THE JOURNAL OF CHEMICAL PHYSICS VOLUME 54, NUMBER 8 15 APRIL 1971

Molecular Theory of Brownian Motion for Several Particles*

J. M. DEUTCH
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
AND
IRWIN OPPENHEIM†
Chemical Physics Department, Weizmann Institute of Science, Rehovoth, Israel
(Received 4 November 1970)

A molecular derivation is presented for the coupled Langevin equations that describe the motion of heavy particles in a fluid. In contrast to the case of a single heavy particle, the friction tensors which appear depend upon the instantaneous separations between the particles. A Fokker–Planck equation describing the reduced distribution function for the heavy particles is also obtained. Calculations with these equations require evaluation of the friction tensors. The friction tensors are evaluated in two ways, by an approximate macroscopic hydrodynamic calculation and an approximate hydrodynamic fluctuation calculation. Both calculations lead to identical expressions for the friction tensors which are shown to have a long-range character at large interparticle separations. Finally, it is shown that these long-range effects cancel in the calculation of the diffusion constant for each particle but remain in the calculation of the relative diffusion constant.

I. INTRODUCTION

In recent years the molecular theory of Brownian motion of a single heavy particle in a fluid has been studied by a variety of techniques.[1–7] In this paper we examine the molecular theory of Brownian motion for a collection of identical heavy particles in a fluid. Our motivation for undertaking this problem is to provide a basis for a theory of the hydrodynamic behavior of a suspension of colloidal particles in solution.

In the first section we use the techniques developed by Mazur and Oppenheim[6] and by Albers, Oppenheim, and Deutch[7] to derive a generalized Langevin equation for the motion of the heavy particles. The generalized Langevin equation we obtain leads simultaneously to a Fokker–Planck equation for the reduced distribution function of the Brownian particles and coupled Langevin particles and coupled Langevin equations describing the equation of motion for the momentum of each Brownian particle. These latter equations, for the momentum, will be referred to here as momentum Langevin equations.

The momentum Langevin equations are valid when the ratio of the mass m of a bath particle to the mass M of a Brownian particle is sufficiently small, and when all of the pertinent relaxation times of the bath, τ_b, are short compared to the relaxation times for the momentum of a Brownian particle. In addition the velocity of a Brownian particle must be small compared to the velocity of a bath particle. The condition on the velocity assures that the disturbance caused by the Brownian particle can be distributed in the bath.

These conditions are identical to those obtained for single particle Brownian motion.[6,7] The important difference is that when more than a single heavy particle is present the longest relaxation time characterizing the bath τ_b is of order (R/c) where R is a typical distance between two fixed heavy particles and c is the speed of sound in the bath.

For the special case of two heavy particles, the generalized Langevin equation we obtain results in a Fokker–Planck equation more general than the equation recently obtained by Mazo.[8] For long times $t \gg \tau_b$ our result reduces to that found by Mazo. The momentum Langevin equations we obtain for two particles contain two friction tensors that describe the self- and cross- relaxation for each particle. These two friction tensors depend upon the instantaneous separation of the two particles. Calculations with the Langevin equation or the corresponding Fokker–Planck equation cannot be accomplished until the dependence on the interparticle separation is known.

In this paper we evaluate the molecular expression obtained for the friction tensor by modification of an approximate hydrodynamic fluctuation theory argument developed by Zwanzig.[9] The dependence of the friction tensors on interparticle separation, $\mathbf{R}_{12}$, is obtained to lowest order in (a/R_{12}) where a is the radius of the Brownian particles. This expression is compared to the expression for the friction tensors obtained from an approximate solution of the macroscopic hydrodynamic equations that describe flow past two fixed spheres. Exact agreement is found between the two calculations to lowest order in (a/R_{12}).

Our final step is to use the approximate expressions for the friction tensors to compute the change in the diffusion constant of each Brownian particle arising from the presence of the other particle. The friction tensors have a long-range dependence on interparticle separation. It is interesting that the long-range modifications of the friction tensor effect the relative and center of mass diffusion constants but cancel in the calculation of the diffusion constant of the individual particles. This feature suggests to us that in colloidal suspensions an analytic concentration expansion for the effective friction tensors is unlikely, while such expansions may be valid for individual particle diffusion constants.

II. DERIVATION OF THE GENERALIZED LANGEVIN EQUATION

We consider a system consisting of n Brownian particles of mass M and N bath particles of mass m. The positions and momenta of the Brownian particles will be denoted by $\mathbf{R}^n$ and $\mathbf{P}^n$, respectively, while the positions of the N bath particles will be denoted by $\mathbf{r}^N$ and their momenta by $\mathbf{p}^N$. The Hamiltonian for the system is

$$H=H_B+H_0,$$

where H_B is the Hamiltonian for the n Brownian particles in the absence of the bath particles,

$$H_B=[(\mathbf{P}^n\cdot\mathbf{P}^n)/2M]+V(\mathbf{R}^n), \quad (2.1)$$

$V(\mathbf{R}^n)$ is the short-range interaction between the Brownian particles, and H_0 is the Hamiltonian for the N bath particles in the potential field of the n Brownian particles held fixed at positions $\mathbf{R}^n$,

$$H_0=(\mathbf{p}^N\cdot\mathbf{p}^N/2m)+U(\mathbf{r}^N)+\sum_{\mu=1}^{n}\Phi_\mu(\mathbf{r}^N,\mathbf{R}_\mu). \quad (2.2)$$

Here $U(\mathbf{r}^N)$ denotes the short-range intermolecular potential energy among the bath particles, and Φ_μ is the short-range potential energy of interaction between Brownian particle μ and the N bath particles. The quantity Φ_μ will be assumed to be the sum of pair interactions

$$\Phi_\mu(\mathbf{r}^N,\mathbf{R}_\mu)=\sum_{l=1}^{N}\phi(|\mathbf{R}_\mu-\mathbf{r}_l|), \quad (2.3)$$

which depends on the scalar distance between the centers of mass of the particles involved.

The Liouville operator for the system is given by

$$iL=iL_0+iL_B,$$

where

$$iL_0=(\mathbf{p}^N/m)\cdot\nabla_{\mathbf{r}^N}-\nabla_{\mathbf{r}^N}(U+\sum_{\mu=1}^{n}\Phi_\mu)\cdot\nabla_{\mathbf{p}^N} \quad (2.4)$$

and

$$iL_B=(\mathbf{P}^n/M)\cdot\nabla_{\mathbf{R}^n}+\mathbf{F}^n\cdot\nabla_{\mathbf{P}^n}, \quad (2.5)$$

and where $\mathbf{F}_\nu$, the force on the Brownian particle ν, is given by

$$\mathbf{F}_\nu=-\nabla_{\mathbf{R}_\nu}(V+\Phi_\nu), \qquad \nu=1,2,3,\cdots. \quad (2.6)$$

We define a projection operator $\mathcal{P}$ by the equation

$$\mathcal{P}A\equiv\langle A\rangle\equiv Z^{-1}\int d\mathbf{r}^N d\mathbf{p}^N\exp[-\beta H_0]A, \quad (2.7)$$

where

$$Z\equiv Z(\mathbf{R}^n)=\int d\mathbf{r}^N d\mathbf{p}^N\exp[-\beta H_0]. \quad (2.8)$$

A potential of mean force χ may be defined from Eq. (2.8)

$$Z(\mathbf{R}^n)=C(\beta,N,V)\exp[-\beta\chi(\mathbf{R}^n)], \quad (2.9)$$

so that

$$\langle\nabla_{\mathbf{R}_\mu}\Phi_\mu\rangle=(-\beta)^{-1}\nabla_{\mathbf{R}_\mu}\ln Z(\mathbf{R}^n)=\nabla_{\mathbf{R}_\mu}\chi(\mathbf{R}^n) \quad (2.10)$$

and hence

$$\langle\mathbf{F}_\mu\rangle=-\langle\nabla_{\mathbf{R}_\mu}[V+\Phi_\mu]\rangle=-\nabla_{\mathbf{R}_\mu}[V+\chi(\mathbf{R}^n)]. \quad (2.11)$$

We now operate with the identity

$$\exp[i(1-\mathcal{P})Lt]=\exp[iLt]-\int_0^t d\tau\exp[iL(t-\tau)]\mathcal{P}iL\exp[i(1-\mathcal{P})L\tau] \quad (2.12)$$

on

$$K(0)=(1-\mathcal{P})iL\phi(\mathbf{R}^n,\mathbf{P}^n), \quad (2.13)$$

where

$$\phi(0)\equiv\phi(\mathbf{R}^n,\mathbf{P}^n) \quad (2.14)$$

is an arbitrary function of the positions and momenta of the Brownian particles. The result is

$$\dot\phi(t)=A(t)+K^+(t)+\int_0^t d\tau e^{iL(t-\tau)}\langle iL_BK^+(\tau)\rangle \quad (2.15)$$

where

$$\dot\phi(t)=\exp[iLt]iL\phi(0), \quad (2.16)$$

$$A(t)=\exp[iLt]\langle iL_B\rangle\phi(0), \quad (2.17)$$

and

$$K^+(t)=\exp[i(1-\mathcal{P})Lt][iL\phi(0)-\langle iL_B\rangle\phi(0)]. \quad (2.18)$$

In order to obtain Eqs. (2.15), (2.17), and (2.18), we have made use of the fact that $\mathcal{P}iL_0(\cdots)\equiv\langle iL_0(\cdots)\rangle=0$.

To proceed with the development several of the terms in Eq. (2.15) must be expressed in a different form. The term $A(t)$ explicitly is

$$A(t)=\exp[iLt]\sum_{\mu=1}^{n}[(\mathbf{P}_\mu/M)\cdot\nabla_{\mathbf{R}_\mu}+\langle\mathbf{F}_\mu\rangle\cdot\nabla_{\mathbf{P}_\mu}]\phi(0). \quad (2.19)$$

The term $\langle iL_BK^+(\tau)\rangle$ in Eq. (2.15) may be simplified to

$$\langle iL_BK^+(\tau)\rangle=\sum_{\mu=1}^{n}[(\mathbf{P}_\mu/M)\cdot\langle\nabla_{\mathbf{R}_\mu}K^+(\tau)\rangle+\nabla_{\mathbf{P}_\mu}\cdot\langle\mathbf{F}_\mu K^+(\tau)\rangle]. \quad (2.20)$$

The identity

$$\langle\nabla_{\mathbf{R}_\mu}K^+(\tau)\rangle=-\beta\langle\mathbf{E}_\mu K^+(\tau)\rangle, \quad (2.21)$$

where

$$\mathbf{E}_\mu\equiv\mathbf{F}_\mu-\langle\mathbf{F}_\mu\rangle \quad (2.22)$$

is easily verified with the use of the fact that

$$\langle K^+(t)\rangle=\langle K^+\rangle=0. \quad (2.23)$$

It follows from Eqs. (2.21) and (2.23) that

$$\langle iL_BK^+(\tau)\rangle=\sum_\mu[\nabla_{\mathbf{P}_\mu}-(\beta/M)\mathbf{P}_\mu]\cdot\langle\mathbf{E}_\mu(0)K^+(\tau)\rangle. \quad (2.24)$$

Since

$$(1-\mathcal{P})iL\phi(0)=(1-\mathcal{P})iL_B\phi(0)=\sum_{\nu=1}^{n}\mathbf{E}_\nu\cdot\nabla_{\mathbf{P}_\nu}\phi(0), \quad (2.25)$$

the quantity $K^+(t)$ may be expressed as

$$K^+(t)=\exp[i(1-\mathcal{P})Lt]\sum_\nu \mathbf{E}_\nu(0)\cdot\nabla_{\mathbf{P}_\nu}\phi(0). \quad (2.26)$$

With these results Eq. (2.15) takes the form

$$\dot\phi(t)=\sum_\mu\{[\mathbf{P}_\mu(t)/M]\cdot\nabla_{\mathbf{R}\mu(t)}+\mathbf{S}_\mu(t)\cdot\nabla_{\mathbf{P}(t)}\}\phi(t)$$

$$+K^+(t)+\sum_\mu\sum_\nu\int_0^t d\tau\exp[iL(t-\tau)]$$

$$\times\{[\nabla_{\mathbf{P}_\mu}-(\beta/M)\mathbf{P}_\mu]\cdot\langle E_\mu\exp[i(1-\mathcal{P})L\tau]\mathbf{E}_\nu\rangle$$

$$\cdot\nabla_{\mathbf{P}_\nu}\phi(0)\}, \quad (2.27)$$

where we have defined

$$\mathbf{S}_\mu(t)=\exp[iLt]\langle\mathbf{F}_\mu\rangle. \quad (2.28)$$

In order to reduce the exact equation of motion for ϕ, Eq. (2.27), to a generalized Langevin equation, one must undertake an analysis similar to that developed by Mazur and Oppenheim[6] for the single particle momentum Langevin equation and employed by us[7] for the single particle generalized Langevin equation. The reader is referred to these papers for details.

Equation (2.27) can be rewritten in the form

$$\dot\phi(t)=A(t)+K^+(t)+\sum_\mu\sum_\nu e^{iLt}\left[\nabla_{\mathbf{P}_\mu}-\frac{\beta\mathbf{P}_\mu}{M}\right]$$

$$\cdot\int_0^t\langle\mathbf{E}_\mu\mathbf{E}_\nu{}^0(\tau)\rangle\cdot\nabla_{\mathbf{P}_\nu}\phi(0)d\tau+I_1+I_2, \quad (2.29)$$

where

$$\mathbf{E}_\nu{}^0(\tau)\equiv\exp(iL_0\tau)\mathbf{E}_\nu, \quad (2.30)$$

$$I_1\equiv\sum_\mu\sum_\nu\int_0^t e^{iL(t-\tau)}\left[\nabla_{\mathbf{P}_\mu}-\frac{\beta\mathbf{P}_\mu}{M}\right]$$

$$\cdot\{\langle\mathbf{E}_\mu\exp[i(1-\mathcal{P})L\tau]\mathbf{E}_\nu\rangle-\langle\mathbf{E}_\mu\mathbf{E}_\nu{}^0(\tau)\rangle\}\cdot\nabla_{\mathbf{P}_\nu}\phi(0)d\tau \quad (2.31)$$

and

$$I_2\equiv\sum_\mu\sum_\nu\int_0^t(e^{iL(t-\tau)}-e^{iLt})\left[\nabla_{\mathbf{P}_\mu}-\frac{\beta\mathbf{P}_\mu}{M}\right]$$

$$\cdot\langle\mathbf{E}_\mu\mathbf{E}_\nu{}^0(\tau)\rangle\cdot\nabla_{\mathbf{P}_\nu}\phi(0)d\tau. \quad (2.32)$$

We wish to determine the conditions under which it is valid to approximate the exact equation, Eq. (2.29), by an approximate equation with the terms I_1 and I_2 set equal to zero. We assume that: (1) $\langle A\exp[iL_0t]B\rangle=\langle A\rangle\langle B\rangle$ for $t>\tau_b$, where τ_b is the longest relaxation time for the bath in the presence of the Brownian particles fixed in position. In the system considered here, there will be a bath relaxation time which depends on $\mathbf{R}_{ij}$ and which is roughly $[|\mathbf{R}_{ij}|/c]$, where c is the velocity of sound in the bath; and (2) the conditions of Eqs. (3.15)–(3.17) of Ref. (7) are met, where $\mathbf{P}$ and $\mathbf{R}$ can be replaced by any of the $\mathbf{P}_\mu$ and $\mathbf{R}_\mu$. With these assumptions, Eq. (2.29) becomes

$$\dot\phi(t)=A(t)+K^+(t)$$

$$+\sum_\mu\sum_\nu e^{iLt}[\nabla_{\mathbf{P}_\mu}-(\beta/M)\mathbf{P}_\mu]\cdot\boldsymbol{\gamma}_{\mu\nu}(t)\cdot\nabla_{\mathbf{P}_\nu}\phi(0), \quad (2.33)$$

where

$$\boldsymbol{\gamma}_{\mu\nu}(t)\equiv\int_0^t d\tau\langle\mathbf{E}_\mu\mathbf{E}_\nu(\tau)\rangle\equiv\boldsymbol{\gamma}_{\mu\nu}(t,\mathbf{R}^n). \quad (2.34)$$

In this equation we have retained the leading terms in powers of $\lambda\equiv(m/M)^{1/2}\ll1$. In the next section we discuss applications of this equation.

III. PROPERTIES OF THE MOMENTUM LANGEVIN EQUATIONS

The momentum Langevin equation is obtained from the generalized Langevin equation, Eq. (2.33), by the choice $\phi=\mathbf{P}_\nu$,

$$\dot{\mathbf{P}}_\nu(t)=\mathbf{S}_\nu(t)+\mathbf{E}_\nu{}^+(t)-\sum_\mu\mathbf{P}_\mu(t)\cdot\boldsymbol{\zeta}_{\mu\nu}(t,\mathbf{R}^n(t)),$$

$$\nu=1,\cdots,n, \quad (3.1)$$

where $\mathbf{S}_\nu(t)$ is given by Eq. (2.28), the random force

$$\mathbf{E}_\nu{}^+(t)=\exp[i(1-\mathcal{P})Lt]\mathbf{E}_\nu, \quad (3.2)$$

and the friction tensor $\boldsymbol{\zeta}_{\mu\nu}$ is defined by $\boldsymbol{\zeta}_{\mu\nu}(t,\mathbf{R}^n)\equiv(\beta/M)\boldsymbol{\gamma}_{\mu\nu}(t,\mathbf{R}^n)$ and

$$\boldsymbol{\zeta}_{\mu\nu}(t,\mathbf{R}^n(t))\equiv(\beta/M)e^{iLt}\boldsymbol{\gamma}_{\mu\nu}(t,\mathbf{R}^n). \quad (3.3)$$

For time scales of interest, $t\gg\tau_b$, the equation for $\mathbf{P}(t)$ becomes

$$\dot{\mathbf{P}}_\nu(t)=\mathbf{S}_\nu(t)+\mathbf{E}_\nu{}^+(t)-\sum_\mu\mathbf{P}_\mu(t)\cdot\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(t)],$$

$$\nu=1,\cdots,n, \quad (3.4)$$

where

$$\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(t)]\equiv\boldsymbol{\zeta}_{\mu\nu}[\infty,\mathbf{R}^n(t)]. \quad (3.5)$$

The coupled Langevin equations that describe the momentum relaxation of the heavy particles are given by Eq. (3.1) or, for long times, by Eq. (3.5). Note that in these equations the effective friction tensors that describe the momentum damping are time dependent through the instantaneous interparticle separations $\mathbf{R}^n(t)$.

In order to complete our association of Eqs. (3.1) and (3.4) with the Langevin equations for this system, we must discuss the averages of products of the fluctuating force $\mathbf{E}_\nu{}^+(t)$. It follows from Eqs. (2.7), (2.22), and (3.2) that

$$\langle\mathbf{E}_\nu{}^+(t)\rangle=\langle\mathbf{E}_\nu\rangle=0. \quad (3.6)$$

It follows from the arguments in Ref. (6) that

$$\langle\mathbf{E}_\mu(0)\mathbf{E}_\nu{}^+(t)\rangle\simeq\langle\mathbf{E}_\mu(0)\mathbf{E}_\nu{}^0(t)\rangle=2(M/\beta)\zeta_{\mu\nu}(\mathbf{R}^n)\delta(t), \quad (3.7)$$

where the last equality is true on the momentum relaxation time scale $t\gg\tau_b$. In fact, in the weak coupling limit $\lambda\to 0$, $t\to\infty$ $(\lambda^2 t)=\text{constant}$, $\mathbf{E}_\mu$ can be described by a Gaussian stochastic process[6] with mean zero, Eq. (3.6), and with the second moment given by Eq. (3.7).

The next calculation of interest is to determine how the correlation function

$$\mathsf{F}_{\mu\nu}(t,\tau)\equiv\langle\mathbf{E}_\mu^+(t)\mathbf{E}_\nu^+(t+\tau)\rangle \quad (3.8)$$

is related to the correlation function $\mathsf{F}_{\mu\nu}(0,\tau)$. The correlation function $\mathsf{F}_{\mu\nu}(t,\tau)$ satisfies the differential equation,

$$\partial\mathsf{F}_{\mu\nu}(t,\tau)/\partial t=\langle iL_B[\mathbf{E}_\mu^+(t)\mathbf{E}_\nu^+(t+\tau)]\rangle. \quad (3.9)$$

This equation may be expressed as

$$\partial\mathsf{F}_{\mu\nu}(t,\tau)/\partial t=\langle iL_B\rangle\mathsf{F}_{\mu\nu}(t,\tau)+\sum_\alpha[\nabla_{\mathrm{P}\alpha}-(\beta/M)\mathbf{P}_\alpha]\cdot\langle\mathbf{E}_\alpha(0)\mathbf{E}_\mu^+(t)\mathbf{E}_\nu^+(t+\tau)\rangle, \quad (3.10)$$

where use has been made of the fact that

$$\nabla_{\mathrm{R}\alpha}\mathsf{F}_{\mu\nu}=\beta\langle\mathbf{E}_\alpha\mathbf{E}_\mu^+(t)\mathbf{E}_\nu(t+\tau)\rangle+\langle\nabla_{\mathrm{R}\alpha}[\mathbf{E}_\mu^+(t)\mathbf{E}_\nu^+(t+\tau)]\rangle. \quad (3.11)$$

The last term in Eq. (3.10) is of higher order in λ than the other terms for small t and τ. For larger t it has the behavior described in Ref. 6 where for $t>\tau_b$, $\mathbf{E}_\nu^+(t)$ forms a Gaussian random process. Thus, for small λ the solution to Eq. (3.10) can be written

$$\mathsf{F}_{\mu\nu}(t,\tau)=\exp[i\langle L_B\rangle t]\mathsf{F}_{\mu\nu}(0,\tau)=\exp[i\langle L\rangle t]\mathsf{F}_{\mu\nu}(0,\tau). \quad (3.12)$$

This result demonstrates that the correlation function of the random force $\mathsf{F}_{\mu\nu}(t,\tau)$ is *not* stationary in time. Physically this reflects the relative motion of the two Brownian particles. The time dependence, with respect to t, of $\mathsf{F}_{\mu\nu}(t,\tau)$ may be computed using the averaged Liouville operator $\langle L\rangle$.

In one-particle Brownian motion theory, the fluctuation dissipation theorem holds, i.e., the friction constant is equal to the time correlation function of the random force times (β/M). We now demonstrate that in the many particle theory this relationship is more complicated. To lowest order we find from Eqs. (3.3), (3.5), and (3.12) that

$$(\beta/M)\int_0^\infty\mathsf{F}_{\mu\nu}(t,\tau)d\tau=\exp[i\langle L\rangle t]\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(0)] \quad (3.13)$$

which is *not* equal to the effective friction constant $\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(t)]$. If we compute the average friction constant at time t, we obtain

$$\langle\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(t)]\rangle=\langle\exp(iLt)\rangle\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(0)], \quad (3.14)$$

which again is not the same as Eq. (3.13).

The Langevin equations, Eq. (3.4), we obtain for several Brownian particles are considerably more complicated than that for one Brownian particle because of the $\mathbf{R}^n(t)$ dependence of the friction constant. Even at large separations of the Brownian particles where the short range function $\mathbf{S}_{\mu\nu}(t)$ can be set equal to zero, the average of Eq. (3.4) is

$$\langle\dot{\mathbf{P}}_\nu(t)\rangle=-\sum_\mu\langle\mathbf{P}_\mu(t)\cdot\boldsymbol{\zeta}_{\mu\nu}[\mathbf{R}^n(t)]\rangle \quad (3.15)$$

and the average on the right-hand side cannot be rigorously broken.

In this section we have examined the properties of the momentum Langevin equations obtained from the generalized Langevin equation, Eq. (2.33), for the special choice $\phi=\mathbf{P}_\nu$. Clearly, we could examine the equations obtained for other choices of ϕ in a manner completely analogous to that undertaken for a single Brownian particle in Ref. 7. Instead, we shall turn our attention in the next section to a discussion of the Fokker–Planck equation for this system.

IV. THE FOKKER–PLANCK EQUATION

The generalized Langevin equation obtained in Sec. II may be used to obtain a Fokker–Planck equation for the reduced distribution function $\psi(\mathbf{R}^n,\mathbf{P}^n,t)$ for the Brownian particles. The results of Eq. (2.33) may be summarized in an equation of motion for the phase function

$$D(t)\equiv D(\hat{\mathbf{R}}^n,\hat{\mathbf{P}}^n,t\mid\mathbf{R}^n,\mathbf{P}^n)\equiv\exp[iLt]\delta(\mathbf{R}^n-\hat{\mathbf{R}}^n)\delta(\mathbf{P}^n-\hat{\mathbf{P}}^n), \quad (4.1)$$

where $\hat{\mathbf{R}}^n$ and $\hat{\mathbf{P}}^n$ denote arbitrary values of the positions and momenta of the Brownian particles. The equation for D is

$$(\partial/\partial t)D(t)=\exp[iLt]\sum_\mu[(\mathbf{P}_\mu/M)\cdot\nabla_{\mathrm{R}\mu}+\langle\mathbf{F}_\mu\rangle\cdot\nabla_{\mathrm{P}\mu}]D(0)+G^+(t)+\sum_\mu\sum_\nu\exp(iLt)\times[\nabla_{\mathrm{P}\mu}-(\beta/M)\mathbf{P}_\mu]\cdot\boldsymbol{\gamma}_{\mu\nu}(t)\cdot\nabla_{\mathrm{P}\mu}D(0), \quad (4.2)$$

where the random force $G^+(t)$ is

$$G^+(t)=\exp[i(1-\mathcal{P})Lt]\sum_\nu\mathbf{E}_\nu\cdot\nabla_{\mathrm{P}\nu}D(0). \quad (4.3)$$

The generalized Langevin equation, Eq. (2.33), is regained by multiplying Eq. (4.2) by $\phi(\mathbf{R}^n,\hat{\mathbf{P}}^n)$ and integrating over all values of $\hat{\mathbf{R}}^n$ and $\mathbf{P}^n$. It should be emphasized that Eq. (4.2) cannot be justified without an examination of the function ϕ with which the delta function is eventually associated.

The equation for $D(t)$ may be written in an alternative form if one takes into account properties of the delta functions in $D(0)$,[7]

$$\partial D/\partial t+\sum_\mu[(\hat{\mathbf{P}}_\mu/M)\cdot\nabla(\mathbf{R}_\mu)+\langle\mathbf{F}_\mu\rangle\cdot\nabla(\hat{\mathbf{P}}_\mu)]D(t)=G^+(t)+\sum_\mu\sum_\nu\nabla(\hat{\mathbf{P}}_\nu)\cdot\boldsymbol{\gamma}_{\nu\mu}(t,\hat{\mathbf{R}}^n)\cdot[\nabla(\hat{\mathbf{P}}_\nu)+(\beta/M)\hat{\mathbf{P}}_\mu]D(t). \quad (4.4)$$

In Eq. (4.4) and the following equations $\nabla(\hat{\mathbf{R}}_\mu)$ and

$\nabla(\hat{\mathbf{P}}_\mu)$ denote gradients with respect to $\hat{\mathbf{R}}_\mu$ and $\mathbf{P}_\mu$, respectively. For times $t \gg \tau_b$ one may replace $\boldsymbol{\gamma}_{\nu\mu}(t, \hat{\mathbf{R}}^n)$ by $\boldsymbol{\gamma}_{\nu\mu}(\infty, \hat{\mathbf{R}}^n)$ in Eq. (4.4) to obtain the random Fokker–Planck equation

$$(\partial D/\partial t) + \sum_\mu [(\hat{\mathbf{P}}_\mu/M)\cdot\nabla(\hat{\mathbf{R}}_\mu) + \langle\hat{\mathbf{F}}_\mu\rangle\cdot\nabla(\hat{\mathbf{P}}_\mu)]D(t) = G^+(t) + \sum_\mu\sum_\nu \nabla(\hat{\mathbf{P}}_\nu)\cdot\boldsymbol{\zeta}_{\nu\mu}(\hat{\mathbf{R}}^n)\cdot[\hat{\mathbf{P}}_\mu + (M/\beta)\nabla(\hat{\mathbf{P}}_\mu)]D(t), \quad (4.5)$$

where

$$\boldsymbol{\zeta}_{\nu\mu}(\hat{\mathbf{R}}^n) = (\beta/M)\boldsymbol{\gamma}_{\nu\mu}(\infty, \hat{\mathbf{R}}^n). \quad (4.6)$$

Note that the friction tensor appearing in Eq. (4.5) does not depend explicitly upon time in contrast to the friction tensor that appears in the momentum Langevin equations.

Properties of the random Fokker–Planck equation may be established exactly as in Ref. (7) where the single particle random Fokker–Planck equation is discussed in detail. For example,

$$\langle G^+(0, \hat{\mathbf{R}}'^n, \hat{\mathbf{P}}'^n)G^+(t, \hat{\mathbf{R}}^n, \hat{\mathbf{P}}^n)\rangle = \sum_{\mu,\nu} \nabla_{\mathbf{P}\mu}\delta(\hat{\mathbf{R}}'^n - \mathbf{R}^n)\delta(\hat{\mathbf{P}}'^n - \mathbf{P}^n)\cdot\boldsymbol{\gamma}_{\mu\nu}(t)\cdot\nabla_{\mathbf{P}\nu}\delta(\hat{\mathbf{R}}^n - \mathbf{R}^n)\delta(\hat{\mathbf{P}}^n - \mathbf{P}^n). \quad (4.7)$$

The equation for $D(t)$, Eq. (4.4), may be used to obtain the distribution function for the Brownian particles since[7]

$$\psi(\hat{\mathbf{R}}^n, \hat{\mathbf{P}}^n, t) = \int d\mathbf{r}^N d\mathbf{p}^N d\mathbf{R}^n d\mathbf{P}^n f(0) D(t), \quad (4.8)$$

where $f(0) \equiv f(\mathbf{r}^N, \mathbf{p}^N, \mathbf{R}^n, \mathbf{P}^n)$ is the initial nonequilibrium distribution of the complete $(N+n)$ particle system.

If one assumes, as is usually done,[8] that the initial distribution consists of the bath particles in equilibrium in the field of the fixed Brownian particles,

$$f(0) = \rho_0 g(\mathbf{R}^n, \mathbf{P}^n), \quad (4.9)$$

then Eq. (4.8) becomes

$$\psi(\hat{\mathbf{R}}^n, \hat{\mathbf{P}}^n, t) = \int d\mathbf{R}^n d\mathbf{P}^n g(\mathbf{R}^n, \mathbf{P}^n)\langle D(t)\rangle. \quad (4.10)$$

Because $\langle G^+(t)\rangle = 0$ the quantity $\langle D(t)\rangle$ satisfies the Fokker–Planck equation

$$\partial\langle D(t)\rangle/\partial t = -\sum_\mu [(\hat{\mathbf{P}}_\mu/M)\cdot\nabla(\hat{\mathbf{R}}_\mu) + \langle\hat{\mathbf{F}}_\mu\rangle\nabla(\hat{\mathbf{P}}_\mu)]\langle D(t)\rangle \times \sum_\mu\sum_\nu \nabla(\hat{\mathbf{P}}_\nu)\cdot\boldsymbol{\zeta}_{\nu\mu}(t, \hat{\mathbf{R}}^n)\cdot[\hat{\mathbf{P}}_\mu + (M/\beta)\nabla(\hat{\mathbf{P}}_\mu)]\langle D(t)\rangle, \quad (4.11)$$

where

$$\boldsymbol{\zeta}_{\nu\mu}(t, \hat{\mathbf{R}}^n) = (\beta/M)\boldsymbol{\gamma}_{\nu\mu}(t, \hat{\mathbf{R}}^n). \quad (4.12)$$

For times $t \gg \tau_b \boldsymbol{\zeta}_{\nu\mu}(t, \hat{\mathbf{R}}^n)$ may be replaced by $\boldsymbol{\zeta}_{\nu\mu}(\hat{\mathbf{R}}^n)$, Eq. (4.6). It follows from Eq. (4.10) that $\psi(\hat{\mathbf{R}}^n, \hat{\mathbf{P}}^n, t)$ will satisfy the identical differential equation with initial condition $\psi(0) = g(\hat{\mathbf{R}}^n, \hat{\mathbf{P}}^n)$. For the special case of two particles and $t \gg \tau_b$, Eq. (4.11) corresponds to Mazo's recent result.[8]

There is an important difference between the Fokker–Planck equation for the distribution function, Eq. (4.11), and the momentum Langevin equations, Eq. (3.1), which is not present in the single particle theory. In the momentum Langevin equations even when $t \gg \tau_b$ the effective friction constant depends upon the instantaneous positions of the Brownian particles [see Eqs. (3.1) and (3.3)] while in the Fokker–Planck equation the friction constant depends only on the coordinates $\hat{\mathbf{R}}^n$. As a consequence, the momentum Langevin equation is highly nonlinear while the Fokker–Planck equation remains linear, albeit quite complicated. The difference arises because of the quantities that are implicitly held constant in the two equations. In the momentum Langevin equation it is the initial momenta and positions that are held fixed while in the Fokker–Planck equation it is the momenta and positions at time t that are held fixed.

Calculations cannot take place with either the coupled momentum Langevin equations or the Fokker–Planck equation unless something is known about the dependence of $\boldsymbol{\zeta}_{\mu\nu}(\mathbf{R}^n)$, Eq. (4.6), on particle position. In the next section we undertake an evaluation of the friction tensor for the special case of two particles. For two particles the friction tensor takes the form ($t \gg \tau_b$)

$$\boldsymbol{\zeta}_{\mu\nu}(\mathbf{R}_{12}) = [\beta/M]\int_0^\infty \langle\mathbf{E}_\mu\mathbf{E}_\nu{}^0(t)\rangle dt, \qquad \mu, \nu = 1, 2. \quad (4.13)$$

V. EVALUATION OF THE FRICTION TENSOR

We shall evaluate the friction tensor in two ways. The first is an approximate *macroscopic* calculation of the force experienced by two stationary spheres when the velocity of the fluid is uniform at infinity. The second way proceeds by an approximate *microscopic* calculation, based on fluctuation theory, of the autocorrelation expression for $\zeta_{\mu\nu}$. In both approaches approximations are introduced that are valid in the limit of large particle separation, i.e., for $(a/|\mathbf{R}_{12}|)$ small, where a is the radius of the sphere. To lowest order in this ratio we find, as expected, identical expressions for the friction tensor.

The Macroscopic Approach

Consider a sphere placed at position $\mathbf{R}_2$ in a fluid where the unperturbed velocity field is $\mathbf{v}^0(\mathbf{R})$. It is well known from hydrodynamics that at points $\mathbf{R}_i$ far from the sphere the resulting velocity field $\mathbf{v}(\mathbf{R})$ is described by[10,11]

$$\mathbf{v}(\mathbf{R}_i) = \mathbf{v}^0(\mathbf{R}_i) - \zeta_0\mathsf{T}_{ij}\cdot\mathbf{v}(\mathbf{R}_j), \quad (5.1)$$

where T_{ij} is the Oseen tensor,

$$\mathsf{T}_{ij} = \rho[\mathsf{I} + \hat{\mathbf{R}}_{ij}\hat{\mathbf{R}}_{ij}], \quad \rho = [8\pi\eta_0|\mathbf{R}_{ij}|]^{-1}, \quad (5.2)$$

and $\hat{\mathbf{R}}_{ij}$ is the unit vector in the direction of the interparticle vector. The quantity ζ_0 is the friction constant for a single sphere in the fluid, I is the unit tensor, and η_0 is the viscosity of the fluid in the absence of all particles. Here we are interested in determining $\mathbf{v}(\mathbf{R}_i)$ at the two Brownian particles that are widely separated and held fixed at positions $\mathbf{R}_1$ and $\mathbf{R}_2$. For convenience we choose a coordinate system where the two particles lie on the z axis so that

$$\mathsf{T}_{ij}=\rho[\mathsf{I}+\hat{k}\hat{k}]. \quad (5.3)$$

The perturbed z component of velocity at particle one is given by

$$v_z(\mathbf{R}_1)=\{1/[1-(2\zeta_0\rho)^2]\}v_z^0(\mathbf{R}_1) - \{2\zeta_0\rho/[1-(2\zeta_0\rho)^2]\}v_z^0(\mathbf{R}_2), \quad (5.4)$$

and the perturbed x component of velocity at particle one is

$$v_x(\mathbf{R}_1)=\{1/[1-(\zeta_0\rho)^2]\}v_x^0(\mathbf{R}_1) - \{\zeta_0\rho/[1-(\zeta_0\rho)^2]\}v_x^0(\mathbf{R}_2) \quad (5.5)$$

with an identical expression for the y-component equations. Expressions for the perturbed velocity at $\mathbf{R}_2$ are identical to Eqs. (5.4) and (5.5) with interchange of $\mathbf{R}_1$ and $\mathbf{R}_2$.

The force on each particle may be approximated by

$$\mathbf{F}(\mathbf{R}_i)=-\zeta_0\mathbf{v}(\mathbf{R}_i), \qquad i=1, 2. \quad (5.6)$$

This approximation introduces an error of order $(a/|\mathbf{R}_{12}|)$, which, however, is already implied by the use of Oseen's tensor.

From Eqs. (5.6), (5.4), and (5.5), it follows that

$$\mathbf{F}(\mathbf{R}_i)=\sum_{j=1}^{2} M\boldsymbol{\zeta}_{ij}\cdot\mathbf{v}^0(\mathbf{R}_j), \qquad i=1, 2. \quad (5.7)$$

The nonvanishing elements of the four friction tensors are given by

$$[M\boldsymbol{\zeta}_{11}]_{zz}=[M\boldsymbol{\zeta}_{22}]_{zz}=\{\zeta_0/[1-(2\zeta_0\rho)^2]\} =\zeta_0[1+(2\zeta_0\rho)^2+O(\zeta_0\rho)^4], \quad (5.8)$$

$$[M\boldsymbol{\zeta}_{11}]_{xx}=[M\boldsymbol{\zeta}_{11}]_{yy}=[M\boldsymbol{\zeta}_{22}]_{xx}=[M\boldsymbol{\zeta}_{22}]_{yy} =\{\zeta_0/[1-(\zeta_0\rho)^2]\}=\zeta_0[1+(\zeta_0\rho)^2+O(\zeta_0\rho)^4] \quad (5.9)$$

for the "self-friction tensors, and

$$[M\boldsymbol{\zeta}_{12}]_{zz}=[M\boldsymbol{\zeta}_{21}]_{zz}=\{-2\zeta_0^2\rho/[1-(2\zeta_0\rho)^2]\} =-2\zeta_0^2\rho[1+O(\zeta_0\rho)^2], \quad (5.10)$$

$$[M\boldsymbol{\zeta}_{12}]_{xx}=[M\boldsymbol{\zeta}_{12}]_{yy}=[M\boldsymbol{\zeta}_{21}]_{xx}=[M\boldsymbol{\zeta}_{21}]_{yy} =\{-\zeta_0^2\rho/[1-(\zeta_0\rho)^2]\}=-\zeta_0^2\rho[1+O(\zeta_0\rho)^2] \quad (5.11)$$

for the cross friction tensor. In the special coordinate system chosen, all off diagonal elements are zero. Note that if $\zeta_0=6\pi\eta_0 a$, then

$$(\zeta_0\rho)=(3/4)(a/|\mathbf{R}_{12}|), \quad (5.12)$$

and that all of the expression for $\boldsymbol{\zeta}_{ij}$ in Eqs. (5.8)–(5.11) have been expanded to lowest nonvanishing order in this parameter consistent with the approximations introduced in the calculation.

The modification introduced by the presence of a second Brownian particle is of order $(a/|\mathbf{R}_{12}|)^2$ for the "self"-friction tensors and of order $(a/|\mathbf{R}_{12}|)$ for the "cross" friction tensors. It is important to note that both these modifications are long ranged which is a necessary consequence of the long range hydrodynamic interaction effects that are present in incompressible fluids.

The Microscopic Approach

We next evaluate the friction tensors by a direct calculation of the time integral of the equilibrium time correlation function expression given in Eq. (4.13). This procedure is based on a calculation by Zwanzig[9] for the friction constant of a single Brownian particle. We imagine an arbitrary fluctuation in the local velocity of an unperturbed fluid $\mathbf{v}^0(\mathbf{R}, t)$ at time t. If two heavy particles are fixed in the fluid the resulting velocity field $\mathbf{v}(\mathbf{R}, t)$ may be approximately related to $\mathbf{v}_0$ by an argument identical to that used above. In a coordinate system where the z axis lies along the interparticle vector, we have from Eqs. (5.4) and (5.5)

$$v_\alpha(\mathbf{R}_i, t)=(1-L_\alpha^2)^{-1}[v_\alpha^0(\mathbf{R}_i, t)-L_\alpha v_\alpha^0(\mathbf{R}_j, t)] \qquad (i\neq j=1, 2), \quad (5.13)$$

where $\alpha=x, y, z$ and

$$L_x=L_y=\zeta_0\rho, \qquad L_z=2\zeta_0\rho. \quad (5.14)$$

The velocity fluctuations average to zero at any time and will, of course, vary appreciably over a spatial length of order a. Accordingly, the effective force on each Brownian particle, assumed spherical, is computed by a modification of Eq. (5.6) to include an average over the particle surface,

$$\mathbf{F}(\mathbf{R}_i, t)=-[\zeta_0/(4\pi)]\int d\Omega_i\mathbf{v}(\mathbf{R}_i, t). \quad (5.15)$$

This force may be expressed in terms of Fourier coefficients of $v^0(\mathbf{R}, t)$,

$$\mathbf{v}^0(\mathbf{R}, t)=\int d\mathbf{k}\tilde{\mathbf{v}}^0(\mathbf{k}, t)\exp[i\mathbf{k}\cdot\mathbf{R}],$$

by use of Eq. (5.13). One finds

$$F_\alpha(\mathbf{R}_i, t)=[-\zeta_0/(1-L_\alpha^2)]\int d\mathbf{k}(\sin ka/ka) \times[\exp(i\mathbf{k}\cdot\mathbf{R}_i)]-L_\alpha[\exp(i\mathbf{k}\cdot\mathbf{R}_j)]\tilde{\mathbf{v}}_\alpha^0(\mathbf{k}, t), \; i\neq j=1, 2. \quad (5.16)$$

The "cross" force correlation function is

$$\langle F_\alpha(\mathbf{R}_1, t)F_\beta(\mathbf{R}_2, 0)\rangle=[\zeta_0^2/(1-L_\alpha^2)(1-L_\beta^2)] \times\int d\mathbf{k}_1 d\mathbf{k}_2(\sin k_1a/k_1a)(\sin k_2a/k_2a) \times\{\exp[i(\mathbf{k}_1\cdot\mathbf{R}_1+\mathbf{k}_2\cdot\mathbf{R}_2)]-L_\alpha\exp[i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}_2] -L_\beta\exp[i(\mathbf{k}_2+\mathbf{k}_1)\cdot\mathbf{R}_1]+L_\alpha L_\beta\exp[i(\mathbf{k}_1\cdot\mathbf{R}_2+\mathbf{k}_2\cdot\mathbf{R}_1)]\} \times\langle\tilde{\mathbf{v}}_\alpha^0(\mathbf{k}_1, t)\tilde{\mathbf{v}}_\beta^0(\mathbf{k}_2, 0)\rangle\equiv G_{\alpha\beta}(|\mathbf{R}_{12}|, t). \quad (5.17)$$

The "self"-force correlation function is

$$\langle F_\alpha(\mathbf{R}_1, t)F_\beta(\mathbf{R}_1, 0)\rangle = [\zeta_0^2/(1-L_\alpha^2)(1-L_\beta^2)] \times \int d\mathbf{k}_1 d\mathbf{k}_2 (\sin k_1 a/k_1 a)(\sin k_2 a/k_2 a) \times\{\exp[i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}_1] - L_\alpha \exp[i(\mathbf{k}_1\cdot\mathbf{R}_2+\mathbf{k}_2\cdot\mathbf{R}_1)] - L_\beta \exp[i(\mathbf{k}_2\cdot\mathbf{R}_2+\mathbf{k}_1\cdot\mathbf{R}_1)] + L_\alpha L_\beta \exp[i(\mathbf{k}_1+\mathbf{k}_2)\cdot\mathbf{R}_2]\} \times\langle \tilde{\mathbf{v}}_\alpha^0(\mathbf{k}_1, t)\tilde{\mathbf{v}}_\beta^0(\mathbf{k}_2, t)\rangle \equiv K_{\alpha\beta}(|\mathbf{R}_{12}|, t). \quad (5.18)$$

The force correlation functions are thus related to velocity fluctuations in an unperturbed fluid. The unperturbed velocity correlations are obtained from usual hydrodynamic fluctuation theory. They are[12]

$$\langle \tilde{\mathbf{v}}_\alpha^0(\mathbf{k}_1, t)\tilde{\mathbf{v}}_\beta^0(\mathbf{k}_2, 0)\rangle = (2k_bT/\eta_0 k_1^2) \times[\delta(t)/(2\pi)^3]\delta(\mathbf{k}_1+\mathbf{k}_2)[\delta_{\alpha\beta}-(k_1^\alpha k_1^\beta/k_1^2)], \quad (5.19)$$

where k_b is Boltzmann's constant. When this expression for the velocity correlations is substituted into Eqs. (5.17) and (5.18) the force correlations may be evaluated. The results for the nonvanishing force correlations are as follows. For the longitudinal "cross" force correlation,

$$G_{zz}(R_{12}, t) = [A\delta(t)/(1-L_z^2)^2] \times[(1+L_z^2)I_1(R_{12}/a) - \tfrac{8}{3}L_z]; \quad (5.20)$$

and for the transverse "cross" force correlation,

$$G_{xx}(R_{12}, t) = G_{yy}(R_{12}, t) = [\delta(t)A/(1-L_x^2)^2] \times[(1+L_x^2)I_2(R_{12}/a) - \tfrac{8}{3}L_x]. \quad (5.21)$$

For the longitudinal "self"-force correlation,

$$K_{zz}(R_{12}, t) = [A\delta(t)/(1-L_z^2)] \times[\tfrac{4}{3}(1+L_z^2) - 2L_z I_1(R_{12}/a)]; \quad (5.22)$$

and for the transverse "self"-force correlation,

$$K_{xx}(R_{12}, t) = K_{yy}(R_{12}, t) = [A\delta(t)/(1-L_x^2)] \times[\tfrac{4}{3}(1+L_x^2) - 2L_x I_2(R_{12}/a)]. \quad (5.23)$$

In these equations

$$A = [\zeta_0^2 k_b T/(4\pi a\eta_0)] \quad (5.24)$$

and the integrals $I_1(R_{12}/a)$ and $I_2(R_{12}/a)$ are defined as

$$I_1(R_{12}/a) = (2/\pi)\int_{-1}^{+1} du \int_0^\infty dk \exp[iku(R_{12}/a)] \times(\sin^2 k/k^2)[1-u^2], \quad (5.25)$$

$$I_2(R_{12}/a) = (2/\pi)\int_{-1}^{+1} du \int_0^\infty dk \exp[iku(R_{12}/a)] \times(\sin^2 k/k^2)[(1+u^2)/2]. \quad (5.26)$$

These integrals may be evaluated exactly. The result is

$$I_1(x) = (2/x) - (4/3)x^{-3}, \qquad x \geq 2, \quad (5.27)$$

$$I_1(x) = (4/3) - (x/4), \qquad x < 2, \quad (5.28)$$

and

$$I_2(x) = (1/x) + (2/3)x^{-3}, \qquad x \geq 2, \quad (5.29)$$

$$I_2(x) = (4/3) - (3/8)x, \qquad x < 2. \quad (5.30)$$

To lowest order in (a/R_{12}) the force correlation functions are found to be

$$G_{zz}(R_{12}, t) = -2A\delta(t)(a/R_{12}), \quad (5.31)$$

$$G_{xx}(R_{12}, t) = -A\delta(t)(a/R_{12}) = G_{yy}(R_{12}, t), \quad (5.32)$$

$$K_{zz}(R_{12}, t) = (4A/3)\delta(t)[1+(3a/2R_{12})^2], \quad (5.33)$$

$$K_{xx}(R_{12}, t) = (4A/3)\delta(t)[1+(3a/4R_{12})^2] = K_{yy}(R_{12}, t). \quad (5.34)$$

Our final step in the calculation is to compute the friction tensor $M\boldsymbol{\zeta}_{ij}$ from the force correlation functions according to Eq. (4.13). The average force that is involved in Eq. (4.13) may be taken to be zero since the Brownian particles are widely separated and this force extends for only a few molecular diameters. Note that through the use of Stokes law,

$$\zeta_0 = 6\pi\eta_0 a,$$

which may legitimately be employed within the context of this approximate calculation, the constant A may be expressed as

$$A = (3\zeta_0/2\beta).$$

Since in Eq. (4.13) the time integral runs from $t=0$ to $t=\infty$, one picks up only one-half of the delta function. The results for the friction tensors $M\boldsymbol{\zeta}_{ij}$ from the hydrodynamic fluctuation calculation are in complete agreement with the results presented in Eq. (5.8)–(5.11), obtained from purely macroscopic hydrodynamic arguments. This agreement between the two methods, while at first sight surprising, is to be expected. Hydrodynamic fluctuation theory is constructed so that an evaluation of the time correlation function expressions gives identical results to macroscopic hydrodynamics, provided, of course, that consistent approximations are used in both calculations. In the two calculations presented here the important approximations implied by use of Oseen's tensor are: (a) low Reynolds number flow, (b) an incompressible fluid, (c) large separation between the two Brownian particles. It would be interesting, but quite difficult, to relax any of these assumptions.

VI. CALCULATION OF DIFFUSION CONSTANTS

The results for the friction tensors determined in the previous section may be used to compute the diffusion constants of the Brownian particles. Of particular interest is the modification in the diffusion of one particle caused by the other. At large particle separations the coupled Langevin equations, Eq. (4.4) may be written as

$$\dot{P}_{1\alpha}(t) = -\zeta_\alpha P_{1\alpha}(t) - \Gamma_\alpha P_{2\alpha}(t) + E_{1\alpha}(t) \quad (6.1)$$

and

$$\dot{P}_{2\alpha}(t) = -\zeta_\alpha P_{2\alpha}(t) - \Gamma_\alpha P_{1\alpha}(t) + E_{2\alpha}(t), \quad (6.2)$$

where $\alpha = x, y, z$, and we have adopted a coordinate system whose z axis points along the interparticle direction at all times. It follows that the nonvanishing elements of the friction tensors at time t are given by Eq. (5.8) to (5.13). For ease of notation we have defined

$$\zeta_\alpha = (\boldsymbol{\zeta}_{11})_{\alpha\alpha} = (\zeta_{22})_{\alpha\alpha} \quad (6.3)$$

and

$$\Gamma_\alpha = (\boldsymbol{\zeta}_{12})_{\alpha\alpha} = (\boldsymbol{\zeta}_{21})_{\alpha\alpha}. \quad (6.4)$$

The term $\mathbf{A}_i(t)$ appearing in Eq. (3.4) is not present in Eqs. (6.1) and (6.2) because it vanishes at large interparticle separations.

These stochastic equations are, in fact, highly nonlinear as a consequence of the friction coefficients' dependence on the instantaneous interparticle separation. However, in the case where the interparticle separation is large, a simplifying assumption is possible. The momentum of each particle relaxes in a time of the order ζ_0^{-1}. For times long compared to ζ_0^{-1}, the particles will diffuse with a diffusion constant of the order $(kT/M\zeta_0)$. The distance $l(t)$ which they travel may be estimated from the usual theory to be $l(t) = [(kT/M\zeta_0)t]^{1/2}$, so that at time t the interparticle separation $\mathbf{R}_{12}(t)$ is approximately

$$\mathbf{R}_{12}(t) = \mathbf{R}_{12}(0) + l(t). \quad (6.5)$$

We shall restrict our attention in our calculation of diffusion to times sufficiently short so that $l(t) \ll R_{12}(t)$. Under these circumstances $\mathbf{R}_{12}(t)$ may be approximated by $\mathbf{R}_{12}(0)$ in the friction coefficients and random forces appearing in Eqs. (6.1) and (6.2). The friction tensors remain diagonal in the coordinate system where the z axis is directed along the initial interparticle direction. Of course, our calculation for the diffusion constant will only be valid for times within which each particle has not moved appreciably compared to $\mathbf{R}_{12}(0)$. From these approximations and Eq. (3.7) it follows that the correlation functions of the random forces are

$$\langle E_{1\alpha} E_{1\beta}(t) \rangle = \langle E_{2\alpha} E_{2\beta}(t) \rangle = 2Mk_bT\zeta_\alpha\delta_{\alpha\beta}\delta(t) \quad (6.6)$$

and

$$\langle E_{1\alpha} E_{2\beta}(t) \rangle = \langle E_{2\alpha} E_{1\beta}(t) \rangle = 2Mk_bT\Gamma_\alpha\delta_{\alpha\beta}\delta(t). \quad (6.7)$$

The analysis of the coupled Langevin equations is simplified if one transforms to the variables

$$p_\alpha = P_{1\alpha} - P_{2\alpha}, \qquad P_\alpha = P_{1\alpha} + P_{2\alpha},$$

$$r_\alpha = R_{1\alpha} - R_{2\alpha}, \qquad R_\alpha = R_{1\alpha} + R_{2\alpha}. \quad (6.8)$$

With this transformation, Eqs. (6.1) and (6.2) become

$$\dot{p}_\alpha(t) = -(\zeta_\alpha - \Gamma_\alpha) p_\alpha(t) + e_\alpha(t) \quad (6.9)$$

and

$$\dot{P}_\alpha(t) = -(\zeta_\alpha + \Gamma_\alpha) P_\alpha(t) + E_\alpha(t), \quad (6.10)$$

where

$$e_\alpha(t) = E_{1\alpha}(t) - E_{2\alpha}(t) \quad (6.11)$$

and

$$E_\alpha(t) = E_{1\alpha}(t) + E_{2\alpha}(t). \quad (6.12)$$

From Eqs. (6.6) and (6.7) it follows that

$$\langle e_\alpha(0) e_\beta(t) \rangle = 4Mk_bT[\zeta_\alpha - \Gamma_\alpha]\delta_{\alpha\beta}\delta(t), \quad (6.13)$$

$$\langle E_\alpha(0) E_\beta(t) \rangle = 4Mk_bT[\zeta_\alpha + \Gamma_\alpha]\delta_{\alpha\beta}\delta(t), \quad (6.14)$$

and

$$\langle e_\alpha(0) E_\beta(t) \rangle = \langle E_\alpha(0) e_\beta(t) \rangle = 0. \quad (6.15)$$

Expectation values of the random forces are zero. The uncoupled equations are easily integrated to give

$$p_\alpha(t) = \exp[-(\zeta_\alpha - \Gamma_\alpha)t]p_\alpha(0) + \int_0^t d\tau \exp[-(\zeta_\alpha - \Gamma_\alpha)(t-\tau)]e_\alpha(\tau) \quad (6.16)$$

and

$$P_\alpha(t) = \exp[-(\zeta_\alpha - \Gamma_\alpha)t]P_\alpha(0) + \int_0^t d\tau \exp[-(\zeta_\alpha + \Gamma_\alpha)(t-\tau)]E_\alpha(\tau). \quad (6.17)$$

These two equations may be used with Eqs. (6.13)–(6.14) to verify the approach of the Brownian particles' momenta to their equilibrium value,

$$\lim_{t\to\infty} \langle p_\alpha^2(t) \rangle = \lim_{t\to\infty} \langle P_\alpha^2(t) \rangle = 2Mk_bT. \quad (6.18)$$

The relevant diffusion constants may be computed in either of two equivalent ways. First, one may integrate Eqs. (6.16) and (6.17) to obtain expressions for $r_\alpha(t)$ and $R_\alpha(t)$. The relative diffusion tensor $D_{\alpha\beta}^{(r)}$ and the center of mass diffusion tensor $D_{\alpha\beta}^{(R)}$ are related to these two quantities according to

$$\lim_{t\to\infty} \langle\langle \Delta r_\alpha(t) \Delta r_\beta(t) \rangle\rangle = 2D_{\alpha\beta}^{(r)}t \quad (6.19)$$

and

$$\lim_{t\to\infty} \langle\langle \Delta R_\alpha(t) \Delta R_\beta(t) \rangle\rangle = 2D_{\alpha\beta}^{(R)}t, \quad (6.20)$$

where $\Delta r_\alpha(t) = r_\alpha(t) - r_\alpha(0)$, etc. Alternatively, we may compute the diffusion tensor according to the time correlation function formulas

$$D_{\alpha\beta}^{(r)} = \frac{1}{M^2}\int_0^\infty dt \langle\langle p_\alpha(t) p_\beta(0) \rangle\rangle_B = \frac{1}{M^2}\int_0^\infty dt \langle\langle p_\alpha(t) \rangle p_\beta(0) \rangle_B \quad (6.21)$$

and

$$D_{\alpha\beta}^{(R)} = \frac{1}{M^2}\int_0^\infty dt \langle\langle P_\alpha(t) P_\beta(0) \rangle\rangle_B = \frac{1}{M^2}\int_0^\infty dt \langle\langle P_\alpha(t) \rangle P_\beta(0) \rangle_B. \quad (6.22)$$

The angular bracket with subscript B in Eqs. (6.19)–

(6.22) denotes an equilibrium average of initial momenta of the two Brownian particles. From Eqs. (6.9) and (6.10) one finds

$$\langle p_\alpha(t)\rangle_B = \exp[-(\zeta_\alpha - \Gamma_\alpha)t]p_\alpha(0) \qquad (6.23)$$

and

$$\langle P_\alpha(t)\rangle_B = \exp[-(\zeta_\alpha + \Gamma_\alpha)t]P_\alpha(0) \qquad (6.24)$$

which leads to the following results for the center of mass and relative diffusion tensors:

$$D_{\alpha\beta}^{(r)} = \frac{2(k_bT/M)\delta_{\alpha\beta}}{(\zeta_\alpha - \Gamma_\alpha)} = 2D_0\delta_{\alpha\beta}[1 - f_\alpha(a/R_{12}) + O(a/R_{12})^3] \qquad (6.25)$$

and

$$D_{\alpha B}^{(R)} = \frac{2(k_bT/M)\delta_{\alpha\beta}}{(\zeta_\alpha + \Gamma_\alpha)} = 2D_0\delta_{\alpha\beta}[1 + f_\alpha(a/R_{12}) + O(a/R_{12})^3] \qquad (6.26)$$

where $D_0 = (kT/M\zeta_0)$ and $f_x = f_y = (f_z/2) = 3/4$.

The diffusion tensor for particle one (or equivalently for particle two) may be obtained in an analagous manner. From Eqs. (6.23) and (6.24) one finds

$$\langle p_1^{(\alpha)}(t)\rangle_B = \exp[-(\zeta_\alpha - \Gamma_\alpha)t][p_\alpha(0)/2] + \exp[(\zeta_\alpha + \Gamma_\alpha)t][P_\alpha(0)/2]. \qquad (6.27)$$

The definition of the diffusion tensor for particle one is

$$D_{\alpha\beta}^{(1)} = \frac{1}{M^2}\int_0^\infty dt \langle\langle p_1^{(\alpha)}(t)\, p_1^{(\beta)}(0)\rangle\rangle_B, \qquad (6.28)$$

which leads to the result

$$D_{\alpha\beta}^{(1)} = (k_bT/M)[\delta_{\alpha\beta}\zeta_\alpha/(\zeta_\alpha^2 - \Gamma_\alpha^2)] = D_0\delta_{\alpha\beta}. \qquad (6.29)$$

The important feature of this result is that the long-range effects that appeared in the momentum relaxation of each particle cancel, leading to a single particle diffusion constant which is unmodified by the presence of the distant sphere to second order in a/R. The cancellation is suggested in the Langevin equations, Eqs. (6.1) and (6.2) where it can be seen that the second particle has two compensating effects; the decrease in the frictional force due to the second particle ($\Gamma_\alpha < 0$) is offset by an increase of the frictional force by an enhancement of the direct or "self"-friction constant ($\zeta_\alpha > \zeta_0$).

CONCLUDING REMARKS

It is important to mention two reservations about the calculations just presented. The first concerns the long-range nature of the friction tensors. The long range arises as a consequence of the Oseen tensor which implies low Reynolds number flow and the neglect of convective terms in the Navier Stokes equations. At distances sufficiently far from a sphere, these convective terms must be taken into account and this may well introduce a natural cutoff in the effective range of the hydrodynamic interaction. Oseen has presented an argument[11] indicating that the modifications must be introduced when the Reynolds number, $\mathrm{Re} = va\rho/\eta_0$, is comparable to (a/R_{12}). Consequently, the macroscopic hydrodynamic calculation presented in Sec. III will only be valid provided

$$\mathrm{Re} \ll (a/R_{12})$$

which implies an upper limit on the interparticle distance. Presumably, at very large separations, similar difficulties are present in the fluctuation calculation. It should be mentioned that no precise theory exists for dealing with the case of extremely large R_{12}.

The second reservation concerns the exact cancellation found in Eq. (6.29) for the single particle diffusion tensor $D_{\alpha\beta}^{(1)}$. The exact cancellation might not be exhibited for the Langevin equation which includes the instantaneous $\mathbf{R}_{12}(t)$ in the friction tensors. However a perturbation analysis, too lengthy to include here, suggests that the cancellation will still be present. The main conclusion, however, that the distance dependence is of shorter effective range for the diffusion tensors than for the friction tensors will not be changed.

Future work will be concerned with systems containing many heavy particles and an examination of their hydrodynamic properties.

* Supported in part by the National Science Foundation.

† On leave from the Department of Chemistry, M.I.T., Cambridge, Mass.

[1] J. L. Lebowitz and E. Rubin, Phys. Rev. **131,** 2381 (1963).
[2] P. Resibois and H. T. Davis, Physica **30,** 1077 (1964).
[3] J. L. Lebowitz and P. Resibois, Phys. Rev. **139,** 1001A (1965).
[4] R. I. Cukier and J. M. Deutch, Phys. Rev. **177,** 240 (1969).
[5] P. Mazur and I. Oppenheim, J. Phys. Soc. Japan Suppl. **26,** 35 (1969).
[6] P. Mazur and I. Oppenheim, "Molecular Theory of Brownian Motion," Physica (to be published).
[7] J. Albers, J. M. Deutch, and I. Oppenheim, J. Chem. Phys. **54,** 3541 (1971), preceding paper.
[8] R. M. Mazo, J. Stat. Phys. **1,** 559 (1969).
[9] R. W. Zwanzig, J. Res. Natl. Bur. Std. **B68,** 143 (1964).
[10] See, for example, J. Riseman and J. G. Kirkwood, in *Rheology Theory and Applications* (Academic, New York, 1956), Chap. 13, p. 495.
[11] C. W. Oseen, *Hydrodynamik* (Akademische Verlag, Leipzig, 1927). See also, J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Prentice-Hall, Englewood Cliffs, N.J., 1965), Chap. 6.
[12] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, London, 1959), Chap. 17.