Langevin approach to the dynamics of interacting Brownian particles

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Abstract. We describe an approach to the dynamics of particles in liquid suspension, based on Langevin equations, which allows rather direct calculation of power series expansions in time τ of such quantities as the particle velocity autocorrelation function, mean-square displacement and dynamic structure factors. The expansions are evaluated to order τ^3 if hydrodynamic interactions are neglected, but only to order τ in their presence. The longer-time diffusion coefficients are also considered, and the importance of the structural relaxation time τ_1 to the theoretical development is emphasised. Further similarities between the dynamics of particle suspensions and atoms in simple fluids are pointed out.

1. Introduction

The dynamics of interacting spherical microscopic particles suspended in a liquid are frequently described theoretically by the generalised Smoluchowski equation, essentially a many-particle diffusion equation. In this way, for example, Ackerson (1976) calculated the first two terms in a MacLaurin power series expansion in time τ of the dynamic structure factor $F(K, \tau)$ (which can be measured by inelastic light or neutron scattering). Here we develop an alternative (though equivalent, see e.g. Zwanzig 1969) approach, based on Langevin equations, which has two advantages. Firstly, the physical principles and assumptions involved are displayed clearly, particularly because of the more explicit treatment of particle velocities inherent in the Langevin approach and the natural emergence of characteristic timescales (see § 2.1). Secondly, the calculations can be considerably simplified. Thus, if hydrodynamic interactions are neglected, we are able to calculate $F(K, \tau)$ to order τ^3 as well as obtaining, apparently for the first time, short-time expansions for the particle velocity autocorrelation function $\phi(\tau)$ and the related mean-square particle displacement (§ 2).

Incorporation into this approach of hydrodynamic interactions, the coupling of the motions of different particles through hydrodynamic flows induced in the suspending liquid, has proved more difficult than originally expected and will be discussed elsewhere. However, as described in § 3, we have been able to calculate rather directly, to order τ, a short-time expansion of $F(K, \tau)$ which includes the effects of hydrodynamic interactions.

The approach described here also allows direct derivation of formal expressions for the *long-time* macroscopic collective and self-diffusion coefficients of the Brownian particle system (§ 4).

In §§ 2–4 we attempt a logical development of the theory without detailed reference to previous work. In § 5 our results are discussed both in general and in the light of

previous work. In particular we emphasise the importance of the structural relaxation time τ_I (§ 2.1) to the theoretical development (see § 5.3). In § 5.2 we also consider the similarities, which have been recognised for some time, between the dynamical properties of particle suspensions and those of atoms in dense simple liquids.

2. Short times, no hydrodynamic interactions

2.1. The theoretical framework

Throughout § 2 hydrodynamic interactions will be neglected. In practice, neglect of hydrodynamic interactions is only justified in dilute suspensions, for example at volume fractions ϕ less than about 0.01. In this case the typical interparticle spacing is many times the particle radius, so that the direct interparticle interactions must be of long range if their effect is not also to be negligible. The best known example of this is the repulsive Coulombic interaction between highly charged particles for which it has been established experimentally (e.g. Brown *et al* 1975, Pusey 1978) that, in dilute suspensions ($\phi < 10^{-3}$) at low electrolyte concentrations, the long-range Coulombic interactions have a strong influence on the particle dynamics whereas the effect of hydrodynamic interactions is essentially undetectable. Nevertheless, the *hypothetical* situation of arbitrary shorter-range direct interactions (which only affect particle dynamics at higher volume fraction) but negligible hydrodynamic interactions is of considerable theoretical interest (see § 5.2). Thus in § 2, although we neglect hydrodynamic interactions, we will not specify the nature of the direct interaction.

The starting point is the Langevin equation for particle j in a suspension containing N identical interacting spheres (see e.g. Uhlenbeck and Ornstein 1930, reprinted in Wax 1954):

$$m\frac{\mathrm{d}v_{j1}(t)}{\mathrm{d}t} = -fv_{j1}(t) + \mathscr{F}_{j1}(t) - \frac{\partial U[\{r_i(t)\}]}{\partial r_{j1}}. \tag{2.1}$$

Here r and v are particle positions and velocities and the subscript 1 indicates a single Cartesian component; m is the particle mass and f its friction coefficient; $\mathscr{F}$ is the solvent-induced 'random force' which is assumed to fluctuate rapidly compared with any other process of interest; $U[\{r_i(t)\}]$ is the potential energy of the direct interaction which depends on the instantaneous positions $\{r_i(t)\}$ of all the particles; $-\partial U/\partial r_{j1}$ is thus one component of the instantaneous interaction force on particle j. Equation (2.1) can be integrated to give the displacement $\Delta r_{j1}(\tau)$ of particle j in time τ (Uhlenbeck and Ornstein 1930, p 831):

$$\Delta r_{j1}(\tau) \equiv r_{j1}(\tau) - r_{j1}(0)$$

$$= \Delta r_{Bj1}(\tau) + \frac{1}{f}\int_0^\tau \mathrm{d}t\frac{\partial U[\{r_i(t)\}]}{\partial r_{j1}}\left[\exp\left(-\frac{\tau-t}{\tau_B}\right)-1\right]. \tag{2.2}$$

Here $\Delta r_{Bj}(\tau)$ is the random or 'Brownian' displacement of particle j which would occur in the absence of interparticle interactions; τ_B, defined by

$$\tau_B = m/f, \tag{2.3}$$

can be taken as the fluctuation time of the particle velocities in response to the solvent forces. (For a particle of radius 250 Å, for example, $\tau_B \approx 1.5 \times 10^{-10}$ s (Pusey 1975); in this short time the particle moves only about 0.3 Å, 1/800th of its radius.) We now

specialise to a timescale where $\tau \gg \tau_B$; this is the regime of validity of the generalised Smoluchowski equation and that investigated by most experiments on particle suspensions. Equation (2.2) then simplifies to

$$\Delta r_{j1}(\tau) = \Delta r_{Bj1}(\tau) - \frac{1}{f} \int_0^\tau dt \frac{\partial U[\{r_i(t)\}]}{\partial r_{j1}}. \tag{2.4}$$

The interaction force is expanded as a Taylor series in particle displacements:

$$\frac{\partial U[\{r_i(t)\}]}{\partial r_{j1}} = \frac{\partial U}{\partial r_{j1}} + \sum_k \sum_\alpha \frac{\partial^2 U}{\partial r_{j1}\, \partial r_{k\alpha}} \Delta r_{k\alpha}(t) + \frac{1}{2} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^3 U}{\partial r_{j1}\, \partial r_{k\alpha}\, \partial r_{l\beta}} \Delta r_{k\alpha}(t)\, \Delta r_{l\beta}(t)$$

$$+ \frac{1}{6} \sum_{k,l,m} \sum_{\alpha,\beta,\gamma} \frac{\partial^4 U}{\partial r_{j1}\, \partial r_{k\alpha}\, \partial r_{l\beta}\, \partial r_{m\gamma}} \Delta r_{k\alpha}(t)\, \Delta r_{l\beta}(t)\, \Delta r_{m\gamma}(t) + \ldots . \tag{2.5}$$

Here italic subscripts are particle labels and run from 1 to N: greek subscripts indicate Cartesian components and run from 1 to 3; we have also adopted the notation $U \equiv U[\{r_i(0)\}]$. Iterative use of (2.4) and (2.5) gives an expression for the total particle displacement in terms of zero-time spatial derivatives of U and the *random* displacements $\{\Delta r_{Bi}\}$:

$$\Delta r_{j1}(\tau) = \Delta r_{Bj1}(\tau) - \frac{\tau}{f} \frac{\partial U}{\partial r_{j1}} - \frac{1}{f} \sum_k \sum_\alpha \frac{\partial^2 U}{\partial r_{j1}\, \partial r_{k\alpha}} \int_0^\tau dt\, \Delta r_{Bk\alpha}(t) + \frac{\tau^2}{2f^2} \sum_k \sum_\alpha \frac{\partial^2 U}{\partial r_{j1}\, \partial r_{k\alpha}} \frac{\partial U}{\partial r_{k\alpha}}$$

$$+ \frac{1}{f^2} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^2 U}{\partial r_{j1}\, \partial r_{k\alpha}} \frac{\partial^2 U}{\partial r_{k\alpha}\, \partial r_{l\beta}} \int_0^\tau dt \int_0^t dt'\, \Delta r_{Bl\beta}(t')$$

$$- \frac{1}{2f} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^3 U}{\partial r_{j1}\, \partial r_{k\alpha}\, \partial r_{l\beta}} \int_0^\tau dt\, \Delta r_{Bk\alpha}(t)\, \Delta r_{Bl\beta}(t)$$

$$+ \frac{1}{f^2} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^3 U}{\partial r_{j1}\, \partial r_{k\alpha}\, \partial r_{l\beta}} \frac{\partial U}{\partial r_{l\beta}} \int_0^\tau dt\, t\, \Delta r_{Bk\alpha}(t)$$

$$- \frac{1}{6f} \sum_{k,l,m} \sum_{\alpha,\beta,\gamma} \frac{\partial^4 U}{\partial r_{j1}\, \partial r_{k\alpha}\, \partial r_{l\beta}\, \partial r_{m\gamma}} \int_0^\tau dt\, \Delta r_{Bk\alpha}(t)\, \Delta r_{Bl\beta}(t)\, \Delta r_{Bm\gamma}(t) + \ldots . \tag{2.6}$$

By definition

$$\Delta r_{j1}(\tau) = \int_0^\tau v_{j1}(t)\, dt \tag{2.7}$$

and

$$\Delta r_{Bj1}(\tau) = \int_0^\tau v_{Bj1}(t)\, dt, \tag{2.8}$$

where $v_{Bj}(t)$ is the 'Brownian component' of particle velocity, the velocity particle j would have in the absence of interparticle interactions. Thus differentiation of (2.4) gives

$$v_{j1}(\tau) = v_{Bj1}(\tau) + v_{Ij1}(\tau), \tag{2.9}$$

where the 'interaction component' of particle velocity, $v_{Ij1}(\tau)$, is given by

$$v_{Ij1}(\tau) = -\frac{1}{f} \frac{\partial U[\{r_i(\tau)\}]}{\partial r_{j1}} \tag{2.10}$$

and describes the 'drifting around' of particle j in the interparticle force field. The Brownian component of velocity has a large mean-square value $\langle v_{Bj1}^2 \rangle \approx kT/m$ (k is Boltzmann's constant, T the temperature) and fluctuates rapidly on timescale τ_B (see above). Direct calculation (Pusey 1975) shows that the interaction component typically has mean-square value $\langle v_I^2 \rangle \ll \langle v_B^2 \rangle$; however, it fluctuates much more slowly on the timescale τ_I ($\tau_I \gg \tau_B$), characteristic of significant changes in the spatial configuration $\{r_i(t)\}$ of particles which cause a significant change in the force $\partial U/\partial r_{j1}$ (equation (2.10)). Nevertheless, the quantities $\langle v_B^2 \rangle \tau_B$ and $\langle v_I^2 \rangle \tau_I$, which, roughly speaking, describe the relative contributions of solvent forces and interaction forces to the particle diffusion coefficients, can often be comparable in magnitude (Pusey 1978, Phillies and Wills 1981). In (2.9), $v_{Ij1}(\tau)$ can be expanded to give (most directly by differentiation of (2.6))

$$v_{j1}(\tau) = v_{Bj1}(\tau) - \frac{1}{f} \frac{\partial U}{\partial r_{j1}} - \frac{1}{f} \sum_k \sum_\alpha \frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \Delta r_{Bk\alpha}(\tau) + \frac{\tau}{f^2} \sum_k \sum_\alpha \frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \frac{\partial U}{\partial r_{k\alpha}}$$

$$+ \frac{1}{f^2} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \frac{\partial^2 U}{\partial r_{k\alpha} \partial r_{l\beta}} \int_0^\tau dt \, \Delta r_{Bl\beta}(t)$$

$$- \frac{1}{2f} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^3 U}{\partial r_{j1} \partial r_{k\alpha} \partial r_{l\beta}} \Delta r_{Bk\alpha}(\tau) \Delta r_{Bl\beta}(\tau)$$

$$+ \frac{\tau}{f^2} \sum_{k,l} \sum_{\alpha,\beta} \frac{\partial^3 U}{\partial r_{j1} \partial r_{k\alpha} \partial r_{l\beta}} \frac{\partial U}{\partial r_{l\beta}} \Delta r_{Bk\alpha}(\tau)$$

$$- \frac{1}{6f} \sum_{k,l,m} \sum_{\alpha,\beta,\gamma} \frac{\partial^4 U}{\partial r_{j1} \partial r_{k\alpha} \partial r_{l\beta} \partial r_{m\gamma}} \Delta r_{Bk\alpha}(\tau) \Delta r_{Bl\beta}(\tau) \Delta r_{Bm\gamma}(\tau) + \dots . \quad (2.11)$$

It appears, however, that since f is undefined for $\tau \ll \tau_B$ we must write

$$v_{j1}(0) = v_{Bj1}(0). \quad (2.12)$$

This is justified *a posteriori* by the calculations below (§§ 2.2 and 2.3).

Equations (2.6) and (2.8)–(2.12) are the basic results to be used in this paper. The calculations involve evaluating ensemble averages of functions of the $\{\Delta r_i\}$ and the $\{v_i\}$. In doing these we exploit the fact that the *random* displacements $\{\Delta r_{Bi}(\tau)\}$ and velocities $\{v_{Bi}\}$ are statistically independent of the particle positions $\{r_i(0)\}$, and hence of the zero-time spatial derivatives of U. Thus, averages over the $\{\Delta r_{Bi}\}$ and the $\{v_{Bi}\}$ can be performed separately from those over the U derivatives and other functions of the $\{r_i\}$. In evaluating the former we use equation (2.8), the assumption that $\tau \gg \tau_B$ and the statistical independence of the Brownian velocities v_B of different particles (valid when hydrodynamic interactions are neglected), which give

$$\langle v_{Bk\alpha}(t) v_{Bl\beta}(t') \rangle \approx 2D_0 \delta_{kl} \delta_{\alpha\beta} \delta(t - t'). \quad (2.13)$$

Here the angular brackets indicate an ensemble average, δ_{kl} is the Kronecker delta and $\delta(t - t')$ the Dirac delta function; D_0 is the 'free-particle' diffusion constant given by the Kubo relationship

$$D_0 \equiv \frac{kT}{f} = \int_0^\infty dt \langle v_{Bk\alpha}(0) v_{Bk\alpha}(t) \rangle. \quad (2.14)$$

Two further identities, valid for systems in thermal equilibrium, are useful in the calculations:

(i) the 'stationarity condition' for statistically stationary variables A and B,

$$\frac{\mathrm{d}\langle A(t)B(t+\tau)\rangle}{\mathrm{d}t} \equiv 0 = \langle \dot{A}(t)B(t+\tau)\rangle + \langle A(t)\dot{B}(t+\tau)\rangle$$

so that

$$\langle \dot{A}(0)B(\tau)\rangle = -\langle A(0)\dot{B}(\tau)\rangle; \tag{2.15}$$

(ii) the 'Yvon identity' for any regular function $G[\{r_i\}]$ of particle positions (Yvon 1943, de Gennes 1959)

$$\left\langle G\frac{\partial U}{\partial r_{k\alpha}}\right\rangle = kT\left\langle \frac{\partial G}{\partial r_{k\alpha}}\right\rangle. \tag{2.16}$$

2.2. The mean-square displacement

The mean-square displacement of a particle is obtained by squaring equation (2.6) and following the averaging procedure outlined at the end of § 2.1. As an illustration we calculate the first two terms in $\langle \Delta r_{j1}^2(\tau)\rangle$, which come from the first three terms in (2.6), in some detail. To order τ^2 we have

$$\langle \Delta r_{j1}^2(\tau)\rangle = \langle \Delta r_{Bj1}^2(\tau)\rangle - \frac{2\tau}{f}\left\langle \frac{\partial U}{\partial r_{j1}}\Delta r_{Bj1}(\tau)\right\rangle + \frac{\tau^2}{f^2}\left\langle \left(\frac{\partial U}{\partial r_{j1}}\right)^2\right\rangle$$

$$- \frac{2}{f}\sum_k\sum_\alpha\left\langle \frac{\partial^2 U}{\partial r_{j1}\,\partial r_{k\alpha}}\int_0^\tau \mathrm{d}t\,\Delta r_{Bj1}(\tau)\,\Delta r_{Bk\alpha}(t)\right\rangle. \tag{2.17}$$

The first term is clearly $2D_0\tau$, the mean-square displacement of a free particle, as can be verified by use of (2.8) and (2.13). In the second term the averages over U and Δr can be performed separately; since the system is spatially isotropic, $\langle \partial U/\partial r_{j1}\rangle = \langle \Delta r_{Bj1}\rangle = 0$. Use of (2.16) and (2.14) gives, for the third term,

$$\frac{\tau^2}{f^2}\left\langle \left(\frac{\partial U}{\partial r_{j1}}\right)^2\right\rangle = \frac{D_0\tau^2}{f}\left\langle \frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle.$$

After separation of averages and use of (2.8) and (2.13), the fourth term becomes

$$-\frac{2}{f}\sum_k\sum_\alpha\left\langle \frac{\partial^2 U}{\partial r_{j1}\,\partial r_{k\alpha}}\right\rangle 2D_0\delta_{jk}\delta_{1\alpha}\frac{\tau^2}{2} = -\frac{2D_0\tau^2}{f}\left\langle \frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle.$$

Higher terms can be evaluated similarly; in appendix 1 we discuss the square of the third term in (2.6). After collecting terms, the final result, to order τ^3, is

$$\langle \Delta r_{j1}^2(\tau)\rangle = 2D_0\tau - \frac{D_0\tau^2}{f}\left\langle \frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle + \frac{D_0\tau^3}{3f^2}\sum_k\sum_\alpha\left\langle \left(\frac{\partial^2 U}{\partial r_{j1}\,\partial r_{k\alpha}}\right)^2\right\rangle + \ldots. \tag{2.18}$$

2.3. The velocity autocorrelation function

By multiplying (2.11) by (2.12) and averaging we get

$$\phi(\tau) \equiv \langle v_{j1}(0)v_{j1}(\tau)\rangle$$

$$= 2D_0\delta(\tau) - \frac{D_0}{f}\left\langle \frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle + \frac{D_0\tau}{f^2}\sum_k\sum_\alpha\left\langle \left(\frac{\partial^2 U}{\partial r_{j1}\,\partial r_{k\alpha}}\right)^2\right\rangle + \ldots. \tag{2.19}$$

It is easily verified that (2.18) and (2.19) obey the identity

$$\langle \Delta r_{j1}^2(\tau) \rangle = 2 \int_0^\tau (\tau - t) \phi(t) \, dt \qquad (2.20)$$

which follows from (2.7). This provides the *a posteriori* justification for equation (2.12).

2.4. The dynamic structure factor $F(K, \tau)$

For a system of N identical Brownian spheres the dynamic structure factor $F(K, \tau)$, measured by inelastic scattering techniques, is

$$F(K, \tau) = N^{-1} \sum_{i,j} \langle \exp\{i\boldsymbol{K} \cdot [r_i(0) - r_j(\tau)]\} \rangle. \qquad (2.21)$$

Here $\boldsymbol{K}$ is the scattering vector which is now taken to be in the '1' direction. Adopting the notation

$$r_i(0) - r_j(0) \equiv r_{ij} \qquad (2.22)$$

we get

$$F(K, \tau) = N^{-1} \sum_{i,j} \langle \exp(iKr_{ij1}) \exp[-iK \Delta r_{j1}(\tau)] \rangle. \qquad (2.23)$$

$F(K, \tau)$ can now be evaluated by expanding the second exponential in (2.23), using (2.6) and averaging. In fact the calculations are greatly simplified if we start from

$$\frac{d^2 F(K, \tau)}{d\tau^2} = -K^2 N^{-1} \sum_{i,j} \langle v_{i1}(0) v_{j1}(\tau) \exp(iKr_{ij1}) \exp[-iK \Delta r_{j1}(\tau)] \rangle \qquad (2.24)$$

which follows from (2.21) with use of (2.15). The coefficients $\lim_{\tau \to 0'} d^n F/d\tau^n$ of a MacLaurin series expansion of $F(K, \tau)$ are obtained by expansion of the last exponential in (2.24) and use of (2.6), (2.8) and (2.11)–(2.16); it should be remembered that, because of (2.13), the true $\tau \to 0$ limit is not taken and all results apply at $\tau \gg \tau_B$.

Obviously

$$\lim_{\tau \to 0'} F(K, \tau) = F(K, 0) \equiv S(K), \qquad (2.25)$$

where $S(K)$ is the static structure factor. A single integration of (2.24) gives

$$\lim_{\tau \to 0'} \frac{dF(K, \tau)}{d\tau} = -K^2 N^{-1} \sum_{i,j} \langle \exp(iKr_{ij1}) \rangle \int_0^\tau \langle v_{Bi1}(0) v_{Bj1}(t) \rangle \, dt$$

$$= -D_0 K^2. \qquad (2.26)$$

It can also be shown that

$$\lim_{\tau \to 0'} \frac{d^2 F(K, \tau)}{d\tau^2} = D_0^2 K^4 + \frac{D_0 K^2}{Nf} \sum_{i,j} \left\langle \exp(iKr_{ij1}) \frac{\partial^2 U}{\partial r_{i1} \, \partial r_{j1}} \right\rangle \qquad (2.27)$$

and

$$\lim_{\tau \to 0'} \frac{d^3 F(K, \tau)}{d\tau^3}$$

$$= -D_0^3 K^6 - \frac{3D_0^2 K^4}{Nf} \sum_j \left\langle \frac{\partial^2 U}{\partial r_{j1}^2} \right\rangle - \frac{D_0 K^2}{Nf^2} \sum_{i,j,k} \sum_\alpha \left\langle \exp(iKr_{ij1}) \frac{\partial^2 U}{\partial r_{i1} \, \partial r_{k\alpha}} \frac{\partial^2 U}{\partial r_{k\alpha} \, \partial r_{j1}} \right\rangle. \qquad (2.28)$$

2.5. The self-dynamic structure factor $F_s(K, \tau)$

The self-dynamic structure factor $F_s(K, \tau)$ for a system of identical Brownian particles is

$$F_s(K, \tau) = \langle \exp[-iK \Delta r_{j1}(\tau)] \rangle. \tag{2.29}$$

Its MacLaurin expansion can be found either by direct calculation or by setting $i = j$ in equations (2.25)–(2.28). The results are

$$\lim_{\tau \to 0} F_s(K, \tau) = 1, \tag{2.30}$$

$$\lim_{\tau \to 0} \frac{dF_s(K, \tau)}{d\tau} = -L'_0 K^2, \tag{2.31}$$

$$\lim_{\tau \to 0} \frac{d^2 F_s(K, \tau)}{d\tau^2} = D_0^2 K^4 + \frac{D_0 K^2}{f} \left\langle \frac{\partial^2 U}{\partial r_{j1}^2} \right\rangle, \tag{2.32}$$

$$\lim_{\tau \to 0} \frac{d^3 F_s(K, \tau)}{d\tau^3} = -D_0^3 K^6 - \frac{3 D_0^2 K^4}{f} \left\langle \frac{\partial^2 U}{\partial r_{j1}^2} \right\rangle - \frac{D_0 K^2}{f^2} \sum_k \sum_\alpha \left\langle \left(\frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \right)^2 \right\rangle. \tag{2.33}$$

3. Short times (to order τ) with hydrodynamic interactions

Equation (2.24) is an exact expression for a system of classical interacting particles which thus applies in the presence of hydrodynamic interactions. After an integration (2.24) can be written in vectorial notation:

$$\frac{dF(K, \tau)}{d\tau} = -N^{-1} \sum_{i,j} \int_0^\tau dt \langle K \cdot v_i(0) v_j(t) \cdot K \exp(iK \cdot r_{ij}) \exp[-iK \cdot \Delta r_j(t)] \rangle. \tag{3.1}$$

Hydrodynamic interactions have two related effects: firstly, due to correlations between the fluctuating solvent forces at different points in the liquid, the Brownian displacements Δr_B (and velocities v_B) of different particles are no longer independent; secondly, the interaction or drift displacement of particle j (the second term in (2.4)) depends not only on the interaction force on particle j but also on the forces on all other particles. It is in treating the second effect that we have encountered difficulties. However, to first order in τ, we can write, following the treatment of § 2.4,

$$\lim_{\tau \to 0} \frac{dF(K, \tau)}{d\tau} = -N^{-1} \sum_{i,j} \int_0^\tau dt \langle K \cdot v_{Bi}(0) v_{Bj}(t) \cdot K \exp(iK \cdot r_{ij}) \rangle, \tag{3.2}$$

where the velocities $\{v_i\}$ have been replaced by their rapidly fluctuating components $\{v_{Bi}\}$ and $\Delta r_j(t)$ set to zero. Simplification of (3.2) is more difficult than that of (2.24) since the $\{v_{Bi}\}$ correlations depend on the instantaneous spatial configuration $\{r_i\}$ of the particles. However, we can exploit the separation of timescales inherent in Brownian motion, i.e. the fact that the fluctuation time τ_B of the $\{v_{Bi}\}$ is much smaller than the 'structural relaxation time' τ_I over which significant changes occur in the spatial configuration $\{r_i\}$ (§ 2.1). Thus we first average the rapidly fluctuating velocities $\{v_{Bi}\}$ over a sub-ensemble, all members of which have the same configuration $\{r_i\}$, and then perform the spatial average. This gives

$$\left. \frac{dF(K, \tau)}{d\tau} \right|_{\tau_B \ll \tau \ll \tau_I} = -N^{-1} \sum_{i,j} \langle K \cdot D'_{ij}(\{r_i\}) \cdot K \exp(iK \cdot r_{ij}) \rangle. \tag{3.3}$$

The diffusion tensors are given by

$$\mathbf{D}'_{ij} = \int_0^\infty dt \langle v_{Bi}(0) v_{Bj}(t) \rangle \tag{3.4}$$

and depend, in general, on the instantaneous positions of all the particles. The short-time effective diffusion coefficient $D_{eff}(K)$ (which describes the initial decay of the *normalised* correlation function $F(K, \tau)/S(K)$) is thus

$$D_{eff}(K) = [NK^2 S(K)]^{-1} \sum_{i,j} \langle \mathbf{K} \cdot \mathbf{D}'_{ij}(\{r_i\}) \cdot \mathbf{K} \exp(i\mathbf{K} \cdot r_{ij}) \rangle. \tag{3.5}$$

$D_{eff}(K)$ describes the motion of the particle system away from an initial configuration over times $\tau_B \ll \tau \ll \tau_I$ and therefore over distances much less than the interparticle spacing (indeed much less than the particle radius), averaged over all possible starting configurations.

A physical interpretation of (3.4) is provided by a linear-response treatment of the Fokker–Planck equation describing N interacting Brownian particles subject to a set of constant external forces $\{F_i\}$. Hess (1980) used this method in a discussion of the long-time ($\tau \gg \tau_I$) friction coefficient of the suspension. This approach is easily adapted to the 'plateau' timescale $\tau_B \ll \tau \ll \tau_I$ with the result

$$\langle v_i \rangle_F = \sum_j \mathbf{b}'_{ij}(\{r_i\}) \cdot \mathbf{F}_j, \tag{3.6}$$

where $\langle v_i \rangle_F$ is the coarse-grained (drift) velocity of particle i, and $\langle \ \rangle_F$ indicates an average over the rapid fluctuations in v_{Bi}. The mobility tensors $\{\mathbf{b}'_{ij}\}$ are given by

$$\mathbf{b}'_{ij} = (kT)^{-1} \mathbf{D}'_{ij}. \tag{3.7}$$

From (3.6), $\mathbf{b}'_{ii}$ is interpreted as the mobility of particle i modified by the presence of other particles, whereas $\mathbf{b}'_{ij}$ describes the increment in the velocity of particle i caused by a force on particle j.

This interpretation allows, in principle, the calculation of the mobility tensors from macroscopic hydrodynamics. To date it has only proved possible to treat analytically the hydrodynamic interaction between an isolated pair of particles at fixed separation. Thus we are forced to consider particle concentrations low enough that the probability of finding two particles in a suitable small volume element greatly exceeds that of finding higher-order clusters. Using low-Reynolds-number, two-body hydrodynamics (for an incompressible fluid) Felderhof (1977) has obtained expressions for the $\mathbf{D}'_{ij}$ in convenient series form. With stick boundary conditions these become

$$\mathbf{D}'_{11}(r_{12}) = D_0 \mathbf{1} + \mathbf{A}(r_{12}) \qquad \mathbf{D}'_{12}(r_{12}) = \mathbf{B}(r_{12}), \tag{3.8}$$

where

$$\mathbf{A}(r_{12}) = D_0 \left[-\frac{15}{4} \frac{a^4}{r_{12}^4} \mathbf{P} - \frac{1}{16} \frac{a^6}{r_{12}^6} (171 - 105\mathbf{P}) + O\left(\frac{a^8}{r_{12}^8}\right) \right], \tag{3.9}$$

$$\mathbf{B}(r_{12}) = D_0 \left[\frac{3}{4} \frac{a}{r_{12}} (\mathbf{1} + \mathbf{P}) + \frac{1}{2} \frac{a^3}{r_{12}^3} (\mathbf{1} - 3\mathbf{P}) + \frac{75}{4} \frac{a^7}{r_{12}^7} \mathbf{P} + O\left(\frac{a^8}{r_{12}^8}\right) \right], \tag{3.10}$$

$\mathbf{1}$ is the unit dyadic, $\mathbf{P} = r_{12} r_{12}/r_{12}^2$, $r_{12} = |r_{12}|$ and a is the particle radius. The much used Oseen (or point-particle) approximation takes the lowest-order terms in (3.8):

$$\mathbf{D}'_{ij} = D_0 \left(\mathbf{1} \delta_{ij} + \frac{3}{4} \frac{a}{r_{ij}} (\mathbf{1} + \mathbf{P})(1 - \delta_{ij}) \right). \tag{3.11}$$

Combination of (3.5) and (3.8) gives

$$D_{\text{eff}}(K) = [S(K)]^{-1}\left(D_0 + nK^{-2}\int d^3r\, g(r)K \cdot [A(r) + \exp(iK \cdot r)B(r)] \cdot K\right), \tag{3.12}$$

where n is the number of particles per unit volume and $g(r)$ is the radial distribution function. Use of (3.9) and (3.10) in (3.12) gives

$$D_{\text{eff}}(K) = \frac{D_0}{S(K)}[1 + \phi(\lambda_O^K + \lambda_D^K + \lambda_S^K + \lambda_A)], \tag{3.13}$$

where

$$\phi = \tfrac{4}{3}\pi a^3 n \tag{3.14}$$

is the volume fraction of particles in the suspension and

$$\lambda_O^K = \frac{9}{2a^2}\int_0^\infty dr\, r[g(r)-1]\left(\frac{\sin Kr}{Kr} + \frac{\cos Kr}{(Kr)^2} - \frac{\sin Kr}{(Kr)^3}\right), \tag{3.15}$$

$$\lambda_D^K = 1 + 3\int_0^\infty \frac{dr}{r}[g(r)-1]j_2(Kr), \tag{3.16}$$

$$\lambda_S^K = \frac{225a^4}{4}\int_0^\infty \frac{dr}{r^5}g(r)\left(\frac{\sin Kr}{Kr} + \frac{2\cos Kr}{(Kr)^2} - \frac{2\sin Kr}{(Kr)^3}\right), \tag{3.17}$$

$$\lambda_A = \frac{3}{a^3}\int_0^\infty dr\, r^2 g(r)\left(\frac{9}{8}\frac{a^6}{r^6} - \frac{5}{4}\frac{a^4}{r^4}\right), \tag{3.18}$$

where $j_2(Kr)$ is a spherical Bessel function. In replacing $g(r)$ by $g(r)-1$ in the Oseen contribution λ_O^K we have exploited the identity (Altenberger and Deutch 1973)

$$K \cdot \int \frac{d^3r}{r}\exp(iK \cdot r)(1+P) = 0, \tag{3.19}$$

thereby ensuring its convergence.

The effective diffusion coefficient D_{eff}^s describing the initial ($\tau_B \ll \tau \ll \tau_I$) decay of the self-dynamic structure factor $F_s(K, \tau)$ (equation (2.29)) can be calculated by a similar procedure (or simply by taking the $i = j$ terms in (3.2)) to give

$$D_{\text{eff}}^s = \int_0^\infty dt\langle v_{Bi1}(0)v_{Bi1}(t)\rangle = \langle K \cdot D_{11}'(r_{12}) \cdot K\rangle/K^2 = D_0(1 + \lambda_A\phi). \tag{3.20}$$

Identification between expressions (3.4) and (3.8)–(3.10) for the diffusion tensors D_{ij}' can also be made through the Landau–Lifshitz (1959) theory of fluctuating hydrodynamics. For point particles, the particle velocity v_{Bi} can be taken as the fluid velocity $V(r_i)$ at the position r_i of particle i. A compact form, derived in appendix 2, for the velocity correlation ($i \neq j$) is then, for $\tau > 0$

$$\langle v_{Bi}(0)v_{Bj}(\tau)\rangle$$

$$= \langle V[r_i(0)]V[r_j(\tau)]\rangle$$

$$= \frac{kT}{\rho}\left\{ 1\left[\frac{2}{3}(4\pi\nu\tau)^{-3/2}\exp\left(-\frac{r_{ij}^2}{4\nu\tau}\right) - \frac{1}{3}(\pi r_{ij}^2)^{-3/2}\gamma\left(\frac{5}{2}, \frac{r_{ij}^2}{4\nu\tau}\right)\right] \right.$$

$$\left. + P(\pi r_{ij}^2)^{-3/2}\gamma\left(\frac{5}{2}, \frac{r_{ij}^2}{4\nu\tau}\right)\right\}, \tag{3.21}$$

where ρ is the fluid density, $\nu = \eta/\rho$ its kinematic viscosity and γ is an incomplete gamma function (Abramowitz and Stegun 1965, p 260). This correlation function is seen to decay·on a timescale

$$\tau_{\rm H} = r_{ij}^2/\nu \tag{3.22}$$

characteristic of shear diffusion between the particles. Typically $\tau_{\rm H}$ is much smaller than the structural relaxation time $\tau_{\rm I}$. On the timescale $\tau \gg \tau_{\rm H}$, typical of many experiments, we may replace (3.21) by the form obtained if transient inertial effects are omitted from the analysis (see appendix 2):

$$\langle v_{{\rm B}i}(0)v_{{\rm B}j}(\tau)\rangle = \frac{kT\delta(\tau)}{4\pi\eta r_{ij}}(1+\mathbf{P}). \tag{3.23}$$

Thus, in the point-particle limit, we can identify $\mathbf{D}'_{ij}$ with the Oseen tensor (with use of (3.4) and (3.11) for $i \neq j$), and a calculation relaxing the point-particle approximation would be expected to yield Felderhof's full expressions (3.8)–(3.10). Indeed Mazur (1981) has recently obtained terms to order a^3/r_{ij}^3 in $\mathbf{D}'_{ij}$ by this approach.

4. Long-time, $K \to 0$ limit

In the $K \to 0$ limit, the dynamic structure factor $F(K, \tau)$ describes the fluctuating growth and decay of a spatial Fourier component of particle number density with wavelength $2\pi/K$ much greater than any characteristic length in the suspension (e.g. the range of the interparticle interaction) and on a timescale much greater than any characteristic time in the system (e.g. the structural relaxation time $\tau_{\rm I}$, § 2.1). Such macroscopic number density fluctuations are expected to be small in amplitude (compared with the average number density) so that they decay according to a linear diffusive mechanism (Weissman and Ware 1978). Thus we expect

$$\lim_{K \to 0} F(K, \tau)\bigg|_{\tau \gg \tau_{\rm I}} = S(0) \exp(-D_{\rm c}K^2\tau), \tag{4.1}$$

where $D_{\rm c}$ is the same collective diffusion coefficient as would be measured in conventional gradient diffusion experiments. By comparing the long-time, small-K limit of (3.1) with (4.1) we obtain a microscopic expression for $D_{\rm c}$:

$$D_{\rm c} = [NS(0)]^{-1} \sum_{i,j} \int_0^\infty \mathrm{d}t \langle v_{i1}(0)v_{j1}(t)\rangle = [NS(0)]^{-1} \sum_{i,j} \frac{\langle \mathbf{K} \cdot \mathbf{D}_{ij}(\{r_i\}) \cdot \mathbf{K}\rangle}{K^2}, \tag{4.2}$$

where the diffusion tensors $\mathbf{D}_{ij}$ are given by

$$\mathbf{D}_{ij} = \int_0^\infty \mathrm{d}t \langle v_i(0)v_j(t)\rangle \tag{4.3}$$

and differ from the $\mathbf{D}'_{ij}$ of (3.4) in that it is the full particle velocities $\{v_i\}$, rather than their Brownian components $\{v_{{\rm B}i}\}$, which enter.

For the case where hydrodynamic interactions can be neglected, substitution of (2.9) and (2.12) in (4.2) gives

$$D_{\rm c} = [NS(0)]^{-1}\left(\sum_{i,j}\int_0^\infty \mathrm{d}t\langle v_{{\rm B}i1}(0)v_{{\rm B}j1}(t)\rangle + \sum_{i,j}\int_0^\infty \mathrm{d}t\langle v_{{\rm B}i1}(0)v_{{\rm I}j1}(t)\rangle\right). \tag{4.4}$$

If the interparticle potential is taken to be pairwise additive, it follows from (2.10) that

$$\sum_j v_{I/1}(t) = 0, \tag{4.5}$$

since pairs of particles exert equal and opposite forces on each other. Thus the second term in (4.4) is zero, and comparison with (3.5) shows that

$$D_c = \lim_{K \to 0} D_{eff}(K), \tag{4.6}$$

giving the result, rather surprising at first sight, that the drift velocity components $\{v_I\}$ do not contribute to collective diffusion and that, at $K \to 0$, the short-time, $\tau_B \ll \tau \ll \tau_I$, and long-time, $\tau \gg \tau_I$, decays of $F(K, \tau)$ are described by the same diffusion coefficient. By use of a memory-function approach, Ackerson (1978) has shown that this conclusion holds also in the presence of two-body hydrodynamic interactions.

Use of (3.13)–(3.18) in (4.6) gives (see also Felderhof 1978)

$$D_c = D_0[1 + \phi(\lambda_O + \lambda_D + \lambda_S + \lambda_A)]/(1 + \phi\lambda_V), \tag{4.7}$$

where

$$\lambda_O = \frac{3}{a^2} \int_0^\infty dr\, r[g(r) - 1], \tag{4.8}$$

$$\lambda_D = 1, \tag{4.9}$$

$$\lambda_S = \frac{75a^4}{4} \int_0^\infty \frac{dr}{r^5} g(r), \tag{4.10}$$

$$\lambda_A = \frac{3}{a^3} \int_0^\infty dr\, r^2 g(r) \left(\frac{9}{8} \frac{a^6}{r^6} - \frac{5}{4} \frac{a^4}{r^4} \right), \tag{4.11}$$

$$\lambda_V = \frac{3}{a^3} \int_0^\infty dr\, r^2 [g(r) - 1]. \tag{4.12}$$

For hard spheres, to first order in ϕ, one has

$$g(r) = 0, \qquad r < 2a,$$
$$g(r) = 1, \qquad r > 2a, \tag{4.13}$$

giving

$$D_c = D_0(1 + 1.56\phi). \tag{4.14}$$

The long-time self-diffusion coefficient D_s, which describes the long-time ($\tau \gg \tau_I$) decay of $F_s(K, \tau)$ and can be identified as the macroscopic tracer diffusion coefficient, follows from taking the $i = j$ terms in (4.4) (or directly from the Kubo relationship):

$$D_s = \int_0^\infty dt \langle v_{i1}(0) v_{i1}(t) \rangle = \int_0^\infty dt \langle v_{Bi1}(0) v_{Bi1}(t) \rangle + \int_0^\infty dt \langle v_{Bi1}(0) v_{Ii1}(t) \rangle. \tag{4.15}$$

The first term in (4.15) is simply the short-time effective diffusion coefficient D_{eff}^s (equation (3.20)). However, by contrast with collective diffusion (equation (4.4)), the second term in (4.15) is *not* zero, since the instantaneous interaction force on a single particle is generally non-zero. Thus the average motion of a single particle in an interacting suspension is characterised by two self-diffusion coefficients: D_{eff}^s, which

describes motion over distances much smaller than the typical interparticle separation and differs from the free-particle value D_0 only because of hydrodynamic interactions; D_s, which describes motions over long distances and depends explicitly on the direct interparticle forces.

5. Discussion

5.1. General comments

Perhaps the main justification for this work is that the more explicit treatment of particle velocities inherent in the Langevin approach, as compared, for example, with approaches based on the generalised Smoluchowski equation, allows (in some cases at least) easier calculations and greater insight into dynamical processes in particle suspensions. It should be mentioned that several of the results discussed in §§ 2–4 are not new but were included in an attempt to provide a logical development. The basic equations (2.6) and (2.11) and the results for the mean-square displacement (2.18) and velocity autocorrelation function (2.19) do not appear to have been quoted before; however, the first two terms of (2.6) form the basis for the 'Brownian dynamics' method of computer simulation (Ermak 1975, Gaylor *et al* 1981). Results (2.26) and (2.27) for $dF/d\tau$ and $d^2F/d\tau^2$ were derived by Ackerson (1976) from the Smoluchowski equation; result (2.33) for $d^3F_s/d\tau^3$ was obtained by W Hess (private communication), whereas equation (2.28) for $d^3F/d\tau^3$ appears to be new. The central result of § 3, expression (3.5) for $D_{eff}(K)$, the K-dependent, short-time diffusion coefficient which includes the effects of hydrodynamic interactions, was derived by Ackerson (1976) and Akcasu and Gurol (1976) (see also Altenberger 1974, 1976, Hess and Klein 1979). Provided the relation (3.4) between diffusion tensors and velocity correlations is accepted (see also Batchelor 1976, Wills 1979), then our derivation of (3.5) is both direct and instructive. Equation (3.13) for $D_{eff}(K)$, which includes a full and explicit treatment of two-body hydrodynamic interactions, has been obtained recently by several authors (Russel and Glendinning 1981, Fijnaut 1981, Pusey and Tough 1982) and will be discussed further in § 5.3. The discussion in § 4 is related to that of Ackerson (1978), Dieterich and Peschel (1979), Hess and Klein (1979) and Hess (1980) who used a memory-function approach to the Smoluchowski equation. Again the approach based on velocity correlations provides a different insight. The existence of two self-diffusion coefficients (see last paragraph of § 4) was also recognised some years ago by Harris (1973) and Jacobs and Harris (1977).

   Since the present paper was essentially completed, Phillies and Wills (1981) have published a similar, though less direct, treatment of the dynamic structure factor $F(K, \tau)$. Their expression for $D_{eff}(K)$ differs from the results of Russel and Glendinning (1981), Fijnaut (1981) and equation (3.13) in that λ_A is erroneously found to be K dependent. Also their expression for $d^2F/d\tau^2$ differs slightly from the results of Ackerson (1976) and equation (2.27). In earlier work Phillies (1977, 1981) also discussed the effects of v_I velocity components on self-diffusion and collective diffusion by a somewhat different approach from that used here.

   We take this opportunity to point out an error in our previous related work. In one of the first derivations of (2.26) Pusey (1975) proposed writing the particle velocity as the sum of two components as in (2.9). There it was assumed that v_B and v_I were uncorrelated. The considerations of § 2.3, in particular, show this assumption to be incorrect (see, also, Phillies and Wills 1981). Indeed $\langle v_B v_I \rangle$ correlations play a central

role in the theory, the value of the drift component $v_i(\tau)$ at time τ depending, through (2.10), on the particle configuration $\{r_i(\tau)\}$ at time τ and hence on the past history of random (and drift) displacements. Fortunately this incorrect assumption did not affect the conclusion of the paper.

Except in § 4, we do not, in this paper, evaluate the expressions obtained for specific systems. In some cases this would be very difficult; for example, evaluation of $d^3F/d\tau^3$ (equation (2.28)) would require knowledge of the three-particle distribution function. It should be emphasised that the value of the results derived here is that they are *exact* (at least to the same extent that Langevin and Smoluchowski equations provide an exact description of Brownian motion). Thus approximate theories, based for example on mode-coupling memory-function approaches, can be tested against them. A similar situation exists in theories of simple liquids (e.g. Boon and Yip 1980, p 44), and it is instructive to pursue this analogy further.

5.2. Comparison with simple liquids

The similar functional forms of the derivatives $dF/d\tau$ and $d^2F/d\tau^2$, (2.26) and (2.27), of the dynamic structure factor $F(K, \tau)$ of particle suspensions, and the derivatives $d^2F/d\tau^2$ and $d^4F/d\tau^4$ for simple atomic liquids (de Gennes 1959) were pointed out by Ackerson (1976) (see also Pusey 1975). Here we concentrate on the velocity autocorrelation function and mean-square displacement.

For atom j in a simple liquid we can expand the velocity in time τ (Nijboer and Rahman 1966):

$$v_{j1}(\tau) = v_{j1}(0) + \dot{v}_{j1}(0)\tau + \ddot{v}_{j1}(0)\tau^2/2 + \dots . \tag{5.1}$$

Newton's second law gives

$$\dot{v}_{j1}(0) = -\frac{1}{m}\frac{\partial U[\{r_i(0)\}]}{\partial r_{j1}}, \tag{5.2}$$

so that

$$\ddot{v}_{j1} = -\frac{1}{m}\sum_k\sum_\alpha\frac{\partial^2 U}{\partial r_{j1}\,\partial r_{k\alpha}}v_{k\alpha}, \text{ etc.} \tag{5.3}$$

Use of (5 1)–(5.3), the equipartition theorem and the fact that, for a system of classical interacting particles, the velocity of particle j at time zero is uncorrelated with the zero-time positions and velocities of all other particles gives

$$\phi(\tau) \equiv \langle v_{j1}(0)v_{j1}(\tau)\rangle$$

$$= \frac{kT}{m} - \frac{kT\tau^2}{2m^2}\left\langle\frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle + \frac{kT\tau^4}{24m^3}\sum_k\sum_\alpha\left\langle\left(\frac{\partial^2 U}{\partial r_{j1}\partial r_{k\alpha}}\right)^2\right\rangle + \dots . \tag{5.4}$$

Substitution of (5.4) into (2.20) gives

$$\langle\Delta r_{j1}^2(\tau)\rangle = \frac{kT\tau^2}{m} - \frac{kT\tau^4}{12m^2}\left\langle\frac{\partial^2 U}{\partial r_{j1}^2}\right\rangle + \frac{kT\tau^6}{360m^3}\sum_k\sum_\alpha\left\langle\left(\frac{\partial^2 U}{\partial r_{j1}\partial r_{k\alpha}}\right)^2\right\rangle + \dots . \tag{5.5}$$

Comparison of (5.5) and (2.18) shows further the formal similarities (and differences) between the dynamics of particle suspensions (if hydrodynamic interactions are neglected) and simple liquids. Remembering that $D_0 = kT/f$ (equation 2.14)), we see, aside from numerical factors, two main differences. Firstly, the friction

coefficient f in a suspension plays the role of the atom's mass in a liquid. This is apparently associated with different 'equations of motion', equation (2.10) which connects the force with a drift *velocity* and Newton's law (5.2) which, of course, connects force and *acceleration*. Secondly, the powers of τ in the expansions are different. In the case of a simple classical liquid (5.5) applies down to the true $\tau = 0$ limit and the motion must be time reversible, so that only even powers of τ are found. Equation (2.18) for a suspension applies only for $\tau \gg \tau_B$; the rapidly fluctuating motion caused by the suspending liquid is averaged over and time reversibility is not required.

The above considerations are clearly related to the idea, developed by Hess and Klein (1981), that the particles in a colloidal suspension can be viewed as forming an 'overdamped fluid'.

Another point of similarity with simple liquids concerns the statistics of the displacement $\Delta r_{j1}(\tau)$. If these are Gaussian we have

$$F_s(K, \tau) \; (\equiv \langle \exp[-iK\,\Delta r_{j1}(\tau)]\rangle) = \exp\!\left(-\frac{K^2}{2}\langle \Delta r_{j1}^2(\tau)\rangle\right), \qquad (5.6)$$

whereas in the general case we must write (e.g. Nijboer and Rahman 1966)

$$F_s(K, \tau) = \exp\!\left(-\frac{K^2}{2}\langle \Delta r_{j1}^2(\tau)\rangle + K^4\gamma(\tau) + \ldots\right). \qquad (5.7)$$

For simple liquids the lowest-order contribution to the non-Gaussian term $\gamma(\tau)$ goes as τ^8 (Schofield 1961). Expansion of both sides of (5.7) and use of (2.18) and (2.31)–(2.33) show that, for particle suspensions, $\gamma(\tau)$ contains no terms of order less than τ^4. Thus, as with simple liquids, the Gaussian approximation (5.6) for $F_s(K, \tau)$, which must be correct at short ($\tau \ll \tau_I$) and long ($\tau \gg \tau_I$) times, is probably not too bad at all times for particle suspensions. This conclusion is supported by the recent Brownian dynamics computer simulations of Gaylor *et al* (1981).

5.3. Timescales in theories of diffusion of interacting Brownian particles

An advantage of the approach used in this paper is that characteristic timescales enter the problem naturally and explicitly. In equation (2.9) the particle velocity is written as the sum of a drift component v_I, caused by the interparticle forces, which fluctuates on timescale τ_I characteristic of significant changes in the spatial arrangement of the particles, and a solvent-induced component v_B which fluctuates much more rapidly on timescale τ_B ($\ll \tau_I$) over which the particle configuration barely changes. The diffusion coefficients describing the particle dynamics are expressed in terms of integrals over time correlation functions of these velocity components (equations (4.4) and (4.15)). In general, therefore, one would expect both fast and slow processes to contribute to these coefficients.

In fact there has been some confusion concerning the timescales over which recent theories apply (see also Marqusee and Deutch 1980, Pusey and Tough 1982 for further discussion). Batchelor (1976) generalised Einstein's discussion of Brownian motion to include the effects of interparticle interactions, whereas Felderhof (1978) reduced the Smoluchowski equation to a diffusion equation in the particle density via a BBGKY-type hierarchy. To anticipate our conclusion, it appears that both these authors expected their theories to apply on the macroscopic timescale $\tau \gg \tau_I$, whereas, in fact, they apply on the intermediate or 'plateau' timescale $\tau_B \ll \tau \ll \tau_I$. For collective diffusion Felderhof

obtained equations (4.7)–(4.14), while for hard spheres to first order in ϕ Batchelor obtained

$$D_c = D_0(1 + 1.45\phi) \tag{5.8}$$

which differs from (4.14) in that hydrodynamic interactions were treated in a slightly different way. However, the essentially equivalent results of Batchelor, Felderhof and equation (4.14) do not contribute to the discussion of timescales, since the collective diffusion constant is, for pairwise-additive interactions, expected to be the same on both short, $\tau_B \ll \tau \ll \tau_I$, and long, $\tau \gg \tau_I$, timescales (Ackerson 1978 and § 4).

Difficulties appear, however, with self-diffusion. By considering the diffusion of tagged particles at low concentration in a suspension of otherwise identical particles Batchelor (1976) and Jones (1979) (who extended Felderhof's approach to suspensions containing two species of particle) derived a result for the self-diffusion coefficient essentially identical to (3.20). (Because of their different treatments of hydrodynamic interactions, Batchelor found $\lambda_A = -1.83$, Jones found $\lambda_A = -1.73$.) This is clearly a short-time, $\tau_B \ll \tau \ll \tau_I$, result (see § 3) and does not contain the extra term (the second term in (4.15)) which includes the longer-time, $\tau \approx \tau_I$, effects of direct interactions.

The reason why Batchelor's (1976) theory is 'short-time' seems clear: he specifically assumed that the change in particle configuration during the relaxation time of the particle velocity correlation function was negligible and thereby neglected possible effects of long-lived v_I correlations. The problem with the approach of Felderhof (1978) and Jones (1979) is less obvious, but may be inherent in the low-density expansion they use to decouple the BBGKY-type hierarchy of equations obtained from the N-particle Smoluchowski equation. As was pointed out by Bogoliubov (1962), results obtained from such low-density expansions are valid only over short times before 'drift' (v_I) motions become important.

Recently Russel and Glendinning (1981) and Fijnaut (1981) have obtained expressions for a wavevector-dependent diffusion coefficient which extend earlier work of Altenberger (1976) by a more complete treatment of hydrodynamic interactions. None of these authors discusses timescales in any detail; however, their results are essentially the same as those of equations (3.13)–(3.18) and must therefore be recognised as applying only at short times, $\tau_B \ll \tau \ll \tau_I$. This restriction to short times seems to stem from linearisations, inherent in all the treatments, which are not generally valid at non-zero wavevector (see e.g. Ackerson 1978, Weissman and Ware 1978) but apply only to small (short-time) displacements from a given initial configuration of particles. By contrast, Phillies and Wills (1981) clearly recognised the short-time nature of their calculation (discussed in § 5.1 above).

The considerations of this section thus show that the main theoretical challenge in this field remains a full description of the dynamic structure factor $F(K, \tau)$ away from the $K \to 0$ and $\tau \ll \tau_I$ limits. Although not discussed here, significant progress has been made in this direction by the projection-operator, memory-function approach of Ackerson (1978), Dieterich and Peschel (1979) and Hess and Klein (1979, 1980, 1981) (also Hess 1981); however, hydrodynamic interactions have yet to be incorporated fully in these theories. Recently there have also been several discussions of the second term in (4.15), the long-time contribution to the self-diffusion coefficient (Marqusee and Deutch 1980, Pusey and Tough 1982, G K Batchelor 1981, private communication). The structure of the long-time contribution to the particle velocity autocorrelation function was also discussed earlier by Harris (1973) for charged particles and by Jacobs and Harris (1977) for hard spheres. These authors found power-law long-time decays

similar to the 'long-time tails' found in the velocity autocorrelation functions of atoms in simple dense liquids.

Finally we note that much of the theoretical development in this paper has assumed the existence of a continuous, differentiable interparticle potential U. This, therefore, excludes the commonly considered case, conceptually simple but not encountered in reality, of true hard spheres. As is the case with hard-sphere simple liquids (e.g. Boon and Yip 1980), we expect that hard-sphere colloidal suspensions will require special theoretical treatment. Nevertheless, it is generally possible to define a relaxation time τ_I for the decay of local structure around a given particle so that the conclusions reached in this section concerning timescales should be valid for arbitrary direct (and hydrodynamic) interactions.

Acknowledgments

Appendix 1. Calculations for § 2.2

Evaluation of the term in $\langle \Delta r_{j1}^2 (\tau) \rangle$ (see § 2.2) which comes from squaring the third term in (2.6) requires care. Use of (2.8) and (2.13) gives

$$\frac{1}{f^2} \sum_{k,l} \sum_{\alpha,\beta} \left\langle \frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \frac{\partial^2 U}{\partial r_{j1} \partial r_{l\beta}} \right\rangle \int_0^\tau dt \int_0^\tau dt' \langle \Delta r_{Bk\alpha}(t) \Delta r_{Bl\beta}(t') \rangle$$

$$= \frac{2D_0}{f^2} \sum_k \sum_\alpha \left\langle \left(\frac{\partial^2 U}{\partial r_{j1} \partial r_{k\alpha}} \right)^2 \right\rangle \int_0^\tau dt \int_0^\tau dt' \int_0^t dt'' \int_0^{t'} dt''' \, \delta(t'' - t''').$$

The quadruple integral is re-ordered and integrated by parts to give

$$\int_0^\tau dt \int_0^t dt'' \int_0^\tau dt' \int_0^{t'} dt''' \, \delta(t'' - t''')$$

$$= \int_0^\tau dt \int_0^t dt'' \left(\tau \int_0^\tau dt''' \, \delta(t'' - t''') - \int_0^\tau dt' \, t' \, \delta(t'' - t') \right)$$

$$= \tau^3/3.$$

Collection of similar terms in the square of (2.6) then leads to equation (2.18).

Appendix 2. Derivation of equation (3.21)

From the Landau–Lifshitz (1959, ch 17) theory of fluctuating hydrodynamics we see that the correlation function of Cartesian components (α, β) of the spatial and temporal Fourier components of the velocity in an incompressible fluid with shear viscosity η and density ρ is

$$\langle V_\alpha(\omega, k) V_\beta(\omega', k') \rangle = \frac{kT\eta}{8\pi^4} \frac{\delta(k + k')\delta(\omega + \omega')(k^2 \delta_{\alpha\beta} - k_\alpha k_\beta)}{(i\omega\rho + \eta k^2)(-i\omega\rho + \eta k^2)}. \qquad \text{(A2.1)}$$

Fourier inversion gives, for $\tau > 0$

$$\langle V_\alpha[r_i(0)] V_\beta[r_j(\tau)]\rangle = \frac{kT}{\rho} \int d^3k \, \exp(i\mathbf{k} \cdot \mathbf{r}_{ij} - k^2\nu\tau)\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right). \quad (A2.2)$$

We express $\delta_{\alpha\beta} - k_\alpha k_\beta/k^2$ and $\exp(i\mathbf{k} \cdot \mathbf{r}_{ij})$ in terms of rotationally irreducible sets of quantities (in the latter case by means of the Rayleigh plane-wave expansion and the spherical harmonic addition theorem (Brink and Satchler 1968, p 151)). The angular integrals are then carried out straightforwardly; the integrals over k are of the form

$$\int_0^\infty j_l(kr_{ij}) \exp(-k^2\nu\tau)k^2 \, dk, \qquad l = 0, 2, \qquad (A2.3)$$

where $j_l(kr_{ij})$ is a spherical Bessel function. The integrals (A2.3) can be evaluated using a result given by Watson (1944, equation (13.3.2)) to give (3.21). In the $\tau \gg \tau_H$ limit, transient inertial effects will have decayed, as is expressed formally by setting $\rho = 0$ in (A2.1). The result (3.23) is obtained by performing the Fourier inversion procedure outlined above. Finally, we note that the analysis leading to (3.21) also provides a new form of the Green function appropriate to unsteady creeping flow which is more compact than that quoted by Altenberger (1979) and Oseen's integral representation quoted by Happel and Brenner (1973, p 83).

References

Abramowitz M and Stegun I A 1965 *Handbook of Mathematical Functions* (Washington, DC: National Bureau of Standards)
Ackerson B J 1976 *J. Chem. Phys.* **64** 242–6
—— 1978 *J. Chem. Phys.* **69** 684–90
Akcasu Z and Gurol H 1976 *J. Polym. Sci.: Polym. Phys. Ed.* **14** 1–10
Altenberger A R 1974 *Acta Phys. Pol.* A **46** 661–6
—— 1976 *Chem. Phys. (Netherlands)* **15** 269–77
—— 1979 *J. Polym. Sci.: Polym. Phys. Ed.* **17** 1317–24
Altenberger A R and Deutch J M 1973 *J. Chem. Phys.* **59** 894–8
Batchelor G K 1976 *J. Fluid Mech.* **74** 1–29
Bogoliubov N N 1962 in *Studies in Statistical Mechanics* vol 1, ed J de Boer and G E Uhlenbeck (Amsterdam: North-Holland)
Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)
Brink D M and Satchler G R 1968 *Angular Momentum* (Oxford: Clarendon)
Brown J C, Pusey P N, Goodwin J W and Ottewill R H 1975 *J. Phys. A: Math. Gen.* **8** 664–82
Dieterich W and Peschel I 1979 *Physica* **95A** 208–24
Ermak D L 1975 *J. Chem. Phys.* **62** 4189–96, 4197–203
Felderhof B U 1977 *Physica* **89A** 373–84
—— 1978 *J. Phys. A: Math. Gen.* **11** 929–37
Fijnaut H M 1981 *J. Chem. Phys.* **74** 6857–63
Gaylor K, Snook I and van Megen W 1981 *J. Chem. Phys.* **75** 1682–9
de Gennes P G 1959 *Physica* **25** 825–39
Happel J and Brenner H 1973 *Low Reynolds Number Hydrodynamics* (Leiden: Noordhoff)
Harris S 1973 *Mol. Phys.* **26** 953–7
Hess W 1980 in *Light Scattering in Liquids and Macromolecular Solutions* ed V Degiorgio, M Corti and M Giglio (New York: Plenum)
—— 1981 *Physica* **A** in press
Hess W and Klein R 1979 *Physica* **99A** 463–93
—— 1980 *J. Phys. A: Math. Gen.* **13** L5
—— 1981 *Physica* **105A** 552–76

Jacobs G and Harris S 1977 *J. Chem. Phys.* **67** 5655–7

Jones R B 1979 *Physica* **97A** 113–26

Landau L D and Lifshitz E M 1959 *Fluid Mechanics* (Oxford: Pergamon)

Marqusee J A and Deutch J M 1980 *J. Chem. Phys.* **73** 5396–7

Mazur P 1981 *preprint*

Nijboer B R A and Rahman A 1966 *Physica* **32** 415–32

Phillies G D J 1977 *J. Chem. Phys.* **67** 4690–5

—— 1981 *J. Chem. Phys.* **74** 2436–40

Phillies G D J and Wills P R 1981 *J. Chem. Phys.* **75** 508–14

Pusey P N 1975 *J. Phys. A: Math. Gen.* **8** 1433–40

—— 1978 *J. Phys. A: Math. Gen.* **11** 119–35

Pusey P N and Tough R J A 1982 in *Dynamic Light Scattering: Applications of Photon Correlation Spectroscopy* ed R Pecora (New York: Plenum)

Russel W B and Glendinning A B 1981 *J. Chem. Phys.* **74** 948–52

Schofield P 1961 *Proc. IAEA Symp., Vienna* (Vienna: International Atomic Energy Agency) p 39

Uhlenbeck G E and Ornstein L S 1930 *Phys. Rev.* **36** 823–41

Watson G N 1944 *Theory of Bessel Functions* (Cambridge: University Press)

Wax N (ed) 1954 *Selected Papers on Noise and Stochastic Processes* (New York: Dover)

Weissman M B and Ware B R 1978 *J. Chem. Phys.* **68** 5069–76

Wills P R 1979 *J. Chem. Phys.* **70** 5865–74

Yvon J 1943 *Cahiers de Physique* **14** 1–17

Zwanzig R 1969 *Adv. Chem. Phys.* **15** 325–33