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Diffusion of Brownian particles in shear flows

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The coupling of Brownian displacements and shear-induced convection of spherical colloidal particles in dilute suspensions is examined using solutions of appropriate convective diffusion equations for the time-dependent probability density and also by calculation of relevant statistical quantities for an ensemble of diffusing particles from Langevin equations. Based on a fundamental solution for convective diffusion from a point in a general linear field, analytical expressions for the probability density $f_\alpha(\mathbf{r}; t)$ are given for the case of an arbitrary, two-dimensional linear flow field. The parameter α, which characterizes the flow, may range from -1 (pure rotation), through zero (simple shear), to $+1$ (pure elongation). The Langevin approach offers interesting insights into the physical mechanism of diffusive–convective coupling, and may also be used to obtain rigorous expressions for moments of the probability density appropriate to a particle diffusing in an unbounded quadratic (Poiseuille) flow. Preliminary experiments are described which qualitatively verify the theoretical predictions for Poiseuille flow, and which suggest a simple, direct method for measuring particle diffusivities. Finally the effect of bounding walls on convective diffusion is considered by means of Monte Carlo calculations. Results show that particle–wall interactions significantly affect the average behaviour of particles located initially within distances of a few particle radii of the wall, since the frictional force is no longer isotropic.

1. Introduction

The importance of Brownian motion in a field of force derives both from its practical aspects, such as those involved in sedimentation (Chandrasekhar 1943), electrophoresis (Booth 1950), or coagulation (van de Ven & Mason 1977), and from its applicability to general problems such as the escape over potential barriers (Kramers 1940) and the diffusion theory of chemical reactions (Brinkman 1956). Investigation of Brownian motion in a field of force continues to be of considerable interest in, for example, polymer physics and colloid science, where, in dealing with solutions of macromolecules or colloidal suspensions, the particular field is often a superposition of an external one (electromagnetic, gravitational) together with an internal one (shear, interparticle interaction). Such situations commonly arise in experiments designed to investigate rheo-optical (flow-birefringence) and rheo-electrical (Kerr) effects, as well as in certain separation techniques, such as 'field-flow fractionation' (Giddings 1966; Krishnamurthy & Subramanian 1977). In view of the importance assumed by internal shear fields in many of these systems, an understanding of the basic physical processes through which random motions of suspended particles couple to the bulk shearing motion of the liquid is desirable. Our investigation here is confined specifically to the translational Brownian motion of isolated spherical colloidal particles in various velocity fields, although coupling of rotary Brownian motion and shear-induced rotation in suspensions of non-spherical particles is an equally important subject, with a variety of consequences as well (Vadas *et al.* 1976; Zuzovsky, Priel & Mason 1979; Leal & Hinch 1971).

There are in general two approaches to the problem of Brownian motion (Chandrasekhar 1943). The motion of a Brownian particle may either be described in terms of a Langevin equation together with statistical or correlation properties of the random force, or it may be described by a probability density in phase space wich satisfies a Fokker–Planck, or 'diffusion' equation with given initial and boundary conditions. As Adelman (1976) has pointed out the equivalence of Langevin and Fokker–Planck approaches has been established only when the random force is assumed to have Gaussian–Markov character. With this assumption one may derive the Fokker–Planck equation by means of the Langevin equation. As is well known for times long compared to the relaxation of the velocity autocorrelation for the Brownian particle the Fokker–Planck equation reduces to the familiar phenomenological diffusion equation corresponding to Fick's second law. This reduction constitutes the so-called 'diffusion limit' and will be our main concern in the calculations which follow. However, as we show, the dynamics of the Brownian particle in a velocity field over small time intervals (accessible only through a Langevin approach) offer interesting insights into the coupling of random Brownian and convective motions of the particle. For this reason we make use of both approaches.

In § 2 the problem of Brownian motion of spherical particles in general linear two-dimensional flows is examined by solving the convective diffusion equation. Aspects of diffusive–convective coupling are revealed in § 3 by means of the Langevin equation for a spherical particle in simple shear. Section 4 treats Brownian motion in a non-linear (Poiseuille) flow first by means of Langevin equation, then, on the basis of moments of the probability distribution calculated by this approach, we construct series expansions of the probability valid near and far away from the point of maximum velocity in the flow profile. Finally in § 5 we seek to answer some questions concerning the effect of bounding walls on the diffusion of colloidal particles by means of Monte Carlo calculations. Before proceeding we should re-emphasize that our calculations are for particles of colloidal rather than molecular dimension, so that quantitative predictions based on this theory are valid only for the former, even though we may in many circumstances expect qualitative agreement for the latter.

2. Brownian motion in linear shear fields: solution of the convective diffusion equation

The diffusion of a spherical colloidal particle in a linear shear field $\mathbf{v}(\mathbf{r}; t)$ is characterized, for times much greater than the relaxation of the velocity autocorrelation, by a flux in probability space given by

$$\mathbf{J}(\mathbf{r}; t) = -D\nabla f(\mathbf{r}; t) + \mathbf{v}(\mathbf{r}; t) f(\mathbf{r}; t), \quad \mathbf{r}(x, y, z), \tag{2.1}$$

which is the sum of a diffusive contribution $-D\nabla f$, where D is the scalar diffusivity ($= k_B T/\zeta$, ζ being the Stokes' frictional coefficient, k_B Boltzmann's constant and T the

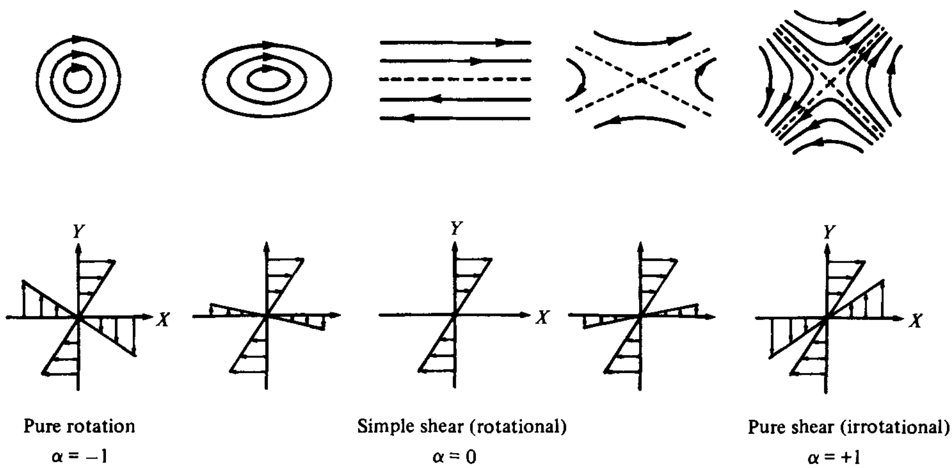

FIGURE 1. General two-dimensional linear flows characterized by the parameter α which can vary from -1 (pure rotation) to $+1$ (pure shear) (after Mason, 1976).

absolute temperature) and a convective contribution $\mathbf{v}f$. Here $f(\mathbf{r}; t)$ is the probability density at $\mathbf{r}$ and t. Since the probability must be conserved according to

$$\partial f/\partial t = -\nabla . \mathbf{J}, \tag{2.2}$$

the probability $f(\mathbf{r}; t)$ obeys the convective diffusion equation

$$\partial f/\partial t + (\mathbf{v} . \nabla) f = D\nabla^2 f \tag{2.3}$$

with the initial condition

$$f(\mathbf{r}; 0) = \delta(\mathbf{r}), \tag{2.4}$$

and, since in this section we will be concerned with diffusion in an infinite medium, we require that f vanish at infinity:

$$\lim_{\mathbf{r}\to\infty} f(\mathbf{r}; t) = 0. \tag{2.5}$$

Obviously the liquid medium is assumed to be incompressible, hence (2.3) is in accord with the equation of continuity $\nabla . \mathbf{v} = 0$.

It is sufficient for our purposes here to deal with the general two-dimensional linear shear field $\mathbf{v}(\mathbf{r})$ which can be expressed in component form (Mason 1976; Kao, Cox & Mason 1977) as

$$v_x = Gy, \quad v_y = \alpha G x, \tag{2.6}$$

where G is the shear rate (a constant) and the parameter α may range from -1 (pure rotation), through zero (simple shear), to $+1$ (pure elongation). Figure 1 illustrates this general field in some of its possible forms.

Now, as we show in appendix A, the solution of the convective diffusion equation (2.3) for arbitrary linear fields (a special case given by (2.6)] with the initial and boundary conditions (2.4) and (2.5) is the generalized Gaussian

$$f(\mathbf{r}; t) = (2\pi)^{-1} (\det \boldsymbol{\beta})^{\frac{1}{2}} \exp\{-\tfrac{1}{2}[\beta_{xx} x^2 + 2\beta_{xy} xy + \beta_{yy} y^2]\}, \tag{2.7}$$

where $\det \boldsymbol{\beta}$ is the determinant of the coefficients β_{ij}, with $i, j = x, y$. As explained in appendix A, the complete solution requires that we determine all of the second moments of the distribution (2.7), which are related to the inverse matrix $\boldsymbol{\beta}^{-1}(t)$, i.e.

$$\langle \mathbf{rr} \rangle = \boldsymbol{\beta}^{-1}(t), \quad \mathbf{r} = \mathbf{r}(x, y), \tag{2.8}$$

where $\langle \mathbf{rr} \rangle$ is the mean-squared displacement tensor and the angular brackets denote an ensemble average.

According to equation (A 11) in appendix A, the elements of $\boldsymbol{\beta}^{-1}$ (or the second moments) obey the following first-order differential equations in t:

$$\frac{d\beta_{xx}^{-1}}{dt} = 2D + 2G\beta_{xy}^{-1}; \tag{2.9}$$

$$\frac{d\beta_{xy}^{-1}}{dt} = G\beta_{yy}^{-1} + \alpha G\beta_{xx}^{-1}; \tag{2.10}$$

$$\frac{d\beta_{yy}^{-1}}{dt} = 2D + 2\alpha G\beta_{xy}^{-1}; \tag{2.11}$$

with $\beta_{xx}^{-1}(0) = \beta_{xy}^{-1}(0) = \beta_{yy}^{-1}(0) = 0$, which is sufficient to ensure that the distribution (2.7) satisfies the initial condition (2.4) (see appendix A).

Solution of (2.9)–(2.11) is straightforward. We find

$$\beta_{xx}^{-1}(=\langle x^2\rangle) = \frac{\alpha+1}{2\alpha^{\frac{3}{2}}G} D\sinh(2\alpha^{\frac{1}{2}}Gt) + \frac{\alpha-1}{\alpha} Dt, \tag{2.12}$$

$$\beta_{xy}^{-1}(=\langle xy\rangle) = \frac{\alpha+1}{2\alpha G} D[\cosh(2\alpha^{\frac{1}{2}}Gt) - 1] \tag{2.13}$$

and

$$\beta_{yy}^{-1}(=\langle y^2\rangle) = \frac{\alpha+1}{2\alpha^{\frac{1}{2}}G} D\sinh(2\alpha^{\frac{1}{2}}Gt) - (\alpha-1)Dt, \tag{2.14}$$

which are easily converted into the desired coefficients β_{xx}, β_{xy} and β_{yy}:

$$\beta_{xx} = \frac{\alpha^{\frac{3}{2}}\psi(t)}{\chi(t)}, \tag{2.15}$$

$$\beta_{xy} = \frac{-\alpha(\alpha+1)\phi(t)}{\chi(t)} \tag{2.16}$$

and

$$\beta_{yy} = \frac{\alpha^{\frac{1}{2}}\Lambda(t)}{\chi(t)}, \tag{2.17}$$

where

$$\psi(t) = (\alpha+1)\sinh(2\alpha^{\frac{1}{2}}Gt) + 2\alpha^{\frac{1}{2}}(1-\alpha)Gt,$$
$$\chi(t) = DG^{-1}\{(\alpha+1)^2[\cosh(2\alpha^{\frac{1}{2}}Gt) - 1] - 2\alpha(\alpha-1)^2G^2t^2\},$$
$$\Lambda(t) = (\alpha+1)\sinh(2\alpha^{\frac{1}{2}}Gt) - 2\alpha^{\frac{1}{2}}(1-\alpha)Gt$$

and

$$\phi(t) = \cosh(2\alpha^{\frac{1}{2}}Gt) - 1.$$

One additional requirement for the coefficients β must be met in order that (2.7) be a solution which can be normalized in an infinite medium for all time: the quadratic form $\beta_{xx}x^2 + 2\beta_{xy}xy + \beta_{yy}y^2$ must be always positive-definite. Clearly this means that we must have

$$(a)\ \ \beta_{xx} \geqslant 0, \quad \beta_{yy} \geqslant 0 \quad \text{for all } t,$$

and

$$(b)\ \ \beta_{xx}\beta_{yy} \geqslant \beta_{xy}^2 \quad \text{for all } t.$$

These two conditions are satisfied for all α between -1 and $+1$.

Thus the probability distribution takes the explicit form for the general two-dimensional flow given by (2.6):

$$f(\mathbf{r};t) = \frac{\alpha}{2\pi}\left(\frac{2G}{D\chi(t)}\right)^{\frac{1}{2}} \exp\{-\frac{\alpha^{\frac{1}{2}}}{2\chi(t)}[\alpha\psi(t)x^2 + \Lambda(t)y^2 - 2\alpha^{\frac{1}{2}}(\alpha+1)\phi(t)xy]\}. \tag{2.18}$$

It is worthwhile to consider three special cases of the general flow field (2.6) and the coupling between diffusion and convection which is revealed by the behaviour of the probability $f_\alpha(\mathbf{r}; t)$ with time.

Case 1. *Pure rotation* ($\alpha = -1$). When $\alpha = -1$ equations (2.12), (2.13) and (2.14) give the second moments

$$\langle x^2 \rangle = \langle y^2 \rangle = 2Dt, \quad \langle xy \rangle = 0,$$

with the corresponding simple Gaussian probability

$$f_{\alpha=1}(\mathbf{r}; t) = (4\pi Dt)^{-1} \exp\left[-\frac{x^2+y^2}{4Dt}\right]. \tag{2.19}$$

We conclude that, despite the shear, diffusion proceeds uninfluenced by the bulk rotation of the liquid.

Case 2. *Simple shear* ($\alpha = 0$). In the limit $\alpha = 0$ we find

$$\langle x^2 \rangle = 2Dt[1 + \tfrac{1}{3}(Gt)^2], \quad \langle y^2 \rangle = 2Dt, \quad \langle xy \rangle = DGt^2,$$

which determines the probability distribution as

$$f_{\alpha=0}(\mathbf{r}; t) = (4\pi Dt)^{-1} \left(\frac{3}{(Gt)^2+12}\right)^{\frac{1}{2}} \exp\left\{-\frac{3[x-\frac{1}{2}yGt]^2}{Dt[(Gt)^2+12]} - \frac{y^2}{4Dt}\right\}. \tag{2.20}$$

This is identical to the solution obtained by Elrick (1963) for convective diffusion from a point source in simple shear. The results for the second moments agree with the analysis given by van de Ven (1977), with the exception of the cross-term $\langle xy \rangle = DGt^2$, which he mistakenly concluded was zero. Coupling between diffusion in the y direction perpendicular to the flow is illustrated by the average $\langle x^2 \rangle$, which is greater than the Einstein term $2Dt$ by the factor $[1 + \frac{1}{3}(Gt)^2]$. The physical basis of enhanced diffusion is rooted in the fact that when the random motion of a particle results in its displacement into a region where the liquid velocity differs from that at the original point, subsequent convection of the particle with the new velocity tends on the average to augment pure diffusion. This effect is a familiar one on a molecular scale in flow-induced dispersion (Taylor 1953; Lighthill 1966; Gill & Sankarasubramanian 1970; Chatwin 1977), and is also analogous to the coupling of molecular and turbulent diffusion described by Saffman (1960). The purpose of the following section is to examine this coupling for colloidal particles in more detail using the appropriate Langevin equation, but for the moment we examine one more special case of the flow (2.6).

Case 3. *Pure elongation* ($\alpha = 1$). For $\alpha = 1$ the second moments exhibit a high degree of enhancement over simple diffusion, to wit

$$\langle x^2 \rangle = \langle y^2 \rangle = DG^{-1} \sinh(2Gt), \quad \langle xy \rangle = DG^{-1}[\cosh(2Gt) - 1],$$

with the probability density

$$f_{\alpha=1}(\mathbf{r}; t) = \frac{G}{2^{\frac{3}{2}}\pi D[\cosh(2Gt)-1]^{\frac{1}{2}}} \exp\left\{\frac{-G}{4D}\left[\frac{\sinh(2Gt)}{\cosh(2Gt)-1}\right](x^2+y^2) + \frac{G}{2D}xy\right\}. \tag{2.21}$$

As is well known simple shear ($\alpha = 0$) is a superposition of pure rotational and pure elongational flows, yet the diffusive–convective coupling is not simply additive. In fact, the rotational component of simple shear acts to retard convective enhancement

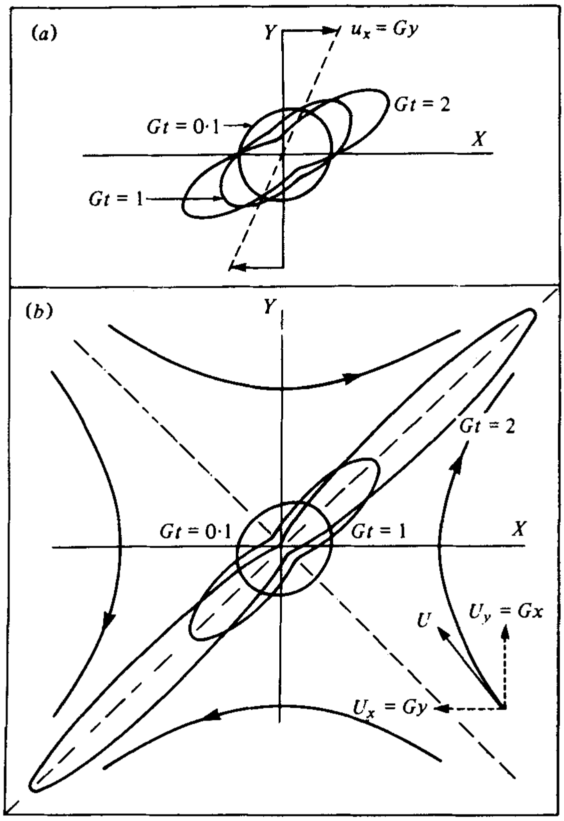

FIGURE 2. Orientation distribution functions $p(\phi)$ for simple shear (a) and pure shear or elongation (b) for various dimensionless times Gt. For a particle at the origin at $t = 0$, $p(\phi)\,d\phi$ is the probability of finding the particle between ϕ and $\phi + d\phi$ at time t. Notice that in pure shear the orientation distribution is stretched out much more than in simple shear and that its maximum always points in the same direction; this is due to the absence of a rotational component in such a flow.

of diffusion relative to pure elongation. This is illustrated graphically by polar plots of the probabilities $p_{\alpha=0}(\phi)$ and $p_{\alpha=1}(\phi)$ (figure 2) which are the probabilities that a particle situated initially at the origin will have been displaced in a dimensionless time Gt such that a line connecting the particle centre and the origin will make an angle ϕ with the X axis. $p_\alpha(\phi)$ is obtained from $f_\alpha(\mathbf{r}; t)$ by transforming to the polar co-ordinates r, ϕ, with

$$x = r\cos\phi, \quad y = r\sin\phi,$$

then integrating the result over all possible values of r from zero to infinity. For simple shear ($\alpha = 0$) and pure elongation ($\alpha = 1$) the results are

$$p_{\alpha=0}(\phi) = [\pi g(\phi; t)]^{-1}\left[\frac{3}{(Gt)^2+12}\right]^{\frac{1}{2}}, \tag{2.22}$$

where
$$g(\phi; t) = \frac{12(\cos\phi - (Gt/2)\sin\phi)^2}{(Gt)^2+12} + \sin^2\phi,$$

and
$$p_{\alpha=1}(\phi) = \frac{[\cosh(2Gt)-1]^{\frac{1}{2}}}{2^{\frac{1}{2}}\pi\sinh(2Gt) - [\cosh(2Gt)-1]\sin 2\phi}. \tag{2.23}$$

For comparison the simple Gaussian distribution (2.19) which of course shows no effect of coupling has the polar representation

$$p(\phi) = 1/2\pi$$

since all angles are equally probable when the displacements are completely random. Apparently the differences illustrated by plots of (2.22) and (2.23) between simple shear and pure elongation are attributable to the rotational component of simple shear. Indeed, the spreads in the distribution, as evidenced by the time-dependences of the respective second moments for $t \ll G^{-1}$, are practically identical, for example

$$\langle x^2 \rangle_{\alpha=0} = 2Dt[1+\tfrac{1}{3}(Gt)^2] \quad \text{simple shear,}$$

$$\langle x^2 \rangle_{\alpha=1} \simeq 2Dt[1+\tfrac{2}{3}(Gt)^2] \quad \text{elongation.}$$

In this short time rotation has not yet displaced a particle from a 'stretching' into a 'compressing' quadrant (see figure 1) in simple shear. For longer times, even though the elongational component of simple shear will continue to influence convection of the particle, the rotational component inhibits rapid increasing of the spread which characterizes pure elongation, where all particles eventually find themselves in regions of flow where 'stretching' takes place. Thus in simple shear the balance between 'stretching' and 'compression' results in an enhanced diffusion, but nowhere near the magnitude of that for pure elongation. The effect of the rotational component on simple shear is also manifest in the clockwise rotation of the maximum in $p_{\alpha=0}(\phi)$ for increasing times Gt, while $p_{\alpha=1}(\phi)$ always has a maximum at $\phi = \frac{1}{4}\pi$.

Although the analysis of convective diffusion for times greater than the relaxation of the velocity autocorrelation is complete with the determination of the probability $f(\mathbf{r}; t)$, there are still important aspects of the coupling which are revealed when we consider the Langevin equation for a spherical colloidal particle subject to a velocity field. In the following section we approach the problem from this point of view.

3. Brownian motion in shear fields: Langevin analysis

(i) *The Langevin equation.* The basic assumption which enables us to construct a Langevin equation for a spherical particle subjected to an internal velocity field, is that the force which determines the motion of the particle can be written as the sum of (*a*) a systematic frictional drag due to the velocity of the particle relative to the bulk motion of the liquid in its immediate vicinity, and (*b*) a random force which arises (at least in the phenomenological point of view) from fluctuations of the liquid velocity field about its average bulk value in the vicinity of the particle (Chow & Hermans 1972, 1972*a*; Bedeaux & Mazur 1974). From the molecular point of view both (*a*) and (*b*) are the result of collisions between the particle and the liquid molecules, which exhibit constant thermal motion and, in the case of a bulk laminar flow, large-scale cooperative motion as well. Thus for an isolated Brownian particle of mass m, subject to no external field, the Langevin equation is

$$m\ddot{\mathbf{r}} = \mathbf{F}_{\text{fric}} + \mathbf{F}_{\text{rand}(t)} \tag{3.1}$$

The dots denote differentiation with respect to the time t.

We assume that the frictional drag $\mathbf{F}_{\text{fric}}$ is proportional to the relative velocity

$$\dot{\mathbf{r}} - \mathbf{v}(\mathbf{r}),$$

$\mathbf{v}(\mathbf{r})$ being the value of the liquid (bulk) velocity which coincides with the particle centre of mass. Strictly speaking the drag on the particle should be evaluated in terms of Faxén's theorem (Happel & Brenner 1973), but for a spherical Brownian particle of radius b such that

$$b/l \ll 1,$$

where l is a characteristic length scale over which significant variations in $\mathbf{v}$ occur, one may substitute for a surface average of the velocity field the value of $\mathbf{v}$ coincident with the centre of the sphere. For our purposes† here the proportionality constant between the drag and the relative velocity is the familiar Stokes' constant $\zeta = 6\pi\eta b$, η being the liquid viscosity.

The Langevin equation is then a stochastic differential equation for the position $\mathbf{r}(t)$ of the Brownian particle:

$$\ddot{\mathbf{r}} + \beta[\dot{\mathbf{r}} - \mathbf{v}(\mathbf{r})] = \mathbf{F}(t), \tag{3.2}$$

where $\beta = \zeta/m$ is the reciprocal relaxation time for the velocity autocorrelation of the particle (Chandrasekhar 1943) and the random force per unit mass $\mathbf{F}(t)$ is assumed to be Gauss–Markov with the correlation properties (Wang & Uhlenbeck 1945)

$$\langle \mathbf{e}_i . \mathbf{F}(t_1)\, \mathbf{e}_j . \mathbf{F}(t_2) \rangle = (2k_B T \zeta/m^2)\, \delta_{ij}\, \delta(t_1 - t_2), \tag{3.3}$$

$$\langle \mathbf{e}_i . \mathbf{F}(t_1)\, \mathbf{e}_i . \mathbf{F}(t_2) \ldots \mathbf{e}_i . \mathbf{F}(t_{2n+1}) \rangle = 0, \tag{3.4}$$

$$\langle \mathbf{e}_i . \mathbf{F}(t_1)\, \mathbf{e}_i . \mathbf{F}(t_2) \ldots \mathbf{e}_i . \mathbf{F}(t_{2n}) \rangle = \sum_{\substack{\text{all}\\ \text{pairs}}} \langle \mathbf{e}_i . \mathbf{F}(t_\alpha)\, \mathbf{e}_i . \mathbf{F}(t_\beta) \rangle \langle \mathbf{e}_i . \mathbf{F}(t_\delta)\, \mathbf{e}_i . \mathbf{F}(t_\gamma) \rangle, \quad i,j = x,y,z \quad \text{and} \quad n \geqslant 0. \tag{3.5}$$

The delta-function correlation (3.3) means that, as far as appreciable changes in the velocity of the particle (or its position) are concerned, the random force is totally uncorrelated with its value at a previous time. The strength of this correlation follows from the equipartition of energy which we assume existed at time $t = 0$, i.e. the initial distribution of velocities available to the particle was Maxwellian. In determining higher-order correlations by means of (3.5) the sum is taken over all of the *unique* correlation products one may construct by dividing the $2n$ times into pairs.

Before we make use of (3.2) and the properties (3.3)–(3.5) for the specific case of simple shear, the initial conditions for solution of the Langevin equation should be made clear. As we have just stated, for all times $t \leqslant 0$, the system (Brownian particle plus liquid medium) is in thermal equilibrium. At some time $t > 0$, we create a velocity field $\mathbf{v}(\mathbf{r})$ in the liquid which of course disturbs this equilibrium. In the calculations which follow, we will for the most part be interested specifically in times

† Actually Stokes' result for steady flow is insufficient to characterize the resistance of a Brownian particle, as was pointed out originally by Lorentz (1921), when the mass density of the particle is of the same order as the density of the suspending medium. Replacing the Stokes' constant ζ by a time-dependent operator has interesting consequences in connection with persistence of the random force and velocity autocorrelations (Chow & Hermans 1972), the intrinsic viscosity of rod-like particles (Foister & Hermans 1977) and the mean-squared displacement of spherical particles (Saffman 1976). For a discussion of the theoretical basis of the Langevin equation with non-steady friction from the fluid-mechanical point of view, see Hinch (1975).

far removed from $t = 0$ as well as the time when the flow $\mathbf{v}(\mathbf{r})$ was fully established. This also corresponds to the 'diffusion limit' which refers to times t satisfying

$$t \gg \beta^{-1}.$$

For times satisfying this condition, the Fokker–Planck equation becomes the convective diffusion equation (Chandrasekhar 1943) and the initial conditions (velocities) no longer influence the particle motion. However in some cases it is necessary to take the initial conditions into account, especially if we are concerned with times which are less than this relaxation time.

(ii) *Calculations for simple shear.* In this section we deal specifically with simple shear flow [$\alpha = 0$ in (2.6)] although it is possible to show that equations (2.12)–(2.14) for the second moments (arbitrary α) follow from the Langevin equation using the field (2.6) for times $t \gg \beta^{-1}$ (appendix B). The nature of coupling between convection and diffusion is clearly illustrated simply by considering the case $\alpha = 0$, so it is not necessary to discuss the general flow in terms of the Langevin equation.

We suppose that a Cartesian co-ordinate system (x, y) is located such that its origin coincides with the initial position of the particle centre. For the simple shear $\mathbf{v} = Gy\mathbf{e}_x$ equation (3.2) can be expressed in component form as

$$\ddot{x} + \beta(\dot{x} - Gy) = X(t), \tag{3.6}$$

$$\ddot{y} + \beta\dot{y} = Y(t), \tag{3.7}$$

where $X(t)$ and $Y(t)$ are components of the random force per unit mass. Obviously motion in the direction of flow (x) is coupled to motion in the direction of the velocity gradient (y) due to the spatial dependence of the shear field.

We may solve (3.6) and (3.7) for an assembly of particles all of which initially have a given velocity with components $\dot{x}(0)$ and $\dot{y}(0)$:

$$x(t) = \frac{\dot{x}(0)}{\beta}(1 - e^{-\beta t}) + \frac{1}{\beta}\int_0^t d\lambda\,[1 - e^{-\beta(t-\lambda)}]\,[X(\lambda) + \beta G y(\lambda)], \tag{3.8}$$

$$y(t) = \frac{\dot{y}(0)}{\beta}(1 - e^{-\beta t}) + \frac{1}{\beta}\int_0^t d\lambda\,[1 - e^{-\beta(t-\lambda)}]\,Y(\lambda). \tag{3.9}$$

The mean squared displacement in the flow direction is obtained by squaring (3.8) and performing the ensemble average, which includes an average over all possible initial velocities which are distributed according to the equilibrium law (in two dimensions)

$$p(\mathrm{v})\,d\mathrm{v} = \frac{m}{2\pi k_B T}\exp\left[-m\mathrm{v}^2/2k_B T\right]d\mathrm{v}, \quad \mathrm{v} = \mathrm{v}(\dot{x}, \dot{y}),$$

with zero mean and second moment in accordance with the equipartition of energy:

$$\tfrac{1}{2}m\langle v^2\rangle = k_B T.$$

We find, using the appropriate correlation properties of the random force components,

$$\langle x^2(t)\rangle = \frac{2k_B T}{m\beta^2}(\beta t - 1 + e^{-\beta t}) + G^2\int_0^t d\lambda \int_0^t d\lambda'[1 - e^{-\beta(t-\lambda)}]\,[1 - e^{-\beta(t-\lambda')}]\,\langle y(\lambda)\,y(\lambda')\rangle. \tag{3.10}$$

The first term is the result of pure diffusion, while the second term, proportional to G^2, is the result of diffusive–convective coupling. The evaluation of (3.10) is fairly straightforward. However, rather than writing out the general result, we may look at two special cases.

Case 1. $t \gg \beta^{-1}$, *the 'diffusion limit'*. The first term on the right-hand side of (3.10) yields

$$2\frac{k_B T}{\zeta}t$$

or simply $2Dt$ with the 'Einstein relation' between the diffusion and frictional coefficients. Making use of (3.9) and neglecting terms of relative order $(\beta t)^{-1}$ or less, the second term reduces to

$$2G^2 D\int_0^t d\lambda \int_0^t d\lambda' \int_0^\lambda ds \int_0^{\lambda'} ds'\, \delta(s-s'), \tag{3.11}$$

which is evaluated by exchanging orders of integration $(\lambda \leftrightarrow s)$ and $(\lambda' \leftrightarrow s')$. For fixed s (or s'), $\lambda(\lambda')$ ranges from $s(s')$ to t. Thus

$$2G^2 D\int_0^t ds' \int_0^t ds\,(t-s)(t-s')\,\delta(s-s') = \tfrac{2}{3}G^2 D t^3.$$

This may be combined with the pure diffusion result $2Dt$ to yield a value of the mean-squared displacement $\langle x^2\rangle$ in agreement with the corresponding second moment of the distribution (2.20).

Case 2. $t \ll \beta^{-1}$. In this limit one finds (Chandrasekhar 1943) that particle inertia will dominate the mean-squared displacement in the absence of shear. Thus the first term in (3.10) contributes to $\langle x^2\rangle$ the amount

$$\frac{k_B T}{m}t^2 = \langle \dot{x}^2\rangle t^2,$$

which is the average of the squared displacement a particle would have if it moved in a time t with a steady velocity $\dot{x}(t)$ which is distributed among the ensemble according to the Maxwell–Boltzmann law. The second term reduces to

$$\frac{2G^2 k_B T}{m}\int_0^t ds \int_0^s ds'(ss') = \frac{k_B T}{4m}G^2 t^4,$$

which means that the result *in the absence* of shear, $k_B T t^2/m$, is increased by the factor $[1+\frac{1}{8}(Gt)^2]$ when shear influences the motion of the particle via the resistance factor in the Langevin equation.

Coupling for small as well as 'large' times (i.e. $t \gg \beta^{-1}$) is also revealed in the correlation between the Y component of the random force, $Y(t')$, at time t' and the displacement $x(t)$ at time t. Multiplying (3.8) by $Y(t')$ and averaging, yields:

$$\langle x(t)\,Y(t')\rangle = \frac{2Gk_B T}{m}\int_0^t ds \int_s^t d\lambda\,[1-e^{-\beta(t-\lambda)}-e^{-\beta(\lambda-s)}+e^{-(t-s)}]\,\delta(s-t'),$$

where averages such as $\langle \dot{x}(0)\,Y(t')\rangle$ vanish owing to causality for $t' > 0$ and $\langle X(t)\,Y(t')\rangle = 0$ since different components of the random force are always uncorrelated. Integration of this expression gives

$$\langle x(t)\,Y(t')\rangle = \begin{cases} 0 \quad \text{for} \quad t' \geqslant t, \\ \dfrac{2Gk_B T}{m}\left\{\dfrac{2}{\beta}e^{-\beta(t-t')}-1]+(t-t')\,[1+e^{-\beta(t-t')}]\right\} \quad \text{for} \quad t > t'. \end{cases} \tag{3.12}$$

For $(t-t') \ll \beta^{-1}$, $\langle x(t)\,Y(t')\rangle \simeq k_B T m^{-1} G\beta^2 (t-t')^3$, while, at the other extreme, $(t-t') \gg \beta^{-1}$, $\langle x(t)\,Y(t')\rangle \simeq k_B T m^{-1} G(t-t')$, showing that the correlation between the

x component of position at time t and the y component of random force at an earlier time t' always increases with the time difference $(t-t')$. In contrast we find that the correlation between the x component of position and the x component of the random force is given by

$$\langle x(t)\,X(t')\rangle = \begin{cases} 0 \quad \text{for} \quad t' \geqslant t, \\ \dfrac{2k_B T}{m}\,[1-e^{-\beta(t-t')}] \quad \text{for} \quad t > t', \end{cases} \tag{3.13}$$

which approaches a constant value of $(2k_B T/m)$ when $(t-t') \gg \beta^{-1}$. The difference between (3.12) and (3.13) is due, of course, to the coupling of displacement due to convection and the random force component which determines the particular value of the velocity field which influences the convective displacement. The fact that the correlation (3.12) attains a strength comparable to (3.13) only for time differences on the order of G^{-1} is in agreement with the observation that the coupling term in the mean-squared displacement becomes comparable to the pure diffusion result whenever $t \sim G^{-1}$ [see equation (3.11)].

In concluding the treatment of diffusion in linear shear flows we emphasize that, although the Langevin equation predicts diffusive–convective coupling for extremely small as well as large times, as a practical matter this coupling will be observable only for times t on the order of the reciprocal shear rate G^{-1}. This conforms qualitatively to the experimental observations of Vadas *et al.* (1976) on the rotary Brownian motion of doublets of colloidal spheres in Poiseuille flow, where because of diffusive–convective coupling the mean-squared angular displacements (with respect to rotating co-ordinates) begin to differ from the pure diffusion result for times on the order of G^{-1}.

The following section deals with the diffusion of particles in Poiseuille flow. Here the velocity field is a quadratic function of the co-ordinates, so that the general method of appendix A is insufficient to determine the full solution for the probability which satisfies the convective diffusion equation. We approach this problem instead by calculating moments of the probability distribution using the Langevin equation. From our knowledge of the moments we then construct approximate solutions of the convective-diffusion equation for local regions in the flow field.

4. Brownian motion in Poiseuille flow

(*a*) *Calculations of second moments from the Langevin equation*

The velocity field for Poiseuille (pipe) flow with respect to a fixed Cartesian system (x', y', z') (see figure 3) is

$$v'_{x'} = \gamma(R_0^2 - y'^2 - z'^2), \quad v'_{y'} = v'_{z'} = 0, \tag{4.1}$$

where $\gamma = (V_{\max}/R_0^2)$, $V_{\max}$ being the maximum velocity at the centre of the tube and R_0 the tube radius. By our definition of co-ordinates x' is along the tube axis, and $(y'^2+z'^2)^{\frac{1}{2}}$ defines the radial distance from the centre.

Consider now a particle which is initially situated at the point $[x'(0), y'(0), z'(0)]$. If we define a new translating system (x, y, z) related to (x', y', z') by

$$x = x' - [x'(0) + v'(0)\,t],$$
$$y = y' - y'(0),$$
$$z = z' - z'(0),$$

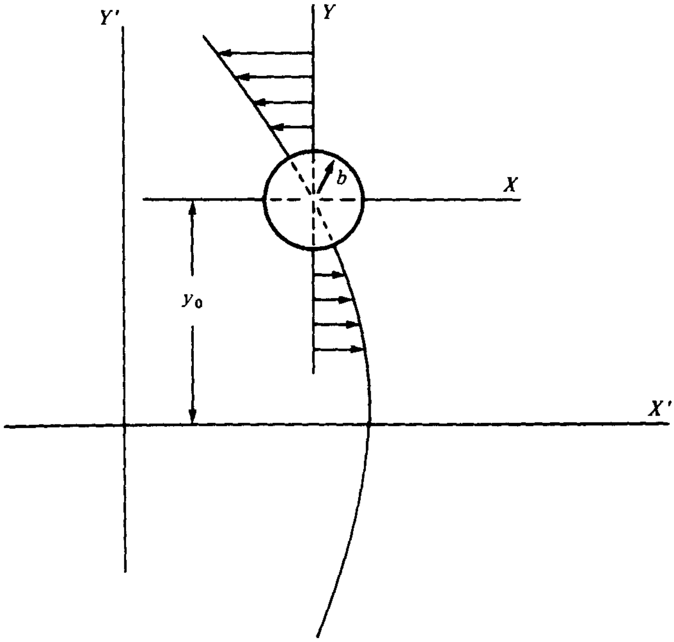

FIGURE 3. Relation in Poiseuille flow between the initial velocity co-ordinates X, Y of a sphere at time $t = 0$ at distance y_0 from the centre and the space-fixed co-ordinates X', Y'. The Z axis (not shown) is directed towards the viewer.

with $$v'(0) = \gamma[R_0^2 - y'^2(0) - z'^2(0)],$$

then the velocity field (4.1) becomes, in the new system,

$$\left.\begin{aligned} v_x &= -\gamma[y^2 + z^2 + 2\{(yy'(0) + zz'(0)\}], \\ v_y &= v_z = 0. \end{aligned}\right\} \tag{4.2}$$

Equation (4.2) defines a field relative to the (x, y, z) system which translates at all times with a velocity determined by the initial position of the particle, i.e. by $y'(0)$ and $z'(0)$. With this choice of co-ordinates the flow consists of a linear and a parabolic region for all $y'(0)$ and $z'(0)$ except at the tube centre, where the flow is completely parabolic. Consequently, for particles with $y'(0) \neq 0$ and/or $z'(0) \neq 0$, we expect enhancement of diffusion similar to that calculated in the previous section for simple shear. This type of behaviour will persist for as long as the particle has not had sufficient time to diffuse out of the linear region. This time for an ensemble of diffusing particles will be roughly

$$[y'^2(0) + z'^2(0)]/D.$$

On the other hand we may expect a qualitative difference in the enhancement of diffusion between simple shear (or two-dimensional linear) flows and Poiseuille flow for particles situated at or very near the tube centre where $y'(0)$ and $z'(0)$ are small and the quadratic term plays a role in the resistance. The calculations below bear out these qualitative observations.

Taking the field (4.2) into account and writing $y'(0) = y_0$ and $z'(0) = z_0$ the Langevin equations for displacements along each of the co-ordinate axes are

$$\ddot{x}+\beta\dot{x}+\beta\gamma[y^2+z^2+2(yy_0+zz_0)] = X(t), \tag{4.3}$$

$$\ddot{y}+\beta\dot{y} = Y(t), \tag{4.4}$$

and

$$\ddot{z}+\beta\dot{z} = Z(t). \tag{4.5}$$

As in the case of simple shear these equations may be integrated formally to give

$$x(t) = \frac{\dot{x}(0)}{\beta}(1-e^{-\beta t})+\frac{1}{\beta}\int_0^t d\lambda\{[1-e^{-\beta(t-\lambda)}]X(\lambda)-\beta\gamma[y^2(\lambda)+z^2(\lambda)+2(y_0y(\lambda)+z_0z(\lambda))]\}; \tag{4.6}$$

$$y(t) = \frac{\dot{y}(0)}{\beta}(1-e^{-\beta t})+\frac{1}{\beta}\int_0^t d\lambda[1-e^{-\beta(t-\lambda)}]\,Y(\lambda); \tag{4.7}$$

$$z(t) = \frac{\dot{z}(0)}{\beta}(1-e^{-\beta t})+\frac{1}{\beta}\int_0^t d\lambda[1-e^{-\beta(t-\lambda)}]\,Z(\lambda). \tag{4.8}$$

Here x is coupled to y and z, but there is no coupling between y and z, so it is sufficient to consider the related problem of Brownian motion in plane Poiseuille (channel) flow, using only equations (4.6) and (4.7) above and taking $z_0 = 0$.

To determine $\langle x^2(t)\rangle$ we square (4.6) and perform the ensemble average,† using once again the correlation properties (3.3), (3.4) and (3.5) together with the initial conditions discussed previously. Subtracting for the time being the contribution $2Dt$ due to pure longitudinal diffusion and neglecting terms of relative order $(\beta t)^{-1}$ or less since our concern is the 'diffusion limit', we find

$$\langle x^2(t)\rangle = \int_0^t d\lambda\int_0^t d\lambda'\,(\gamma^2\langle y^2(\lambda)\,y^2(\lambda')\rangle+4y_0^2\gamma^2\langle y(\lambda)\,y(\lambda')\rangle$$
$$+4y_0\gamma^2\langle y^2(\lambda)\,y(\lambda')\rangle-2\gamma\beta\langle X(\lambda)\,y^2(\lambda')+2y_0X(\lambda)\,y(\lambda')\rangle). \tag{4.9}$$

The average $\langle y^2(\lambda)\,y(\lambda')\rangle$ vanishes owing to property (3.4), while averages involving the products $X(\lambda)\,y^2(\lambda')$ and $X(\lambda)\,y(\lambda')$ vanish by (3.3). Furthermore the term in (4.9) proportional to $\langle y(\lambda)\,y(\lambda')\rangle$ is just the contribution from the linear region of flow analogous to simple shear which yields a t^3 time dependence. Thus

$$\langle x^2(t)\rangle = \tfrac{8}{3}\gamma^2y_0^2Dt^3+\gamma^2\int_0^t d\lambda\int_0^t d\lambda'\,\langle y^2(\lambda)\,y^2(\lambda')\rangle. \tag{4.10}$$

To evaluate the remaining term in (4.10) which originates from the parabolic region, we make use of (4.4) for $y(t)$. In the diffusion limit

$$\langle y^2(\lambda)\,y^2(\lambda')\rangle = \beta^{-4}\int_0^\lambda ds\int_0^\lambda ds'\int_0^{\lambda'} du\int_0^{\lambda'} du'\,\langle Y(s)\,Y(s')\,Y(u)\,Y(u')\rangle. \tag{4.11}$$

† Cox (private communication) has calculated $\langle x^2\rangle$ in plane Poiseuille flow by solving differential equations which can be derived by multiplying the convective diffusion equation for plane Poiseuille flow by x^2, then integrating over all space. His results are identical to those we calculate here. This is also the method employed by Brenner & Gaydos (1977) who considered convective diffusion of colloidal particles in small pores. Other approaches (Saffman 1960; Chatwin 1977) may be used, but essentially one must calculate the same average quantities from the Langevin equation.

The correlation of the random force component $Y(t)$ at four different times may be found by referring to property (3.5). Now there are three possible ways to arrange the four times s, s', u and u' into correlation pairs:

$$\langle Y(s)\,Y(s')\rangle\langle Y(u)\,Y(u')\rangle,\quad \langle Y(s)\,Y(u)\rangle\langle Y(s')\,Y(u')\rangle,\quad \langle Y(s)\,Y(u')\rangle\langle Y(s')\,Y(u)\rangle.$$

But of these three, only two are unique, since the second and third are equivalent because integrations over $s(u)$ and $s'(u')$ are equivalent. Thus

$$\langle Y(s)\,Y(s')\,Y(u)\,Y(u')\rangle = \left(\frac{2k_B T\zeta}{m^2}\right)^2 \{\delta(s-s')\,\delta(u-u')+\delta(s-u)\,\delta(s'-u')\},$$

which, when used in (4.11), gives

$$\langle y^2(\lambda)\,y^2(\lambda')\rangle = 4D^2\begin{cases}\lambda\lambda'+\lambda'^2 & \text{for} \quad \lambda'<\lambda,\\ \lambda\lambda'+\lambda^2 & \text{for} \quad \lambda<\lambda'.\end{cases}$$

The parabolic contribution then follows by straightforward integration and the *total* mean squared displacement (including pure diffusion) becomes

$$\langle x^2(t)\rangle = 2Dt[1+\tfrac{4}{3}\gamma^2 y_0^2 t^2+\tfrac{7}{6}D\gamma^2 t^3]. \tag{4.12}$$

For three-dimensional pipe flow coupling in the z-direction adds to (4.12) two terms, one of which is equivalent to (4.11) and the other is the cross term involving $\langle y^2(\lambda)\,z^2(\lambda')\rangle$. Evaluation of this average is straightforward, where we again use the property (4.5). Consequently for three dimensions we find:

$$\langle x^2(t)\rangle = 2Dt[1+\tfrac{4}{3}\gamma^2\rho_0^2\, t^2+\tfrac{10}{3}D\gamma^3 t^3], \tag{4.13}$$

where $\rho_0 = (y_0^2+z_0^2)^{\frac{1}{2}}$ is the initial radial position of the particle.

This result is rigorously correct only for particles in an infinite medium. Realistically we expect (4.13) to be valid in pipe flow for times t satisfying

$$t \ll [R_0-\rho_0]^2/D.$$

For colloidal particles D is of order $10^{-8}\,\mathrm{cm^2\,s^{-1}}$. If a particle finds itself initially at, say, $0{\cdot}9R_0$, where R_0 is $100\,\mu\mathrm{m}$, then this time is of order 100 s, which is still quite long enough for the coupling between diffusion and convection to have an effect on the spread of the probability distribution. For molecular diffusion, however, D is several orders of magnitude larger than 10^{-8}, so that the validity of (4.13) for macromolecular particles will be restricted to shorter times, i.e. for initial radial positions near the tube centre. For longer times (i.e. $t \gg R_0^2/D$, which is the characteristic time a particle would take to sample all velocities in the profile) diffusive–convective coupling of the type we have been discussing must yield to 'Taylor dispersion' (Taylor 1953; see also Brenner & Gaydos 1977), where $\langle x^2(t)\rangle$ again increases linearly as t, but with a proportionality constant (the 'dispersion coefficient') inversely proportional to D. We must therefore reiterate that no account is taken in the treatment thus far either of hydrodynamic interactions between the diffusing particle and the bounding wall, or of the rebounding (reflexion) of particles at the wall. These effects are of some interest, even for the time scales relevant here however, and, as § 5 shows, will be very important for particles located initially near the wall.

Other quantities that reflect coupling of convection and diffusion in Poiseuille flow are the elements of the mean squared displacement dyadic $\langle \mathbf{rr} \rangle$, where

$$\langle \mathbf{rr} \rangle = \begin{bmatrix} \langle x^2 \rangle & \langle yx \rangle & \langle zx \rangle \\ \langle xy \rangle & \langle y^2 \rangle & \langle zy \rangle \\ \langle xz \rangle & \langle yz \rangle & \langle z^2 \rangle \end{bmatrix}. \tag{4.14}$$

For isotropic diffusion in a medium with no bulk flow all of the off-diagonal elements in (4.14) are zero. However, for Poiseuille flow it can be shown, using the Langevin equations, that

$$\langle xy \rangle = -2\gamma y_0 Dt^2, \quad \langle xz \rangle = -2\gamma z_0 Dt^2 \quad \text{and} \quad \langle yz \rangle = 0.$$

Furthermore $\langle y^2 \rangle = \langle z^2 \rangle = 2Dt$. Also the trace of $\langle \mathbf{rr} \rangle$ is the vector mean-squared displacement:

$$tr\,\langle \mathbf{rr} \rangle = \langle r^2 \rangle = 6Dt[1 + \tfrac{4}{9}\gamma^2 \rho_0^2\, t^2 + \tfrac{10}{9}\gamma^2 Dt^3]. \tag{4.15}$$

Finally the covariance of $\mathbf{r}(t)$, given by

$$\langle \Delta r^2 \rangle = \langle [\mathbf{r} - \langle \mathbf{r} \rangle] . [\mathbf{r} - \langle \mathbf{r} \rangle] \rangle$$

can be obtained by noting that, from equations (4.6)–(4.8),

$$\langle x \rangle = -2\gamma Dt^2, \quad \langle y \rangle = \langle z \rangle = 0,$$

giving

$$\langle \Delta r^2 \rangle = 6Dt[1 + \tfrac{4}{9}\gamma^2 \rho_0^2 t^2 + \tfrac{4}{9}\gamma^2 Dt^3]. \tag{4.16}$$

The fact that for an infinite medium the mean displacement in the flow direction is on the average negative can be explained by the argument given by Chatwin (1976): owing to the nature of the velocity gradient in Poiseuille flow (increasing linearly as the radial distance from the centre), although radial diffusion itself is isotropic, displacement away from the centre is into a region of flow where the particle will encounter a greater negative change in liquid velocity than an equal displacement toward the tube centre where liquid velocities are greater, but the gradient itself is smaller. Thus on the average the displacement of the particle in the flow direction will be less than that of the origin which travels always with the initial velocity of the particle. In anticipation of the results of § 5, we might note that hydrodynamic interaction of the particle and wall may introduce some anisotropy in diffusion through the different frictional force experienced by the particle as it moves toward or away from the wall. We may expect qualitative differences in mean particle motion as reflected in the mean displacement $\langle x \rangle$ for example, for particles with initial positions near the wall, even though the results for $\langle x \rangle$ above are formally independent of initial position. Again we refer to § 5 for a discussion of these points.

One further remark is in order concerning convection-enhanced diffusion in Poiseuille flow as compared with the linear flows of the previous section, especially that of simple shear. The correlation between the random force perpendicular to flow and displacement in the flow direction is identical in Poiseuille and simple shear since both flows have linear components. It may seem somewhat puzzling at first sight, however, that, for a particle initially located at the exact centre, there will be enhanced diffusion in the flow direction, but the correlation between say $Y(t')$ and $x(t)$ [see equation (3.12)] is zero, as can be verified using the Langevin equations with $y_0 = z_0 = 0$. These two observations are not contradictory, since with respect to the tube centre, the velocity field is radially symmetric. Consequently axial displacements which arise due to positive *or* negative random forces propelling the particle away from the centre, are always negative with respect to the origin travelling at V_{max}. Since we assume that the random force is Gaussian with zero mean the average of products like $x(t)\,Y(t')$ should, because of the symmetry, be zero.

On the basis of the results we have found in this section, especially equation (4.13), we will now calculate some series expansions of the probability distribution for particles diffusing in a two-dimensional (plane) Poiseuille flow (an extension to tube flow is straightforward). The first case is for particles located initially near the point of maximum velocity.

(b) *Series expansions for convective diffusion in Poiseuille flow*

(i) *Expansion near the centre.* Introducing the following dimensionless parameters:

$$t^* = Dt/y_0^2, \quad x^* = x/y_0, \quad y^* = y/y_0, \quad z^* = z/z_0 \quad \text{and} \quad \sigma = \gamma y_0^3/D$$

we can write the convective diffusion equation for plane Poiseuille flow as

$$\partial f/\partial t^* = \nabla^{*2} f + \sigma(2y^* + y^{*2})\,\partial f/\partial x^*. \tag{4.17}$$

Here the dimensionless parameter σ is a local Péclet number and is the ratio of two characteristic times τ_d and τ_c; τ_c is the characteristic convection time y_0/v and τ_d the characteristic diffusion time y_0^2/D. Thus $\sigma = \tau_d/\tau_c$. Near the centre $y_0 \ll 1$ and therefore $\sigma \ll 1$. For initial positions y_0 far from the centre $y^{*2} \ll y^*$ and the equation reduces to the equation for simple shear flow by replacing 2σ by $-Gy_0^2/D$, which is equivalent to replacing $-2\gamma y_0$ by G.

Expressing (4.12) in terms of the above dimensionless parameters we have

$$\langle x^{*2}\rangle = 2t^* + \tfrac{8}{3}\sigma^2 t^{*3}(1 + \tfrac{7}{8}t^*). \tag{4.18}$$

This suggests that (4.17) can be solved as a series expansion in σ and that only terms of order σ^2 contribute to the second moment of the distribution function f.

Let
$$f = f_0 + \sigma f_1 + \sigma^2 f_2 + \dots. \tag{4.19}$$

When $\sigma = 0$ (4.17) reduces to a simple diffusion equation. Consequently

$$f_0 = \frac{1}{8(\pi t^*)^{\frac{3}{2}}}\exp\left[-\frac{x^{*2}+y^{*2}+z^{*2}}{4t^*}\right]. \tag{4.20}$$

Substituting (4.19) into (4.17) and collecting terms of order σ yields

$$\frac{\partial f_1}{\partial t^*} = \nabla^{*2} f_1 + (2y^* + y^{*2})\frac{\partial f_0}{\partial x^*}. \tag{4.21}$$

Making use of (4.20) this can be written as

$$\nabla^{*2} f_1 - \frac{\partial f_1}{\partial t^*} = -h_1(\mathbf{r}^*; t^*), \tag{4.22}$$

which is an inhomogeneous diffusion equation with the source function h_1, given by

$$h_1 = -\frac{x^*(2y^* + y^{*2})}{16\pi^{\frac{3}{2}} t^{*\frac{5}{2}}}\exp\left[-\frac{x^{*2}+y^{*2}+z^{*2}}{4t^*}\right]. \tag{4.23}$$

The Green's function of equation (4.22) is obtained by replacing x^* by $x^* - x'$ etc. and t^* by $t^* - t'$ (Morse & Feshbach, 1953) in (4.20). Thus the Green's function is

$$g(\mathbf{r}^*|\mathbf{r}'; t^*|t') = \frac{1}{8\pi^{\frac{3}{2}}(t^*-t')^{\frac{3}{2}}} \exp\left[-\frac{(x^*-x')^2+(y^*-y')^2+(z^*-z')^2}{4(t^*-t')}\right] \quad \text{when} \quad t^*-t' > 0,$$

$$= 0 \quad \text{otherwise.} \tag{4.24}$$

Hence $$f_1(\mathbf{r}^*, t^*) = \int_{-\infty}^{\infty} d\mathbf{r}' \int_0^{t^*} dt' g(\mathbf{r}^*|\mathbf{r}'; t^*|t')\, h(\mathbf{r}', t').$$

Integration of the source function using (4.24) yields:

$$f_1 = -\frac{x^*(t^*+3y^*+y^{*2})}{48\pi^{\frac{3}{2}}t^{*\frac{3}{2}}} \exp\left[-\frac{x^{*2}+y^{*2}+z^{*2}}{4t^*}\right]. \tag{4.25}$$

The above procedure can be repeated to obtain the solution to order σ^2. Substituting (4.19) into (4.17) and collecting terms of order σ^2 yields an equation for f_2:

$$\frac{\partial f_2}{\partial t^*} = \nabla^{*2} f_2 + (2y^* + y^{*2}) \frac{\partial f_1}{\partial x^*}, \tag{4.26}$$

which can be written as

$$\nabla^{*2} f_2 - \frac{\partial f_2}{\partial t^*} = -h_2(\mathbf{r}^*, t), \tag{4.27}$$

where

$$h_2(\mathbf{r}^*, t^*) = \frac{(1-x^{*2}/2)\,[2y^*t^* + (6+t^*)\,y^{*2} + 5y^{*3} + y^{*4}]}{48\pi^{\frac{3}{2}}\,t^{*\frac{3}{2}}} \exp\left[-\frac{x^{*2}+y^{*2}+z^{*2}}{4t^*}\right]. \tag{4.28}$$

Evaluating the required integral of the source function h_2 using the Green's function (4.24), we find

$$f_2 = (48\pi^{\frac{3}{2}})^{-1}\,[a_0 + a_1 y^* + a_2 y^{*2} + a_3 y^{*3} + a_4 y^{*4} + a_5 x^{*2} + a_6 x^{*2} y^* + a_7 x^{*2} y^{*2} + a_8 x^{*2} y^{*3} + a_9 x^{*2} y^{*4}] \exp\left[-\frac{x^{*2}+y^{*2}+z^{*2}}{4t^*}\right], \tag{4.29a}$$

where the a_i's are all functions of t^*:

$$\left.\begin{aligned} &a_0 = -\tfrac{3}{10}t^{*\frac{3}{2}} - t^{*\frac{1}{2}}, \quad a_1 = -\tfrac{1}{2}t^{*\frac{1}{2}}, \\ &a_2 = -\tfrac{3}{5}t^{*\frac{1}{2}} - 3/2t^{*\frac{1}{2}}, \quad a_3 = -1/t^{*\frac{1}{2}}, \\ &a_4 = -1/6t^{*\frac{1}{2}}, \quad a_5 = \tfrac{3}{20}t^{*\frac{1}{2}} + 1/2t^{*\frac{1}{2}}, \\ &a_6 = 1/t^{*\frac{1}{2}}, \quad a_7 = 3/10t^{*\frac{1}{2}} + 3/4t^{*\frac{3}{2}}, \\ &a_8 = 1/2t^{*\frac{3}{2}}, \quad a_9 = 1/12t^{*\frac{3}{2}}. \end{aligned}\right\} \tag{4.29b}$$

With the aid of (4.25) and (4.29) it is possible to calculate the moments of f up to order σ^2. For instance the contribution of the term of order σ to $\langle r^{*2}\rangle$ is zero while the contribution of the σ^2 term to $\langle r^{*2}\rangle$:

$$\begin{aligned} \langle r^{*2}\rangle &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} (x^{*2}+y^{*2}+z^{*2}) f_2\, dx^*\, dy^*\, dz^* \\ &= a_0 t^{*\frac{5}{2}} + \tfrac{10}{3}a_2 t^{*\frac{7}{2}} + 28a_4 t^{*\frac{9}{2}} + \tfrac{10}{3}a_5 t^{*\frac{7}{2}} + \tfrac{28}{3}a_7 t^{*\frac{9}{2}} + 72a_9 t^{*\frac{11}{2}}. \end{aligned} \tag{4.30}$$

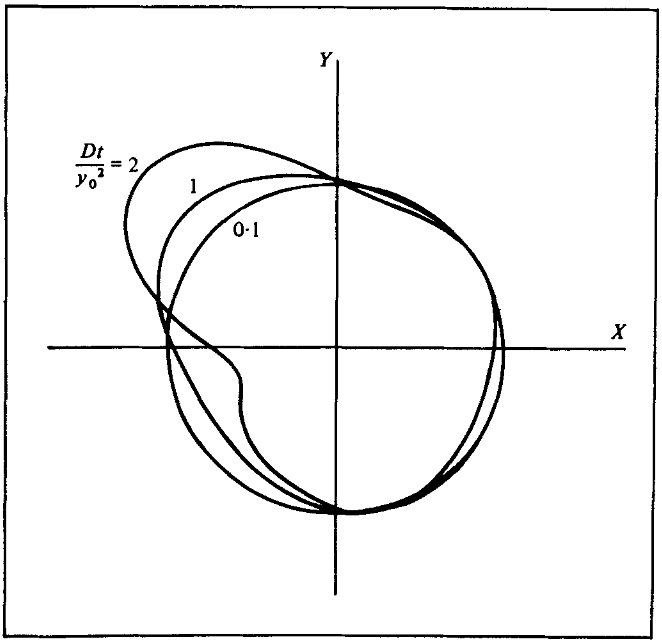

FIGURE 4. Orientation distribution function $p(\phi)$ for particles near the centre of a parabolic flow for the case $\sigma = 0{\cdot}1$. The co-ordinate system shown is the 'initial velocity' co-ordinate system. Its origin is slightly off centre with respect to a space-fixed co-ordinate system (see figure 3).

Substituting (4.29*b*) into (4.30) yields:

$$\langle r^{*2}\rangle = \tfrac{8}{3}t^{*3} + \tfrac{7}{3}t^{*4},$$

in agreement with result derived earlier. The results of the previous section prove that terms of order greater than σ^2 do not contribute to the second moment.

As in § 2, the deviation from Gaussian behaviour for small values of σ can be conveniently described by the polar plot $p(\phi)$, where

$$p(\phi) = \int_0^\infty dr^*r^{*2}\int_0^\pi d\theta\sin\theta[f_0+\sigma f_1+\sigma^2 f_2],$$

with

$$r^{*2} = x^{*2}+y^{*2}+z^{*2}, \quad x^* = r^*\sin\theta\cos\phi, \quad y^* = r^*\sin\theta\sin\phi, \quad z^* = r^*\cos\theta.$$

A typical example of $p(\phi)$ is given in figure 4 for the case $\sigma = 0{\cdot}1$. Note the asymmetry in $p(\phi)$ which appears after a time $Dt/y_0^2 > 0{\cdot}1$. This behaviour is in accord with the asymmetry of the velocity field itself.

(ii) *Solution far removed from the centre.* Introducing the following dimensionless parameters:

$$\tilde{x} = \frac{\gamma\,|y_0|^{\frac{1}{2}}}{D}x, \quad \tilde{y} = \frac{\gamma\,|y_0|^{\frac{1}{2}}}{D}y, \quad \tilde{z} = \frac{\gamma\,|y_0|^{\frac{1}{2}}}{D}z \quad \text{and} \quad \tilde{t} = \gamma\,|y_0|\,t,$$

one can write the convection diffusion equation for plane Poiseuille flow as

$$\frac{\partial f}{\partial \tilde{t}} = \tilde{\nabla}^2 f + [2\tilde{y} + \sigma^{-\frac{1}{2}}\tilde{y}^2]\frac{\partial f}{\partial \tilde{x}}. \tag{4.31}$$

In the limit $\sigma \to \infty$ equation (4.31) reduces to the equation for simple shear by replacing $-2\gamma y_0$ with G. Expressing (4.12) in terms of the above parameters yields

$$\langle \tilde{x}^2 \rangle = 2\tilde{t} + \tfrac{8}{3}\tilde{t}^3 + \frac{7}{3\sigma}\tilde{t}^4. \tag{4.32}$$

Recalling that when $\sigma = \tau_d/\tau_c \gg 1$, the particle will spend a relatively long time sampling the linear region of flow before it diffuses into the parabolic region. This ratio increases as we move farther away from the centre. Equation (4.32) suggests that (4.31) can be solved as a series expansion in $\sigma^{-\frac{1}{2}}$:

$$f = \tilde{f}_0 + \sigma^{-\frac{1}{2}}\tilde{f}_1 + \sigma^{-1}\tilde{f}_2 + \dots. \tag{4.33}$$

The zero-order solution $\tilde{f}_0$ satisfies

$$\frac{\partial \tilde{f}_0}{\partial \tilde{t}} = \tilde{\nabla}^2 \tilde{f}_0 + 2\tilde{y}\frac{\partial \tilde{f}_0}{\partial \tilde{x}}. \tag{4.34}$$

Hence recalling equation (2.20) for simple shear:

$$\tilde{f}_0 = \frac{1}{8(2\pi\tilde{t})^{\frac{3}{2}}}\left(\frac{3}{\tilde{t}^2+3}\right)^{\frac{1}{2}} \exp - \left[\frac{3(\tilde{x}+\tilde{t}\tilde{y})^2}{4\tilde{t}(\tilde{t}^2+3)} + \frac{\tilde{y}^2}{4\tilde{t}} + \frac{\tilde{z}^2}{4\tilde{t}}\right]. \tag{4.35}$$

Substituting (4.33) into (4.31) and collecting terms of order $\sigma^{-\frac{1}{2}}$ and σ^{-1} yields:

$$\tilde{\nabla}^2\tilde{f}_1 - \frac{\partial \tilde{f}_1}{\partial \tilde{t}} - 2\tilde{y}\frac{\partial \tilde{f}_2}{\partial \tilde{x}} = -\tilde{y}^2\frac{\partial \tilde{f}_0}{\partial \tilde{x}}, \tag{4.36a}$$

$$\tilde{\nabla}^2\tilde{f}_2 - \frac{\partial \tilde{f}_2}{\partial \tilde{t}} - 2\tilde{y}\frac{\partial \tilde{f}_2}{\partial \tilde{x}} = -\tilde{y}^2\frac{\partial \tilde{f}_1}{\partial \tilde{x}}. \tag{4.36b}$$

The Green's function of (4.36) is obtained, as can be proved rigorously, by replacing $\tilde{x}$ by $(\tilde{x}-x')$, etc., and $\tilde{t}$ by $\tilde{t}-t'$ in (4.35):

$$g(\tilde{\mathbf{r}}|\mathbf{r}';\tilde{t}|t') = \frac{1}{8(2\pi)^{\frac{3}{2}}(\tilde{t}-t')^{\frac{3}{2}}}\left(\frac{3}{(\tilde{t}-t')^2+3}\right)^{\frac{1}{2}}$$
$$\times \exp\left\{-\frac{3[(\tilde{x}-x')+(\tilde{t}-t')(\tilde{y}-y')]^2}{4(\tilde{t}-t')[(\tilde{t}-t')^2+3]} + \frac{(\tilde{y}-y')^2+(-z')^2\tilde{z}}{4(\tilde{t}-t')}\right\}$$

when $\tilde{t}-t > 0$ but zero otherwise. (4.37)

Spatial integration of the source function $-\tilde{y}^2\dfrac{\partial \tilde{f}_0}{\partial \tilde{x}}$ using (4.37) suggests a solution $\tilde{f}_1$ of the form

$$\tilde{f}_1 = \frac{1}{16}\left(\frac{3}{2\pi}\right)^{\frac{1}{2}}(b_1\tilde{x}+b_2\tilde{y}+b_3\tilde{x}^3+b_4\tilde{x}^2\tilde{y}+b_5\tilde{x}\tilde{y}^2+b_6\tilde{y}^3).\exp - \left[\frac{3(\tilde{x}+\tilde{t}\tilde{y})^2}{4\tilde{t}(\tilde{t}^2+3)} + \frac{(\tilde{y}^2+\tilde{z}^2)}{4\tilde{t}}\right], \tag{4.38}$$

where all of the coefficients b_i are functions of $\tilde{t}$.

Substituting (4.38) into (4.36a) shows that (4.38) is the correct solution and that the functions b_i's are determined by the following set of coupled differential equations:

$$\left.\begin{aligned}
\frac{db_1}{d\tilde{t}} &= -\frac{5b_1}{2\tilde{t}}-\frac{3b_2}{\tilde{t}^2+3}+6b_3+2b_5,\\
\frac{db_2}{d\tilde{t}} &= \frac{2\tilde{t}^2+3}{\tilde{t}^2+3}b_1-\frac{13\tilde{t}^2+15}{2\tilde{t}(\tilde{t}^2+3)}b_2+2b_4+6b_6,\\
\frac{db_3}{d\tilde{t}} &= -\frac{5\tilde{t}^2+27}{2\tilde{t}(\tilde{t}^2+12)}b_3-\frac{3b_4}{\tilde{t}^2+3},\\
\frac{db_4}{d\tilde{t}} &= \frac{3(2\tilde{t}^2+3)}{\tilde{t}^2+3}b_3-\frac{13\tilde{t}^2+27}{2\tilde{t}(\tilde{t}^2+3)}b_4-\frac{6b_5}{\tilde{t}^2+3},\\
\frac{db_5}{d\tilde{t}} &= \frac{2(2\tilde{t}^2+3)}{\tilde{t}^2+3}b_4-\frac{3(7\tilde{t}^2+9)}{2\tilde{t}(\tilde{t}^2+3)}b_5-\frac{9b_6}{\tilde{t}^2+3}-\frac{1}{\tilde{t}^{\frac{3}{2}}(\tilde{t}^2+3)^{\frac{3}{2}}},\\
\frac{db_6}{d\tilde{t}} &= \frac{2\tilde{t}^2+3}{\tilde{t}^2+3}b_5-\frac{29\tilde{t}^2+27}{2\tilde{t}(\tilde{t}^2+3)}b_6-\frac{1}{\tilde{t}^{\frac{3}{2}}(\tilde{t}^2+3)^{\frac{3}{2}}}.
\end{aligned}\right\} \quad (4.39)$$

Presumably the set of equations (4.39) have analytical solutions, but we were unable to find them. In principle the b_i's can also be found by integrating the source function using (4.37), but this seems, owing to the complexity of the integrand, too laborious a task.

In a manner analogous to that we employ to find $\tilde{f}_1$ it is possible to determine $\tilde{f}_2$. The formal solution is

$$\tilde{f}_2 = \sum_{i=1}^{16} c_i(t)\,\tilde{x}^m\tilde{y}^{n-m}\exp-\left[\frac{3(\tilde{x}+\tilde{t}\tilde{y})^2}{4\tilde{t}(\tilde{t}^2+3)}+\frac{(\tilde{y}^2+\tilde{z}^2)}{4\tilde{t}}\right],$$

where the c_i's are functions of $\tilde{t}$ and $0 \leqslant m \leqslant n$ (m and n are integers) with $m+n = 0, 2, 4$ or 6; this yields 16 terms in total. It is interesting to note that a 16 term expansion contributes just one single term to the second moment $\langle \tilde{r}^2 \rangle$, namely $7\tilde{t}^4/3\sigma$.

5. Wall effects: Monte Carlo calculations

The usual boundary condition taken at the wall for convective diffusion in Poiseuille flow is the no-flux condition (Taylor 1953; Chatwin 1977). This is equivalent to saying that the diffusion coefficient does not change when a particle approaches the wall and that the wall acts as a perfect reflector. However, as shown by Goldman, Cox & Brenner (1967*a*, *b*) the diffusion coefficient is a function of the ratio h/b, h being the distance to the wall and b the particle radius. Furthermore, they showed that the velocity of a particle is slowed down owing to the presence of a wall. For molecular diffusion the region near the wall where wall effects are important is usually very small compared to a tube radius and has little effect on, for example, the concentration of particles averaged over the tube cross-section. However, as we are mainly interested in convective diffusion of colloidal particles in Poiseuille flow, here wall effects can be rather important. For instance, the diffusion constant for a $1\,\mu$m particle in a tube of radius $100\,\mu$m, even at the centre, is about 1 % lower than the value in an unbounded fluid. In order to be able to examine diffusion in systems where wall effects cannot be ignored, we calculated the second moments of the distribution by using Monte Carlo methods.

Three wall corrections have to be taken into account.

(1) Diffusion parallel to the wall: for a particle at a distance h from the wall the tangential diffusion coefficient D_t equals $g_1(h/b)\,D$, where g_1 is a correction factor and D the diffusion coefficient in an infinite medium.

(2) Diffusion perpendicular to the wall: the radial diffusion coefficient D_r equals $g_2(h/b)\,D$. Again g_2 is a correction factor.

(3) The particle velocity U_b near the wall is less than the undisturbed fluid velocity and U_b equals $g_3(h/b)\,U(d)$, U being the undisturbed fluid velocity at a distance $d = h+b$ from the wall.

The functions $g_1(h/b)$, $g_2(h/b)$ and $g_3(h/b)$ are all zero when $h = 0$ and approach one as $h \to \infty$. This means that near the wall diffusion is no longer isotropic, since, the further away a particle is from the wall, the larger its diffusion coefficient will be. Numerical values for the g_i's can be found in the papers by Goldman *et al.* (1967*a*, *b*).

The displacement of Brownian particles in two-dimensional Poiseuille flow is given by the following set of equations (van de Ven 1977):

$$\left.\begin{aligned} dx &= g_3(h/b)\,U(d)\,dt + R_1(t),\\ dh &= R_2(t). \end{aligned}\right\} \tag{5.1}$$

Here $R_1(t)$ and $R_2(t)$ are random displacements. In integrating (5.1) numerically, $R_1(t)$ and $R_2(t)$ are chosen at random in each integration step Δt from Gaussian distribution functions with zero mean and standard deviations $[2g_1(h/b)\,D\Delta t]^{\frac{1}{2}}$ and $[2g_2(h/b)\,D\Delta t]^{\frac{1}{2}}$ respectively. For most calculations (except very near a wall) the position of a particle was determined after 100 steps and the procedure repeated 100 times. For comparison calculations were also performed from the case of the usual no-flux boundary condition. In this case all the g_i's are equal to one and h changes sign when $h+dh < 0$ (reflexion).

The results of such calculations are given in figures 5 and 6 for the case

$$Pe = G_{\max} b^2/D = 100 \quad \text{and} \quad R_0/b = 100,$$

corresponding, for example, to particles of $1\,\mu$m radius in an aqueous solution in a tube of radius $R_0 = 100\,\mu$m with a wall shear rate $G_{\max}$ of about $7\,\mathrm{s}^{-1}$, a typical condition in a 'travelling microtube device' (Vadas, Goldsmith & Mason 1973; van de Ven & Mason, 1976).

In these figures the second moments are expressed, as before, with respect to an observer moving with the velocity of the particle at time $t = 0$; thus $\hat{x} = (x - U_0 t)/b$ and $\hat{y} = (h-h_0)/b$, U_0 and h_0 being the particle velocity and wall distance at time $t = 0$.

It can be seen that taking wall effects into account has a dramatic effect on $\langle \hat{x}^2 \rangle$ and $\langle \hat{y}^2 \rangle$, diminishing the second moments by sometimes several orders of magnitude, especially near the wall. In contrast reflexion has almost no effect on the second moments as compared to the calculations for an unbounded fluid. For the case of reflexion the second moment $\langle \hat{y}^2 \rangle$ can be readily calculated. The probability distribution function for a diffusive point source at $d_0 (= h_0 + b)$, a reflecting wall at $d = 0$ and an image source at $-d_0$ is given by (Chandrasekhar 1943):

$$p(d,t;\,d_0) = \frac{1}{2(\pi D t)^{\frac{1}{2}}}\left\{\exp\left[-\frac{(d-d_0)^2}{4Dt}\right] + \exp\left[-\frac{(d+d_0)^2}{4Dt}\right]\right\} \tag{5.2}$$

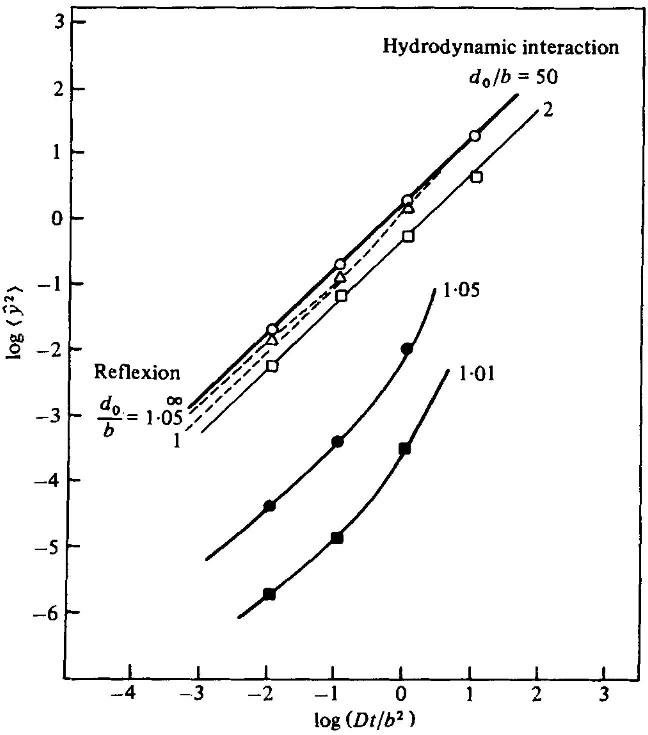

FIGURE 5. Second moment of the probability density function perpendicular to the flow direction as a function of time for various ratios of wall distance to particle radius. The solid line at the top and the dashed lines refer to the exact results for the case of reflexion [equation (5.3)]. Monte Carlo calculations (△) for $d_0/b = 1{\cdot}05$ are included. The solid line on top is indistinguishable from Monte Carlo calculations (○) for $d_0/b = 50$, which take hydrodynamic interactions into account. Other solid lines show Monte Carlo calculations with hydrodynamic interaction for various values of d_0/b. $P_e = 100$ and $R_0/b = 100$.

and hence

$$\langle (d-d_0)^2 \rangle = 2Dt + (2d_0^2 + Dt)\,\mathrm{erfc}\left[\frac{h_0+2b}{2\sqrt{(Dt)}}\right] - Dt\,\mathrm{erfc}\left[\frac{h_0}{2\sqrt{(Dt)}}\right] - h_0\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}\left\{\exp-\left[\frac{h_0^2}{4Dt}\right] + \exp-\left[\frac{(h_0+2b)^2}{4Dt}\right]\right\}, \quad (5.3)$$

The last three terms on the right-hand side of (5.3) are usually small compared to $2Dt$ and affect only slightly a $\log \langle y^2 \rangle$ *vs.* $\log t^*$ plot (see figure 5). From figure 6 it can be seen that also for $\langle x^2 \rangle$ the correction due to reflexion at a wall is rather small. The corrections due to hydrodynamic interactions with the wall are, however, appreciable, especially near the wall.

The calculations have only been carried to times where $\langle x^2 \rangle$ varies as t^3. At much larger times, when particles start reaching the centre of the parabolic flow, $\langle x^2 \rangle$ will of course vary as t^4 in accord with (4.14).

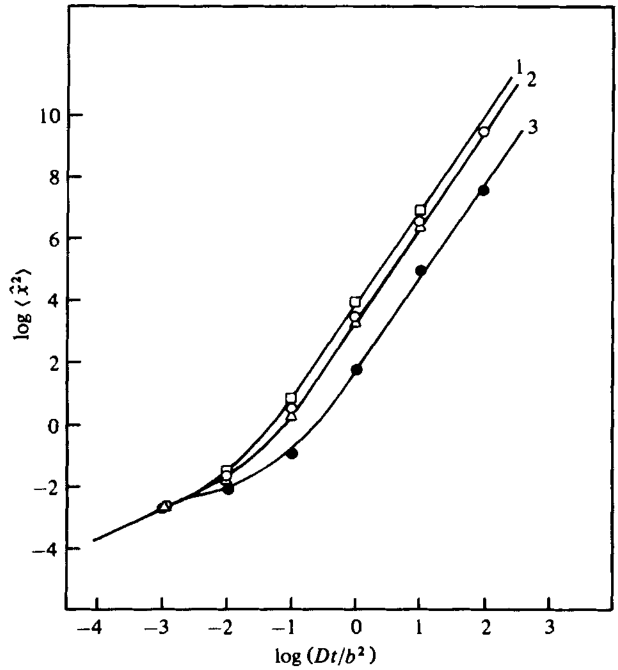

FIGURE 6. Second moment in the direction of flow as a function of time for the case $P_e = 100$ and $R_0/b = 100$.

(1) The solid line is a calculation for the case of an unbounded fluid with $y_0/b = 99$, corresponding to the distance between a particle at the wall and the centre. Monte Carlo calculations (□) for the case of reflexion for $d_0/b \leqslant 1{\cdot}05$ ($y_0/b \geqslant 98{\cdot}95$) fall within computational error on this curve.

(2) The solid line is a theoretical curve for unbounded fluid with $y_0/b = 50$. Monte Carlo calculations for $d/b_0 = 50$ with (○) and without (△) wall effects are shown.

(3) Monte Carlo calculations for $d_0/b \leqslant 1{\cdot}05$ with wall corrections, showing that particles are slowed down appreciably by the presence of a wall. Calculations for $1{\cdot}05 < d_0/b < 50$ fall smoothly in between curves 2 and 3.

6. Discussion

In general coupling between random motions of colloidal particles and convection due to shear can be elucidated by a consideration of both the probability density as a function of time and also the motion of the particle as it is revealed by its stochastic (Langevin) equation of motion. Our results for the linear flows of § 2, which include solutions of the convective diffusion equation appropriate to the particular flow field, indicate that the degree of coupling increases as we move from pure rotational, through simple shear to elongational flows. Here one is reminded of analogous behaviour which can be observed in the shear-induced breakup of aggregates composed of spherical particles with no appreciable Brownian motion (Kao, Powell & Mason 1979), where the least efficient flows are those dominated by rotation and the most efficient those dominated by elongation.

Our calculations for Poiseuille flow using the Langevin approach are in general qualitative agreement with the theory of molecular dispersion of soluble matter in tubes, initiated originally by Taylor (1953), and subsequently extended by Gill &

Sankarasubramanian (1970, 1971), Chatwin (1977), and numerous others. Also, the results given by equation (4.13) for the mean-squared displacement in the flow direction suggest the following interesting possibility for determining diffusion coefficients in a mono-disperse flowing colloidal suspension. A plot of $\ln\langle x^2\rangle$ *vs.* $\ln t$ should, for $t \ll R_0^2/D$, have three linear regions corresponding to slopes of 1, 3 and 4 respectively. Preliminary experiments using the 'travelling micro-tube technique' (Vadas, *et al.* 1973) indicate that the linear region with slope 3 is readily accessible even for a relatively small number of measurements on a few selected particles. In fact plotting data for only six polystyrene latex spheres (radius $\sim 1\,\mu$m) suspended in water flowing with a maximum velocity of $\sim 50\,\mu$m/s in a $200\,\mu$m diameter capillary, we find that this linear region has a slope of 3·1. With improved accuracy the intercept of this region should yield a value of the average self-diffusion coefficient D which is characteristic of the particles in the dilute suspension. Experiments are now under way to test the general predictions of the theory and also to carry out measurements of diffusion coefficients in this manner.

Finally the methods employed in this paper may be extended to the coupling of rotary Brownian motion and rotation due to hydrodynamical shear torques in suspension of spheroids with potentially useful application in the analysis of spreads in measured periods of rotation and other related problems (van de Ven, Takamura & Mason 1979).

Appendix A. Solution of the convective diffusion equation for a point source at the origin in a linear field

Consider the flux $\mathbf{J}(\mathbf{r};t)$ given by

$$\mathbf{J}(\mathbf{r};t) = -D\nabla f(\mathbf{r};t)+\mathbf{H}(\mathbf{r};t)f(\mathbf{r};t), \tag{A 1}$$

where $f(\mathbf{r};t)$ is the probability density at $\mathbf{r}$ and t, D is a scalar which is independent of $\mathbf{r}$ and t and $\mathbf{H}(\mathbf{r};t) = \mathbf{A}(t).\mathbf{r}$ is a generalized field linear in the co-ordinates $\mathbf{r}$. For an incompressible liquid the trace of $\mathbf{A}(t)$ will vanish in accord with the equation of continuity, but in what follows we refrain from this assumption for the sake of generality.

The probability $f(\mathbf{r};t)$ obeys the conservation law

$$\frac{\partial f(\mathbf{r};t)}{\partial t}+\nabla.\mathbf{J} = 0, \tag{A 2}$$

which may be combined with (A 1) to yield the convective diffusion equation

$$\frac{\partial f}{\partial t}+\nabla.(\mathbf{H}f) = D\nabla^2 f, \tag{A 3}$$

or, in alternative form, employing the summation convention for repeated indices

$$\frac{\partial f}{\partial t}+A_{ij}x_j\frac{\partial f}{\partial x_i}+A_{ii}f = D\delta_{ij}\frac{\partial^2 f}{\partial x_i\,\partial x_j}. \tag{A 4}$$

Here $H_i = A_{ij}x_j$ and $i,j = 1,2,3$. We seek a fundamental solution of (A 4) in an infinite medium; that is, we require

$$\lim_{t\to 0} f(\mathbf{r};t) = \delta(\mathbf{r}) \tag{A 5}$$

and
$$\lim_{r\to\infty} f(\mathbf{r};t) = 0. \tag{A 6}$$

As a trial solution we take the generalized Gaussian distribution

$$f(\mathbf{r};t) = B(t)\exp -[\tfrac{1}{2}\beta_{kl}x_k x_l] \tag{A 7}$$

with $\beta_{kl} = \beta_{lk}$, and we assume that $\beta_{kl}(t)\,x_k x_l$ is a positive-definite quadratic form in order to satisfy (A 6). $B(t)$ is a normalization constant to be determined by

$$\int d\mathbf{r} f(\mathbf{r};t) = 1 \quad \text{for all } t.$$

Substitution of (A 7) into (A 4) shows that the generalized Gaussian is indeed a solution provided the coefficients β_{kl} satisfy

$$\frac{d\beta_{kl}}{dt} + A_{ik}\beta_{il} + A_{il}\beta_{ki} + 2D\beta_{il}\beta_{ik} = 0, \tag{A 8}$$

and that $B(t)$ satisfy

$$\frac{1}{B}\frac{dB}{dt} + A_{ii} + 2D\beta_{ii} = 0. \tag{A 9}$$

The nonlinearity of (A 8) makes solution of the set of coupled equations for the coefficients β_{kl} a difficult task in all but the simplest cases. It is preferable therefore to try to determine first the matrix of coefficients inverse to the matrix of β_{kl}. To obtain an equation for β^{-1}_{kl} equivalent to (A 8) for β_{kl} we first write (A 8) in the form

$$\frac{d\beta_{ij}}{dt} + A_{mi}\beta_{mj} + A_{mj}\beta_{im} + 2D\beta_{mj}\beta_{mi} = 0. \tag{A 10}$$

Multiplying (A 10) from the right by β^{-1}_{li} we find

$$\frac{d\beta^{-1}_{il}}{dt}\beta_{ij} - A_{mi}\beta_{mj}\beta^{-1}_{li} - A_{mj}\delta_{lm} - 2D\beta_{mj}\delta_{ml} = 0,$$

where we have used $\beta_{ij}\beta^{-1}_{li} = \delta_{jl}$. Multiplying now from the left by β^{-1}_{jk}, we have the following equation for β^{-1}_{kl}:

$$\frac{d\beta^{-1}_{kl}}{dt} - A_{ki}\beta^{-1}_{li} - \beta^{-1}_{ik}A_{li} - 2D\delta_{kl} = 0. \tag{A 11}$$

In order to specify initial conditions for the solution of (A 11) and (A 9), we must investigate the conditions under which the distribution (A 7) becomes a delta function in the limit $t \to 0$. Obviously we must have

$$\lim_{t\to 0}\int d\mathbf{r} f(\mathbf{r};t) = 1.$$

This requirement is satisfied by taking

$$B(t) = (2\pi)^{-\frac{3}{2}}(\det \boldsymbol{\beta})^{\frac{1}{2}}$$

or, equivalently,

$$B(t) = (2\pi)^{-\frac{3}{2}}\{\det \boldsymbol{\beta}^{-1}\}^{-\frac{1}{2}}. \tag{A 12}$$

In addition with $B(t)$ given by (A 12) one can show by a straightforward calculation, using equation (A 11) for $d\beta^{-1}_{kl}/dt$, that the differential equation (A 9) for $B(t)$ is satisfied. Consequently the distribution will remain normalized for all t.

The condition that (A 7) with (A 12) reduce to $\delta(\mathbf{r})$ at $t = 0$ will also require that

$$(a)\quad \lim_{\substack{t\to 0\\ \mathbf{r}=0}} (2\pi)^{-\frac{3}{2}} (\det \boldsymbol{\beta}^{-1})^{-\frac{1}{2}} \exp\left[-\tfrac{1}{2}\beta_{kl} x_k x_l\right] = \infty$$

and

$$(b)\quad \lim_{\substack{t\to 0\\ \mathbf{r}\neq 0}} (2\pi)^{-\frac{3}{2}} (\det \boldsymbol{\beta}^{-1})^{-\frac{1}{2}} \exp\left[-\tfrac{1}{2}\beta_{kl} x_k x_l\right] = 0.$$

Now (a) is satisfied if we take all $\beta_{kl}^{-1}(0)$ identically equal to zero. That this condition also satisfies (b) can be verified in the following manner.

The determinant of $\boldsymbol{\beta}^{-1}$ appearing in the normalization constant may be written in alternative form (Happel & Brenner 1973) as

$$\det \boldsymbol{\beta}^{-1} = \tfrac{1}{6}\beta_{pq}^{-1}\beta_{rs}^{-1}\beta_{tu}^{-1}\epsilon_{pqt}\epsilon_{rsu},$$

where ϵ_{ijk} is the unit alternating tensor. Obviously $(\det \boldsymbol{\beta}^{-1})^{\frac{1}{2}}$ approaches zero as $(\beta_{kl}^{-1})^{\frac{3}{2}}$ if we take $\beta_{kl}^{-1}(0) = 0$. The limit of $\exp[-\frac{1}{2}\beta_{kl} x_k x_l]$, on the other hand, is determined by the behaviour of β_{kl} as $t \to 0$. If $\beta_{kl}^{-1} \to 0$ as $t \to 0$ then β_{kl} approaches infinity in the limit as can be seen by repeated application of l'Hôpital's rule to β_{kl} in the form

$$\beta_{kl} = (\beta_{im}^{-1}\beta_{jn}^{-1}\epsilon_{imk}\epsilon_{jnl})/6 \det \boldsymbol{\beta}^{-1}$$

and use of equation (A 11) for the time derivatives. Thus $\exp[-\frac{1}{2}\beta_{kl} x_k x_l]$ approaches zero exponentially for fixed $r \neq 0$, while $(\det \boldsymbol{\beta}^{-1})^{\frac{1}{2}}$ approaches zero only as $(\beta_{kl}^{-1})^{\frac{3}{2}}$. The ratio of these two quantities appearing in (b) must therefore approach zero, which is the desired behaviour. It should also be pointed out (Landau & Lifshitz 1969) that the second moments of the generalized Gaussian are related to the inverse elements β_{kl}^{-1} as

$$\langle x_k x_l \rangle = \beta_{kl}^{-1}, \tag{A 13}$$

so that requiring $\beta_{kl}^{-1}(0) = 0$ is equivalent to saying that the probability is initially a point source at the origin. Furthermore, an equation for $\langle x_k x_l \rangle$ identical to (A 11) may be derived by multiplying (A 4) by $x_k x_l$, integrating over all space, and utilizing the boundary conditions at infinity.

In conclusion then, solving (A 11) with $\beta_{kl}^{-1}(0) = 0$ completes the determination of the fundamental solution of the convective diffusion equation for an arbitrary linear field. A word of caution should be injected here, however, since we have assumed that $\beta_{kl}(t)\, x_k x_l$ will always be positive-definite. Actually the field is arbitrary only inasmuch as the solution of the appropriate equations for $\beta_{kl}^{-1}(t)$ maintains this positive-definite character. Once this has been verified for any specific case, then the analysis here will provide the correct distribution. The determination of the fundamental solution for a general point source (not necessarily at the origin) which may be used to calculate the solution of (A 3) for any arbitrary initial distribution, requires some modification of the procedure above.

Appendix B. Mean squared displacements in general two-dimensional flow from the Langevin equation†

If we neglect terms in the Langevin equation which are of relative order $(\beta t)^{-1}$ or less, then formal integration of the Langevin equations with the general flow (2.6) yields

$$x(t) = \frac{1}{\beta}\int_0^t d\lambda\,[X(\lambda)+\beta G y(\lambda)], \tag{B 1}$$

$$y(t) = \frac{1}{\beta}\int_0^t d\lambda\,[Y(\lambda)+\alpha\beta G x(\lambda)]. \tag{B 2}$$

Differentiation of (B 1) and (B 2) gives an equation for $x(t)$:

$$\ddot{x}-\alpha G^2 x = \frac{1}{\beta}\dot{X}(t)+\frac{1}{\beta}G\,Y(t). \tag{B 3}$$

This non-homogeneous equation has the solution

$$x(t) = \frac{1}{\beta}\int_0^t ds\,X(s)\cosh\,[\alpha^{\frac{1}{2}}G(t-s)]+\frac{1}{\alpha^{\frac{1}{2}}\beta}\int_0^t ds\,Y(s)\sinh\,[\alpha^{\frac{1}{2}}G(t-s)], \tag{B 4}$$

where $x(0) = 0$. With a similar initial condition on $y(t)$ we find

$$y(t) = \frac{\alpha^{\frac{1}{2}}}{\beta}\int_0^t ds\,X(s)\sinh\,[\alpha^{\frac{1}{2}}G(t-s)]+\frac{1}{\beta}\int_0^t ds\,Y(s)\cosh\,[\alpha^{\frac{1}{2}}G(t-s)]. \tag{B 5}$$

With (B 4) and (B 5), equations (2.12)–(2.14) follow by appropriate averaging over the ensemble.

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