

Application of the Langevin equation to fluid suspensions

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Brownian motion of particles suspended in a fluid is studied, and expressions derived for the particle diffusivity and velocity autocorrelation function. The theory of thermal noise in a general linear system is applied to both the particles and the fluid in a novel formulation. This enables the recent modification of the Langevin equation to include the effect of fluid inertia to be seen as just a necessary but simple reinterpretation of the original analysis, without introducing the theory of non-Markovian processes.

1. Introduction

This paper is concerned with suspensions of particles which are small enough to perform Brownian motions. Although small, the particles will be considered sufficiently large compared with the solvent molecules that the fluid can be described by incompressible hydrodynamics rather than a full kinetic theory. The Brownian movements of the individual particles give rise to diffusion processes in the bulk suspension. As well as translational dispersion, there can also be diffusion of the orientation, shape and particle-separation statistics, all of which can influence the bulk rheological and optical properties. The effectiveness of the Brownian movements in producing diffusion is characterized by a diffusivity \mathbf{D} . In complex situations this diffusivity is a second-rank tensor field defined over the same space as the statistics. It is determined by the strength of the thermal agitations and by the ease with which the particles can move through the fluid, measured respectively by the Boltzmann temperature kT and by the mobility or admittance ζ^{-1} (the velocity resulting from a steady unit force). There are two independent arguments which yield the Stokes–Einstein relation

$$\mathbf{D} = kT\zeta^{-1}, \quad (1.1)$$

which has been experimentally verified in many types of diffusion.

The simplest and most direct calculation of the diffusivity was given by Einstein (1905). He considered the equilibrium of diffusion opposing a steady potential force $-\nabla V$. With a particle concentration c , the flux of particles in response to the steady force if there were no diffusion would be $-c\zeta^{-1}\cdot\nabla V$. In thermodynamic equilibrium such a flux must be balanced by a diffusional flux $-\mathbf{D}\cdot\nabla c$. But in thermodynamic equilibrium the concentration must have the

Maxwell-Boltzmann distribution $c \propto \exp(-V/kT)$. Using this distribution and equating the net flux to zero produces the result (1.1). This argument, which is applicable to any type of diffusion, makes three assumptions: that potential forces can be constructed, that the system has a meaningful thermodynamic temperature, and that the friction force is linear in the particle velocity for steady motions. These assumptions are satisfied by Brownian particles.

The alternative method of calculating the diffusivity uses a Langevin equation of motion. This is the momentum equation for the particle with a random forcing for the thermal agitations and with a friction force linear in the instantaneous velocity. If the magnitude of the velocity fluctuations is known from an equipartition of energy, the magnitude of the random forcing can be found. This enables calculation of the rate of increase of particle dispersion (mean-square position), which is just twice the diffusivity. The advantage of the Langevin method is that it allows further details of the Brownian motion to be calculated, including the velocity autocorrelation function (the correlation of the present particle velocity with the velocity at other times). The details of these calculations are delayed until the next section. The assumptions required for the calculations are that the random forcing appears as white noise on the time scale of a particle slowing down owing to friction after an impulse, that the mean kinetic energy of a particle is $\frac{1}{2}kT$ for each degree of freedom, and that the friction force is linear in the instantaneous velocity. The white-noise assumption is satisfied when the particles are much larger than the solvent molecules without being much less dense. The friction law is, however, incorrect. While for small particles the friction force is linear in the velocity because the Reynolds number of the solvent flow will be small, the force does not involve only the instantaneous velocity. The time scale of principal interest is the time taken by a particle to slow down after receiving an impulse. For not too different densities of particle and solvent, this time is the time for vorticity to diffuse over the length of the particle. Thus the frictional force can not have attained its steady-state value, and fluid inertia must be included along with the particle inertia. There is therefore a paradox in the traditional Langevin treatment: the correct diffusivity is obtained with the wrong friction law. At this point it should be recalled that Einstein's argument cannot be similarly faulted, as it requires only the velocity response to a steady potential force.

The first indication of a deficiency in the Langevin equation came in some numerical simulations of the molecular motions in liquids. Rahman (1964) and Alder & Wainwright (1967) found a long-tailed decay in the velocity correlation function. After a few molecular vibration times the velocity correlation should be correctly predicted by the macroscopic hydrodynamic theory. The standard Langevin result using the instantaneous friction law, however, predicts a rapid exponential decay. Alder & Wainwright (1968) realized that there was a cooperative effect from the surrounding molecules, i.e. the developing hydrodynamic motion which was not fully described by the steady Stokes drag. Solving numerically the Navier-Stokes equations for time-dependent flow outside a rigid sphere, Alder & Wainwright (1970) were able to predict their observed $t^{-\frac{3}{2}}$ asymptotic decay in the correlation function of the linear velocity. The calculation of the

asymptotic decay in the velocity correlation function has been repeated by Zwanzig & Bixon (1970) using the explicit generalization of the Stokes drag for transient motions of an arbitrary frequency. There is a different frequency-dependent friction for rotation, for which Ailawadi & Berne (1971) found a $t^{-\frac{1}{2}}$ asymptotic decay in the angular velocity correlation function. For the general mode of motion, a friction law with an arbitrary frequency dependence has been discussed by Case (1971). When the friction law does depend on frequency, the random motion of the particles is not Markovian.

While the modification of the Langevin equation for frequency-dependent friction corrected the velocity correlations, it led to some difficulties with the diffusivity relation (1.1). The high frequency part of the friction law is dominated by an added-mass term, which describes the rate of change of fluid inertia in incompressible inviscid potential flow past an accelerating particle. Using the new version of the Langevin equation for the particle Widom (1971) found a diffusivity which, as pointed out by Chow & Hermans (1972) and others, was too high by the ratio of the particle mass to the combined particle and added mass. This error is rectified by not making the mean particle kinetic energy kT , but rather assigning this kinetic energy to the combination of the fluid and the particle. Just why this appealing alternative is correct and how it corresponds to sharing the energy in proportion to the particle mass and the added mass of incompressible inviscid theory need some clarification. In order to avoid any assumption about the mean particle kinetic energy, Hauge & Martin-Löf (1973) calculated the statistics of the random force on a single particle starting from the theory of Brownian fluctuations in fluid continua. Their analysis applied to a rigid spherical particle gave the correct results for the velocity correlation function and for the diffusivity. Chow & Hermans (1972, 1974) also calculated the statistics of this random force. Then, proceeding to the velocity correlation function, they omitted the fluid inertia (by using mkT in equations (38) and (39) in the 1972 paper) and assumed the mean kinetic energy of the particle to be $\frac{1}{2}kT$ (immediately after their equation (41)), both of which are incorrect in my view.

The purpose of this paper is to show how the diffusivity and the velocity correlation function can be correctly obtained from the original Langevin analysis, with an instantaneous friction law. The key to the unification of the recent results and the traditional approach is the application of the Langevin equation to the fluid as well as the particles. As incidental results, the theory of fluctuations in fluids will be recovered and the role of the added mass will be explained. In §2 the classical Langevin theory for an arbitrary system will be restated, the application to fluid systems being made in §3. The successful application of the traditional Langevin analysis avoids the introduction of the theory of non-Markovian processes and the evaluation of the statistics of the random force acting on a particle.

2. The Langevin theory for a system

We start with a general system whose instantaneous configuration is described by the state vector \mathbf{x} . In the application to the fluid \mathbf{x} will belong to an infinite-dimensional space. This is not very desirable, e.g. the system has infinite energy in its thermal motions; but as such infinities result solely from the mathematical idealization of replacing the large number of small solvent molecules by a continuum, their existence can be tolerated. The rate of change of the system is given by the state velocity vector $\dot{\mathbf{x}}$. The scalar inner product of two state vectors will be denoted by $\mathbf{x}_1 \cdot \mathbf{x}_2$.

The system is endowed with a generalized inertia, which will be a second-rank tensor field $\mathbf{m}(\mathbf{x})$. Thus the kinetic energy of the changing system is $\frac{1}{2}\dot{\mathbf{x}} \cdot \mathbf{m} \cdot \dot{\mathbf{x}}$, while its generalized momentum is $\mathbf{m} \cdot \dot{\mathbf{x}}$. As the definition of the inertia really comes in the kinetic energy, it is only meaningful to consider a symmetric \mathbf{m} . In addition to inertia, we consider the free (cold) system to suffer from friction which is linear in the instantaneous velocity, and which will thus be represented in the momentum equation by a term $\boldsymbol{\zeta} \cdot \dot{\mathbf{x}}$. Attention is restricted to systems in which the second-rank tensor field $\boldsymbol{\zeta}(\mathbf{x})$ describing the friction is symmetric. The fluid system of eventual interest does comply with this restriction. In fact all systems which are not far from equilibrium in some appropriate sense have a symmetric $\boldsymbol{\zeta}$ through Onsager's unproven principle.

The Langevin equation of motion for the system is completed by driving the thermal motions with a random force $\mathbf{f}(t)$. In general the inertia and resistance tensors $\mathbf{m}(\mathbf{x})$ and $\boldsymbol{\zeta}(\mathbf{x})$ will depend on the instantaneous configuration of the system. We now assume the length scale for these variations in the tensors to be sufficiently large compared with a thermal displacement (more precisely, a displacement during which the velocity has some coherence) so that the tensors can be replaced by their local (constant) values. This assumption is satisfied by a suspension of particles which are larger and more massive than the solvent molecules. With this linearization, the Langevin equation to be studied becomes

$$\mathbf{m} \cdot \ddot{\mathbf{x}} + \boldsymbol{\zeta} \cdot \dot{\mathbf{x}} = \mathbf{f}(t). \quad (2.1)$$

This will be solved subject to initial conditions

$$\mathbf{x}(0) = \dot{\mathbf{x}}(0) = \mathbf{0}.$$

Considering a system started a finite time ago, rather than at $t = -\infty$, avoids the complication of infinite drifts in the displacement. Once the approximation of small thermal displacements has been made there is no loss of generality in choosing the trivial initial conditions.

The diffusivity and the velocity correlation function are found by solving the Langevin equation (2.1) for each random forcing $\mathbf{f}(t)$ and then relating the required statistics of the solution to two assumptions involving other statistics. The first assumption is that the random forcing is stationary white noise: when an ensemble average is taken, to be denoted by an overbar, the force has no

correlation with its value at different times and the magnitude of the fluctuations does not change in time, i.e.

$$\overline{\mathbf{f}(t')\mathbf{f}(t)} = \delta(t' - t) \mathbf{F}, \tag{2.2}$$

where the symmetric second-rank correlation tensor \mathbf{F} is a constant, independent of time. In reality the force does have a very short but non-zero correlation time; in liquids it is the vibration time of a molecule. Thus attention is here restricted to much longer macroscopic events, which sense only the integral force correlation

$$\mathbf{F} = \int_{-\infty}^{\infty} \overline{\mathbf{f}(t)\mathbf{f}(t+\tau)} d\tau.$$

The second assumption is that the system has a well-defined temperature associated with an equipartition of energy. This assumption will fix the magnitude of the thermal fluctuations and in particular determine the force correlation \mathbf{F} . The system under consideration possesses just kinetic energy in possibly many different modes. The relevant normal modes are those which diagonalize the inertia tensor \mathbf{m} . By the temperature assumption each mode has a mean kinetic energy of $\frac{1}{2}kT$ and an instantaneous velocity which is independent of the other modes:

$$\lim_{t \rightarrow \infty} \overline{\dot{\mathbf{x}}(t)\dot{\mathbf{x}}(t)} = kT\mathbf{m}^{-1}. \tag{2.3}$$

The limit of time tending to infinity has to be taken in order to forget the initial state of rest. To tolerate the infinite energy granted by (2.3) to an infinite-dimensional system, it must be realized that the infinite dimensionality is a mathematical idealization.

The calculation of the magnitude of the force correlation can now proceed. The solution of the Langevin equation (2.1) subject to the initial conditions is

$$\dot{\mathbf{x}}(t) = \int_0^t dt' \exp\{\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}(t' - t)\} \cdot \mathbf{m}^{-1} \cdot \mathbf{f}(t'). \tag{2.4}$$

When the system has more than one degree of freedom, the argument of the exponential is a tensor instead of a scalar, so that the exponential must be interpreted as the classical power series or in the co-ordinates which diagonalize $\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}$. In infinite-dimensional systems the exponential is usually called the Green's function. Using solution (2.4) the correlation of the velocity with itself at the same instant can be formed:

$$\overline{\dot{\mathbf{x}}(t)\dot{\mathbf{x}}(t)} = \int_0^t dt' \int_0^t dt'' \exp\{\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}(t' - t)\} \cdot \mathbf{m}^{-1} \cdot \overline{\mathbf{f}(t')\mathbf{f}(t'')} \cdot \mathbf{m}^{-1} \cdot \exp\{\boldsymbol{\zeta} \cdot \mathbf{m}^{-1}(t'' - t)\}.$$

At this stage the white-noise assumption (2.2) gives

$$\overline{\dot{\mathbf{x}}(t)\dot{\mathbf{x}}(t)} = \int_0^t dt' \exp\{\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}(t' - t)\} \cdot \mathbf{m}^{-1} \cdot \mathbf{F} \cdot \mathbf{m}^{-1} \cdot \exp\{\boldsymbol{\zeta} \cdot \mathbf{m}^{-1}(t' - t)\}$$

and integrating by parts

$$\begin{aligned} \overline{\dot{\mathbf{x}}(t)\dot{\mathbf{x}}(t)} = & \boldsymbol{\zeta}^{-1} \cdot \mathbf{F} \cdot \mathbf{m}^{-1} - \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}t\} \cdot \boldsymbol{\zeta}^{-1} \cdot \mathbf{F} \cdot \mathbf{m}^{-1} \cdot \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}t\} \\ & - \boldsymbol{\zeta}^{-1} \cdot \mathbf{m} \cdot \overline{\dot{\mathbf{x}}\dot{\mathbf{x}}} \cdot \boldsymbol{\zeta} \cdot \mathbf{m}^{-1}. \end{aligned}$$

Finally, taking the limit $t \rightarrow \infty$ and substituting for the velocity correlation from the temperature assumption (2.3) yields

$$\mathbf{F} = 2kT\boldsymbol{\zeta}. \quad (2.5)$$

This result is one of the so-called fluctuation-dissipation theorems for the system. It relates the magnitudes of the random fluctuating force and the mean friction force, both forces having the same physical origin at the molecular level.

Having determined the strength of the random force it is possible to proceed directly to the diffusivity. A more enlightening approach, however, can be made in terms of the velocity correlation function, which will first be studied. The velocity correlation function is defined as

$$\mathbf{R}(\tau) = \lim_{t \rightarrow \infty} \overline{\dot{\mathbf{x}}(t+\tau) \dot{\mathbf{x}}(t)},$$

the limiting process again being needed to forget the initial rest state. One value of the function is known already, namely $\mathbf{R}(0)$, from the temperature assumption. Using the solution of the Langevin equation (2.4), the correlation of the velocities at two different times may be formed:

$$\begin{aligned} \overline{\dot{\mathbf{x}}(t+\tau) \dot{\mathbf{x}}(t)} &= \int_0^{t+\tau} dt' \int_0^t dt'' \\ &\times \exp\{\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}(t' - t - \tau)\} \cdot \mathbf{m}^{-1} \cdot \overline{\mathbf{f}(t') \mathbf{f}(t'')} \cdot \mathbf{m}^{-1} \cdot \exp\{\boldsymbol{\zeta} \cdot \mathbf{m}^{-1}(t'' - t)\}. \end{aligned}$$

The white-noise assumption reduces this to

$$\begin{aligned} \overline{\dot{\mathbf{x}}(t+\tau) \dot{\mathbf{x}}(t)} &= \int_0^{\min(t+\tau, t)} dt' \\ &\times \exp\{\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}(t' - t - \tau)\} \cdot \mathbf{m}^{-1} \cdot \mathbf{F} \cdot \mathbf{m}^{-1} \cdot \exp\{\boldsymbol{\zeta} \cdot \mathbf{m}^{-1}(t' - t)\}. \end{aligned}$$

At this stage it is necessary to separate the two cases $\tau \geq 0$. Only the intermediate steps for $\tau \geq 0$ are presented. For this case the upper limit of the integral becomes t . Factorizing out the τ part of the exponential leads to

$$\overline{\dot{\mathbf{x}}(t+\tau) \dot{\mathbf{x}}(t)} = \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}\tau\} \cdot \overline{\dot{\mathbf{x}}(t) \dot{\mathbf{x}}(t)}, \quad \tau \geq 0.$$

This expression has a simple physical explanation. First note that if there were no forcing after the time t then the free system would decay according to

$$\dot{\mathbf{x}}(t+\tau) = \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}\tau\} \cdot \dot{\mathbf{x}}(t).$$

The expression for the correlation between the velocities at t and $t+\tau$ means, therefore, that the forcing in the intervening period has no coherent effect, which is clearly just a result of the white-noise assumption. The desired velocity correlation function is finally obtained by taking the limit $t \rightarrow \infty$ and using the temperature assumption (2.3):

$$\mathbf{R}(\tau) = \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}\tau\} \cdot \mathbf{R}(0) = kT \exp\{-\mathbf{m}^{-1} \cdot \boldsymbol{\zeta}\tau\} \cdot \mathbf{m}^{-1}, \quad \tau \geq 0. \quad (2.6)$$

This result is a simple embodiment of the white-noise and temperature assumptions, for the right-hand side is precisely the response of the free system to a

single impulse of magnitude kT at $\tau = 0$. The appropriate form of the result for negative τ may be derived without any additional effort by making a shift in the origin of time in the definition of the correlation function:

$$\mathbf{R}(\tau) = \mathbf{R}^T(-\tau) = kT\mathbf{m}^{-1} \cdot \exp\{\boldsymbol{\zeta} \cdot \mathbf{m}^{-1}\tau\}, \quad \tau \leq 0,$$

where the superscript T denotes the transpose of the tensor.

While the mean displacement of the system has been made to vanish ($\overline{\mathbf{x}(t)} = 0$), the thermal fluctuations give rise to an increasing variance of the displacement $\overline{\mathbf{x}(t) \mathbf{x}(t)}$. The present displacement can be thought of as the sum of a number of effectively independent random increments, a displacement increment achieving independence of the past once the velocity has lost coherence. Applying the central limit theorem for a large number of increments, the present random displacement will have a Gaussian distribution with a variance equal to the variance of an increment multiplied by the number of increments. Now the size of an independent increment is the velocity multiplied by the persistence time of the velocity, while the number of increments is the present time divided by this time required to make an increment. Hence after several velocity correlation times, the variance of the present displacement will be growing linearly in time with a growth rate given by the velocity correlation time multiplied by the square of the magnitude of the velocity. The Gaussian distribution of the present displacement, with a variance proportional to time, provides the link between the statistics of the ensemble and the diffusion process, by identifying the fundamental solution of the diffusion equation with the statistical Gaussian distribution. The diffusivity is therefore half the eventual rate of growth of the variance of the displacement:

$$\mathbf{D} = \lim_{t \rightarrow \infty} \frac{1}{2} d[\overline{\mathbf{x}(t) \mathbf{x}(t)}] / dt.$$

A formal derivation of the magnitude of \mathbf{D} requires a few short manipulations. First the time differential is commuted with the ensemble averaging and the displacements written as integrals of the velocity from the initial zero conditions:

$$\mathbf{D} = \lim_{t \rightarrow \infty} \frac{1}{2} \int_0^t \overline{d\tau \dot{\mathbf{x}}(t) \dot{\mathbf{x}}(t-\tau) + \dot{\mathbf{x}}(t-\tau) \dot{\mathbf{x}}(t)}.$$

Here the velocity correlation function can be recognized, yielding

$$\mathbf{D} = \frac{1}{2} \int_0^\infty [\mathbf{R}(\tau) + \mathbf{R}^T(\tau)] d\tau.$$

This expression makes precise the earlier physical statement that the rate of increase in the displacement variance is the velocity correlation time multiplied by the velocity magnitude squared. Finally, substituting the formula for the velocity correlation (2.6) and performing the τ integration yields the classical Stokes-Einstein result (1.1).

3. Application to a fluid system

In this section the Langevin theory will be applied to a suspension of rigid particles in an incompressible Newtonian fluid. As a preliminary, it is necessary to recast the familiar governing equations into the simplifying notation of (2.1). We start by considering a cold suspension, with no thermal motions, the fluctuations being added more easily at a later stage.

Let the n th particle be at the position \mathbf{x}_n with an orientation $\boldsymbol{\theta}_n$ (which can be defined by the location of a fixed point in the particle and by Euler angles respectively), be moving with a translational velocity \mathbf{u}_n and with an angular velocity $\boldsymbol{\omega}_n$, and have a mass M_n and moment-of-inertia tensor \mathbf{I}_n . The number of particles is left arbitrary and can be infinite. Let the fluid be in the volume V and have a velocity field $\mathbf{u}(\mathbf{x})$, $\mathbf{x} \in V$. Attention is restricted to velocity fields which are sufficiently smooth, and in particular, continuous at the surfaces of the particles:

$$\mathbf{u}(\mathbf{x}) = \mathbf{u}_n + \boldsymbol{\omega}_n \wedge (\mathbf{x} - \mathbf{x}_n)$$

on the n th particle's surface. Attention is further restricted to solenoidal velocity fields, which requires a pressure field in the momentum equation. For simplicity the density ρ and the viscosity μ of the fluid are assumed to be constants in V .

When thermal driving is added to the cold suspension, the motions of interest will have a small amplitude. Three linearizations are made. These neglect the nonlinear fluid inertia term,† changes in the moment inertia tensor as the particles rotate, and changes in the shape of the fluid volume as the particles move. The momentum equations for the components of the suspension then become for a point in the fluid

$$\left. \begin{aligned} \nabla \cdot \mathbf{u} &= 0, \\ \rho \partial \mathbf{u} / \partial t &= -\nabla p + \mu \nabla^2 \mathbf{u} \\ \text{and for the } n\text{th particle} \\ M_n \frac{d\mathbf{u}_n}{dt} &= \oint_n \mathbf{n} \cdot \boldsymbol{\sigma}, \\ \mathbf{I}_n \cdot \frac{d\boldsymbol{\omega}_n}{dt} &= \oint_n (\mathbf{x} - \mathbf{x}_n) \wedge \mathbf{n} \cdot \boldsymbol{\sigma}, \end{aligned} \right\} \quad (3.1)$$

where the fluid stress tensor is given by

$$\boldsymbol{\sigma} = -p\mathbf{I} + \mu(\nabla\mathbf{u} + \nabla\mathbf{u}^T)$$

and the integrals are taken around the surface of the particle with \mathbf{n} the outward normal.

To recast the cold suspension in terms of the general system of the preceding section, the configuration of the system is defined by an infinite-dimensional state vector \mathbf{x} . This is a partitioned vector: the first group of components is the

† Chow & Hermans (1972) questioned whether the low Reynolds number approximation may be made because vorticity diffuses on an increasing length scale during the decay after an impulse. While the length scale is increasing, the velocity scale is however decreasing more rapidly, so that the Reynolds number starts small and only decreases.

continuum of points in the fluid, while the second group is the position and the third the orientation of the particles, i.e.

$$\mathbf{x} = (\mathbf{x}, \mathbf{x}_n, \boldsymbol{\theta}_n),$$

where it is implied that \mathbf{x} ranges over the fluid volume V and n ranges over all the particles. The idea of treating the fluid as additional generalized co-ordinates was used by Thompson & Tait (1879). The difficulty of the volume V changing as the particles move does not enter the linearized problem for small amplitude motions, and could be completely avoided by adopting a Lagrangian description of the fluid. The motion of the suspension is contained in the state velocity vector

$$\dot{\mathbf{x}} = (\mathbf{u}(\mathbf{x}), \mathbf{u}_n, \boldsymbol{\omega}_n), \tag{3.2}$$

where \mathbf{u} is always constrained to be smooth and solenoidal. The appropriate inner product for the system involves an integral over the fluid and translational and rotational sums over the particles, e.g. that between two generalized velocities (although such a product has no physical significance because it is not dimensionally consistent) is

$$\dot{\mathbf{x}}' \cdot \dot{\mathbf{x}} = \int_V d^3x \mathbf{u}'(\mathbf{x}) \cdot \mathbf{u}(\mathbf{x}) + \sum_n (\mathbf{u}'_n \cdot \mathbf{u}_n + \boldsymbol{\omega}'_n \cdot \boldsymbol{\omega}_n).$$

From the generalized momentum

$$\mathbf{m} \cdot \dot{\mathbf{x}} = (\rho \partial \mathbf{u}(\mathbf{x}) / \partial t, M_n d\mathbf{u}_n / dt, \mathbf{l}_n \cdot d\boldsymbol{\omega}_n / dt)$$

it is clear that the second-rank inertia tensor \mathbf{m} is diagonal (and symmetric):

$$\mathbf{m} = \begin{pmatrix} \rho \mathbf{l} \delta(\mathbf{x}' - \mathbf{x}) & 0 & 0 \\ 0 & M_n \mathbf{l} \delta_{n'n} & 0 \\ 0 & 0 & \mathbf{l}_n \delta_{n'n} \end{pmatrix}. \tag{3.3}$$

The symmetric friction tensor is not so immediately apparent. The friction force for the velocity $\dot{\mathbf{x}}$ is

$$\boldsymbol{\zeta} \cdot \dot{\mathbf{x}} = - \left(-\nabla p + \mu \nabla^2 \mathbf{u}, \oint_n \mathbf{n} \cdot \boldsymbol{\sigma}, \oint_n (\mathbf{x} - \mathbf{x}_n) \wedge \mathbf{n} \cdot \boldsymbol{\sigma} \right)$$

and so the rate at which this force does work on the velocity $\dot{\mathbf{x}}$ is

$$\dot{\mathbf{x}}' \cdot \boldsymbol{\zeta} \cdot \dot{\mathbf{x}} = - \int_V d^3x \mathbf{u}' \cdot (-\nabla p + \mu \nabla^2 \mathbf{u}) - \sum_n \oint_n (\mathbf{u}'_n + \boldsymbol{\omega}'_n \wedge (\mathbf{x} - \mathbf{x}_n)) \cdot \mathbf{n} \cdot \boldsymbol{\sigma}.$$

Using the definition of the stress tensor $\boldsymbol{\sigma}$, the continuity of the velocity on the surfaces of the particles and the divergence theorem yields

$$= \int_V d^3x \mu (\nabla \mathbf{u}' : \nabla \mathbf{u} + \nabla \mathbf{u}' : \nabla \mathbf{u}^T).$$

In this last expression the symmetric form of the friction tensor can be recognized:

$$\boldsymbol{\zeta} = \begin{pmatrix} +\mu \delta(\mathbf{x}' - \mathbf{x}) (\mathbf{l} \overleftarrow{\nabla} \cdot \overrightarrow{\nabla} + \overleftarrow{\nabla} \overrightarrow{\nabla}) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{3.4}$$

where the arrows over the differential operators denote whether the operator acts on what precedes or follows the tensor. This completes the identification of the suspension as a general system: when the definitions (3.2)–(3.4) are substituted into (2.1) with no Brownian forcing, they yield the governing equations (3.1). The advantage of taking the system to be so large and including every fluid point is that the linear friction law becomes instantaneous in nature. The random process \mathbf{x} can thereby remain Markovian.

The thermal fluctuations can now be added to the suspension. Although there exists a well-established theory for the fluctuations in fluids, we choose here to apply the general results of §2 and thereby derive that theory. The Brownian motions are incorporated by restoring to the system equation (2.1) the random fluctuating force $\mathbf{f}(t)$. Substituting the friction tensor (3.4) into the result (2.5) with (2.2) for the strength of the random force yields

$$\overline{\mathbf{f}(t')\mathbf{f}(t)} = 2kT\delta(t'-t) \begin{pmatrix} +\mu\delta(\mathbf{x}'-\mathbf{x})(\overleftarrow{\nabla}\cdot\overrightarrow{\nabla}+\overrightarrow{\nabla}\overleftarrow{\nabla}) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \quad (3.5)$$

This expression shows the structure of the random forcing. It can be partitioned such that it vanishes in the discrete particle components, and it involves the forward derivative of a second-order tensor $\mathbf{s}(\mathbf{x}, t)$:

$$\mathbf{f}(t) = (-\overleftarrow{\nabla}\cdot\mathbf{s}, \quad 0, \quad 0). \quad (3.6a)$$

A more familiar form is obtained by turning the derivative round:

$$\mathbf{f}(t) = (\nabla\cdot\mathbf{s}, \quad \oint_n \mathbf{n}\cdot\mathbf{s}, \quad \oint_n (\mathbf{x}-\mathbf{x}_n) \wedge \mathbf{n}\cdot\mathbf{s}). \quad (3.6b)$$

This exposes the origin of the thermal motions in the suspension. The net stress within the fluid is the sum of a viscous Newtonian stress $\boldsymbol{\sigma}$ and a random fluctuating stress \mathbf{s} . The fluid moves in response to the divergence of this net stress, and the particle moves in response to this net stress integrated over its boundary. Physically the stress exerted across a surface is systematically driven by velocity gradients to have the average viscous value, but at the molecular level is transmitted in discrete units (transfer of particles in a gas and vibrations in a liquid) and so fluctuates about its average. The strength of the stress fluctuations \mathbf{s} is readily extracted from (3.5) by substituting the form (3.6a) for the force $\mathbf{f}(t)$:

$$\overline{s_{i'j'}(\mathbf{x}', t')s_{ij}(\mathbf{x}, t)} = 2kT\mu\delta(t'-t)\delta(\mathbf{x}'-\mathbf{x})[\delta_{i'i}\delta_{j'j}+\delta_{i'j}\delta_{j'i}-\frac{2}{3}\delta_{i'j'}\delta_{ij}]. \quad (3.7)$$

The final product of Kronecker deltas has been inserted to make \mathbf{s} traceless in the mean, which is appropriate to an incompressible fluid, where the trace can be accommodated in the locally indeterminate pressure. The result (3.7) is the basis for the theory of fluctuations in fluids. There is some confusion in that theory (Hauge & Martin-Löf 1973) as to whether the fluctuating stress \mathbf{s} should be directly applied to the particle or only allowed to act indirectly through its divergence, driving fluctuations in the fluid velocity \mathbf{u} and thence the viscous

stress σ on the particles. The expression (3.6*b*) indicates that the direct contribution is to be included: both within the fluid and on the particle surfaces, the real stress is the sum of the viscous and random contributions. If this were not the case, then the conservation of momentum might be violated.

After the fluctuations in the fluid, attention is now turned specifically to the Brownian motions of the particles. In a study of a suspension, the principal interest is usually the various diffusion processes of the particles and not of the fluid. Moreover, the preceding theory can be safely applied to macroscopic Brownian particles, but caution is needed with the fluid, which has been idealized to a continuum with an infinite number of degrees of freedom. From the general results for the diffusivity (1.1) and the velocity correlation function (2.6), only those partitioned components which involve the particles will be discussed. Let p and q be the labels of two typical particle co-ordinates, perhaps involving different particles and different components of particle translation and rotation.

The coefficient of proportionality for the p flux of concentration due to a q gradient of concentration is the pq component of the diffusivity, given from (1.1) by

$$D_{pq} = kT(\zeta^{-1})_{pq}.$$

Instead of explicitly inverting the friction tensor (3.4), which must be done in the class of smooth solenoidal velocity fields, some understanding of the inverse friction (or mobility) can be obtained from the general Langevin equation (2.1). If the general system is subjected to a steady force \mathbf{f}^s instead of the random thermal forcing $\mathbf{f}(t)$, the response after several relaxation times will be a steady velocity

$$\dot{\mathbf{x}} \rightarrow \zeta^{-1} \cdot \mathbf{f}^s, \quad t \rightarrow \infty.$$

Hence the pq component of the inverse friction tensor is the p component of the steady particle velocities resulting in the suspension from a steady force being applied to the q particle component. This is simply the standard particle mobility tensor for steady Stokes flows. By using the elaborate partitioned system defined in (3.2)–(3.4), which has an instantaneous friction law, the particle diffusivity tensor has been shown to be correctly given by the particle mobility tensor for steady flows, even though the particles themselves considered alone as a system do not enjoy an instantaneous friction law.

The correlation between the p and q particle velocity components with a time delay τ is given from (2.6) by

$$\lim_{t \rightarrow \infty} \overline{\dot{\mathbf{x}}_p(t + \tau) \mathbf{x}_q(t)} = kT[\exp\{-\mathbf{m}^{-1} \cdot \zeta \tau\} \cdot \mathbf{m}^{-1}]_{pq}.$$

As discussed in §2, this is just the p particle velocity response after an impulse of magnitude kT in the q particle component. The simultaneous correlation ($\tau = 0+$) is $kT(m^{-1})_{pq}$, and being the immediate response to an impulse is independent of the friction. Caution is needed in taking the inverse of the inertia tensor (3.3): for the self-translation term, $p = q =$ some particle translation, the component of the inverse is not the reciprocal of the particle mass, $(m^{-1})_{pp} \neq 1/m_{pp}$. The diagonal form of the expression (3.3) is deceptive because there is an implied constraint to the subspace of smooth solenoidal (incompressible) fluid velocity

fields. The choice of the reciprocal of the particle mass corresponds to particles moving with the fluid at rest, a situation violating the smoothness constraint. To create a smooth solution fluid motions may be used which have not involved any friction ζ , i.e. incompressible inviscid potential flows driven by the pressure field. Such flows are only able to satisfy the normal boundary conditions on the particles. The full smooth solution requires the action of friction in a thin boundary layer to satisfy the tangential boundary condition. In the idealized limit of an instantaneous impulse the usual smoothness in the velocity field cannot be maintained. The smoothness and solenoidal constraints have therefore brought the fluid inertia into the particle components of the inverse inertia. In particular, for an isolated particle, the particle inverse inertia is the reciprocal of the sum of the particle mass and the fluid added mass as given by incompressible inviscid potential theory.

The result that the impulse kT is distributed between the particle and the fluid is a consequence of the incompressible theory of hydrodynamics. In a constrained system, the equipartition of energy gives a thermal energy of $\frac{1}{2}kT$ to each mode of motion (degree of freedom). The constraint of incompressibility means that a particle in motion must share its $\frac{1}{2}kT$ with the associated motion in the fluid necessitated by the incompressibility. When a small compressibility is taken into account, it is found that the distribution is achieved by sound waves acting after the unconstrained particle has received the full kT (Zwanzig & Bixon 1975). As long as the impulses are treated carefully in the incompressible theory, compressibility need not be introduced because the Brownian motion of macroscopic particles is much slower than the speed of sound.

The coupling of the fluid to the particles introduced by the constraints has an effect on the pq component of the velocity correlation at all time delays. The pq velocity correlation depends on the full friction tensor ζ , and not just the pq component ζ_{pq} or even the entire particle-particle partition. Thus the correlation function for particles involves the decay of an infinite-dimensional system in which the exponential function of time might be misleading. The trouble is that the infinite sum of decaying exponentials in (2.6) need not itself decay exponentially (cf. singularities in Laplace transforms which are not simple poles). Indeed diffusion-like negative half-integral powers of time have been found for isolated particles. Because fluid inertia plays a part in the particle velocity correlation function, the time-dependent Stokes drag should be used to calculate the correct velocity decay after the impulse has been carefully applied to the particle and fluid added mass.

This section has applied the traditional Langevin analysis, with an instantaneous friction law, to both the fluid and the particles. It has thereby been possible to show quite generally that (i) the diffusivity is given by the mobility obtained from the steady Stokes equations and (ii) the velocity correlation function is the velocity response of the cold system to an impulse kT , if the impulse momentum is distributed carefully between the particle and the fluid.

As an example of the application of these two general results we consider the particular case of translational motion of rigid spheres in a suspension which is sufficiently dilute for the hydrodynamic interactions between particles to be

neglected. The mobility according to the steady Stokes equations is $1/6\pi\mu a$, where a is the radius of the spheres and μ the dynamic viscosity of the solvent. Thus the translational diffusivity is $kT/6\pi\mu a$, as obtained by Einstein (1905). The velocity correlation function $R(\tau)$ is the translational velocity of the sphere after receiving an impulse of magnitude kT . The motion after an impulse is found from the time-dependent momentum equation for the particle, using the time-dependent viscous drag. This equation is best Laplace transformed as

$$\frac{4}{3}\pi a^3 \rho' s \hat{R}(s) + \left\{ \frac{2}{3}\pi a^3 \rho s + 6\pi\mu a [(a^2 s/\nu)^{\frac{1}{2}} + 1] \right\} \hat{R}(s) = kT,$$

where ρ' is the average density of the particle, ρ the density of the fluid, ν the kinematic viscosity of the solvent and s the Laplace transform variable. The first term of the equation represents the particle inertia, the term in curly brackets the fluid force and the right-hand side the impulse. In the fluid-force term the first part is the fluid added mass. Solving the equation yields

$$\hat{R}(s) = \frac{kT}{6\pi\mu} \left[1 + \left(\frac{sa^2}{\nu} \right)^{\frac{1}{2}} + \frac{1}{9} \left(1 + 2\frac{\rho'}{\rho} \right) \frac{sa^2}{\nu} \right]^{-1}.$$

The diffusivity, being the time integral of $R(\tau)$, is immediately recognized as $\hat{R}(0)$. The asymptotic behaviour of $R(\tau)$ at long times τ can be found from the expansion of $\hat{R}(s)$ for small s . Thus

$$R(\tau) = \frac{kT}{12\pi^{\frac{3}{2}} a^3 \rho} \left[\left(\frac{a^2}{\nu\tau} \right)^{\frac{3}{2}} + O\left(\left(\frac{a^2}{\nu\tau} \right)^2 \right) \right],$$

showing slow algebraic decay, as obtained by Alder & Wainwright (1970) and Zwanzig & Bixon (1970). The full expression for the correlation function is

$$R(\tau) = \frac{kT}{2\pi a^3 \rho (5 - 8\rho'/\rho)^{\frac{1}{2}}} \left(\frac{a^2}{\nu} \right)^{\frac{1}{2}} [\alpha_+ \exp(\alpha_+^2 t) \operatorname{erfc}(\alpha_+ \sqrt{t}) - \alpha_- \exp(\alpha_-^2 t) \operatorname{erfc}(\alpha_- \sqrt{t})],$$

where

$$\alpha_{\pm} = \left(\frac{\nu}{a^2} \right)^{\frac{1}{2}} \frac{3}{2} \left[3 \pm \left(5 - 8\frac{\rho'}{\rho} \right)^{\frac{1}{2}} \right] / \left(1 + 2\frac{\rho'}{\rho} \right).$$

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