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## Contributions to Non-Equilibrium Thermodynamics. I. Theory of Hydrodynamical Fluctuations\*

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The velocity of a particle in Brownian motion as described by the Langevin equation is a stationary Gaussian-Markov process. Similarly, in the formulation of the laws of non-equilibrium thermodynamics by Onsager and Machlup, the macroscopic variables describing the state of a system lead to an  $n$ -component stationary Gaussian-Markov process, which, in addition, these authors assumed to be even in time. By dropping this assumption, the most general stationary Gaussian-Markov process is discussed. As a consequence, the theory becomes applicable to the linearized hydrodynamical equations and suggests that the Navier-Stokes equations require additional fluctuation terms which were first proposed by Landau and Lifshitz. Such terms and their correlation properties are presented, and these equations are then used to derive the Langevin equation for the Brownian motion of a particle of arbitrary shape.

### I. INTRODUCTION

Several concepts from the theory of stochastic processes will be used throughout this paper. For convenience, a few of the basic definitions will be given here.<sup>1</sup>

Let  $a(t)$  denote a random or stochastic process. The random function  $a(t)$  may represent a single random process or it may represent a collection of  $n$  random processes,  $a_i(t)$ . It is often convenient in the latter case to omit the indices and to use a matrix notation wherein  $a_i(t)$  is written as a column matrix  $\mathbf{a}(t)$ . When indices are used, the summation convention for repeated indices will be invoked.

A random process is defined by a hierarchy of probability distributions of which the first,  $W_1(a, t)$ , is defined as the probability at time  $t$  that the value of  $a(t)$  is between  $a$  and  $a + da$ . The conditional probability distribution function,  $P_2(a_1 t_1 | a_2 t_2)$ , is defined as the probability at time  $t_2$  that the value of

$a(t)$  is between  $a_2$  and  $a_2 + da_2$  given that at time  $t_1 < t_2$   $a(t)$  had the value  $a_1$ .

A stationary process,  $a(t)$ , is defined by the requirement that all distribution functions for it are invariant under time translation. As consequence  $W_1(a, t)$  is independent of  $t$ , and  $P_2(a_1 t_1 | a_2 t_2)$  depends upon time through  $t_2 - t_1$  only. For stationary processes these two distributions will be denoted by  $W_1(a)$  and  $P_2(a_1 | a_2 t)$  where  $t = t_2 - t_1$ .

A stationary process,  $\mathbf{a}(t)$ , is also Gaussian if all its distributions are of Gaussian form. For  $W_1(\mathbf{a})$  and  $P_2(\mathbf{a}_1 | \mathbf{a}_2 t)$  this requires

$$W_1(\mathbf{a}) = W_0 \exp \left[ -\frac{1}{2} \mathbf{a}^\dagger \mathbf{E} \mathbf{a} \right]$$

and

$$P_2(\mathbf{a}_1 | \mathbf{a}_2, t) \\ = P_0 \exp \left[ -\frac{1}{2} \mathbf{a}_1^\dagger \mathbf{A}(t) \mathbf{a}_1 - \mathbf{a}_1^\dagger \mathbf{B}(t) \mathbf{a}_2 - \frac{1}{2} \mathbf{a}_2^\dagger \mathbf{C}(t) \mathbf{a}_2 \right].$$

When  $\mathbf{a}(t)$  is intended to represent an  $n$ -component process, then  $\mathbf{E}$ ,  $\mathbf{A}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  are matrices and  $\mathbf{a}$ ,  $\mathbf{a}_1$ ,

and  $\mathbf{a}_2$  are column matrices.  $\mathbf{a}^\dagger(t)$  is a row matrix adjoint to  $\mathbf{a}(t)$ . The proportionality factors are determined by the normalization conditions

$$\int W_1(\mathbf{a}) d\mathbf{a} = 1 \tag{1}$$

and

$$\int P_2(\mathbf{a}_1 | \mathbf{a}_2, t) d\mathbf{a}_2 = 1.$$

Stationary Gaussian processes are also Markov processes if  $P_2$  satisfies the so-called Smoluchovsky equation

$$P_2(\mathbf{a}_1 | \mathbf{a}_2, t) = \int P_2(\mathbf{a}_1 | \mathbf{a}, t - s) P_2(\mathbf{a} | \mathbf{a}_2, s) d\mathbf{a} \tag{2}$$

for all  $s$  between zero and  $t$ .

The Langevin equation describes the Brownian motion of a slowly moving colloidal particle in a fluid. The equation is

$$M \frac{du(t)}{dt} = -\alpha u(t) + \tilde{F}(t), \tag{3}$$

where  $M$  is the mass of the particle,  $u(t)$  is its velocity,  $\alpha$  is a positive friction constant, and  $\tilde{F}(t)$  is a purely random stationary Gaussian fluctuating force which is defined as a process with mean value zero and correlation formula

$$\langle \tilde{F}(t) \tilde{F}(s) \rangle = 2D \delta(t - s), \tag{4}$$

where  $D$  is a constant and the factor 2 is for convenience as will become evident. Equation (3) with condition (4) has been shown to produce a stationary Gaussian-Markov process in the random variable  $u(t)$ .<sup>1</sup> The  $P_2$  function in this case is

$$P_2(u_0 | u, t) = \{2\pi\sigma^2[1 - \rho^2(t)]\}^{-1/2} \cdot \exp\left(-\frac{[u - u_0\rho(t)]^2}{2\sigma^2[1 - \rho^2(t)]}\right),$$

where  $\sigma^2 = D/\alpha M$  and  $\rho(t) = \exp(-\alpha t/M)$ . The relation

$$\lim_{t \rightarrow \infty} P_2(u_0 | u, t) = W_1(u)$$

may be used to get  $W_1(u)$  which is

$$W_1(u) = \left(2\pi \frac{D}{\alpha M}\right)^{-1/2} \exp\left(-\frac{\alpha M u^2}{2D}\right). \tag{5}$$

Because  $W_1(u)$  is also given by the requirement that it should be the Maxwell distribution

$$W_1(u) = \left(2\pi \frac{K_B T}{M}\right)^{-1/2} \exp\left(-\frac{M u^2}{2K_B T}\right), \tag{6}$$

where  $K_B$  is Boltzmann's constant and  $T$  is the temperature of the fluid, then equality of (5) and (6) results in

$$D = K_B T \alpha. \tag{7}$$

Equation (7) is Einstein's relation and leads to the prototype fluctuation-dissipation theorem

$$\langle \tilde{F}(t) \tilde{F}(s) \rangle = 2K_B T \alpha \delta(t - s). \tag{8}$$

Identity (8) is so named because it connects the mean square correlation of the fluctuating force with the dissipative constant  $\alpha$ .

A generalization of these ideas has been given by Onsager and Machlup in their formulation of the basic laws of non-equilibrium thermodynamics.<sup>2</sup> A system is described by  $n$  macroscopic variables  $\alpha_1(t), \dots, \alpha_n(t)$ . Their equilibrium values are taken to be zero. Near equilibrium the entropy is given by

$$S(t) = S_0 - \frac{1}{2} K_B \alpha_i(t) E_{ij} \alpha_j(t), \tag{9}$$

where  $S_0$  is a constant and  $E_{ij}$  is a symmetric, positive definite matrix. The linear regression equations are assumed to have the form

$$\frac{d}{dt} \alpha_i(t) = -K_B L_{ij} E_{jk} \alpha_k(t) + \tilde{F}_i(t), \tag{10}$$

where  $L_{ij}$  is a matrix which is non-singular and has eigenvalues with positive real parts.  $\tilde{F}_i(t)$  is a purely random stationary Gaussian fluctuating force component satisfying

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2Q_{ij} \delta(t - s), \tag{11}$$

where  $Q_{ij}$  is necessarily symmetric and positive definite. Equations (10) and (11) lead to a proof that the process described by the  $\alpha_i(t)$ 's is an  $n$ -component stationary Gaussian-Markov process. The  $W_1(\alpha)$  and  $P_2(\alpha_0 | \alpha t)$  distributions may be determined.<sup>3</sup> Using

$$\lim_{t \rightarrow \infty} P_2(\alpha_0 | \alpha t) = W_1(\alpha)$$

for  $W_1(\alpha)$  we get the expression

$$W_1(\alpha) = \left[\frac{||\mathbf{M}||}{(2\pi)^n}\right]^{-1/2} \exp[-\frac{1}{2} \alpha^\dagger \mathbf{M} \alpha], \tag{12}$$

where  $||\mathbf{M}||$  is the determinant of the matrix  $\mathbf{M}$  which is defined by

$$2\mathbf{Q} = \mathbf{G}\mathbf{M}^{-1} + \mathbf{M}^{-1}\mathbf{G}^\dagger,$$

where  $\mathbf{G} = K_B \mathbf{L}\mathbf{E}$  and  $\mathbf{G}^\dagger$  is the transpose of the matrix  $\mathbf{G}$ . However, using (9) in the Boltzmann-Planck relationship connecting entropy and probability gives for  $W_1(\alpha)$

$$W_1(\alpha) = \left( \frac{\|\mathbf{E}\|}{(2\pi)^n} \right)^{1/2} \exp \left( -\frac{1}{2} \alpha^\dagger \mathbf{E} \alpha \right). \quad (13)$$

Equality of (12) and (13) requires

$$M_{ii} = E_{ii} \quad (14)$$

which is the analog of (7) and which leads, through the definition of  $M_{ii}$ , to the fluctuation-dissipation theorem

$$\langle \tilde{\mathbf{F}}(t) \tilde{\mathbf{F}}(s) \rangle = [\mathbf{G}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{G}^\dagger] \delta(t - s). \quad (15)$$

Onsager and Machlup further assumed that all of the  $\alpha_i(t)$ 's were even functions of the time  $t$ . This leads to the celebrated reciprocal relations

$$L_{ij} = L_{ji} \quad (16)$$

and reduces the fluctuation-dissipation theorem, (15), to the elegant form

$$\langle \tilde{\mathbf{F}}(t) \tilde{\mathbf{F}}(s) \rangle = 2\mathbf{L} \delta(t - s). \quad (17)$$

## II. THE MOST GENERAL STATIONARY GAUSSIAN-MARKOV PROCESSES

Although Onsager and Machlup treated the case of  $\alpha(t)$ 's which are all odd functions of the time,<sup>4</sup> they did not treat the case in which both even and odd  $\alpha(t)$ 's occur simultaneously. This situation arises physically in the cases of the Brownian motion of a harmonic oscillator, fluctuating hydrodynamics, and the fluctuating Boltzmann equation. The first two cases will be discussed in this paper within the context of the most general stationary Gaussian-Markov processes which do allow simultaneously both even and odd random variables. In this section the derivation of the most general stationary Gaussian-Markov processes will be presented and the case of the Brownian motion of a harmonic oscillator will be given as an example. In the next section fluctuating hydrodynamics will be presented and the fluctuating Boltzmann equation will be reserved for a sequel to this paper.

For the general case the thermodynamical variables will be denoted by  $a_1(t) \cdots a_n(t)$ . Their equilibrium values are zero, and near equilibrium the entropy is given by

$$S = S_0 - \frac{1}{2} K_B a_i E_{ij} a_j, \quad (18)$$

where the matrix  $E_{ij}$  is symmetric and positive definite. As pointed out in the introduction, for a stationary Gaussian process  $W_1(\mathbf{a})$  and  $P_2(\mathbf{a} | \mathbf{a}'t)$  are expressed in the form

$$W_1(\mathbf{a}) = W_0 \exp \left( -\frac{1}{2} \mathbf{a}^\dagger \mathbf{E} \mathbf{a} \right) \quad (19)$$

and

$$P_2(\mathbf{a} | \mathbf{a}', t) = P_0 \exp \left( -\frac{1}{2} \mathbf{a}^\dagger \mathbf{A} \mathbf{a} - \mathbf{a}^\dagger \mathbf{B} \mathbf{a}' - \frac{1}{2} \mathbf{a}'^\dagger \mathbf{C} \mathbf{a}' \right),$$

where  $\mathbf{E}$  is the entropy matrix in (18),  $W_0 = \|\mathbf{E}\|/(2\pi)^n$ ,  $\mathbf{A}$  and  $\mathbf{C}$  are symmetric positive definite matrices depending on  $t$ , and  $\mathbf{B}$  is a  $t$  dependent matrix with no special symmetry properties.  $P_0$  is a normalization constant which will be determined below. Because  $P_2$  must satisfy the normalization condition, (1), it must be of the form

$$P_2(\mathbf{a} | \mathbf{a}', t) = P_0 \exp \left[ -\frac{1}{2} (\mathbf{a}' - \mathbf{D} \mathbf{a})^\dagger \mathbf{C} (\mathbf{a}' - \mathbf{D} \mathbf{a}) \right], \quad (20)$$

where  $P_0^2 = \|\mathbf{C}\|/(2\pi)^n$ . The equality of (19) and (20) determines  $\mathbf{A}$  and  $\mathbf{B}$  in terms of  $\mathbf{C}$  and  $\mathbf{D}$  by

$$\mathbf{A} = \mathbf{D}^\dagger \mathbf{C} \mathbf{D} \quad \text{and} \quad \mathbf{B} = -\mathbf{D}^\dagger \mathbf{C}. \quad (21)$$

The proof of (21) follows directly from the equality of the arguments of the exponentials in (19) and (20). Finally, from the condition

$$\int W_1(\mathbf{a}) P_2(\mathbf{a} | \mathbf{a}', t) d\mathbf{a} = W_1(\mathbf{a}')$$

it may be proved that

$$\mathbf{C}^{-1} = \mathbf{E}^{-1} - \mathbf{D} \mathbf{E}^{-1} \mathbf{D}^\dagger. \quad (22)$$

Therefore,  $P_2$  is completely determined by the two matrices  $\mathbf{E}$  and  $\mathbf{D}$ . The proof of (22) is given in Appendix A.<sup>5</sup>

The form of  $P_2$  in (20) implies that the conditional average for  $\mathbf{a}'$  with given initial values for  $\mathbf{a}$  is given by

$$\langle \mathbf{a}' \rangle^{\mathbf{a}} \equiv \int \mathbf{a}' P_2(\mathbf{a} | \mathbf{a}'t) d\mathbf{a}' = \mathbf{D}(t) \mathbf{a}, \quad (23)$$

where the time dependence of  $\mathbf{D}$  is made explicit.

At this point the Markov property of the process is assumed and is introduced through the Smoluchovskiy equation (2). Therefore, (23) implies

$$\begin{aligned} \mathbf{D}(t) \mathbf{a} &= \iint \mathbf{a}' P_2(\mathbf{a} | \mathbf{a}''t - s) P_2(\mathbf{a}'' | \mathbf{a}'s) d\mathbf{a}'' d\mathbf{a}' \\ &= \int P_2(\mathbf{a} | \mathbf{a}''t - s) \mathbf{D}(s) \mathbf{a}'' d\mathbf{a}'' = \mathbf{D}(s) \mathbf{D}(t - s) \mathbf{a}. \end{aligned}$$

From this it follows that

$$D_{ij}(t) = D_{ik}(s) D_{kj}(t - s). \quad (24)$$

The solution to (24) is the Doob formula

$$\mathbf{D}(t) = \exp(-\mathbf{G}t), \quad (25)$$

where  $\mathbf{G}$  is a time independent matrix with no particular symmetry properties. Putting (25) into (23) and taking the time derivative gives the regres-

sion equations for the average behavior

$$\frac{d}{dt} \langle a_i' \rangle^a = -G_{ii} \langle a_i' \rangle^a. \tag{26}$$

This is the form of the average regression equations for an arbitrary stationary Gaussian-Markov process. In order to guarantee the approach to equilibrium  $G_{ii}$  must have eigenvalues with positive real parts.  $G_{ii}$  may always be written as the sum of an antisymmetric matrix,  $A_{ii}$ , and a symmetric matrix,  $S_{ii}$ . For the applications which will be made of this result it is sufficient to assume that  $G_{ii}$  is non-singular and that the eigenvalues of  $S_{ii}$  are non-negative with at least one of them being positive. Writing  $\mathbf{G} = \mathbf{A} + \mathbf{S}$  and introducing fluctuating forces  $\tilde{\mathbf{F}}$ , Eq. (26) may be considered as the average of a generalized Langevin equation of the form

$$\frac{d}{dt} \mathbf{a}(t) + \mathbf{A}\mathbf{a}(t) + \mathbf{S}\mathbf{a}(t) = \tilde{\mathbf{F}}(t). \tag{27}$$

The fluctuating forces  $\tilde{\mathbf{F}}(t)$  are assumed to be purely random stationary Gaussian processes with average value zero and with correlation formula

$$\langle \tilde{\mathbf{F}}(t)\tilde{\mathbf{F}}(s) \rangle = 2\mathbf{Q} \delta(t - s), \tag{28}$$

where  $\mathbf{Q}$  is symmetric and positive definite. The proofs which lead to (12) and (15) may be used to compute  $W_1(\mathbf{a})$  and  $P_2(\mathbf{a} | \mathbf{a}')$ . The generalized fluctuation-dissipation theorem becomes

$$\langle \tilde{\mathbf{F}}(t)\tilde{\mathbf{F}}(s) \rangle = (\mathbf{G}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{G}^\dagger) \delta(t - s). \tag{29}$$

Derivation of (29) requires use of (18) in analogy with the use of (9) in the Onsager and Machlup case. Recall that some of the  $a_i(t)$ 's may be even while others are odd functions of time. It is this feature which makes (27) and (29) more general than (10) and (15).

The Brownian motion of a harmonic oscillator affords a simple example of all the points requiring the generalized Langevin equation (27). The governing equations are

$$M \frac{dx}{dt} = p, \tag{30}$$

$$\frac{dp}{dt} + M\omega^2 x = -\frac{\alpha}{M} p + \tilde{F},$$

where  $M$  is the mass of the oscillator,  $\omega$  is the harmonic force constant, and  $\alpha$  is the friction constant.  $\tilde{F}$  is a purely random stationary Gaussian process with mean value zero and correlation formula

$$\langle \tilde{F}(t)\tilde{F}(s) \rangle = 2D \delta(t - s). \tag{31}$$

Define  $y$  by  $y \equiv M\omega x$ . The identifications

$$a_i \equiv \begin{pmatrix} y \\ p \end{pmatrix}, \quad A_{ii} \equiv \begin{pmatrix} 0 & -\omega \\ \omega & 0 \end{pmatrix},$$

$$S_{ii} \equiv \begin{pmatrix} 0 & 0 \\ 0 & \frac{\alpha}{M} \end{pmatrix}, \quad \tilde{F}_i \equiv \begin{pmatrix} 0 \\ \tilde{F} \end{pmatrix}$$

permit writing (30) as

$$\frac{d}{dt} \mathbf{a}_i + A_{ii}\mathbf{a}_i + S_{ii}\mathbf{a}_i = \tilde{F}_i. \tag{32}$$

This is an example of (27) in which there are two  $a$ 's with opposite time parity as indicated by (30). Neither  $y$  nor  $p$  alone generates a stationary Gaussian-Markov process.<sup>6</sup> Note also that  $S_{ii}$  has an eigenvalue equal to zero whereas  $G_{ii} = A_{ii} + S_{ii}$  is nevertheless non-singular.

Using the Maxwell-Boltzmann distribution for  $W_1$  gives

$$W_1(y, p) = W_0 \exp \left( -\frac{1}{2} \frac{p^2}{MK_B T} - \frac{1}{2} \frac{y^2}{MK_B T} \right)$$

which leads to an  $E_{ii}$  matrix with the value

$$E_{ii} = \frac{1}{MK_B T} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}.$$

Therefore, the fluctuation-dissipation theorem, (29), becomes in this case,

$$\langle \tilde{\mathbf{F}}_i(t)\tilde{\mathbf{F}}_i(s) \rangle = 2MK_B T S_{ii} \delta(t - s). \tag{33}$$

Using the definition of  $S_{ii}$  and (31) gives  $D = K_B T \alpha$  which is once again the Einstein relation, (7).

### III. HYDRODYNAMICAL FLUCTUATIONS

Hydrodynamics is a macroscopic theory and one should expect, therefore, that the hydrodynamical variables will fluctuate in space and time. To describe these fluctuations Landau and Lifshitz have proposed adding a purely random stress tensor and a purely random heat flux vector to the Navier-Stokes equations.<sup>7</sup> They then tried to derive the correlation properties of these random functions from the Onsager-Machlup theory. Their derivation is not correct because hydrodynamics simultaneously involves even and odd functions of time. The proper framework for a theory of hydrodynamical fluctuations is the generalized theory of stationary Gaussian-Markov processes presented in Sec. II of this paper. It will be shown to lead in a natural and consistent manner to a derivation of the Landau-Lifshitz formulas.

One starts from the classical non-fluctuating

Navier-Stokes equations which are

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial x_\alpha} (\rho u_\alpha) = 0, \tag{34}$$

$$\rho \frac{D}{Dt} u_\alpha = -\frac{\partial}{\partial x_\beta} P_{\alpha\beta}, \tag{35}$$

$$\rho \frac{D}{Dt} \epsilon = -\frac{\partial}{\partial x_\alpha} q_\alpha - P_{\alpha\beta} D_{\alpha\beta}, \tag{36}$$

where  $\rho$  is the mass density,  $u_\alpha$  is the local velocity, and  $\epsilon$  is the interval energy per gram.  $D/Dt$  means the substantial derivative  $\partial/\partial t + u_\alpha \partial/\partial x_\alpha$  and

$$D_{\alpha\beta} = \frac{1}{2} \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right),$$

$P_{\alpha\beta} = p \delta_{\alpha\beta} - 2\eta(D_{\alpha\beta} - \frac{1}{3} D_{\gamma\gamma} \delta_{\alpha\beta}) - \xi D_{\gamma\gamma} \delta_{\alpha\beta}$ , and  $q_\alpha = -K\partial T/\partial x_\alpha$  where  $p$  is the local pressure and  $T$  is the local temperature.  $\eta$ ,  $\xi$ , and  $K$  are the transport coefficients shear viscosity, bulk viscosity, and heat conductivity, respectively. Equations (34), (35), and (36) must be completed by giving the equation of state  $p = p(\rho, T)$  and the thermal equation of state  $\epsilon = \epsilon(\rho, T)$ . These two state equations are not independent and are related through the second law of thermodynamics by

$$\rho^2 \frac{\partial \epsilon}{\partial \rho} = p - T \frac{\partial p}{\partial T}. \tag{37}$$

Writing the first and second laws together as

$$d\epsilon = T ds + \frac{p}{\rho} d\rho \tag{38}$$

and using

$$P_{\alpha\beta} D_{\alpha\beta} = p \frac{\partial}{\partial x_\alpha} u_\alpha - 2\eta D_{\alpha\beta} D_{\alpha\beta} - (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2$$

in (36), and  $(\partial/\partial x_\alpha)u_\alpha = -(1/\rho)(D/Dt)\rho$  from (34) gives for the entropy per gram,  $s$ , the equation

$$\rho T \frac{D}{Dt} s = \frac{\partial}{\partial x_\alpha} \left( K \frac{\partial}{\partial x_\alpha} T \right) + 2\eta D_{\alpha\beta} D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2. \tag{39}$$

This leads, for the time rate of change of the total entropy,  $S(t) = \int \rho s dV$ , to the result

$$\frac{d}{dt} S = \int \left( \frac{K[(\partial/\partial x_\alpha T)][(\partial/\partial x_\alpha)T]}{T^2} + \frac{1}{T} [2\eta D_{\alpha\beta} D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2] \right) dV. \tag{40}$$

The proof of (40) requires application of the divergence theorem and elimination of surface integrals

because there is neither momentum flow nor heat flux across the bounding surface. The form of the integrand in (40) guarantees that  $(d/dt)S \geq 0$ .

It will be shown that when linearized, Eqs. (34), (35), and (36) may be put into the form of the average regression equations for a general stationary Gaussian-Markov process

$$\frac{d}{dt} a_i + A_{ij} a_j = -S_{ij} a_j. \tag{41}$$

Denote the equilibrium density by  $\rho_{eq}$ , the equilibrium temperature by  $T_{eq}$ , and take the equilibrium velocity to be zero. The deviation of the density from  $\rho_{eq}$  is denoted by  $\Delta\rho$ , the deviation of the temperature from  $T_{eq}$  is denoted by  $\Delta T$ , and the velocity deviation is denoted by  $u_\alpha$ . Define constants  $A$ ,  $B$ , and  $C$  by:  $A = (\partial p/\partial \rho)_{eq}$ ,  $B = (\partial p/\partial T)_{eq}$ , and  $C = (\partial \epsilon/\partial T)_{eq}$ . With these preliminaries the linearized equations may be written in the form

$$\frac{\partial}{\partial t} \Delta\rho + \rho_{eq} \frac{\partial}{\partial x_\alpha} u_\alpha = 0, \tag{42}$$

$$\rho_{eq} \frac{\partial u_\alpha}{\partial t} + A \frac{\partial}{\partial x_\alpha} \Delta\rho + B \frac{\partial}{\partial x_\alpha} \Delta T = \frac{\partial}{\partial x_\beta} [2\eta D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma} \delta_{\alpha\beta}], \tag{43}$$

$$\rho_{eq} C \frac{\partial}{\partial t} \Delta T + T_{eq} B \frac{\partial}{\partial x_\alpha} u_\alpha = K \frac{\partial^2}{\partial x_\alpha \partial x_\alpha} \Delta T. \tag{44}$$

In the derivations of (43) and (44) from (35) and (36) one uses (37) and (42). Define  $a_i(\mathbf{r}t)$  for  $i = 1, 2, \dots, 5$  by

$$a_1(\mathbf{r}t) = \rho_{eq}^{-1/2} \Delta\rho(\mathbf{r}t), a_\alpha(\mathbf{r}t) = \left( \frac{\rho_{eq}}{A} \right)^{1/2} u_\alpha(\mathbf{r}t) \text{ for } \alpha = 2, 3, 4, a_5(\mathbf{r}t) = \left( \frac{\rho_{eq} C}{T_{eq} B} \right)^{1/2} \Delta T(\mathbf{r}t). \tag{45}$$

Greek indices,  $\alpha$  and  $\beta$ , will always go from 2 to 4 and will be used for vector and tensor components, whereas Latin indices,  $i$  and  $j$ , are intended for 1, 2, 3, 4, and 5. With these conventions two  $5 \times 5$  matrices are defined by

$$A_{ij}(\mathbf{r}, \mathbf{r}') = \begin{bmatrix} 0 & A_{1\alpha} & 0 \\ A_{\alpha 1} & & A_{\alpha 5} \\ 0 & A_{5\alpha} & 0 \end{bmatrix}, \tag{46}$$

where  $A_{1\alpha} = A_{\alpha 1} = A^{1/2}(\partial/\partial x_\alpha)\delta(\mathbf{r} - \mathbf{r}')$  and  $A_{5\alpha} = A_{\alpha 5} = (B/\rho_{eq})(T_{eq}/C)^{1/2}(\partial/\partial x_\alpha)\delta(\mathbf{r} - \mathbf{r}')$  and

$$S_{ij}(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & S_{\alpha\beta} & 0 \\ 0 & 0 & S_{55} \end{pmatrix}, \quad (47)$$

where  $S_{\alpha\beta} = S_{\beta\alpha} = (1/\rho_{\text{eq}})(\partial^2/\partial x_\mu \partial x'_\nu)\delta(\mathbf{r} - \mathbf{r}') [\eta(\delta_{\alpha\mu}\delta_{\beta\nu} + \delta_{\alpha\nu}\delta_{\beta\mu}) + (\xi - \frac{2}{3}\eta)\delta_{\alpha\mu}\delta_{\beta\nu}]$  and  $S_{55} = (K/\rho_{\text{eq}}C)(\partial^2/\partial x_\mu \partial x'_\nu)\delta(\mathbf{r} - \mathbf{r}')\delta_{\mu\nu}$ . Note that  $A_{ij}(\mathbf{r}, \mathbf{r}') = -A_{ji}(\mathbf{r}', \mathbf{r})$  and that  $S_{ij}(\mathbf{r}, \mathbf{r}') = +S_{ji}(\mathbf{r}', \mathbf{r})$ . Equations (42), (43), and (44) may now be written as

$$\begin{aligned} \frac{\partial}{\partial t} a_i(\mathbf{r}t) + \int A_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r}' \\ = - \int S_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r}'. \end{aligned} \quad (48)$$

By considering  $a_i(\mathbf{r}t)$  as labeled by both  $i$  and  $\mathbf{r}$ , the summation over the labels implied in (41) corresponds to summing over  $i$  and integrating over  $\mathbf{r}'$ . In this manner of thinking, (48) corresponds to a specific instance of (41). The antisymmetry of  $A_{ij}(\mathbf{r}, \mathbf{r}')$  and the symmetry of  $S_{ij}(\mathbf{r}, \mathbf{r}')$  have already been indicated. That the eigenvalues of  $S_{ij}(\mathbf{r}, \mathbf{r}')$  are non-negative may be verified from (47).

Fluctuating hydrodynamical forces,  $\tilde{F}_i(\mathbf{r}t)$ , may be added to (48) in order to get a fluctuating hydrodynamics. These forces have mean value zero and correlation formula

$$\langle \tilde{F}_i(\mathbf{r}t)\tilde{F}_j(\mathbf{r}'t') \rangle = 2Q_{ij}(\mathbf{r}, \mathbf{r}')\delta(t - t'). \quad (49)$$

The fluctuating linearized hydrodynamical equations become

$$\begin{aligned} \frac{\partial}{\partial t} a_i(\mathbf{r}t) + \int A_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r}' \\ = - \int S_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r}' + \tilde{F}_i(\mathbf{r}t). \end{aligned} \quad (50)$$

There remains the problems of determining  $Q_{ij}(\mathbf{r}, \mathbf{r}')$ . This is achieved by deducing an entropy matrix,  $E_{ij}(\mathbf{r}, \mathbf{r}')$ , from the entropy production equation, (40), and substituting it into the fluctuation-dissipation theorem.

From (40) the entropy production near equilibrium may be written up to second order in the hydrodynamical variables as

$$\begin{aligned} \frac{d}{dt} S = \int \left\{ \frac{K}{T_{\text{eq}}^2} \left( \frac{\partial}{\partial x_\alpha} \Delta T \right) \left( \frac{\partial}{\partial x_\alpha} \Delta T \right) \right. \\ \left. + \frac{1}{T_{\text{eq}}} [2\eta D_{\alpha\beta} D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2] \right\} dV. \end{aligned} \quad (51)$$

Substituting (45) and (47) into (51) gives

$$\frac{d}{dt} S = K_B \left( \frac{A}{K_B T_{\text{eq}}} \right) \iint a_i(\mathbf{r}t) S_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r} d\mathbf{r}'. \quad (52)$$

However, from the canonical second-order expression for the entropy

$$S = S_{\text{eq}} - \frac{1}{2} K_B \iint a_i(\mathbf{r}t) E_{ij}(\mathbf{r}, \mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r} d\mathbf{r}' \quad (53)$$

it follows from (48) that

$$\begin{aligned} \frac{d}{dt} S = \frac{1}{2} K_B \iiint a_i(\mathbf{r}t) [S_{ij}(\mathbf{r}, \mathbf{r}') E_{jk}(\mathbf{r}'', \mathbf{r}'') \\ + E_{ij}(\mathbf{r}, \mathbf{r}') S_{jk}(\mathbf{r}'', \mathbf{r}'')] a_k(\mathbf{r}''t) d\mathbf{r} d\mathbf{r}' d\mathbf{r}''. \end{aligned} \quad (54)$$

Comparison of (52) and (54) gives for  $E_{ij}(\mathbf{r}, \mathbf{r}')$

$$E_{ij}(\mathbf{r}, \mathbf{r}') = \frac{A}{K_B T_{\text{eq}}} \delta_{ij} \delta(\mathbf{r} - \mathbf{r}'). \quad (55)$$

Defining  $G_{ij}(\mathbf{r}, \mathbf{r}')$  by  $G_{ij}(\mathbf{r}, \mathbf{r}') = A_{ij}(\mathbf{r}, \mathbf{r}') + S_{ij}(\mathbf{r}, \mathbf{r}')$ , the fluctuation-dissipation theorem in this context is given by

$$\begin{aligned} \langle \tilde{F}_i(\mathbf{r}t)\tilde{F}_j(\mathbf{r}'t') \rangle = \int [G_{ik}(\mathbf{r}, \mathbf{r}'') E_{kj}^{-1}(\mathbf{r}'', \mathbf{r}'') \\ + E_{ik}^{-1}(\mathbf{r}, \mathbf{r}'') G_{jk}(\mathbf{r}'', \mathbf{r}'')] d\mathbf{r}'' \delta(t - t'). \end{aligned} \quad (56)$$

The integration in (56) is easily performed using (55) and yields

$$Q_{ij}(\mathbf{r}, \mathbf{r}') = \frac{K_B T_{\text{eq}}}{A} S_{ij}(\mathbf{r}, \mathbf{r}'). \quad (57)$$

Since  $S_{11}(\mathbf{r}, \mathbf{r}') = 0$ , it follows from (49) and (57) that  $\tilde{F}_1(\mathbf{r}t) = 0$  which means that the continuity equation, (42), has no fluctuating force. This is reasonable since it also does not possess a dissipative constant.

The equations just derived may be rewritten in terms of the usual hydrodynamical variables,  $\Delta\rho$ ,  $u_\alpha$ , and  $\Delta T$ . First, define  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\alpha$  by

$$\tilde{F}_\alpha(\mathbf{r}t) = (\rho_{\text{eq}} A)^{-1/2} \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(\mathbf{r}t), \quad (58)$$

$$\tilde{F}_5(\mathbf{r}t) = (\rho_{\text{eq}} T_{\text{eq}} A C)^{-1/2} \frac{\partial}{\partial x_\alpha} \tilde{g}_\alpha(\mathbf{r}t).$$

This permits rewriting (50) as

$$\frac{\partial}{\partial t} \Delta\rho + \rho_{\text{eq}} \frac{\partial}{\partial x_\alpha} u_\alpha = 0, \quad (59)$$

$$\begin{aligned} \rho_{\text{eq}} \frac{\partial}{\partial t} u_\alpha + \frac{\partial p}{\partial x_\alpha} = \frac{\partial}{\partial x_\beta} [2\eta D_{\alpha\beta} \\ + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma} \delta_{\gamma\beta}] + \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}, \end{aligned} \quad (60)$$

$$\rho_{eq} \frac{\partial \epsilon}{\partial t} + p \frac{\partial u_\alpha}{\partial x_\alpha} = K \frac{\partial^2}{\partial x_\alpha \partial x_\alpha} \Delta T + \frac{\partial}{\partial x_\alpha} \tilde{g}_\alpha. \quad (61)$$

Putting (58) into (49) and using (57) gives as fluctuation-dissipation theorems

$$\langle \tilde{S}_{\alpha\beta}(\mathbf{r}t) \tilde{S}_{\mu\nu}(\mathbf{r}'t') \rangle = 2K_B T_{eq} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') [\eta(\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}) + (\xi - \frac{2}{3}\eta) \delta_{\alpha\beta} \delta_{\mu\nu}], \quad (62)$$

$$\langle \tilde{g}_\alpha(\mathbf{r}t) \tilde{g}_\beta(\mathbf{r}'t') \rangle = 2K_B T_{eq}^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') K \delta_{\alpha\beta}. \quad (63)$$

From (57) it is also seen that  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\gamma$  are uncorrelated.

Equations (62) and (63) are identical to the corresponding formulas proposed by Landau and Lifshitz.  $\tilde{S}_{\alpha\beta}$  may be thought of as a fluctuating stress tensor, and  $\tilde{g}_\alpha$  may be viewed as a fluctuating heat flux. These quantities must always be considered as fluctuating "forces" which are responsible for fluctuations in the hydrodynamical variables.

#### IV. APPLICATION TO THE THEORY OF BROWNIAN MOTION

Applications of the fluctuating hydrodynamical equations require solving equations (59), (60), and (61) as inhomogeneous equations with inhomogeneities given by  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\alpha$ . The linearity of the equations results in giving  $\Delta\rho$ ,  $\Delta T$ , and  $u_\alpha$  as linear functionals of  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\alpha$ . The correlations among  $\Delta\rho$ ,  $\Delta T$ , and  $u_\alpha$  are induced through their functional dependence upon  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\alpha$ , using Eqs. (62) and (63). Note that for a particular problem the fluctuating stress tensor, for example, is obtained by solving for  $u_\alpha$  as a functional of  $\tilde{S}_{\alpha\beta}$  and  $\tilde{g}_\alpha$  and then putting  $u_\alpha$  into the expression  $-2\eta(D_{\alpha\beta} - \frac{1}{3}D_{\gamma\gamma}\delta_{\alpha\beta}) - \xi D_{\gamma\gamma}\delta_{\alpha\beta}$ . This is very different from the fluctuating stress tensor "force,"  $S_{\alpha\beta}$ , and the two should not become confused.

The most simple and straightforward application is the calculation of the fluctuating hydrodynamical quantities around complete equilibrium where  $\rho = \rho_{eq}$ ,  $T = T_{eq}$ , and  $u_\alpha = 0$  in an infinite medium. This has been done by Rytov<sup>8</sup> and Foch,<sup>9</sup> and it explains both the Rayleigh and Brillouin scattering of light by a fluctuating fluid. In the following, application will be made to the problem of a slowly moving particle immersed in a fluid. This is the problem of Brownian motion. It will be shown that the fluctuating hydrodynamical equations give rise to a fluctuating force acting on the particle, as well as to an average frictional force which

slows the average motion of the particle. The resulting situation will be seen to be that which is described by the Langevin equation.<sup>10</sup>

For a slowly moving particle all inertial terms in Eqs. (59), (60), and (61) will be neglected. Equation (59) becomes

$$\frac{\partial}{\partial x_\alpha} u_\alpha(\mathbf{r}t) = 0. \quad (64)$$

Equation (60) in conjunction with (64) becomes

$$\frac{\partial}{\partial x_\beta} P_{\alpha\beta}(\mathbf{r}t) = -\frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(\mathbf{r}t), \quad (65)$$

where

$$P_{\alpha\beta}(\mathbf{r}t) = -p(\mathbf{r}t) \delta_{\alpha\beta} + \eta \left( \frac{\partial u_\alpha(\mathbf{r}t)}{\partial x_\beta} + \frac{\partial u_\beta(\mathbf{r}t)}{\partial x_\alpha} \right).$$

$P_{\alpha\beta}$  does not contain a bulk viscosity term because of (64). Equation (61) in conjunction with (64) is independent of  $u_\alpha$  altogether. Its solution is a uniform temperature field on the average which fluctuates as a result of the presence of the fluctuating heat flux "force"  $\tilde{g}_\alpha$ . Further consideration of the temperature equation is omitted since it does not effect  $u_\alpha$ . Equations (64) and (65) determine the problem when appropriate boundary conditions are given.

The recipe for solving (64) and (65) is first of all to solve the average equations

$$\frac{\partial}{\partial x_\alpha} u_\alpha(\mathbf{r}t) = 0, \quad (66)$$

$$\frac{\partial}{\partial x_\beta} P_{\alpha\beta}(\mathbf{r}t) = 0$$

with appropriate boundary conditions on the surface of the particle,  $S$ , and infinitely far away from  $S$ . The boundary conditions are that  $u_\alpha = U_\alpha$  on  $S$  and that  $u_\alpha = 0$  infinitely far away from  $S$ . This corresponds to the situation in which the particle is moving slowly, with velocity  $U_\alpha$ , through the fluid which is otherwise at rest. The solution to (66) with these boundary conditions gives the average velocity field,  $u_\alpha$ , everywhere outside of the particle. This is called the Stokes' problem, and for a sphere the solution is well known. Next, the fluctuating equations, (64) and (65), must be solved with appropriate boundary conditions on  $S$  and infinitely far away from  $S$ . In order to distinguish this case from the preceding case, the fluctuating velocity field and the fluctuating stress tensor are, respectively, denoted by  $\tilde{u}_\alpha$  and  $\tilde{P}_{\alpha\beta}$ . Equations (64) and (65) are then

$$\begin{aligned} \frac{\partial}{\partial x_\alpha} \tilde{u}_\alpha(\mathbf{r}t) &= 0, & (67) \quad \int_V \left( u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta} \right) dV \\ \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta}(\mathbf{r}t) &= -\frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(\mathbf{r}t). & = \int_V \left[ u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} + \left( \frac{\partial}{\partial x_\beta} u_\alpha \right) \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta} \right. \\ & & \left. - \left( \frac{\partial}{\partial x_\beta} \tilde{u}_\alpha \right) P_{\alpha\beta} \right] dV \\ & & = \int_V \frac{\partial}{\partial x_\beta} (u_\alpha \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha P_{\alpha\beta}) dV \\ & & = \int_S (u_\alpha \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha P_{\alpha\beta}) \hat{n}_\beta d\Omega. \end{aligned}$$

The appropriate boundary conditions are that on  $S$ ,  $\tilde{u}_\alpha = 0$  while infinitely far from  $S$   $\tilde{u}_\alpha$  takes on its complete equilibrium value. The solution to (67) gives the fluctuating velocity field everywhere outside of the particle. In general, both problems given by (66) and (67) with their respective boundary conditions may be solved by the method of Green's functions. For the average equations, (66), this has been extensively discussed by Oseen.<sup>11</sup> However, for the present purposes the explicit solutions are not necessary.

From the average and fluctuating velocity fields,  $u_\alpha$  and  $\tilde{u}_\alpha$ , the average and fluctuating stress tensors may be computed. From each of these, by integrating the normal projections over the surface of the particle,  $S$ , it is possible to obtain the average and fluctuating forces acting on the particle. Call these two forces  $F_\alpha$  and  $\tilde{F}_\alpha$ , respectively. The equation of motion for the particle is then

$$M \frac{dU_\alpha}{dt} = F_\alpha + \tilde{F}_\alpha. \quad (68)$$

It is well known that the solution of the Stokes' problem leads to a force  $F_\alpha$  which is proportional to  $U_\alpha$  with a negative proportionality or friction coefficient. If one can prove that the fluctuating force,  $\tilde{F}_\alpha$ , satisfies a fluctuation-dissipation theorem like (8) then the Langevin equation has been completely derived from and shown to be consistent with the fluctuating hydrodynamical equations.

For the proof, the following identity is required:

$$\begin{aligned} \int_V \left( u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta} \right) dV \\ = \int_S (u_\alpha \tilde{P}_{\alpha\beta} \hat{n}_\beta - \tilde{u}_\alpha P_{\alpha\beta} \hat{n}_\beta) d\Omega, \end{aligned} \quad (69)$$

where the volume integral is over the entire region  $V$  outside of the surface  $S$ .  $\hat{n}_\beta$  is a unit vector normal to  $S$  and directed into the fluid. For the proof of (69) note that  $\partial u_\alpha / \partial x_\alpha = 0 = \partial \tilde{u}_\alpha / \partial x_\alpha$  implies

$$\begin{aligned} \left( \frac{\partial}{\partial x_\beta} u_\alpha \right) \tilde{P}_{\alpha\beta} &= \left( \frac{\partial}{\partial x_\beta} u_\alpha \right) \eta \left( \frac{\partial \tilde{u}_\alpha}{\partial x_\beta} + \frac{\partial \tilde{u}_\beta}{\partial x_\alpha} \right) \\ &= \left( \frac{\partial}{\partial x_\beta} \tilde{u}_\alpha \right) \eta \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) = \left( \frac{\partial}{\partial x_\beta} \tilde{u}_\alpha \right) P_{\alpha\beta}. \end{aligned}$$

Therefore,

Equations (66) and (67) are substituted into the left-hand side of (69), while the boundary conditions for  $u_\alpha$  and  $\tilde{u}_\alpha$  on  $S$  are substituted into the right-hand side. The result is

$$- \int_V u_\alpha \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta} dV = \int_S U_\alpha \tilde{P}_{\alpha\beta} \hat{n}_\beta d\Omega. \quad (70)$$

Since  $U_\alpha$  is a constant, it may be factored out of the integral over  $S$ . The fluctuating force,  $\tilde{F}_\alpha$ , is by definition given by

$$\tilde{F}_\alpha = \int_S \tilde{P}_{\alpha\beta} \hat{n}_\beta d\Omega. \quad (71)$$

Therefore, putting (71) into (70) gives

$$U_\alpha \tilde{F}_\alpha = - \int_V u_\alpha \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta} dV. \quad (72)$$

From (72) and the basic correlation formula (62) it may be proved that

$$U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq} \delta(t-s) \int_S u_\alpha P_{\alpha\beta} \hat{n}_\beta d\Omega. \quad (73)$$

The proof of (73) is in Appendix B

On  $S$ ,  $u_\alpha = U_\alpha$ , so that

$$\int_S u_\alpha P_{\alpha\beta} \hat{n}_\beta d\Omega = U_\alpha \int_S P_{\alpha\beta} \hat{n}_\beta d\Omega.$$

The average frictional force on the particle is by definition given by

$$f_{\alpha\beta} U = \int_S P_{\alpha\beta} \hat{n}_\beta d\Omega, \quad (74)$$

where  $f_{\alpha\beta}$  is the friction tensor. Therefore, (73) and (74) combine to give

$$\langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq} f_{\alpha\beta} \delta(t-s). \quad (75)$$

This is the fluctuation-dissipation theorem for the Langevin equation in a generalized form applicable to particles of arbitrary shape. Note that (75) implies that  $f_{\alpha\beta}$  must be symmetric, a fact which



may be proved directly. For a sphere of radius  $a$ ,  $f_{\alpha\beta} = 6\pi\eta a\delta_{\alpha\beta}$  as is well known from the Stokes' solution for a sphere.

V. CONCLUDING REMARKS

As mentioned in Sec. IV, the explicit solution for the fluctuating velocity field is determined uniquely by Eq. (67) and its boundary conditions. For a sphere the solution can be found from the Green's tensor for the Stokes' equation given by Oseen. Hence, one can find the effect which the motion of the sphere has on the correlation properties of  $\tilde{u}_\alpha$ , which will be different from the corresponding properties in an infinite fluid at rest. Perhaps the effect of the motion of the sphere on the Brillouin scattering of light is observable. It would provide a very searching test for the fluctuating hydrodynamical equations.

It seems reasonable to expect that the fluctuating stress tensor  $\tilde{S}_{\alpha\beta}$  and heat flux vector  $\tilde{g}_\alpha$  remain the same even if the non-linear inertial effects of the hydrodynamical equations can no longer be neglected. It seems to us of special interest to investigate the effect of the fluctuating forces near a hydrodynamical instability point. It is possible that in the neighborhood of such a point the fluctuations and correlation lengths become large, so that the effect on light scattering may be similar to the so-called critical opalescence near the liquid-vapor critical point. Whether the increase in Brillouin scattering observed by Goldstein and Hagen in fluids near the transition from laminar to turbulent flow, which these authors attribute to a kind of pre-turbulence, can be understood as an enhancement of the hydrodynamical fluctuations remains to be seen.<sup>12</sup>

APPENDIX A

The proof of (22) was suggested by deGroot.<sup>5</sup> Using (19), the integration which must be performed to obtain (22) is

$$W_0 P_0 \int \exp[-\frac{1}{2}\mathbf{a}^\dagger(\mathbf{E} + \mathbf{A})\mathbf{a} - \mathbf{a}^\dagger\mathbf{B}\mathbf{a}' - \frac{1}{2}\mathbf{a}'^\dagger\mathbf{C}\mathbf{a}'] da.$$

The exponent may be written as

$$-\frac{1}{2}(\mathbf{a} - \mathbf{K}\mathbf{a}')^\dagger(\mathbf{E} + \mathbf{A})(\mathbf{a} - \mathbf{K}\mathbf{a}') + \frac{1}{2}(\mathbf{K}\mathbf{a}')^\dagger(\mathbf{E} + \mathbf{A})\mathbf{K}\mathbf{a}' - \frac{1}{2}\mathbf{a}'^\dagger\mathbf{C}\mathbf{a}',$$

where  $\mathbf{K}$  is defined by

$$\mathbf{B} = -(\mathbf{E} + \mathbf{A})\mathbf{K}.$$

With the exponent in this form, the  $\mathbf{a}$  integration is easily done and produces a constant factor

$$\left[ \frac{\|\mathbf{E} + \mathbf{A}\|}{(2\pi)^n} \right]^{-1/2}.$$

Therefore, the initial identity becomes

$$W_0 P_0 \left[ \frac{\|\mathbf{E} + \mathbf{A}\|}{(2\pi)^n} \right]^{-1/2} \exp[\frac{1}{2}(\mathbf{K}\mathbf{a}')^\dagger(\mathbf{E} + \mathbf{A})\mathbf{K}\mathbf{a}' - \frac{1}{2}\mathbf{a}'^\dagger\mathbf{C}\mathbf{a}'] = W_0 \exp[-\frac{1}{2}\mathbf{a}'^\dagger\mathbf{E}\mathbf{a}'].$$

From this identity it follows that

$$\mathbf{E} = \mathbf{C} - \mathbf{K}^\dagger(\mathbf{E} + \mathbf{A})\mathbf{K}$$

if

$$P_0 = \left[ \frac{\|\mathbf{E} + \mathbf{A}\|}{(2\pi)^n} \right]^{1/2}.$$

It is convenient to prove this last identity later and for the time being to assume that it is true. Using (21) the defining relation for  $\mathbf{K}$  becomes

$$\mathbf{D}^\dagger\mathbf{C} = (\mathbf{E} + \mathbf{D}^\dagger\mathbf{C}\mathbf{D})\mathbf{K}.$$

The expression  $\mathbf{E} = \mathbf{C} - \mathbf{K}^\dagger(\mathbf{E} + \mathbf{A})\mathbf{K}$  becomes

$$\mathbf{E} = \mathbf{C} + \mathbf{K}^\dagger\mathbf{B} = \mathbf{C} - \mathbf{K}^\dagger\mathbf{D}^\dagger\mathbf{C}.$$

Taking the transpose of this equation gives

$$\mathbf{E} = \mathbf{C} - \mathbf{C}\mathbf{D}\mathbf{K},$$

from which multiplication by  $\mathbf{D}^\dagger$  gives

$$\mathbf{D}^\dagger\mathbf{C} = \mathbf{D}^\dagger\mathbf{E} + \mathbf{D}^\dagger\mathbf{C}\mathbf{D}\mathbf{K}.$$

From the earlier expression for  $\mathbf{D}^\dagger\mathbf{C}$  it follows that

$$\mathbf{E}\mathbf{K} = \mathbf{D}^\dagger\mathbf{E}.$$

Finally, for  $\mathbf{K}$  this gives the identity

$$\mathbf{K} = \mathbf{E}^{-1}\mathbf{D}^\dagger\mathbf{E}.$$

From  $\mathbf{E} = \mathbf{C} - \mathbf{C}\mathbf{D}\mathbf{K}$  this new expression for  $\mathbf{K}$  gives

$$\mathbf{E} = \mathbf{C} - \mathbf{C}\mathbf{D}\mathbf{E}^{-1}\mathbf{D}^\dagger\mathbf{E}.$$

Multiplying from the left with  $\mathbf{C}^{-1}$  and from the right with  $\mathbf{E}^{-1}$  gives

$$\mathbf{C}^{-1} = \mathbf{E}^{-1} - \mathbf{D}\mathbf{E}^{-1}\mathbf{D}^\dagger,$$

which is (22). Now, to prove  $P_0^2 = \|\mathbf{E} + \mathbf{A}\|/(2\pi)^n$  recall that  $P_0^2 = \|\mathbf{C}\|/(2\pi)^n$  so that it is necessary to show that

$$\|\mathbf{C}\| = \|\mathbf{E} + \mathbf{A}\|.$$

From  $\mathbf{K} = \mathbf{E}^{-1}\mathbf{D}^\dagger\mathbf{E}$  it follows that  $\|\mathbf{K}\| = \|\mathbf{D}\|$ . However, the defining identity for  $\mathbf{K}$  using the expression (21) for  $\mathbf{B}$  gives  $\|\mathbf{D}\| \|\mathbf{C}\| = \|\mathbf{E} + \mathbf{A}\| \|\mathbf{K}\|$  which with  $\|\mathbf{K}\| = \|\mathbf{D}\|$  gives the desired result.

APPENDIX B. PROOF OF (73)

Directly from (62),

$$\begin{aligned}
 U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle &= 2K_B T_{eq} \delta(t-s) \eta \\
 &\cdot \int_V \int_V u_\alpha(\mathbf{r}) u_\beta(\mathbf{r}') \frac{\partial^2}{\partial x_\mu \partial x_\nu} \delta(\mathbf{r} - \mathbf{r}') \\
 &\cdot (\delta_{\alpha\beta} \delta_{\mu\nu} + \delta_{\alpha\nu} \delta_{\beta\mu} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\nu}) dV_r dV_{r'} = 2K_B T_{eq} \\
 &\cdot \delta(t-s) \eta \int_V \left[ \frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\alpha}{\partial x_\beta} - \frac{2}{3} \left( \frac{\partial u_\alpha}{\partial x_\alpha} \right)^2 \right] dV.
 \end{aligned}$$

Using  $\partial u_\alpha / \partial x_\alpha = 0$  implies

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta} (u_\alpha u_\beta) = \frac{\partial u_\beta}{\partial x_\alpha} \frac{\partial u_\alpha}{\partial x_\beta}$$

and

$$\frac{\partial^2}{\partial x_\beta \partial x_\beta} (u_\alpha u_\alpha) = 2 \frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\alpha}{\partial x_\beta} + 2u_\alpha \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha.$$

Therefore,

$$\begin{aligned}
 U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle &= 2K_B T_{eq} \delta(t-s) \eta \int_V \left[ \frac{1}{2} \frac{\partial^2}{\partial x_\beta \partial x_\beta} (u_\alpha u_\alpha) \right. \\
 &\left. - u_\alpha \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha + \frac{\partial^2}{\partial x_\alpha \partial x_\beta} (u_\alpha u_\beta) \right] dV.
 \end{aligned}$$

The divergence theorem may be applied. Surface terms infinitely far from  $S$  vanish because of the asymptotic behavior of  $u_\alpha$  at that distance. Applying the divergence theorem and using (66) in the form

$$\eta \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha = \frac{\partial}{\partial x_\alpha} p$$

gives

$$\begin{aligned}
 U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle &= 2K_B T_{eq} \delta(t-s) \eta \\
 &\cdot \left\{ \int_S \left[ \frac{1}{2} \hat{n}_\beta \frac{\partial}{\partial x_\beta} (u_\alpha u_\alpha) + \hat{n}_\alpha \frac{\partial}{\partial x_\beta} (u_\alpha u_\beta) \right] d\Omega \right. \\
 &\left. - \int_V u_\alpha \frac{1}{\eta} \frac{\partial}{\partial x_\alpha} p dV \right\}.
 \end{aligned}$$

However,

$$\int_S \frac{1}{2} \hat{n}_\beta \frac{\partial}{\partial x_\beta} (u_\alpha u_\alpha) d\Omega = \int_S \hat{n}_\beta u_\alpha \frac{\partial u_\alpha}{\partial x_\beta} d\Omega$$

and

$$\begin{aligned}
 - \int_V u_\alpha \frac{1}{\eta} \frac{\partial}{\partial x_\alpha} p dV &= -\frac{1}{\eta} \\
 &\cdot \int_V \frac{\partial}{\partial x_\alpha} (u_\alpha p) dV = -\frac{1}{\eta} \int_S \hat{n}_\beta p \delta_{\alpha\beta} u_\alpha d\Omega
 \end{aligned}$$

and

$$\begin{aligned}
 \int_S \hat{n}_\alpha \frac{\partial}{\partial x_\alpha} (u_\alpha u_\beta) d\Omega &= \int_S \hat{n}_\alpha u_\beta \frac{\partial u_\alpha}{\partial x_\beta} d\Omega = \int_S \hat{n}_\beta u_\alpha \frac{\partial u_\beta}{\partial x_\alpha} d\Omega.
 \end{aligned}$$

Consequently,

$$\begin{aligned}
 U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle &= 2K_B T_{eq} \delta(t-s) \eta \\
 &\cdot \int_S \left[ \hat{n}_\beta u_\alpha \left( \frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) - \hat{n}_\beta u_\alpha \frac{1}{\eta} p \delta_{\alpha\beta} \right] d\Omega \\
 &= 2K_B T_{eq} \delta(t-s) \int_S u_\alpha P_{\alpha\beta} \hat{n}_\beta d\Omega.
 \end{aligned}$$

\* This work is based on the dissertation of R. F. Fox (Rockefeller University, 1969).

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<sup>1</sup> G. E. Uhlenbeck and L. S. Ornstein, *Phys. Rev.* **36**, 823 (1930).

<sup>2</sup> L. Onsager and S. Machlup, *Phys. Rev.* **91**, 1505 (1953).

<sup>3</sup> S. R. deGroot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), p. 119.

<sup>4</sup> S. Machlup and L. Onsager, *Phys. Rev.* **91**, 1512 (1953).

<sup>5</sup> Reference 3, p. 470.

<sup>6</sup> M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.* **17**, 323 (1945).

<sup>7</sup> L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Pergamon, New York, 1959), Chap. 17.

<sup>8</sup> S. M. Rytov, *Zh. Eksp. Teor. Fiz.* **33**, 514, 671 (1957) [*Sov. Phys. JETP* **6**, 401, 513 (1958)].

<sup>9</sup> J. Foch, *Phys. Fluids* **11**, 2336 (1968).

<sup>10</sup> R. Zwanzig, *J. Res. Natl. Bur. Std. (U. S.)* **64B**, 143 (1964). Zwanzig has attempted a similar proof of the Langevin equation for the case of a spherical particle. However, his argument is not satisfactory since he does not follow the recipe for solving the fluctuating hydrodynamical equations outlined in the beginning of this section. Zwanzig appeals to a theorem of Faxen which is not applicable for flows with outside forces as is the case here. Furthermore, in the proof given here the restriction to a sphere is unnecessary.

<sup>11</sup> C. W. Oseen, *Neuer Methoden und Ergebnisse in der Hydrodynamik* (Akad. Verlag, Leipzig, 1927).

<sup>12</sup> R. J. Goldstein and W. F. Hagen, *Phys. Fluids* **10**, 1349 (1967).