}) \mathbf{b}(\mathbf{r}) d\mathbf{r} \sim Pe^3 \int U'_r(\mathbf{R}) \mathbf{B}_0(\mathbf{R}) (Pe^{-3/2} d\mathbf{R}) + o(Pe^{3/2});$$

recalling that the velocity fluctuation is proportional to  $r^{-2}$ , which introduces one factor of  $Pe$ , while  $H_0 = Pe$  introduces another, the scaling of an  $O(Pe^{3/2})$  contribution

becomes clear. However, because the contribution to  $\mathbf{D}_\infty^s$  from the correlation of  $\mathbf{U}'$  with  $\mathbf{b}_0$  has already been determined in the inner region, we must integrate

$$\int \mathbf{U}'_r[\mathbf{B}_0 - \mathbf{b}_0(\mathbf{R})]d\mathbf{R},$$

where  $\mathbf{b}_0(\mathbf{R})$  indicates the dipolar  $\mathbf{b}$ -field in the absence of flow expressed in outer variables. To show explicitly the contributions associated with the homogeneous and particular portions of  $\mathbf{B}_0$ , we express the integrations yielding  $O(Pe^{3/2})$  contributions as

$$\mathcal{D}^h = \text{sym} \frac{1}{2} \int \mathbf{U}'_r[\mathbf{B}_0^h - \mathbf{b}_0(\mathbf{R})]d\mathbf{R} \quad \text{and} \quad \mathcal{D}^p = \text{sym} \frac{1}{2} \int \mathbf{U}'_r \mathbf{B}_0^p d\mathbf{R}, \quad (80)$$

where the forms of  $\mathbf{B}_0^h$  and  $\mathbf{B}_0^p$  are given by (52) and (67), respectively. Although neither integral in (80) is symmetric, it is only the symmetric portions which generate diffusive contributions. The 4-fold integration ( $d\mathbf{R}$  and  $dt$ ) for  $\mathcal{D}^h$  and the 7-fold integration ( $d\mathbf{R}$ ,  $d\mathbf{S}$ , and  $dt$ ) for  $\mathcal{D}^p$  were reduced analytically to 2-fold and 3-fold integrations, respectively, with the remaining integrations performed numerically. Reduction of the integrals follows from the observation that the exponential in the solution has the form of a generalized Gaussian, and may, through a time-dependent change of coordinates, be rewritten as a sum of quadratic terms, allowing the spatial integrals to be evaluated; each volume integration requires integration over an introduced parameter, and thus the reduction is not to the time integrals as might be expected.

By symmetry,  $\mathcal{D}_{i3}^{h,p} = \mathcal{D}_{3i}^{h,p} \equiv 0$  for  $i \neq 3$ . We find

$$\mathcal{D}_{11}^h = -\mathcal{D}_{22}^h \approx 6 \times 10^{-5},$$

while the components  $\mathcal{D}_{12}^h$ ,  $\mathcal{D}_{21}^h$ , and  $\mathcal{D}_{33}^h$  are all found to be smaller than  $10^{-10}$ ; thus,  $\mathcal{D}^h$  is essentially zero. The particular integral yields

$$\mathcal{D}^p = \begin{pmatrix} 3.83 & 0.93 & 0 \\ 0.93 & 1.74 & 0 \\ 0 & 0 & 0.39 \end{pmatrix}. \quad (81)$$

Bringing together all the contributions to  $\mathbf{D}_\infty^s$  we have

$$\mathbf{D}_\infty^s = (1 - 2.07\phi)\mathbf{I} + 0.30\phi Pe \hat{\mathbf{E}} + (0.13\mathbf{I} + \mathcal{D}^h + \mathcal{D}^p)\phi Pe^{3/2} + O(\phi^2, Pe^2). \quad (82)$$

Again, the  $O(Pe)$  term is valid for a general linear flow, while the  $O(Pe^{3/2})$  term is restricted to simple-shear flow.

This completes the evaluation of the leading flow-dependent components of the self-diffusivity for  $Pe \ll 1$  and  $\phi \ll 1$ . In the general case, a non-hard-sphere interparticle potential will generate an  $O(Pe)$  and an  $O(Pe^{3/2})$  diffusivity contribution. Proper evaluation of these contributions requires inclusion of the potential-driven flux in the governing equations for  $g$  and  $\mathbf{b}$ .

#### 4.4. Scaling estimate for the long-time self-diffusivity near maximum packing

For concentrated quiescent colloidal dispersions, Brady (1994) presented a self-consistent approach for the prediction of the long-time self-diffusivity. Very good agreement with experiment for all  $\phi$  is obtained by this method which factors the diffusivity into a hydrodynamic and a structural (or thermodynamic) term. The idea behind this approach is the recognition that the appropriate scale for the diffusivity, both in the equation for the perturbation function and the time derivative

of the structure factor, is the short-time self-diffusivity,  $D_0^s(\phi)$ , at the volume fraction of interest, rather than the infinite dilution value  $D$ . Scaling diffusivity by  $D_0^s(\phi)$ , the relative diffusivity of a pair asymptotes to  $\mathbf{I}$  for widely separated particles, regardless of  $\phi$ . This also implies that the appropriate Péclet number is  $\bar{P}e = \dot{\gamma}a^2/2D_0^s(\phi)$ .

To apply the self-consistent method, the perturbation is expressed

$$f_N = \bar{\mathbf{j}}_1 \cdot \bar{\mathbf{b}}, \quad (83)$$

where the constant flux of particle 1, denoted  $\bar{\mathbf{j}}_1$ , is defined by

$$-\mathbf{k} \cdot \bar{\mathbf{D}}_\infty \cdot \mathbf{k} = (\ln F_s) - 2\bar{P}e(\mathbf{k} \cdot \hat{\mathbf{r}} \cdot \nabla_k \ln F_s + i\mathbf{k} \cdot \langle \mathbf{U}_1 \rangle^0) = i\mathbf{k} \cdot \bar{\mathbf{j}}_1. \quad (84)$$

The overbar of  $\bar{\mathbf{D}}_\infty$  denotes normalization with  $D_0^s(\phi)$ . Replacing  $i\mathbf{k}$  on the right-hand side of (31) by  $\bar{\mathbf{j}}_1$  yields a self-consistent equation for  $f_N$ . Following the procedure of Brady (1994), the long-time self-diffusivity can be expressed in terms of  $\bar{\mathbf{b}}$  for the general case as

$$\mathbf{D}_\infty^s = \mathbf{D}_0^s \cdot \left[ \mathbf{I} - \phi \frac{3}{4\pi} \oint_{r=2} \hat{\mathbf{r}} \cdot \bar{\mathbf{D}}_r \bar{\mathbf{b}} g dS - \phi \frac{3}{4\pi} \int \langle [2\bar{P}e \mathbf{U}'_r + \nabla \cdot \bar{\mathbf{D}}_r - \bar{\mathbf{D}}_r \cdot \nabla V] \bar{\mathbf{b}} \rangle_2 g(\mathbf{r}) d\mathbf{r} \right]^{-1}, \quad (85)$$

where an integration by parts has been performed.

For hard spheres without hydrodynamic interactions,  $\mathbf{U}'_r$  and  $\nabla \cdot \bar{\mathbf{D}}_r$  are zero. Because the equilibrium pair-distribution function diverges as  $g^{eq}(2; \phi) \sim 1.2(1 - \phi/\phi_m)^{-1}$  (Woodcock 1981) where  $\phi_m \approx 0.63$  is the maximum packing fraction, the contact integral of (85) dominates as  $\phi \rightarrow \phi_m$ . Thus, only the contact values of  $g^{eq}$ ,  $p$  and  $\mathbf{b}$  are needed to estimate  $\mathbf{D}_\infty^s$ . Using the low- $\phi$  limit of  $\mathbf{b}$ , which Brady (1994) showed provided a good estimate in the quiescent suspension, we have the estimate

$$\mathbf{D}_\infty^s \sim \mathbf{D}_\infty^s(\phi; \bar{P}e = 0) \cdot \left[ \mathbf{I} - \frac{23}{15} \bar{P}e \hat{\mathbf{E}} - 0.325 \bar{P}e^{3/2} \mathbf{I} \right]^{-1}, \quad \text{as } \phi \rightarrow \phi_m,$$

where the long-time self-diffusivity in the absence of flow is given by

$$\mathbf{D}_\infty^s(\phi; \bar{P}e = 0) \approx \frac{\mathbf{D}_0^s}{2\phi g(2; \phi)}.$$

For small  $\bar{P}e$  we can expand the denominator and  $D_0^s(\phi; \bar{P}e)$  from (41) to obtain

$$\mathbf{D}_\infty^s \sim \mathbf{D}_\infty^s(\phi; \bar{P}e = 0) \left[ \mathbf{I} + \frac{23}{15} \bar{P}e \hat{\mathbf{E}} + 0.325 \bar{P}e^{3/2} \mathbf{I} + O(\bar{P}e^2) \right], \quad \text{as } \phi \rightarrow \phi_m. \quad (86)$$

The coefficients of the  $O(\bar{P}e)$  and  $O(\bar{P}e^{3/2})$  terms are approximate, but the general form displayed by (86) is not sensitive to the approximations made. We emphasize that the requirement for the perturbation analysis is now that  $\dot{\gamma}a^2/2D_0^s(\phi) \ll 1$ , which is a severe restriction on the shear rate because  $D_0^s(\phi)$  vanishes near maximum packing for hydrodynamically interacting particles as  $D_0^s(\phi) \sim 0.85(1 - \phi/\phi_m)$  (Phung 1993).

With hydrodynamic interactions, the contact integrals are identically zero as discussed before. However, for large  $\phi$ , Brady (1994) argued that a contact integral again appears because  $\nabla \cdot \bar{\mathbf{D}}_r$  tends to a delta-function at contact as  $\phi \rightarrow \phi_m$ . Thus, the long-time self-diffusivity is given by the estimate (86) whether or not there are hydrodynamic interactions. The effect of hydrodynamic interactions is only through  $D_0^s(\phi)$  and  $\bar{P}e$ .

Unfortunately, there are no data with which to compare the above predictions. Simulation data of Phung *et al.* (1996) and Phung (1993), while at low  $Pe$ , are not at sufficiently low  $\bar{P}e$  to extract the  $\bar{P}e$  dependence. The prediction that for weak flows the long-time self-diffusivity normalized by the long-time self-diffusivity at  $\bar{P}e = 0$  should be a function of  $\bar{P}e$  may be used to collapse the data for all volume fractions onto a single universal curve. The limited data of these simulation studies do seem to conform to this scaling. It would be interesting to see if this prediction is borne out by experiment and if the first correction to the long-time self-diffusivity in the velocity-gradient direction in simple-shear flow behaves as  $\bar{P}e^{3/2}$ .

## 5. Summary and concluding remarks

Using the Fourier-transform method based upon dynamic light scattering, we have developed a theory for the identification and evaluation of the short- and long-time self-diffusion tensors for suspensions in linear flow at arbitrary Péclet number, including also the influence of non-hydrodynamic interparticle and external forces acting upon the particles. The theory was applied here to determine  $\mathbf{D}_0^s$  and  $\mathbf{D}_\infty^s$  in a dilute suspension in weak simple-shear flow, i.e. in the dual limit  $\phi \ll 1$  and  $Pe \ll 1$ . Although our application of the theory in the present work is limited to small-wavevector variations corresponding to disturbances with large spatial extent, the theory is applicable to disturbances of any lengthscale, and thus for any  $\mathbf{k}$ .

Our work demonstrates that relationships between microstructure and the self-diffusivity which were known for quiescent suspensions (Rallison & Hinch 1986; Brady 1994) apply also to sheared suspensions. The microstructure at an ‘initial’ instant (the steady microstructure at the conditions of interest was taken here as the most natural, but by no means the only, choice) and the perturbation to this microstructure caused by the motion of a tagged particle must be determined for the evaluation of  $\mathbf{D}_\infty^s$ , whereas  $\mathbf{D}_0^s$  requires only an average of the particle mobility within the initial microstructure. Generalizing the definition of the perturbation function given by Brady (1994) to apply to linear bulk flows, we have shown that the definitions and formulae relating the self-diffusivity to the self-intermediate scattering function  $F_s$  also hold for non-equilibrium conditions.

The merit of the approach presented here for the diffusivity in flowing suspensions may be appreciated by noting that the coupling of a straining flow with a diffusive spreading leads to a non-diffusive dispersion and the positional variance of a particle will never, at least in certain directions, grow linearly with time. Thus, one cannot identify the self-diffusivity in terms of the growth rate of the variance as is possible for quiescent suspensions. However, the simple identification of the self-diffusivity with the tensor coefficient of the  $O(k^2)$  term in  $\partial \ln F_s / \partial t$  in the Fourier-transform method yields all components of the tensor. In addition to this simple identification, the theory provides a single method for evaluation of the self-diffusivity for all suspension conditions.

We briefly summarize the primary new results. The short-time self-diffusivity is altered from the Stokes–Einstein value of  $D = k_B T / 6\pi\eta a$  when hydrodynamic interactions are considered, with an  $O(\phi Pe)$  correction proportional to  $\hat{\mathbf{E}}$  resulting from the distortion of the steady pair-distribution from spherical symmetry by straining flow (Batchelor 1977) (the next  $Pe$ -dependence of  $g$ , and hence of  $\mathbf{D}_0^s$ , is  $O(Pe^2)$  as shown by Brady & Vicic (1995), but we do not consider corrections beyond  $O(Pe^{3/2})$ ). The long-time self-diffusivity has first corrections of  $O(\phi Pe)$  and  $O(\phi Pe^{3/2})$ , regardless

of whether hydrodynamic interactions are considered. The  $O(\phi Pe)$  contribution is proportional to  $\hat{\mathbf{E}}$  and, like the correction to  $\mathbf{D}_0^s$  of the same order, is valid for arbitrary linear flow, whereas the  $O(\phi Pe^{3/2})$  correction we determine is specific to simple-shear flow. Although  $\mathbf{D}_\infty^s$  will have a correction of  $O(\phi Pe^{3/2})$  in other linear flows, not only the numerical value but also the tensorial character of the contribution will differ. The  $O(\phi Pe^{3/2})$  contribution to  $\mathbf{D}_\infty^s$  is isotropic in the absence of hydrodynamic interactions. When hydrodynamic interactions are included, this contribution is given by the sum of a tensor proportional to  $\hat{\mathbf{E}}$ , with component form in simple shear of  $\hat{E}_{ij} = (\delta_{i1}\delta_{j2} + \delta_{i2}\delta_{j1})/2$ , and a non-isotropic tensor. The  $O(\phi Pe^{3/2})$  self-diffusivity corrections are equivalent in their order with respect to  $\phi$  and  $Pe$  to those found by Leal (1973) for the influence of a weak simple-shear flow upon the cross-stream effective conductivity of a passive scalar in a dilute suspension of spherical drops or rigid particles. We deduce from the analogy between the present problem and that of Leal that correlation of the velocity and temperature disturbances caused by a particle yields an  $O(\phi Pe)$  correction to the effective conductivity proportional to  $\hat{\mathbf{E}}$ .

Flow-dependent corrections to the self-diffusivity as  $\phi \rightarrow \phi_m$  have been shown to follow the same scaling with respect to  $\phi$  as in the case of  $\bar{P}e = 0$ , for sufficiently small  $\bar{P}e$ ; these scalings were obtained using the method developed by Brady (1994) for the determination of the scaling with  $\phi$  in a concentrated suspension which factorizes  $\mathbf{D}_\infty^s$  into a hydrodynamically influenced term, which is simply  $\mathbf{D}_0^s$ , and a microstructural term which can be written as  $(g(2)f(2))^{-1}$  in the general case as  $\phi \rightarrow \phi_m$  (the argument of 2 is shorthand for  $|\mathbf{r}| = 2$ ). For weak flows, the appropriate Péclet number is that based on the short-time self-diffusivity at the volume fraction of interest,  $\bar{P}e = \dot{\gamma}a^2/2D_0^s(\phi)$ , and  $\mathbf{D}_\infty^s$  can be expressed as the product of  $\mathbf{D}_\infty^s$  at  $\bar{P}e = 0$  times the same function of  $\bar{P}e$  as at small  $\phi$ .

As noted at the beginning of this section, the Fourier-transform method is not limited in applicability to a finite range of  $Pe$ . The phenomenon of shear-induced diffusion of non-colloidal particles (Eckstein *et al.* 1977; Leighton & Acrivos 1987; Acrivos *et al.* 1992) may thus be treated by the Fourier-transform method. This problem, which requires the evaluation of both  $g$  and  $f$  (i.e. the  $\mathbf{b}$ -field, as we have formulated the problem) for  $Pe \gg 1$ , are treated in Morris & Brady (1996), in which the microstructure of a strongly sheared suspension and its impact upon both the rheology and diffusivity are addressed.

This work was supported in part by the National Science Foundation through grant CTS-9420415 and by the Office of Naval Research through grant N00014-95-1-0423. The suggestions of Dr Chris Harris of Shell Research, Amsterdam, for the evaluation of the integrals involved in the diffusivity calculation were very helpful.

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