Journal of Statistical Physics, Vol. 7, No. 3, 1973

Fluctuating Hydrodynamics and Brownian Motion

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Received July 26, 1972

The Langevin equation describing Brownian motion is considered as a contraction from the more fundamental, but still phenomenological, description of an incompressible fluid governed by fluctuating hydrodynamics in which a Brownian particle with stick boundary condition is immersed. First, the derivation of fluctuating hydrodynamics is reconsidered to clarify certain ambiguities as to the treatment of boundaries. Subsequently the contraction is carried out. Since Brownian particles of arbitrary shape are considered, rotations and translations are in general coupled. The symmetry of the 6×6 friction tensor $\Gamma_{ij}(t)$ is proved for arbitrary shape without appeal to microscopic arguments. This symmetry is then used to prove that the fluctuation-dissipation theorem on the contracted level (nonwhite noise in general) follows from the corresponding statement on the level of fluctuating hydrodynamics (white noise). The condition under which the contracted description reduces to the classical Langevin equation is given, and the connection between our theory and related work is discussed.

KEY WORDS: Brownian motion; fluctuating hydrodynamics; Langevin equation; fluctuation-dissipation theorem; autocorrelation functions.

1. INTRODUCTION

The first successful theory of Brownian motion was due to Einstein and to Smoluchowski.[3] In fact, all the classical experiments on that phenomenon

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[3] Some of the classical papers on Brownian motion, together with further references, can be found in Refs. 1a and 1b.

were adequately described by the Einstein–Smoluchowski formulas. Nevertheless, the validity of their theory is restricted to time scales on which the decay time of the velocity of the Brownian particle (B) is negligible. Since this decay time is typically 10^{-7} sec, the corresponding restriction was naturally of no great concern to contemporary experimentalists.

In an attempt to go beyond the Einstein–Smoluchowski approximation, Langevin, however, proposed his equation, which in the absence of external fields reads

$$m\, d\mathbf{U}/dt = -\gamma \mathbf{U}(t) + \tilde{\mathbf{F}}(t) \tag{1}$$

Here m is the mass, $\mathbf{U}(t)$ is the velocity of B, and γ is the friction constant. For a spherical particle in a fluid where the mean free path is small compared to the radius R of the sphere, γ is assumed to be given by Stokes's law, i.e.,

$$\gamma = 6\pi\eta R \tag{2}$$

where η is the viscosity of the fluid. Finally, the fluctuating force $\tilde{\mathbf{F}}(t)$ with vanishing mean is assumed to have a white spectrum,

$$\langle \tilde{F}_i(t) \tilde{F}_j(t') \rangle = 2kT\gamma\, \delta_{ij}\, \delta(t - t') \tag{3}$$

where k is Boltzmann's constant, T is the temperature of the fluid, and δ_{ij} and $\delta(t)$ are the Kronecker and Dirac deltas, respectively.

The Einstein–Smoluchowski theory follows from (1)–(3) as a limiting case for $t \gg m/\gamma$. In addition, the Langevin equation predicts the velocity autocorrelation function

$$C_U(t) \equiv \langle U_x(0) U_x(t) \rangle = (kT/m)\, e^{-\gamma t/m} \tag{4}$$

The Langevin equation has been extremely fruitful in statistical physics, and its immediate generalizations play a central role in all linear theories of fluctuation phenomena. As an important example, one can quote the theory of Gaussian Markov processes used by Onsager and Machlup[(2)] in their formulation of first-order nonequilibrium thermodynamics. A special case within this general framework is that of linearized, fluctuating hydrodynamics due to Landau and Lifshitz[(3)] and Green.[(4)]

Nevertheless, the validity of the Langevin equation in its original context of Brownian motion is not proved by the success of the general point of view it represents. What is in particular open to criticism is the use of Stokes's steady-state friction law (2). Whereas the Markovian character of Navier–Stokes hydrodynamics seems firmly rooted[4] in the basic conservation

[4] Not so firmly rooted as one used to think, however. Difficulties are encountered in the two-dimensional case. See Ref. 19.

laws, the instantaneous friction (2) has the status of the simplest possible assumption consistent with the Einstein–Smoluchowski theory.

Over the last decade several attempts have been made to derive (1), or its Fokker–Planck equivalent, as a limiting law from the Liouville equation for the $(N + 1)$-body problem.[5] In this way it has been shown that (1) is indeed correct to lowest order in the parameter m_f/m, where m_f is the mass of the fluid particles. Although formally correct, these derivations are somewhat misleading since, as will become apparent, the relevant small parameter is not m_f/m, but ρ/ρ_B, where ρ is the mass density of the fluid and $\rho_B = m/V_B = 3m/4\pi R^3$ that of the Brownian particle.

In fact, it was pointed out already by Lorentz[(7)] [6] in his lectures in 1911–12 that the consistency of (2) can be discussed within a purely phenomenological framework. His order-of-magnitude estimate, based on standard hydrodynamics, immediately showed that (2) can only be a good approximation provided that ρ/ρ_B is small. This important insight subsequently fell into oblivion, and was only revived very recently[(8)] when the newly discovered tails[(9–11)] $\sim t^{-3/2}$ in the molecular time correlation functions prompted reconsideration of exponential decays like (4).

Lorentz's argument was restricted to the friction term in (1). The *complete* Langevin equation can be discussed on a purely macroscopic basis, however, if one starts with a Brownian particle coupled by stick boundary condition to a fluid governed by fluctuating hydrodynamics, and proceeds to contract the description to the level of the dynamical variables of B alone. This scheme is implied in a calculation by Zwanzig[(12)] and was stated explicitly by Fox and Uhlenbeck.[(13)] The result of these derivations was again (1), at the expense, however, of the essentially unjustified assumption involved in the neglect of time derivatives of the fluid fields.

In this paper we reconsider the approach to Brownian motion outlined in the previous paragraph. Since we shall not neglect time derivatives of the fluid variables, the velocity field will not automatically be divergence-free. To avoid complications that might obscure the central issues, we shall, however, confine our attention to incompressible fluids. This restriction will, of course, influence some of the detailed results, but the essential features remain unaffected. The equations defining the linearized Navier–Stokes description are given in Section 2.

In the original derivations of fluctuating hydrodynamics, boundaries were not considered, whereas they play a crucial role in the present context. To

[5] The first paper dealing with the problem from this point of view seems to be that of Lebowitz and Rubin.[(5)] Further references can be found in a recent work along these lines.[(6)]

[6] We are indebted to Prof. M. S. Green for bringing this reference to our attention.

clear up existing ambiquities as to the treatment of fluctuating forces at boundaries, we rederive the fluctuating equations in Sections 3 and 4. It is shown that *different* consistent interpretations exist for the fluctuating forces with boundaries present. Moreover, the simplest choice is not the one commonly made.

In Section 5 and 6 we consider the contraction of the description to the level of the dynamical variables of B alone. These variables include the angular velocity $\mathbf{\Omega}(t)$ as well as $\mathbf{U}(t)$. One could, of course, decouple rotations and translations from the outset by restricting one's attention to particles with certain symmetries, in particular, to spheres.[7] In the context of contractions from fluctuating hydrodynamics, however, it seems a matter of principal interest to discuss the procedure for arbitrary shapes. Decoupling is thus precluded. For this general case, then, we prove in Section 6 the fluctuation-dissipation theorem[(15)] for the (in general) non-Markovian Langevin equation on the contracted level as a consequence of the corresponding theorem for the Markovian description given by fluctuating hydrodynamics. Furthermore, the symmetry of the friction tensor is proved in general without appeal to arguments outside our purely phenomenological model. In the realization of this program the appropriate Green's identity is instrumental.

After this investigation of the general features of the contraction, we turn in Section 7 to explicit calculations on the degenerate example of the sphere. The results, and their connections to related theories, are finally discussed in Section 8.

2. THE LINEARIZED NAVIER–STOKES DESCRIPTION

The standard Navier–Stokes equation describing the flow of an incompressible fluid in a volume V reads[(3)]

$$\rho(\partial/\partial t + \mathbf{u} \cdot \nabla)\mathbf{u} = -\nabla p + \eta \nabla^2 \mathbf{u}$$

with (5)

$$\nabla \cdot \mathbf{u} = 0$$

for $\mathbf{x} \in V$. Here $\mathbf{u}(\mathbf{x}, t)$ is the velocity field of the fluid and $p(\mathbf{x}, t)$ the deviation of the hydrostatic pressure field from its equilibrium value p_0. The constant mass density of the fluid is denoted by ρ and its viscosity by η.

A body immersed in the fluid obeys the equations of motion

$$m\, dU_i/dt = F_i(t), \qquad J_{ij}\, d\Omega_j/dt = M_i(t) \tag{6}$$

[7] This restricted problem is considered in a recent paper.[(14)]

where summation over repeated indices is implied. As before, **U** and **Ω** are the velocities of the body and m and J_{ij} its mass and inertia tensor, respectively. The force **F** and torque **M** exerted on the body by the fluid are given in terms of the stress tensor

$$\sigma_{ij} = -(p_0 + p)\,\delta_{ij} + \eta\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) \tag{7}$$

as

$$F_i(t) = -\int_S dS\,\sigma_{ij}(\mathbf{u}, p)\,n_j \tag{8}$$

$$M_i(t) = -\int_S dS\,\epsilon_{ijk}[x_j - X_j(t)]\,\sigma_{kl}n_l \tag{9}$$

Here $\mathbf{n}(\mathbf{x})$ is the unit vector normal to the surface S at $\mathbf{x}$ pointing out of the fluid, i.e., *into* the body. The Levi-Civita symbol ϵ_{ijk} is antisymmetric in all indices, and $\epsilon_{123} = 1$. The position of the center of mass of the body is denoted by $\mathbf{X}(t)$.

To complete the description, the boundary condition for $\mathbf{u}(\mathbf{x}, t)$ on S is needed. We shall adopt the "stick" condition which says that

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{U}(t) + \boldsymbol{\Omega}(t) \times [\mathbf{x} - \mathbf{X}(t)] \tag{10}$$

for $\mathbf{x} \in S$. It is further assumed that $\mathbf{u}(\mathbf{x}, t)$ is everywhere bounded.

We then proceed to linearize the above set of equations. The rationale for linearization in this case is twofold. First, while the linear Langevin theories pose no basic difficulties, their generalizations to nonlinear processes are known to be problematic.[16] Second, from a more practical point of view it is easy to check that in the context of Brownian motion, nonlinear effects are numerically negligible under typical circumstances.

The effects of linearization in $\mathbf{u}$, p, $\mathbf{U}$, and $\boldsymbol{\Omega}$ on the equations above are the following: (i) The convection term on the left of (5) is dropped. (ii) The position $\mathbf{X}(t)$ of the body, which apart from a trivial constant is the time integral of $\mathbf{U}(t)$, gives rise to nonlinear terms in (9) and (10). Consequently, $\mathbf{X}$ is dropped. (iii) For a body of arbitrary shape, rotations will cause the surface S to change in time with respect to a nonrotating frame. This again [in (8)–(10)] gives rise to nonlinear terms which for consistency should be neglected. Points (ii) and (iii) can be restated equivalently as follows: The frame of reference can be changed to one fixed to the body. The inertial and convection terms resulting from this transformation are nonlinear and should be neglected. Consequently, the velocities should still be measured with respect to the stationary frame.

The linearized set of equations then reads

$$\rho\, \partial \mathbf{u}/\partial t = -\nabla p + \eta \nabla^2 \mathbf{u} \tag{11}$$

$$m\, dU_i/dt = F_i = -\int_S dS\, \sigma_{ij}(\mathbf{u}, p)\, n_j \tag{12}$$

$$J_{ij}\, d\Omega_j/dt = M_i = -\int_S dS\, \epsilon_{ijk} x_j \sigma_{kl}(\mathbf{u}, p)\, n_l \tag{13}$$

with the constraints

$$\nabla \cdot \mathbf{u}(\mathbf{x}, t) = 0 \qquad \text{for} \quad \mathbf{x} \in V \tag{14}$$

$$\mathbf{u}(\mathbf{x}, t) = \mathbf{U}(t) + \boldsymbol{\Omega}(t) \times \mathbf{x} \qquad \text{for} \quad \mathbf{x} \in S \tag{15}$$

The next step is to regard Eqs. (11)–(13) as the equations for the *averages* of $\mathbf{u}$, $\mathbf{U}$, and $\boldsymbol{\Omega}$ and to add random force terms on the right to get stochastic equations for the fluctuating velocities. The forces are constructed by appeal to the analogous case of the finite-dimensional Gaussian Markov process to which the subsequent section is devoted.

3. THE GAUSSIAN MARKOV PROCESS

In this section we shall briefly recall the properties of a finite-dimensional Gaussian Markov process $a(t)$, where a stands for the coloumn vector $\{a_1, ..., a_n\}$. The contact with physical systems as provided by nonequilibrium thermodynamics will be made in the standard way and the results put in a form convenient for our purposes.

The process a, for which the equilibrium average $\langle a \rangle$ vanishes by definition, is assumed to obey the linear Langevin equation

$$da/dt = -Ga + g \tag{16}$$

where G is a matrix of no particular symmetry, the eigenvalues of which have positive real parts. Since a is Markovian, the spectrum of the random noise g must be white, and since a Gaussian a implies a Gaussian g, the random forces are completely specified by the correlation matrix

$$\langle g(s)\, g^T(t) \rangle = 2Q\, \delta(s - t) \tag{17}$$

where g^T denotes the transpose of g and Q is a symmetric, positive-semidefinite matrix.

The stationary solution of (16) is

$$a(t) = \int_{-\infty}^{t} ds\, e^{-(t-s)G} g(s) \tag{18}$$

from which the equilibrium correlations follow as

$$R \equiv \langle aa^T \rangle = 2 \int_0^\infty d\tau \exp(-\tau G) Q \exp(-\tau G^T) \tag{19}$$

where we have used (17). On the other hand, since a is assumed to be Gaussian, its equilibrium distribution must be of the form

$$W(a) = \text{const} \times \exp(-\tfrac{1}{2}a^T E a) \tag{20}$$

where E is a symmetric matrix. If R can be inverted, then clearly

$$E = R^{-1} \tag{21}$$

On the other hand, (19) and (21) show that E, G, and Q are not independent, and their interrelation is what amounts to the "fluctuation-dissipation theorem" on this level. Its most attractive form is obtained by partial integration of (19) which, together with (21), yields

$$2Q = GE^{-1} + E^{-1}G^T \tag{22}$$

In this context (22) should be considered the *prescription* by which the appropriate random forces in the Langevin equation (16) are *constructed.*

As is evident from Section 2, we shall be interested in processes where the components fluctuate subject to some linear constraints [see Eqs. (14) and (15)]. The matrix R is then singular and defines a null space $\bar{A}$ by $Ra = 0$. Equations (20) and (21) are clearly meaningless for $a \in \bar{A}$. These relations will, however, only be used for a in the orthogonal subspace A where R^{-1} is defined in the ordinary way ($R^{-1}Ra = RR^{-1}a = a$), and the singular nature of R thus creates no problems.

The contact between the purely formal development up to this point and a wide class of physical systems is provided by the postulates of nonequilibrium thermodynamics. These postulates offer a physical interpretation of the matrices E and G and by (22) permit the construction of the random forces appropriate to the system.

The first postulate relates E to thermodynamics by stating that the stationary probability distribution $W(a)$ of the fluctuating quantities $\{a_1, \ldots a_n\}$ is given for closed systems as

$$W(a) = \text{const} \times e^{\Delta S/k} \tag{23}$$

Here $\Delta S(a)$ is the deviation of the entropy from its equilibrium value $S(0)$ and k is Boltzmann's constant. Comparison with (20) yields

$$\Delta S(a) = -\tfrac{1}{2}ka^T Ea \tag{24}$$

The second postulate is the well-known regression hypothesis: The fluctuations decay on the average according to the linear macroscopic laws. Instead of direct comparison between the equations of motion, however, a procedure involving the entropy production $d(\Delta S)/dt$ is more convenient for our purposes. From (24) one has

$$\frac{d\,\Delta S}{dt} = -\frac{k}{2}\left(\frac{da^T}{dt}Ea + a^T E\frac{da}{dt}\right) \tag{25}$$

The regression hypothesis here amounts to the interpretation of the time derivatives on the right of (25) as being given by the averaged equation (16), and on the left as having the meaning defined by the linear macroscopic laws [Eqs. (11)–(15) in our case].

Use of the averaged equation (16) in (25) gives

$$d(\Delta S)/dt = \tfrac{1}{2}ka^T(G^T E + EG)a \tag{26}$$

and appeal to (22) yields the simple result

$$d(\Delta S)/dt = ka^T EQEa \tag{27}$$

Since the left-hand sides of (24) and (27) are easily deduced from the thermodynamics and the transport properties of the system, and since Q follows directly from (27) when Ea is known, these two equations form a particularly convenient basis for the construction of the random forces.

4. CONSTRUCTION OF THE RANDOM FORCES

We are now ready to return to the specific problem announced at the end of Section 2: the construction of the random forces appropriate to the system consisting of a Brownian particle immersed in an incompressible fluid. The basic object to be defined is the random variable $a(t)$, which now stands for the column vector (of infinite dimensionality)

$$a(t) = \{\mathbf{u}(\mathbf{x}, t), p(\mathbf{x}, t), \mathbf{U}(t), \boldsymbol{\Omega}(t)\} \tag{28}$$

The subspace A in which $a(t)$ is constrained to fluctuate is defined by the relations (14) and (15).

For the identification of E we need an expression for the entropy. In a fluctuating, incompressible fluid the reduction of the entropy from its maximum value is caused by conversion of internal energy into the kinetic energy $\mathscr{E}$ associated with the fluctuations, i.e.,

$$\begin{aligned}\Delta S &= -\mathscr{E}/T \\ &= -(1/T)\left(\tfrac{1}{2}\rho\int_V d^3x\,\mathbf{u}^2 + \tfrac{1}{2}m\mathbf{U}^2 + \tfrac{1}{2}\boldsymbol{\Omega}\cdot\mathbf{J}\boldsymbol{\Omega}\right)\end{aligned} \tag{29}$$

Comparison of (24), (28), and (29) shows that Ea has the form

$$Ea = (1/kT)\{\rho\mathbf{u}(\mathbf{x}, t), 0, m\mathbf{U}, \mathbf{J}\boldsymbol{\Omega}\} \tag{30}$$

for $a \in A$.

The entropy production in an incompressible fluid follows from hydrodynamics[3] as

$$\frac{d\,\Delta S}{dt} = \frac{\eta}{T}\int_V d^3x \left(\frac{\partial u_i}{\partial x_j}\frac{\partial u_i}{\partial x_j} + \frac{\partial u_i}{\partial x_j}\frac{\partial u_j}{\partial x_i}\right) \equiv \frac{D(\mathbf{u}, \mathbf{u})}{T} \tag{31}$$

where $D(\mathbf{u}, \mathbf{u})$, according to (29), is the rate of dissipation of kinetic energy

$$D(\mathbf{u}, \mathbf{u}) = -d\mathscr{E}/dt \tag{32}$$

The basic equation (27) can then with the aid of (17) and (31) be put in the form

$$a^T(t)\, E\langle g(t)\, g^T(t')\rangle\, Ea(t') = 2\delta(t - t')\, D(\mathbf{u}, \mathbf{u})/kT \tag{33}$$

for $a \in A$.

The remaining problem is the interpretation of (33) as defining the random forces that should be added to Eqs. (11)–(13). For convenience we write

$$g(t) = \{\rho^{-1}\mathbf{f}(\mathbf{x}, t), 0, m^{-1}\mathbf{K}(t), \mathbf{J}^{-1}\mathbf{L}(t)\} \tag{34}$$

which amounts to adding the fluctuating forces $\mathbf{f}(\mathbf{x}, t)$, $\mathbf{K}(t)$, and $\mathbf{L}(t)$ on the right-hand sides of Eqs. (11)–(13), respectively. With the convention (34), the crucial quantity on the left of (33) becomes, by (30),

$$a^TEg = (1/kT)\left[\int_V d^3x\, \mathbf{u}\cdot\mathbf{f} + \mathbf{U}\cdot\mathbf{K} + \boldsymbol{\Omega}\cdot\mathbf{L}\right] \tag{35}$$

The simplest choice for $\mathbf{f}$, $\mathbf{K}$, and $\mathbf{L}$ that satisfies (33) is

$$\mathbf{K} = \mathbf{L} = 0 \tag{36}$$

while the correlations of $\mathbf{f}$ are determined by

$$\left\langle \int_V d^3x\, \mathbf{u}(\mathbf{x})\cdot\mathbf{f}(\mathbf{x}, t) \int_V d^3x'\, \mathbf{f}(\mathbf{x}', t')\cdot\mathbf{u}(\mathbf{x}')\right\rangle = 2kT\,\delta(t - t')\, D(\mathbf{u}, \mathbf{u}) \tag{37}$$

for an arbitrary field $\mathbf{u}(\mathbf{x})$ satisfying (14) and (15).

This is not the only possible interpretation of (33), however, nor is it the standard one. It is customary to base the discussion on a random stress tensor $s_{ik}(\mathbf{x}, t)$ rather than on the force, which is then given by the divergence

$$f_i(\mathbf{x}, t) = \partial s_{ik}(\mathbf{x}, t)/\partial x_k \tag{38}$$

By Gauss's theorem, the integral in (35) can be written

$$\int_V d^3x \, u_i \frac{\partial s_{ik}}{\partial x_k} = \int_{S \cup S_0} dS \, u_i s_{ik} n_k - \int_V d^3x \frac{\partial u_i}{\partial x_k} s_{ik} \tag{39}$$

where $\int dS$ goes over the surface S of the Brownian particle *and* over the large outer surface S_0.

In terms of s_{ik} one can thus satisfy (33) by the stipulation

$$\mathbf{K} = \mathbf{L} = 0 \tag{40}$$

$$s_{ik}(\mathbf{x}, t) = 0 \qquad \text{for} \quad \mathbf{x} \in S \cup S_0 \tag{41}$$

whereby the last term in (39) inserted into (35) and (33) yields

$$\langle s_{ik}(\mathbf{x}, t) \, s_{jl}(\mathbf{x}', t') \rangle = 2kT\eta\delta(t - t') \, \delta(\mathbf{x} - \mathbf{x}')[\delta_{ij}\delta_{kl} + \delta_{il}\delta_{kj}] \tag{42}$$

for $\mathbf{x}, \mathbf{x}' \in V$ but $\mathbf{x}, \mathbf{x}' \notin S \cup S_0$. Equation (42) is, of course, the standard formula[3] specialized to the case of an incompressible fluid.

There exists an alternative to (40)–(42) however, due to the constraint imposed by the boundary condition (15) on S. If one disregards the contribution to (39) from S_0 and uses (15), the surface integral in (39) can be put in the form

$$U_i \int_S dS \, s_{ik} n_k + \Omega_i \int_S dS \, \epsilon_{ijk} x_j s_{kl} n_l \tag{43}$$

Comparison with (35) and (12)–(13) then shows that by defining

$$K_i = -\int_S dS \, s_{ik} n_k \tag{44}$$

$$L_i = -\int_S dS \, \epsilon_{ijk} x_j s_{kl} n_l \tag{45}$$

and letting (42) be valid for $\mathbf{x}, \mathbf{x}' \in V$, $\mathbf{x}, \mathbf{x}' \in S$ *included*, one again satisfies (33).

These two distinct possibilities on the choice of s_{ik}, $\mathbf{K}$ and $\mathbf{L}$, have not always been recognized as such in the literature, and a measure of obscurity has resulted. In our opinion it is safer, and indeed simpler, to abandon the use of s_{ik} altogether and base calculations on $\mathbf{f}$, $\mathbf{K}$, and $\mathbf{L}$ as defined by (36)–(37).

5. CONTRACTION OF THE DESCRIPTION

We shall now turn to a study of the contraction from the Markovian description of the system in terms of the infinite-dimensional vector $a(t) =$

$\{\mathbf{u}(\mathbf{x}, t), p(\mathbf{x}, t), \mathbf{U}(t), \boldsymbol{\Omega}(t)\}$ to a description in terms of the six-component quantity

$$b(t) = \{\mathbf{U}(t), \boldsymbol{\Omega}(t)\} \tag{46}$$

i.e., we shall eliminate explicit consideration of the fluid variables to produce stochastic equations for the dynamical variables of the Brownian particle alone. The classical Langevin equation for Brownian motion will then emerge as a limiting case. The equation of motion for $b(t)$ is, however, in general non-Markovian, as should be expected.

The first task is to show how the fluid variables can, in principle, be eliminated. To this end one splits $\mathbf{u}, p$ into a systematic and a random part,

$$\mathbf{u}(\mathbf{x}, t) = \bar{\mathbf{u}}(\mathbf{x}, t) + \tilde{\mathbf{u}}(\mathbf{x}, t), \qquad p(\mathbf{x}, t) = \bar{p}(\mathbf{x}, t) + \tilde{p}(\mathbf{x}, t) \tag{47}$$

which obey separate equations,

$$\left.\begin{aligned} \rho\, \partial\bar{\mathbf{u}}/\partial t &= -\nabla\bar{p} + \eta\nabla^2\bar{\mathbf{u}} \qquad (48)\\ \nabla\cdot\bar{\mathbf{u}} &= 0 \qquad (49)\end{aligned}\right\} \quad \text{for} \quad \mathbf{x}\in V$$

$$\bar{\mathbf{u}}(\mathbf{x}, t) = \mathbf{U}(t) + \boldsymbol{\Omega}(t) \times \mathbf{x} \qquad \text{for} \quad \mathbf{x}\in S \tag{50}$$

and

$$\left.\begin{aligned} \rho\, \partial\tilde{\mathbf{u}}/\partial t &= -\nabla\tilde{p} + \eta\nabla^2\tilde{\mathbf{u}} + \mathbf{f} \qquad (51)\\ \nabla\cdot\tilde{\mathbf{u}} &= 0 \qquad (52)\end{aligned}\right\} \quad \text{for} \quad \mathbf{x}\in V$$

$$\tilde{\mathbf{u}}(\mathbf{x}, t) = 0 \qquad \text{for} \quad \mathbf{x}\in S \tag{53}$$

One further assumes that $\bar{\mathbf{u}}(\mathbf{x}, t), \bar{p}(\mathbf{x}, t) \to 0$ as $|\mathbf{x}| \to \infty$, and that $\tilde{\mathbf{u}}(\mathbf{x}, t)$ is everywhere bounded. Addition of the two sets of equations leads of course, back to Eqs. (11), (14), and (15) with the random force added to (11). The important property of the above splitting is that $\bar{\mathbf{u}}(\mathbf{x}, t), \bar{p}(\mathbf{x}, t)$ only depends on $\mathbf{U}(s), \boldsymbol{\Omega}(s)$ for $s \leqslant t$, and $\tilde{\mathbf{u}}(\mathbf{x}, t), \tilde{p}(\mathbf{x}, t)$ only on $\mathbf{f}(\mathbf{x}', s)$ for $s \leqslant t$. It is an immediate consequence that the quantities in (51)–(53) are *independent*[14] of those in (48)–(50).

Since the force $\mathbf{F}(t)$ and torque $\mathbf{M}(t)$ on B, as given by (12) and (13), depend linearly on $\mathbf{u}$ and p through the stress tensor σ_{ij}, one can also split those quantities in such a way that $\bar{\mathbf{F}}(t)$ and $\bar{\mathbf{M}}(t)$ are given by $\sigma_{ij}(\bar{\mathbf{u}}, \bar{p})$ at t on S, and $\tilde{\mathbf{F}}(t)$ and $\tilde{\mathbf{M}}(t)$ similarly follow from $\sigma_{ij}(\tilde{\mathbf{u}}, \tilde{p})$.

Solving (47)–(50), one can then in principle obtain $\bar{\mathbf{F}}$ and $\bar{\mathbf{M}}$ as linear functions of $\mathbf{U}$ and $\boldsymbol{\Omega}$:

$$\bar{F}_i(t) = -\int_{-\infty}^{t} ds\, [\gamma_{ij}(t-s)\, U_j(s) + \phi_{ij}(t-s)\, \Omega_j(s)] \tag{54}$$

$$\bar{M}_i(t) = -\int_{-\infty}^{t} ds\, [\psi_{ij}(t-s)\, U_j(s) + \mu_{ij}(t-s)\, \Omega_j(s)] \tag{55}$$

where

$$\begin{pmatrix} \gamma(t) & \phi(t) \\ \psi(t) & \mu(t) \end{pmatrix} \equiv \Gamma(t) \tag{56}$$

plays the role of a 6×6 friction tensor (nonlocal in time). Its explicit form depends on the geometry of the Brownian particle, and is known in simple cases. As we shall see, all that is needed in the context of the fluctuation-dissipation theorem is its symmetry, proved in Appendix B.

Defining the six-dimensional force $h = \bar{h} + \tilde{h}$ by

$$h(t) = \{\mathbf{F}(t), \mathbf{M}(t)\} \tag{57}$$

where $\mathbf{F}(t)$ and $\mathbf{M}(t)$ are defined by (12) and (13), and the 6×6 inertia tensor L by

$$L = \begin{pmatrix} mI & 0 \\ 0 & J \end{pmatrix} \tag{58}$$

one can then on the basis of the above considerations write the generalized Langevin equation in the compact form

$$L\, db/dt = h(t) = -\int_{-\infty}^{t} ds\, \Gamma(t-s)\, b(s) + \tilde{h}(t) \tag{59}$$

Since (59) is non-Markovian (except in limiting cases, see Section 8), it is of particular interest to verify that the fluctuation-dissipation theorem relating $\Gamma(t)$ to the (nonwhite) spectrum of $\tilde{h}$ follows from the corresponding statement (37) on the (Markovian) level of $a(t)$.

6. GREEN'S IDENTITY AND THE FLUCTUATION-DISSIPATION THEOREM FOR THE CONTRACTED DESCRIPTION

In this section we prove that the fluctuation-dissipation theorem on the level of $b(t)$ follows from that on the level of $a(t)$. The tool needed to construct this proof is a Green's identity for solutions of Eqs. (48)–(50) and (51)–(53) This identity is proved in Appendix A and reads as follows: If $\bar{\mathbf{u}}$, $\bar{p}$ satisfy the former equations for some prescribed motion of B, i.e., with *given* $b(t)$, and $\tilde{\mathbf{u}}$, $\tilde{p}$ the latter, and they are suitably bounded, then

$$-\int_{-\infty}^{\infty} dt \int_S dS\, \bar{u}_i(\mathbf{x}, -t)\, \tilde{\sigma}_{ik} n_k = \int_{-\infty}^{\infty} dt \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, -t) \cdot \mathbf{f}(\mathbf{x}, t) \tag{60}$$

where

$$\tilde{\sigma}_{ik} = \sigma_{ik}(\tilde{\mathbf{u}}(\mathbf{x}, t), \tilde{p}(\mathbf{x}, t)) \tag{61}$$

If (50) is inserted on the left-hand side of (60) ($\equiv I$) and use is made of the definitions of $\tilde{\mathbf{F}}$ and $\tilde{\mathbf{M}}$ [(12), (13), and splitting as stated above (54)], one finds

$$\begin{aligned} I &= -\int_{-\infty}^{\infty} dt \int_S dS\, [U_i(-t) + \epsilon_{ijl}\Omega_j(-t)\, x_l]\, \tilde{\sigma}_{ik} n_k \\ &= \int_{-\infty}^{\infty} dt\, [\mathbf{U}(-t) \cdot \tilde{\mathbf{F}}(t) + \mathbf{\Omega}(-t) \cdot \tilde{\mathbf{M}}(t)] \end{aligned} \tag{62}$$

Introducing the notation of (57), one can consequently rewrite (60) as

$$I \equiv \int_{-\infty}^{\infty} dt\, b^T(-t)\, \tilde{h}(t) = \int_{-\infty}^{\infty} dt \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, -t) \cdot \mathbf{f}(\mathbf{x}, t) \tag{63}$$

The mean square of (63) is then

$$\begin{aligned} \langle I^2 \rangle &= \iint_{-\infty}^{\infty} ds\, dt\, b^T(-t) \langle \tilde{h}(t)\, \tilde{h}^T(s) \rangle\, b(-s) \\ &= \iint_{-\infty}^{\infty} ds\, dt \left\langle \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, -t) \cdot \mathbf{f}(\mathbf{x}, t) \int_V d^3x'\, \bar{\mathbf{u}}(\mathbf{x}', -s) \cdot \mathbf{f}(\mathbf{x}', s) \right\rangle \\ &= 2kT \int_{-\infty}^{\infty} dt\, D(\bar{\mathbf{u}}(t), \bar{\mathbf{u}}(t)) \end{aligned} \tag{64}$$

where (37) has been used and the substitution $t \to -t$ made in the final expression. Since by (32), $D(\bar{\mathbf{u}}, \bar{\mathbf{u}})$ is the rate at which the total kinetic energy $\mathscr{E}(t)$ associated with the solution $\bar{\mathbf{u}}(\mathbf{x}, t)$ is dissipated, the last integral in (64) equals

$$-\mathscr{E}(\infty) + \mathscr{E}(-\infty) - \int_{-\infty}^{\infty} dt\, b^T(t)\, \bar{h}(t)$$

If the given velocities $\mathbf{U}(t)$ and $\mathbf{\Omega}(t)$ of the Brownian particle vanish as $t \to -\infty$ and if the total energy put into the fluid by B is finite, then

$$\mathscr{E}(-\infty) = \mathscr{E}(+\infty) = 0 \tag{65}$$

Use of the expressions (54)–(56) for the drag $\bar{h}(t)$ then yields

$$\int_{-\infty}^{\infty} dt\, D(\bar{\mathbf{u}}, \bar{\mathbf{u}}) = \iint_{t \geqslant s} dt\, ds\, b^T(t)\, \Gamma(t - s)\, b(s) \tag{66}$$

On the other hand, from (63) it follows that, due to the symmetry $s \rightleftarrows t$,

$$\begin{aligned} \langle I^2 \rangle &= \iint_{-\infty}^{\infty} ds\, dt\, b^T(t) \langle \tilde{h}(-t)\, \tilde{h}^T(-s) \rangle\, b(s) \\ &= 2 \iint_{t \geqslant s} ds\, dt\, b^T(t) \langle \tilde{h}(0)\, \tilde{h}^T(t - s) \rangle\, b(s) \end{aligned} \tag{67}$$

where the time translation invariance of the equilibrium average has been used. Since $b(t)$ is an arbitrary function at our disposal, comparison of (64), (66), and (67) gives

$$\langle \tilde{h}(0)\, \tilde{h}^T(t-s) \rangle = kT\Gamma(t-s) \tag{68}$$

for $t \geqslant s$.

Equation (68) is almost the relation we seek. What is missing is clearly the corresponding statement for $t \leqslant s$. The gap is filled in Appendix B, where we prove, on the basis of Green's identity, that Γ is a symmetric matrix, i.e., $\Gamma^T = \Gamma$. As a consequence, we have

$$\langle \tilde{h}(0)\, \tilde{h}^T(t-s) \rangle = \langle \tilde{h}(t-s)\, \tilde{h}^T(0) \rangle = \langle \tilde{h}(0)\, \tilde{h}^T(s-t) \rangle \tag{69}$$

where again the time translation invariance of an equilibrium average was used in the second step. Combination of (68) and (69) finally yields

$$\langle \tilde{h}(0)\, \tilde{h}^T(t) \rangle = kT\Gamma(|\, t\,|) \tag{70}$$

for *all* t.

The relation (70) is the appropriate fluctuation-dissipation theorem expressing the autocorrelation of the six-component random force $\tilde{h}(t)$ in terms of the friction matrix $\Gamma(t)$. It has been proved here for arbitrary shape of the Brownian particle and by arguments completely within our chosen phenomenological framework. In particular, no reference to the time reversibility of the underlying microscopic equations has been made.

The reasoning leading from (68) to (70) plays, in fact, the role of an *inverse* Onsager argument.[(17)] Here the symmetry of Γ is deduced from the averaged equations of motion, and is subsequently used to prove the reversibility (69) of the random force.[8]

7. EXAMPLE. THE SPHERICAL PARTICLE

In the previous section we proved the fluctuation-dissipation theorem for the six-dimensional process $b(t) = \{\mathbf{U}(t), \mathbf{\Omega}(t)\}$. From the point of view of explicit calculations the problem is thus essentially reduced to that of finding the friction tensor $\Gamma(t)$, obtainable from Eqs. (48)–(50) for the average motion. Since the calculation of Γ is a problem in classical hydrodynamics and is not of central concern in this paper, we shall be content with quoting the results for the case of maximum degeneracy, namely the sphere.

These results have been known for a long time.[9] Their relevance to the

[8] All components of h are trivially odd functions of the momenta in the $(N+1)$-body Hamiltonian.

[9] See Lamb.[(18)] In particular, the equivalent of (72) was found by Stokes in 1851.

problem of Brownian motion, which was pointed out by Lorentz,[7] has only recently been appreciated, however.[8,14] They will be restated here as providing a concrete example within the general formalism, but also because they will facilitate the discussion of the connection between our approach and related work, and will enable us to check the validity of certain approximations commonly made.

Define the functions

$$\hat{f}^{+}(\omega) = \int_0^\infty dt\, e^{i\omega t} f(t), \qquad \hat{f}^{-}(\omega) = \int_{-\infty}^0 dt\, e^{i\omega t} f(t) \tag{71}$$

Thus, $\hat{f}(\omega) = \hat{f}^{+}(\omega) + \hat{f}^{-}(\omega)$ is the Fourier transform of $f(t)$, and $\hat{f}^{+}(iz)$ is its Laplace transform. For a spherical particle both the inertia tensor L and the friction tensor $\Gamma(t)$ are trivially diagonal. With reference to Eqs. (54)–(56) and to (71) a standard calculation[3] yields (see footnote 9)

$$\hat{\gamma}_{ij}^{+}(\omega) \equiv \delta_{ij}\hat{\gamma}(\omega) = \delta_{ij} 6\pi\eta R[1 + R(-i\omega/\nu)^{1/2} - (i\omega R^2/9\nu)] \tag{72}$$

$$\hat{\mu}_{ij}^{+}(\omega) \equiv \delta_{ij}\hat{\mu}(\omega) = \delta_{ij} 8\pi\eta R^3 \left[1 - \frac{i\omega R^2/3\nu}{1 + R(-i\omega/\nu)^{1/2}}\right] \tag{73}$$

$$\phi(t) = \psi(t) = 0 \tag{74}$$

where we have used the fact that, as a result of causality, $\hat{\gamma}^{-} = \hat{\mu}^{-} = 0$. Furthermore, R is the radius of the particle, $\nu = \eta/\rho$ is the kinematic viscosity of the fluid, and $(-i\omega)^{1/2}$ is uniquely defined by a cut along the negative imaginary ω axis.

From (72)–(74) it follows that all components of $b(t)$ are independent and that rather than the generalized Langevin equation (59), one can study the two scalar equations

$$m\dot{U}(t) = -\int_{-\infty}^{t} ds\, \gamma(t-s)\, U(s) + \tilde{F}(t) \tag{75}$$

$$J\dot{\Omega}(t) = -\int_{-\infty}^{t} ds\, \mu(t-s)\, \Omega(s) + \tilde{M}(t) \tag{76}$$

where we have written $J_{ij} = \delta_{ij}J$ and where U, $\tilde{F}$ and Ω, $\tilde{M}$ denote any component of the corresponding vectors.

Since the autocorrelation functions of the fluctuating forces depend on the time difference only, one has

$$\langle \hat{\tilde{F}}(\omega)\, \hat{\tilde{F}}(\omega') \rangle = \hat{C}_F(\omega)\, \delta(\omega + \omega') \tag{77}$$

where $\hat{C}_F(\omega)$ is the so-called power spectrum of $\tilde{F}$, defined as the Fourier transform of the autocorrelation $C_F(t) = \langle \tilde{F}(0)\tilde{F}(t) \rangle$. From the fluctuation-dissipation theorem (70) the spectra of $\tilde{F}$ and $\tilde{M}$ are given in terms of the friction kernels as

$$\hat{C}_F(\omega) = kT[\hat{\gamma}(\omega) + \hat{\gamma}(-\omega)] \tag{78}$$

$$\hat{C}_M(\omega) = kT[\hat{\mu}(\omega) + \hat{\mu}(-\omega)] \tag{79}$$

The corresponding spectra of the stationary processes U and Ω are derived by taking the Fourier transforms of (75) and (76) using (77) to get

$$\hat{C}_U(\omega) = [\hat{C}_F(\omega)/| -i\omega m + \hat{\gamma}(\omega)|^2] = \{kT/[-i\omega m + \hat{\gamma}(\omega)]\} + \text{c.c.} \tag{80}$$

$$\hat{C}_\Omega(\omega) = \{kT/[-i\omega J + \hat{\mu}(\omega)]\} + \text{c.c.} \tag{81}$$

where c.c. stands for complex conjugate.

The transformation of (80)–(81) to time language with $\hat{\gamma}$, $\hat{\mu}$ given by (72)–(73) is carried out in Appendix C. For long times t the asymptotic results are

$$C_U(t) \simeq \tfrac{2}{3}(kT/\rho)(4\pi\nu \mid t \mid)^{-3/2} \tag{82}$$

$$C_\Omega(t) \simeq \pi(kT/\rho)(4\pi\nu \mid t \mid)^{-5/2} \tag{83}$$

The values at $t = 0$ give the mean square fluctuations of U and Ω, which are found to be

$$C_U(0) = kT/(m + 2\pi R^3\rho/3) \tag{84}$$

$$C_\Omega(0) = kT/J \tag{85}$$

Some comments on the above results are in order:

1. In this paper we have treated the fluid surrounding B as incompressible. For real fluids this amounts to an approximation which is valid for sufficiently slowly varying phenomena. In particular, the first two terms in the expression (72) for the friction $\hat{\gamma}(iz) = \hat{\gamma}(\omega)$ remain valid for compressible fluids. As can be seen from Appendix C, it is these two terms that determine the asymptotic decay (82).

2. The effective mass which occurs in the variance (84) is an artifact of the model, however. Its derivation depends on the third term in (72), which is *not* correct with finite compressibility. From statistical mechanics one knows, of course, that the exact result for the variance is kT/m.

3. Since pure rotations of a sphere do not couple to longitudinal sound waves, the results (73) and (85) remain valid for a compressible fluid.

4. The above calculations were based on the stick boundary condition. The "slip" condition, which states that tangential forces on the boundary vanish, would lead to different coefficients in (72). It would not, however,

influence the asymptotic decay (82). In fact, any condition intermediate between stick and slip would yield the same asymptotic decay, coefficient included.[10]

8. DISCUSSION

The contraction from the Markovian description of a Brownian particle immersed in a fluctuating fluid produced the non-Markovian Langevin equation (59) for the dynamical variables of B. This is the general situation: Contractions of Markovian descriptions produce non-Markovian ones. The crucial question is rather under which circumstances the contracted description is again Markovian to a sufficient approximation.

The condition determining when the non-Markovian equation (75) reduces to (one component of) the classical Langevin equation (1) can be read off (80) with the aid of (72). When only the constant term in (72) is kept, (75) coincides with the classical equation, and (80) has a simple pole at $\omega_{\wp} = -i\hat{\gamma}(0)/m$. This pole determines the characteristic time scale of the velocity fluctuations and on this scale the second (and third) terms in (72) can be neglected provided that[7,8,14]

$$1 \gg R \mid \omega_{\wp}/\nu \mid^{1/2} = [\tfrac{9}{2}\rho/(3m/4\pi R^3)]^{1/2} = (\tfrac{9}{2}\rho/\rho_{\mathrm{B}})^{1/2} \tag{86}$$

The numerical coefficient in (86) is a result of the spherical geometry. The qualitative conclusion that the ratio of the mass *densities* is the crucial parameter is, however, of general validity.

There is nevertheless no contradiction between the above results and the formal theories,[6] from which the classical Langevin equation (1) emerges as correct to lowest order in $(m_f/m)^{1/2}$. In those theories one keeps the mass m_f of the fluid particles, the density, *and* the interaction (in particular the radius of the Brownian particle) fixed when passing to the limit $m \to \infty$. In that limit *both* $(m_f/m)^{1/2}$ and $(\rho/\rho_{\mathrm{B}})^{1/2}$ become small.

The distinction between the two parameters is significant in practice, however. The mass density ratio shows that the classical Langevin equation offers a good description of, say, solid dust particles in air (with due account taken of the presence of gravity). But it does *not* apply to pollen in water, i.e., to Brownian motion in its historically accurate meaning.

Also, no matter how small ρ/ρ_{B} is, (75) with (72) leads to the asymptotic result (82) rather than to an exponential decay. But as ρ/ρ_{B} decreases, the time τ at which the exponential decay yields to (82) increases. When τ has become so large that $mC_U(\tau)/kT \ll 1$ the non-Markovian effects can be neglected.

[10] This follows, for example, from the results of Zwanzig and Bixon.[10]

From the general assumption that an essentially arbitrary initial state rapidly evolves into one close to local equilibrium, Ernst *et al.*(11,19) showed that the molecular time correlation functions have tails $\sim t^{-3/2}$. A straightforward application of their method to the $(N + 1)$-body problem yields the asymptotic formula

$$C_U(t) \simeq \tfrac{2}{3}(kT/\rho)[4\pi(\nu + D)|\, t\,|]^{-3/2} \tag{87}$$

where D is the diffusion coefficient of the Brownian particle.[11] Comparison shows that (87) is identical with our result (82)[12] except that ν has been replaced by $(\nu + D)$.[13] This discrepancy should not be surprising. It is clear(19) that a purely macroscopic theory like the one presented in this paper will not embody the effects represented by D in (87). This is not a fatal flaw, however. For Brownian particles larger than molecular size, $D/\nu \ll 1$. Our continuum theory is thus an approximation correct to zeroth order in D/ν.

The importance of the last remark becomes apparent when one compares the formula (72) for $\hat{\gamma}(\omega)$ and the work of Refs. 11 and 19. From those papers it follows that in three dimensions all transport coefficients have a first correction term $\sim\sqrt{\omega}$. This correction to the viscosity would compete with the crucial second term in (72). However, one can show that the viscosity correction as compared to this term is of relative order D/ν. Consistency thus requires that it should be neglected.

It is important to realize that both the classical Langevin equation (1) and the corrected version (75) contain the Einstein–Smoluchowski theory as a limiting case when $t \gg \hat{\gamma}(0)/m$. In that theory the single parameter determining the evolution of the probability density $P(\mathbf{r}, t)$ of B in space is the diffusion coefficient. From Einstein's work(1a) one knows that

$$D = \int_0^\infty dt\, \langle U(0)\, U(t)\rangle = \tfrac{1}{2}\hat{C}_U(0) \tag{88}$$

which, by (80), yields

$$D = kT/\hat{\gamma}(0) = kT/6\pi\eta R \tag{89}$$

This celebrated relation is thus a consequence of (75) as well as of (1), and the classical experiments cannot distinguish between the two.

In conclusion, we therefore point out that the non-Markovian effects beyond the Einstein–Smoluchowski limit represent a standing challenge to the experimentalists!

[11] The corresponding argument for $C_\Omega(t)$ has been made by Ailawadi and Berne.(20)

[12] The coefficient in the corresponding result of Ref. 8 is not quite correct, due to inconsistent treatment of the effective mass.

[13] On this background the independence of (82)–(83) on the details of the boundary condition and on the compressibility becomes clear.

APPENDIX A. PROOF OF GREEN'S IDENTITY

Let $\bar{\mathbf{u}}$, $\bar{p}$ be a solution of Eqs. (48)–(50) for some given $\mathbf{U}$, $\mathbf{\Omega}$, and let $\tilde{\mathbf{u}}$, $\tilde{p}$ be a solution of Eqs. (51)–(53) for some given $\mathbf{f}$, not necessarily random. Then one has

$$\begin{aligned}\Delta_T &\equiv \rho \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, -T) \cdot \tilde{\mathbf{u}}(\mathbf{x}, T) - \rho \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, T) \cdot \tilde{\mathbf{u}}(\mathbf{x}, -T) \\ &= \int_{-T}^{T} dt \int_V d^3x \left[\rho \frac{\partial \bar{\mathbf{u}}(\mathbf{x}, -t)}{\partial t} \cdot \tilde{\mathbf{u}}(\mathbf{x}, t) + \bar{\mathbf{u}}(\mathbf{x}, -t) \cdot \rho \frac{\partial \tilde{\mathbf{u}}(\mathbf{x}, t)}{\partial t}\right] \\ &= \int_{-T}^{T} dt \int_V d^3x\, [\tilde{\mathbf{u}} \cdot (\nabla \bar{p} - \eta \nabla^2 \bar{\mathbf{u}}) + \bar{\mathbf{u}} \cdot (-\nabla \tilde{p} + \eta \nabla^2 \tilde{\mathbf{u}} + \mathbf{f})] \end{aligned} \tag{A.1}$$

The following identity holds:

$$\bar{\mathbf{u}} \cdot \nabla^2 \tilde{\mathbf{u}} - \tilde{\mathbf{u}} \cdot \nabla^2 \bar{\mathbf{u}} = \frac{\partial}{\partial x_k}\left(\bar{u}_i \frac{\partial \tilde{u}_i}{\partial x_k} - \tilde{u}_i \frac{\partial \bar{u}_i}{\partial x_k}\right) \tag{A.2}$$

and since $\nabla \cdot \bar{\mathbf{u}} = \nabla \cdot \tilde{\mathbf{u}} = 0$,

$$\tilde{\mathbf{u}} \cdot \nabla \bar{p} - \bar{\mathbf{u}} \cdot \nabla \tilde{p} = \nabla \cdot (\bar{p}\tilde{\mathbf{u}} - \tilde{p}\bar{\mathbf{u}}) \tag{A.3}$$

$$\frac{\partial}{\partial x_k}\left(\bar{u}_i \frac{\partial \tilde{u}_k}{\partial x_i} - \tilde{u}_i \frac{\partial \bar{u}_k}{\partial x_i}\right) = 0 \tag{A.4}$$

Use of (A.2)–(A.4) in (A.1) and Gauss's theorem gives

$$\begin{aligned}\Delta_T = \int_{-T}^{T} dt \int_{S \cup S_0} dS \left[\eta \left(\bar{u}_i \frac{\partial \tilde{u}_i}{\partial x_k} + \bar{u}_i \frac{\partial \tilde{u}_k}{\partial x_i} - \tilde{u}_i \frac{\partial \bar{u}_i}{\partial x_k} - \tilde{u}_i \frac{\partial \bar{u}_k}{\partial x_k}\right) + \bar{p}\tilde{u}_k - \tilde{p}\bar{u}_k\right] n_k \\ + \int_{-T}^{T} dt \int_V d^3x\, \bar{\mathbf{u}} \cdot \mathbf{f}\end{aligned}$$

or, by the definition of the stress tensor (7),

$$\Delta_T = \int_{-T}^{T} dt \int_{S \cup S_0} dS\, [\bar{u}_i \sigma_{ik}(\tilde{\mathbf{u}}, \tilde{p}) - \tilde{u}_i \sigma_{ik}(\bar{\mathbf{u}}, \bar{p})]\, n_k + \int_{-T}^{T} dt \int_V d^3x\, \bar{\mathbf{u}} \cdot \mathbf{f} \tag{A.5}$$

The contribution from the outer surface S_0 can be made to vanish if one imposes the boundary condition $\bar{\mathbf{u}} = \tilde{\mathbf{u}} = 0$ on S_0 and regards the two solutions as the limits of the corresponding solutions when the volume goes to infinity. The volume integration then extends over the entire space except that occupied by B.

To prove (60) from (A.5), one first notes that the second boundary term in (A.5) vanishes since $\tilde{\mathbf{u}} = 0$ on S. It remains to be shown that the left-hand side of (A.5) vanishes as $T \to \infty$. Since Δ_T is a random variable, this amounts to proving that $\lim_{T\to\infty}\langle \Delta_T^2 \rangle = 0$. Let $\mathbf{U}(t) = \boldsymbol{\Omega}(t) = 0$ for $t < -T_0$, where T_0 is some large but fixed t. It follows that $\mathbf{u}(\mathbf{x}, t) = 0$, $\bar{p}(\mathbf{x}, t) = 0$ for $t < -T_0$. Thus, for $T > T_0$ only the lower limit contributes to Δ_T:

$$\Delta_T = -\rho \int_V d^3x\, \bar{\mathbf{u}}(\mathbf{x}, T) \cdot \tilde{\mathbf{u}}(\mathbf{x}, -T) \tag{A.6}$$

Consequently,

$$\langle \Delta_T^2 \rangle = \rho^2 \int_V d^3x\, d^3x'\, \bar{u}_i(\mathbf{x}, T)\, \bar{u}_j(\mathbf{x}', T) \langle \tilde{u}_i(\mathbf{x}, -T)\, \tilde{u}_j(\mathbf{x}', -T) \rangle \tag{A.7}$$

The average in (A.7) represents an equilibrium correlation function. Furthermore, since $-T < -T_0$, $\bar{\mathbf{u}}(\mathbf{x}, -T) = 0$ and $\tilde{\mathbf{u}}(\mathbf{x}, -T) = \mathbf{u}(\mathbf{x}, -T)$. It is therefore tempting to go back to the expressions (28) and (30) for E which, by (19) and (21), define such correlation functions for all $a \in A$. Here, since $-T < -T_0$, we are interested in the case with the additional constraints $\mathbf{U} = \boldsymbol{\Omega} = 0$, so that $\mathbf{u} = 0$ on S aside from $\nabla \cdot \mathbf{u} = 0$.

From (28) and (30) one immediately concludes that

$$\langle u_i(\mathbf{x}, -T)\, u_j(\mathbf{x}', -T) \rangle = kT\rho^{-1}\delta_{ij}\, \delta(\mathbf{x} - \mathbf{x}')$$

which inserted in (A.7) gives

$$\langle \Delta_T^2 \rangle = kT\rho \int d^3x\, |\, \bar{\mathbf{u}}(\mathbf{x}, T)|^2 \tag{A.8}$$

Since (A.8) is proportional to the total kinetic energy in the fluid at time T, and since energy, according to (32), is dissipated at the rate given by $D(\bar{\mathbf{u}}, \bar{\mathbf{u}})$, it follows that

$$\lim_{T\to\infty} \langle \Delta_T^2 \rangle = 0$$

provided that the total energy put into the fluid by the prescribed motion $\mathbf{U}(t)$, $\boldsymbol{\Omega}(t)$ of B is finite. This completes the proof of (60).

Rather than base the argument on the analogy with the finite-dimensional process, one could also derive (A.8) by using nothing but the equations of motion (48)–(53) and the prescription (37) for the random forces. This derivation, which again makes use of (A.5), is, however, somewhat involved, and for that reason we shall be content with the simple argument given above.

In Appendix B a slightly different version of Green's identity will also be needed. In that case $(\bar{\mathbf{u}}, \bar{p}) = (\mathbf{u}, p)$ and $(\tilde{\mathbf{u}}, \tilde{p}) = (\mathbf{u}', p')$ are both solutions of Eqs. (48)–(50) for the average motion. If one stipulates that for both solutions the corresponding $\mathbf{U}(t)$, $\boldsymbol{\Omega}(t)$ vanish for $t \leqslant -T_0$ and if $T > T_0$, then by its definition (A.1), $\Delta_T = 0$. Thus (B.1) of Appendix B immediately follows.

APPENDIX B. PROOF OF THE SYMMETRY OF Γ

At the end of Appendix A Green's identity was proved in the form

$$\int_{-\infty}^{\infty} dt \int_S dS\,[u_i'(\mathbf{x}, t)\,\sigma_{ik} - u_i(\mathbf{x}, -t)\,\sigma_{ik}']\,n_k = 0 \tag{B.1}$$

where

$$\sigma_{ik} = \sigma_{ik}(\mathbf{u}(\mathbf{x}, -t), p(\mathbf{x}, -t)), \qquad \sigma_{ik}' = \sigma_{ik}(\mathbf{u}'(\mathbf{x}, t), p'(\mathbf{x}, t))$$

Here $\mathbf{u}$, p and $\mathbf{u}'$, p' are both solutions of Eqs. (48)–(50). Use of the boundary condition (50) in (B.1) gives

$$\int_{-\infty}^{\infty} dt \int_S dS\,\{[U_i'(t) + \epsilon_{ijl}\Omega_j'(t)\,x_l]\,\sigma_{ik} - [U_i(-t) + \epsilon_{ijl}\Omega_j(-t)\,x_l]\,\sigma_{ik}'\}\,n_k$$

$$= -\int_{-\infty}^{\infty} dt\,[\mathbf{U}'(t)\cdot\mathbf{F}(-t) + \mathbf{\Omega}'(t)\cdot\mathbf{M}(-t) - \mathbf{U}(-t)\cdot\mathbf{F}'(t) - \mathbf{\Omega}(-t)\cdot\mathbf{M}'(t)]$$

$$= -\int_{-\infty}^{\infty} dt\,[b'^T(t)\,\bar{h}(-t) - b^T(-t)\,\bar{h}'(t)] = 0 \tag{B.2}$$

After the substitution $t \to -t$ in the first term, this can, with the aid of (54)–(56), be written as

$$\iint_{t\geqslant s} dt\,ds\,b'^T(-t)\,\Gamma(t-s)\,b(s) = \iint_{t\geqslant s} dt\,ds\,b^T(-t)\,\Gamma(t-s)\,b'(s) \tag{B.3}$$

Change of variables $-t \to s$, $s \to -t$ on the right-hand side of (B.3) yields

$$\iint_{t\geqslant s} dt\,ds\,b'^T(-t)\,\Gamma(t-s)\,b(s) = \iint_{t\geqslant s} dt\,ds\,b'^T(-t)\,\Gamma^T(t-s)\,b(s) \tag{B.4}$$

and since $b'(-t)$ and $b(s)$ are arbitrary functions, one concludes that Γ is a symmetric matrix:

$$\Gamma^T(t) = \Gamma(t), \qquad t \geqslant 0 \tag{B.5}$$

Note that in this proof, which was based on the Navier–Stokes equation alone, no special assumptions on the shape of the body were invoked.

APPENDIX C. TRANSFORMATION OF (80)–(81)

In this appendix some of the details in the derivation of (82)–(85) from (80)–(81) are given. The transform of (80) reads

$$C_U(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\,e^{-i\omega t}\left\{\frac{kT}{-i\omega m + \hat{\gamma}(\omega)} + \text{c.c.}\right\} \tag{C.1}$$

Since $\gamma(t)$ is a real function, $\hat{\gamma}(-\omega) = \hat{\gamma}^*(\omega)$. Furthermore, since the system is dissipative, the first term in (C.1) has no singularities in the upper half ω plane [cf. (72)]. For $t > 0$ ($t < 0$) the contour of integration can be closed in the lower (upper) half ω plane and consequently the second (first) term in (C.1) does not contribute. For $t \neq 0$, therefore,

$$C_U(t) = \frac{kT}{2\pi} \int_{\mathscr{C}} d\omega \, \frac{e^{-i\omega|t|}}{-i\omega m + \hat{\gamma}(\omega)} \tag{C.2}$$

where $\mathscr{C}$ is the contour closed in the lower half plane:

A more convenient expression for $C_U(t)$ is found if one turns to the variable $z = -i\omega$ and notes that the only singularity in the left half z plane is the cut along the negative real z axis. Deformation of the contour yields

$$C_U(t) = \frac{kT}{2\pi i} \int_{-\infty}^{0} dz \, e^{z|t|} \left\{ \frac{1}{zm + \hat{\gamma}[i(z - i0)]} - \frac{1}{zm + \hat{\gamma}[i(z + i0)]} \right\} \tag{C.3}$$

Writing (72) as

$$\hat{\gamma}(iz) = a(1 + b\sqrt{z} + cz) \tag{C.4}$$

where $a = 6\pi\eta R$, $b = R/\sqrt{\nu}$, and $c = R^2/9\nu = b^2/9$, one finds from (C.3)

$$C_U(t) = \frac{kTab}{\pi} \int_0^\infty dx \, e^{-x|t|} \frac{\sqrt{x}}{[a - (m + ac)x]^2 + a^2 b^2 x} \tag{C.5}$$

The asymptotic form of $C_U(t)$ follows from (C.5) when the denominator in the integrand is replaced by a^2. Thus

$$C_U(t) \simeq (kTb/\pi a \mid t \mid^{3/2}) \int_0^\infty dy \, \sqrt{y} \, e^{-y} = \tfrac{2}{3}(kT/\rho)(4\pi\nu \mid t \mid)^{-3/2} \tag{C.6}$$

in agreement with (82). The corresponding result for $C_\Omega(t)$, (83), is derived in a completely analogous fashion.

The variance of U, $C_U(0)$, is most easily found by going back to (C.1). For $t = 0$ the two terms are equal. The first term is analytic in the upper half-plane, so that by closing the contour, the sum of the integrals along the real axis and along the upper semicircle vanishes. The last integral is trivial, so that

$$C_U(0) = -\frac{kT}{\pi} \int_0^\pi i \, d\varphi \, \frac{\omega}{-i\omega(m + ac)} = \frac{kT}{m + \frac{2}{3}\pi R^3 \rho} \tag{C.7}$$

$C_\Omega(0)$ is determined by the same method.

From (C.5) it can also be verified directly that $C_U(t)$ converges to the classical Langevin correlation $(kT/m)\, e^{-\alpha|t|/m}$ when $9\rho/2\rho_B = b^2a/m = 9ca/m$ approaches zero, because then the integrand in (C.5) becomes sharply peaked around $x = a/m$.

ACKNOWLEDGMENTS

Both authors were fortunate enough to spend the academic year 1970–71 with the group in statistical physics at The Rockefeller University, New York, where the major part of this work was carried out. It is a pleasure to thank the members of that distinguished group for advice and encouragement. Finally, one of us (E.H.H.) gratefully acknowledges support from The National Science Foundation.

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