

THE PHYSICS OF FLUIDS

VOLUME 13, NUMBER 12

DECEMBER 1970

Contributions to Nonequilibrium Thermodynamics. II. Fluctuation Theory for the Boltzmann Equation*

RONALD FORREST FOX†

Department of Physics, University of California, Berkeley, California 94720

AND

GEORGE E. UHLENBECK

The Rockefeller University, New York, New York 10021

(Received 9 April 1970)

The theory of the nonequilibrium phenomena in a dilute gas as described by the Boltzmann equation is extended in order to also include the fluctuations of the distribution function of the molecules. It is shown that in a first approximation this extension leads to the Landau-Lifshitz fluctuation terms in the hydrodynamical equations.

I. INTRODUCTION

The theory of general stationary, Gaussian Markov processes which was developed in Ref. 1 is applied to the fluctuation theory of a gas as described by the Boltzmann equation. The result is a Boltzmann equation with fluctuation terms (Sec. II). An adaptation of the Enskog procedure for deriving hydrodynamics from the Boltzmann equation is presented and leads to a derivation of the hydrodynamical equations with fluctuations² (Secs. III and IV). Since both fluctuating hydrodynamics and the Boltzmann equation with fluctuations are stationary Gaussian Markov processes, their connection through the Enskog procedure suggests a general theorem for such processes. This is discussed in Sec. V and leads to a general criterion for the over-all consistency of the stationary Gaussian Markov process approach to nonequilibrium thermodynamics.

II. FLUCTUATIONS IN μ SPACE

The state of a dilute and monoatomic gas is described by a distribution function $f(\mathbf{r}, \mathbf{p}, t)$ which gives the number of particles at time t in the element $d\mathbf{r} d\mathbf{p}$ of the six-dimensional phase space (μ space) of a molecule. The change of f with time is governed

by the Boltzmann equation³ and one shows that for $t \rightarrow \infty$ $f(\mathbf{r}, \mathbf{p}, t)$ approaches, if there are no outside forces, the Maxwell equilibrium distribution:

$$f_{eq}(\mathbf{p}) = n_{eq}(2\pi mk_B T_{eq})^{-3/2} \exp\left(-\frac{\mathbf{p}^2}{2mk_B T_{eq}}\right),$$

where n_{eq} is the equilibrium density, T_{eq} is the equilibrium temperature, m is the mass of a molecule, and k_B is the Boltzmann constant. When $f(\mathbf{r}, \mathbf{p}, t)$ is near $f_{eq}(\mathbf{p})$, one can write

$$f(\mathbf{r}, \mathbf{p}, t) = f_{eq}(\mathbf{p})[1 + h(\mathbf{r}, \mathbf{p}, t)],$$

where $h(\mathbf{r}, \mathbf{p}, t)$ fulfills the linearized Boltzmann equation

$$\begin{aligned} \frac{\partial h}{\partial t} + \frac{\mathbf{p}_a}{m} \frac{\partial h}{\partial x_a} \\ = \int f_{eq}(\mathbf{p}) g I(g, \theta) [h' + h'_1 - h - h_1] d\Omega d\mathbf{p}_1. \quad (1) \end{aligned}$$

The right-hand side of (1) describes the effect of binary collisions on the change of $h(\mathbf{r}, \mathbf{p}, t)$ with time. The prime and the subscript 1 on the h 's refer to its momentum variable $\mathbf{p}$ only. For instance h'_1 means $h(\mathbf{r}, \mathbf{p}'_1, t)$. The four momentum variables refer to the binary collision $(\mathbf{p}, \mathbf{p}_1) \rightleftharpoons (\mathbf{p}', \mathbf{p}'_1)$; g is the relative velocity which turns through the angle

θ in the solid angle $d\Omega$ during the collision and $I(g, \theta)$ is the differential collision cross section, which depends on the intermolecular force.

It will be shown that (1) may be rewritten such that it has the form of the average regression equations of a stationary Gaussian Markov process:

$$\frac{da_i}{dt} + A_{ii}a_i = -S_{ii}a_i, \quad (2)$$

where $A_{ii} = -A_{ii}$, $S_{ii} = S_{ii}$, and S_{ii} has non-negative eigenvalues. In analogy with the treatment of the hydrodynamical variables in Ref. 1, the $a_i(t)$ in (2) for this case will be $h(\mathbf{r}, \mathbf{p}, t)$. Therefore, the summations over the repeated indices in (2) correspond to integrations over the labels $\mathbf{r}$ and $\mathbf{p}$. After establishing the form (2) in this sense for (1), fluctuations will be introduced transforming the linearized Boltzmann equation into a generalized Langevin equation.

First, we observe that the right-hand side of (1) may be written in the form

$$-\int d\mathbf{p}' f_{\text{eq}}(\mathbf{p}) K(\mathbf{p}, \mathbf{p}') h(\mathbf{r}, \mathbf{p}', t) \quad (3)$$

as was shown by Hilbert⁴ and Enskog⁵ who also proved that the kernel $K(\mathbf{p}, \mathbf{p}')$ is symmetric, isotropic, and has nonnegative eigenvalues. From the five conservation laws for a binary collision it follows that $K(\mathbf{p}, \mathbf{p}')$ has five zero eigenvalues. Not much is known about the eigenvalue spectrum in general. For a repulsive intermolecular force $\sim r^{-5}$ (Maxwell model) the spectrum is discrete and goes to infinity.⁶ For hard spheres the spectrum begins with a discrete series which converges to a continuous spectrum which extends to infinity.⁷ In the following we assume that the spectrum is discrete. This is merely a formal convenience since no specific properties of the spectrum beyond those already mentioned will be used. Also we will not be concerned with the convergence of eigenfunction expansions so that they must be considered as formal series.

Now define $a(\mathbf{r}, \mathbf{p}, t)$, $A(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$, and $S(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$ by

$$a(\mathbf{r}, \mathbf{p}, t) = f_{\text{eq}}^{1/2}(\mathbf{p}) h(\mathbf{r}, \mathbf{p}, t),$$

$$A(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') = f_{\text{eq}}^{1/2}(\mathbf{p}) \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}'), \quad (4)$$

$$S(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') = f_{\text{eq}}^{1/2}(\mathbf{p}) f_{\text{eq}}^{1/2}(\mathbf{p}') K(\mathbf{p}, \mathbf{p}') \delta(\mathbf{r} - \mathbf{r}'),$$

then, using (3), one easily verifies that (1) can be written in the form

$$\begin{aligned} \frac{\partial}{\partial t} a(\mathbf{r}, \mathbf{p}, t) + \iint d\mathbf{r}' d\mathbf{p}' A(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') a(\mathbf{r}', \mathbf{p}', t) \\ = - \iint d\mathbf{r}' d\mathbf{p}' S(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') a(\mathbf{r}', \mathbf{p}', t). \end{aligned} \quad (5)$$

$A(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$ is antisymmetric because of the factor $(\partial/\partial x_\alpha) \delta(\mathbf{r} - \mathbf{r}')$ and $S(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$ is symmetric with nonnegative eigenvalues because of the factor $K(\mathbf{p}, \mathbf{p}')$. Therefore, thinking of $\mathbf{r}$ and $\mathbf{p}$ as labels, the linearized Boltzmann equation (5) has the same form as the average regression equations of a stationary Gaussian Markov process of type (2).

The linearized Boltzmann equation gives a contracted description of the behavior of a dilute gas, since for a precise description the Liouville equation would be required. Hence, $h(\mathbf{r}, \mathbf{p}, t)$ must be considered to fluctuate in time. The form (5) of the linearized Boltzmann equation suggests that the fluctuation may be described by adding to the regression equation (5) a fluctuating force term $f_{\text{eq}}^{1/2}(\mathbf{p}) \tilde{C}(\mathbf{r}, \mathbf{p}, t)$ which makes (5) a generalized Langevin equation. Going back to $h(\mathbf{r}, \mathbf{p}, t)$, one then obtains, for the linearized Boltzmann equation with fluctuations,

$$\begin{aligned} \frac{\partial h}{\partial t} + \frac{p_\alpha}{m} \frac{\partial h}{\partial x_\alpha} \\ = - \int d\mathbf{p}' K(\mathbf{p}, \mathbf{p}') f_{\text{eq}}(\mathbf{p}') h(\mathbf{r}, \mathbf{p}', t) + \tilde{C}(\mathbf{r}, \mathbf{p}, t). \end{aligned} \quad (6)$$

$\tilde{C}(\mathbf{r}, \mathbf{p}, t)$ is assumed to have mean value zero and to satisfy the correlation formula

$$\begin{aligned} \langle \tilde{C}(\mathbf{r}, \mathbf{p}, t) \tilde{C}(\mathbf{r}', \mathbf{p}', t') \rangle \\ = 2Q(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') \delta(t - t'). \end{aligned} \quad (7)$$

$Q(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$ may be explicitly determined by invoking the fluctuation-dissipation theorem [Ref. 1, Eq. (29)] once the "entropy matrix" $E(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}')$ has been determined. E follows from the expression for the entropy of a dilute gas

$$S(t) = -k_B \iint d\mathbf{r} d\mathbf{p} f(\mathbf{r}, \mathbf{p}, t) \ln f(\mathbf{r}, \mathbf{p}, t). \quad (8)$$

Near equilibrium, replacing f by $f_{\text{eq}}(1 + h)$, and expanding (8) up to second order in h , one obtains

$$\begin{aligned} S(t) = S_{\text{eq}} - k_B \iint d\mathbf{r} d\mathbf{p} \left[f_{\text{eq}}(\mathbf{p}) h(\mathbf{r}, \mathbf{p}, t) \right. \\ \left. + f_{\text{eq}}(\mathbf{p}) h(\mathbf{r}, \mathbf{p}, t) \left(\ln [n_{\text{eq}} (2\pi m k_B T_{\text{eq}})^{-3/2}] - \frac{p^2}{2mk_B T} \right) \right. \\ \left. + \frac{1}{2} f_{\text{eq}}(\mathbf{p}) h^2(\mathbf{r}, \mathbf{p}, t) \right] \end{aligned}$$

with

$$S_{\text{eq}} = -k_B \iint dr dp f_{\text{eq}}(p) \ln f_{\text{eq}}(p).$$

Since the total number of gas molecules and the total kinetic energy are constants of the motion, the terms linear in h vanish, so that with the definition (4) for $a(r, p, t)$ one gets

$$S(t) = S_{\text{eq}} - \frac{1}{2} k_B \iint dr dp a^2(\mathbf{r}, \mathbf{p}, t) \quad (9)$$

from which one reads off that the entropy matrix E is given by

$$E(\mathbf{r}, \mathbf{p}; \mathbf{r}', \mathbf{p}') = \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{p} - \mathbf{p}'). \quad (10)$$

Putting this in the fluctuation-dissipation theorem, one finds that (7) becomes

$$\begin{aligned} \langle \tilde{C}(\mathbf{r}, \mathbf{p}, t) \tilde{C}(\mathbf{r}', \mathbf{p}', t') \rangle \\ = 2K(\mathbf{p}, \mathbf{p}') \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (11)$$

The results (6) and (11) can be put in another form by introducing the eigenvalues λ_i (formally assumed to be discrete) and eigenfunctions $\phi_i(\mathbf{p})$ of the kernel $K(\mathbf{p}, \mathbf{p}')$. The ϕ_i 's are orthonormal with respect to the weight function $f_{\text{eq}}(p)/n_{\text{eq}}$, so that

$$\int d\mathbf{p} \frac{1}{n_{\text{eq}}} f_{\text{eq}}(p) \phi_i(\mathbf{p}) \phi_j(\mathbf{p}) = \delta_{ij}. \quad (12)$$

$K(\mathbf{p}, \mathbf{p}')$ has the expansion

$$K(\mathbf{p}, \mathbf{p}') = \sum_{i=1}^{\infty} \lambda_i \phi_i(\mathbf{p}) \phi_i(\mathbf{p}') \quad (13)$$

and expanding $\tilde{C}$ one can write

$$\tilde{C}(\mathbf{r}, \mathbf{p}, t) = \sum_{i=1}^{\infty} \tilde{F}_i(\mathbf{r}, t) \phi_i(\mathbf{p}). \quad (14)$$

Because $K(\mathbf{p}, \mathbf{p}')$ has five zero eigenvalues, which will be taken as the first five corresponding to $i = 1, 2 \dots 5$, the expansions (13) and (14) become sums from $i = 6$ to $i = \infty$. For (13) this is obvious, while for (14) it follows from (11), since (11) requires that $\tilde{F}_i(\mathbf{r}, t) = 0$ for $i = 1, 2 \dots 5$. Finally, by expanding $h(r, p, t)$ in the form

$$h(\mathbf{r}, \mathbf{p}, t) = \sum_{i=1}^{\infty} a_i(\mathbf{r}, t) \phi_i(\mathbf{p}) \quad (15)$$

one easily shows that (6) becomes

$$\begin{aligned} \frac{\partial}{\partial t} a_i(\mathbf{r}, t) + \int B_{ik, \alpha} \frac{\partial}{\partial x_\alpha} a_k(\mathbf{r}', t) dr' \\ = -\lambda_i a_i(\mathbf{r}, t) + \tilde{F}_i(\mathbf{r}, t), \end{aligned} \quad (16)$$

where $B_{ik, \alpha}$ is defined by

$$B_{ik, \alpha} = \int d\mathbf{p} \frac{1}{n_{\text{eq}}} f_{\text{eq}}(p) \phi_i(\mathbf{p}) \frac{p_\alpha}{m} \phi_k(\mathbf{p}), \quad (17)$$

and the fluctuating $\tilde{F}_i$ have average value zero and satisfy

$$\begin{aligned} \langle \tilde{F}_i(\mathbf{r}, t) \tilde{F}_k(\mathbf{r}', t') \rangle \\ = 2\lambda_i \delta_{ik} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (18)$$

The form (16) of the Boltzmann equation with fluctuations will be used in the following two sections of this paper.

III. CONSISTENCY WITH FLUCTUATING HYDRODYNAMICS

In Ref. 1 it was shown that the theory of hydrodynamical fluctuations leads to the Langevin equation for the motion of a Brownian particle. It is, therefore, of interest to see if the theory of μ -space fluctuations can give rise to the theory of hydrodynamical fluctuations. We saw that for the complete description of the gas in μ space *all* the functions $a_i(\mathbf{r}, t)$ are required, while for the theory of hydrodynamical fluctuations only the five hydrodynamical variables are needed. Note that these five variables are related to the first five coefficients $a_i(\mathbf{r}, t)$ in the expansion (15) of $h(\mathbf{r}, \mathbf{p}, t)$ and that these are associated with the five zero eigenvalues of the kernel $K(\mathbf{p}, \mathbf{p}')$. One should expect, therefore, that the first five of the $a_i(\mathbf{r}, t)$ will vary in time much slower than the other $a_i(\mathbf{r}, t)$, which is the reason why a contraction of the description from μ space to hydrodynamics is possible. An unambiguous mathematical procedure for effecting such a contraction was first developed by Enskog,^{5,8} who used it for the derivation of the Navier-Stokes equations from the Boltzmann equation. We will use the same method to derive the hydrodynamical fluctuations from the μ -space fluctuations.

We first note that the five zero-eigenvalue eigenfunctions of $K(\mathbf{p}, \mathbf{p}')$ are explicitly⁹

$$\begin{aligned} \phi_1(\mathbf{p}) = 1; \quad \phi_\alpha(\mathbf{p}) = (mk_B T_{\text{eq}})^{-1/2} p_\alpha, \\ \phi_5(\mathbf{p}) = \left(\frac{2}{3}\right)^{1/2} (k_B T_{\text{eq}})^{-1} \left(\frac{p^2}{2m} - \frac{3}{2} k_B T_{\text{eq}}\right). \end{aligned} \quad (19)$$

To check the orthonormality conditions one needs the integrals

$$\begin{aligned} \int d\mathbf{p} \frac{1}{n_{\text{eq}}} f_{\text{eq}}(p) p_\alpha p_\beta = mk_B T_{\text{eq}} \delta_{\alpha\beta}, \\ \int d\mathbf{p} \frac{1}{n_{\text{eq}}} f_{\text{eq}}(p) \frac{p^2}{2m} p_\alpha p_\beta = \frac{5}{2} m (k_B T_{\text{eq}})^2 \delta_{\alpha\beta}. \end{aligned}$$

The five hydrodynamical variables: density, local velocity, and local temperature, are defined in the linearized regime by

$$\begin{aligned}\Delta n(\mathbf{r}, t) &\equiv n(\mathbf{r}, t) - n_{\text{eq}} = \int d\mathbf{p} f_{\text{eq}}(\mathbf{p}) h(\mathbf{r}, \mathbf{p}, t), \\ n_{\text{eq}} u_{\alpha}(\mathbf{r}, t) &= \int d\mathbf{p} f_{\text{eq}}(\mathbf{p}) \frac{p_{\alpha}}{m} h(\mathbf{r}, \mathbf{p}, t), \\ \frac{3}{2} k_B \Delta T(\mathbf{r}, t) &+ \frac{3}{2} \frac{k_B T_{\text{eq}}}{n_{\text{eq}}} \Delta n(\mathbf{r}, t) \\ &= \frac{1}{n_{\text{eq}}} \int d\mathbf{p} f_{\text{eq}}(\mathbf{p}) \frac{p^2}{2m} h(\mathbf{r}, \mathbf{p}, t),\end{aligned}\quad (20)$$

where $\Delta T(\mathbf{r}, t) = T(\mathbf{r}, t) - T_{\text{eq}}$. Note that the left-hand side of (20) is also $(3/2n_{\text{eq}}) \Delta p(\mathbf{r}, t)$ where $\Delta p(\mathbf{r}, t)$ is the deviation of the pressure from the equilibrium value.

Following Enskog we now introduce a scaling parameter θ and expand $h(\mathbf{r}, \mathbf{p}, t)$ formally in a series in $1/\theta$

$$h(\mathbf{r}, \mathbf{p}, t) = h_0(\mathbf{r}, \mathbf{p}, t) + \frac{1}{\theta} h_1(\mathbf{r}, \mathbf{p}, t) + \frac{1}{\theta^2} h_2(\mathbf{r}, \mathbf{p}, t) + \cdots$$

Similarly, the time derivative is formally expanded

$$\frac{\partial}{\partial t} = \frac{\partial_0}{\partial t} + \frac{1}{\theta} \frac{\partial_1}{\partial t} + \frac{1}{\theta^2} \frac{\partial_2}{\partial t} + \cdots$$

Finally, we assume $K(\mathbf{p}, \mathbf{p}')$ to be of order θ and $\tilde{C}(\mathbf{r}, \mathbf{p}, t)$ to be of order zero in θ . Putting $K = \theta \bar{K}$, then $\bar{K}$ is of order zero and has eigenvalues $\bar{\lambda}_i = \lambda_i/\theta$. Introducing these expansions in the linearized Boltzmann equation with fluctuations (6) and equating equal powers of θ , one obtains the set of equations

$$\int d\mathbf{p}' \bar{K}(\mathbf{p}, \mathbf{p}') f_{\text{eq}}(\mathbf{p}') h_0(\mathbf{r}, \mathbf{p}', t) = 0, \quad (21)$$

$$\begin{aligned}\left(\frac{\partial_0}{\partial t} + \frac{p_{\alpha}}{m} \frac{\partial}{\partial x_{\alpha}}\right) h_0 \\ = - \int d\mathbf{p}' \bar{K}(\mathbf{p}, \mathbf{p}') f_{\text{eq}}(\mathbf{p}') h_1(\mathbf{r}, \mathbf{p}', t) + \tilde{C}(\mathbf{r}, \mathbf{p}, t),\end{aligned}\quad (22)$$

$$\begin{aligned}\left(\frac{\partial_0}{\partial t} + \frac{p_{\alpha}}{m} \frac{\partial}{\partial x_{\alpha}}\right) h_1 + \frac{\partial_1}{\partial t} h_0 \\ = - \int d\mathbf{p}' \bar{K}(\mathbf{p}, \mathbf{p}') f_{\text{eq}}(\mathbf{p}') h_2(\mathbf{r}, \mathbf{p}', t),\end{aligned}\quad (23)$$

$$\begin{aligned}\left(\frac{\partial_0}{\partial t} + \frac{p_{\alpha}}{m} \frac{\partial}{\partial x_{\alpha}}\right) h_2 + \frac{\partial_1}{\partial t} h_1 + \frac{\partial_2}{\partial t} h_0 \\ = - \int d\mathbf{p}' \bar{K}(\mathbf{p}, \mathbf{p}') f_{\text{eq}}(\mathbf{p}') h_3(\mathbf{r}, \mathbf{p}', t),\end{aligned}\quad (24)$$

and so on!

The solutions of these equations are obtained by invoking solubility and uniqueness conditions at each order of $1/\theta$. The uniqueness conditions are expressed by assuming that in the eigenfunction expansions of the successive approximations $h_n(\mathbf{r}, \mathbf{p}, t)$ only $h_0(\mathbf{r}, \mathbf{p}, t)$ contains the first five eigenfunctions (19). Therefore if

$$h_n(\mathbf{r}, \mathbf{p}, t) = \sum_i a_i^{(n)}(\mathbf{r}, t) \phi_i(\mathbf{p}), \quad (25)$$

then it is assumed that

$$a_i^{(n)}(\mathbf{r}, t) = 0 \quad \text{for } l = 1, 2 \cdots 5 \quad \text{and } n > 0. \quad (26)$$

That this leads to uniqueness of the solutions for $h_n(\mathbf{r}, \mathbf{p}, t)$ will become evident as the computation proceeds.

Clearly from (21) it follows that h_0 is a linear combination of the first five eigenfunctions. Therefore

$$h_0(\mathbf{r}, \mathbf{p}, t) = \sum_{i=1}^5 a_i^{(0)}(\mathbf{r}, t) \phi_i(\mathbf{p}). \quad (27)$$

The uniqueness conditions (26) imply that the hydrodynamical quantities (20) are determined exclusively by $h_0(\mathbf{r}, \mathbf{p}, t)$. In fact, one easily obtains

$$\begin{aligned}a_1^{(0)}(\mathbf{r}, t) &= n_{\text{eq}}^{-1} \Delta n(\mathbf{r}, t), \\ a_{\alpha}^{(0)}(\mathbf{r}, t) &= \left(\frac{m}{k_B T_{\text{eq}}}\right)^{1/2} u_{\alpha}(\mathbf{r}, t), \\ a_5^{(0)}(\mathbf{r}, t) &= \left(\frac{3}{2}\right)^{1/2} T_{\text{eq}}^{-1} \Delta T(\mathbf{r}, t).\end{aligned}\quad (28)$$

In order to solve (22) one must impose the solubility condition that the left-hand side is orthogonal to the first five eigenfunctions since from our assumptions it follows that the right-hand side is orthogonal to these functions. This leads to the conditions

$$\frac{\partial_0}{\partial t} a_i^{(0)}(\mathbf{r}, t) + \sum_{k=1}^5 B_{ik,\alpha} \frac{\partial}{\partial x_{\alpha}} a_k^{(0)}(\mathbf{r}, t) = 0 \quad (29)$$

for $l = 1, 2 \cdots 5$. The $B_{ik,\alpha}$ are defined by (17) and can easily be calculated for $l, k = 1, 2 \cdots 5$. Using (28) one then verifies that (29) are just the linearized Euler hydrodynamical equations:

$$\begin{aligned}\frac{\partial_0}{\partial t} \Delta n(\mathbf{r}, t) + n_{\text{eq}} \frac{\partial}{\partial x_{\alpha}} u_{\alpha}(\mathbf{r}, t) &= 0, \\ mn_{\text{eq}} \frac{\partial_0}{\partial t} u_{\alpha}(\mathbf{r}, t) &= - \frac{\partial}{\partial x_{\alpha}} \Delta p(\mathbf{r}, t),\end{aligned}\quad (30)$$

$$n_{\text{eq}} k_B \frac{\partial_0}{\partial t} \Delta T(\mathbf{r}, t) = - \frac{2}{3} n_{\text{eq}} k_B T_{\text{eq}} \frac{\partial}{\partial x_{\alpha}} u_{\alpha}(\mathbf{r}, t).$$

These equations may be viewed as defining the zero-order time derivative $\partial_0/\partial t$. Note that to this

order of approximation the fluctuating forces $\tilde{C}(\mathbf{r}, \mathbf{p}, t)$ do not contribute, corresponding to the fact that the Euler equations do not contain any dissipative effects. Finally, if the conditions (29) are satisfied, then the uniqueness condition guarantees that (22) leads to a unique solution for $h_i(\mathbf{r}, \mathbf{p}, t)$, and one finds, for the expansion coefficients,

$$a_i^{(1)}(\mathbf{r}, t) = \frac{1}{n_{eq}\bar{\lambda}_i} \left(\tilde{F}_i(\mathbf{r}, t) - \sum_{k=1}^5 B_{ik,\alpha} \frac{\partial}{\partial x_\alpha} a_k^{(0)}(\mathbf{r}, t) \right) \quad (31)$$

for $l > 5$.

In this way one can go on. The solubility conditions for (23) become

$$\frac{\partial}{\partial t} a_i^{(0)}(\mathbf{r}, t) = - \sum_{k=6}^{\infty} B_{ik,\alpha} \frac{\partial}{\partial x_\alpha} a_k^{(1)}(\mathbf{r}, t) \quad (32)$$

for $l = 1, 2 \dots 5$. Substituting (31) into (32) gives

$$\begin{aligned} \frac{\partial}{\partial t} a_i^{(0)}(\mathbf{r}, t) &= \frac{1}{n_{eq}} \sum_{k=6}^{\infty} \sum_{j=6}^{\infty} B_{ik,\alpha} \frac{1}{\bar{\lambda}_k} B_{kj,\beta} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} a_j^{(0)}(\mathbf{r}, t) \\ &\quad - \frac{1}{n_{eq}} \sum_{k=6}^{\infty} B_{ik,\alpha} \frac{1}{\bar{\lambda}_k} \frac{\partial}{\partial x_\alpha} \tilde{F}_k(\mathbf{r}, t). \end{aligned} \quad (33)$$

For the case of spherically symmetric intermolecular potentials, which is the case we always have in mind, the $\phi_i(\mathbf{p})$ are either even or odd under the reflection operation $\mathbf{p} \leftrightarrow -\mathbf{p}'$. From the definition (17) of the $B_{ik,\alpha}$ one then shows that¹⁰

$$B_{ik,\alpha} \frac{1}{\bar{\lambda}_k} B_{kj,\beta} = 0 \quad (34)$$

unless $\phi_i(\mathbf{p})$ and $\phi_j(\mathbf{p})$ have the same parity under $\mathbf{p} \leftrightarrow -\mathbf{p}'$. Keeping this in mind, and using the following definitions:

$$\Pi_{\alpha\beta} = \frac{m}{\theta} \sum_{k=6}^{\infty} B_{\mu k,\alpha} \frac{1}{\bar{\lambda}_k} B_{k\nu,\beta}, \quad (35)$$

$$Q_{\alpha\beta} = \frac{3k_B}{2\theta} \sum_{k=6}^{\infty} B_{5k,\alpha} \frac{1}{\bar{\lambda}_k} B_{k5,\beta},$$

$$P_{\alpha\beta}^{(1)}(\mathbf{r}, t) = -\Pi_{\alpha\beta,\mu\nu} \frac{\partial}{\partial x_\nu} u_\mu(\mathbf{r}, t), \quad (36)$$

$$q_\alpha^{(1)}(\mathbf{r}, t) = -Q_{\alpha\beta} \frac{\partial}{\partial x_\beta} \Delta T(\mathbf{r}, t),$$

$$\tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}, t) = (mk_B T_{eq})^{1/2} \frac{1}{\theta} \sum_{k=6}^{\infty} B_{\alpha k,\beta} \frac{1}{\bar{\lambda}_k} \tilde{F}_k(\mathbf{r}, t), \quad (37)$$

$$\tilde{q}_\alpha^{(1)}(\mathbf{r}, t) = \left(\frac{3}{2}\right)^{1/2} \frac{k_B T_{eq}}{\theta} \sum_{k=6}^{\infty} B_{5k,\alpha} \frac{1}{\bar{\lambda}_k} \tilde{F}_k(\mathbf{r}, t),$$

Eqs. (33) can be written in the form

$$\frac{\partial}{\partial t} \Delta n(\mathbf{r}, t) = 0,$$

$$mn_{eq} \frac{\partial}{\partial t} u_\alpha(\mathbf{r}, t) = -\theta \frac{\partial}{\partial x_\beta} (P_{\alpha\beta}^{(1)} + \tilde{P}_{\alpha\beta}^{(1)}), \quad (38)$$

$$\frac{3}{2} n_{eq} k_B \frac{\partial}{\partial t} \Delta T(\mathbf{r}, t) = -\theta \frac{\partial}{\partial x_\alpha} (q_\alpha^{(1)} + \tilde{q}_\alpha^{(1)}),$$

where we have again introduced the hydrodynamical variables by (28). These equations can be looked upon as defining the first-order time derivative $\partial/\partial t$. Combining (30) and (38) then gives the hydrodynamical equations with fluctuations to order $1/\theta$. One gets

$$\frac{\partial}{\partial t} \Delta n(\mathbf{r}, t) + n_{eq} \frac{\partial}{\partial x_\alpha} u_\alpha(\mathbf{r}, t) = 0,$$

$$\begin{aligned} mn_{eq} \frac{\partial}{\partial t} u_\alpha(\mathbf{r}, t) + \frac{\partial}{\partial x_\alpha} \Delta p(\mathbf{r}, t) \\ = -\frac{\partial}{\partial x_\beta} (P_{\alpha\beta}^{(1)} + \tilde{P}_{\alpha\beta}^{(1)}), \end{aligned} \quad (39)$$

$$\begin{aligned} \frac{3}{2} n_{eq} k_B \frac{\partial}{\partial t} \Delta T(\mathbf{r}, t) + n_{eq} k_B T_{eq} \frac{\partial}{\partial x_\alpha} u_\alpha(\mathbf{r}, t) \\ = \frac{\partial}{\partial x_\alpha} (q_\alpha^{(1)} + \tilde{q}_\alpha^{(1)}). \end{aligned}$$

Finally using the correlation formula (18) for the fluctuating forces $\tilde{F}(\mathbf{r}, t)$ from (37) one obtains the correlation formula for the fluctuating stress and heat flux in the form

$$\begin{aligned} \langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}, t) \tilde{P}_{\mu\nu}^{(1)}(\mathbf{r}', t') \rangle \\ = 2k_B T_{eq} \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') \Pi_{\alpha\beta,\mu\nu}, \\ \langle \tilde{q}_\alpha^{(1)}(\mathbf{r}, t) \tilde{q}_\beta^{(1)}(\mathbf{r}', t') \rangle \\ = 2k_B T_{eq}^2 \delta(t - t') \delta(\mathbf{r} - \mathbf{r}') Q_{\alpha\beta}, \\ \langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}, t) \tilde{q}_\gamma^{(1)}(\mathbf{r}', t') \rangle = 0, \end{aligned} \quad (40)$$

where Π and Q are defined by (35). Except for the explicit form of the stress tensor and heat flux in terms of the transport coefficients, Eqs. (39) and (40) have precisely the form of the Navier-Stokes equations with fluctuations presented in Ref. 1. In the next section we will show that for spherically symmetric intermolecular potentials the conventional form for $P_{\alpha\beta}$ and q_α follows from (36) and that Eqs. (40) reduce to the Landau-Lifshitz correlation formula.

By continuing the Enskog procedure one obtains the so-called higher order hydrodynamical equation of which the second order was developed in detail

by Burnett.¹¹ With our adaptation of the Enskog procedure one obtains, in second order, the linearized Burnett equations with new fluctuation terms. Since the method is straightforward, we only present the results. Using the following list of definitions:

$$D_{\mu\alpha, \nu\beta} = \frac{m}{n_{\text{eq}}\theta^2} \sum_{k=6}^{\infty} B_{\mu k, \alpha} \frac{1}{(\bar{\lambda}_k)^2} B_{k\nu, \beta},$$

$$D'_{\alpha\beta} = \frac{3k_B}{2n_{\text{eq}}\theta^2} \sum_{k=6}^{\infty} B_{5k, \alpha} \frac{1}{(\bar{\lambda}_k)^2} B_{k5, \beta}, \quad (41)$$

$$Q_{\mu\alpha, \beta\gamma} = \frac{1}{n_{\text{eq}}\theta^2} \left(\frac{3}{2} m k_B T_{\text{eq}} \right)^{1/2} \sum_{k=6}^{\infty} B_{\mu k, \alpha} \frac{1}{\bar{\lambda}_k} \sum_{i=6}^{\infty} B_{ki, \beta} \frac{1}{\bar{\lambda}_i} B_{i5, \gamma},$$

$$P_{\alpha\beta}^{(2)}(\mathbf{r}, t) = \frac{1}{T_{\text{eq}}} Q_{\alpha\beta, \mu\nu} \frac{\partial^2}{\partial x_\mu \partial x_\nu} \Delta T(\mathbf{r}, t) + D_{\alpha\beta, \mu\nu} \frac{\partial}{\partial x_\nu} \frac{\partial_0}{\partial t} u_\mu(\mathbf{r}, t), \quad (42)$$

$$q_\alpha^{(2)}(\mathbf{r}, t) = Q_{\mu\nu, \alpha\beta} \frac{\partial^2}{\partial x_\nu \partial x_\beta} u_\mu(\mathbf{r}, t) + D'_{\alpha\beta} \frac{\partial}{\partial x_\beta} \frac{\partial_0}{\partial t} \Delta T(\mathbf{r}, t),$$

$$\tilde{P}_{\alpha\beta}^{(2)}(\mathbf{r}, t) = -\frac{(mk_B T_{\text{eq}})^{1/2}}{n_{\text{eq}}\theta^2} \sum_{k=6}^{\infty} B_{\alpha k, \beta} \left(\frac{1}{(\bar{\lambda}_k)^2} \frac{\partial_0}{\partial t} \tilde{F}_k(\mathbf{r}, t) + \frac{1}{\bar{\lambda}_k} \sum_{i=6}^{\infty} B_{ki, \gamma} \frac{\partial}{\partial x_\gamma} \frac{1}{\bar{\lambda}_i} \tilde{F}_i(\mathbf{r}, t) \right), \quad (43)$$

$$\tilde{q}_\alpha^{(2)}(\mathbf{r}, t) = -\left(\frac{3}{2}\right)^{1/2} \frac{k_B T_{\text{eq}}}{n_{\text{eq}}\theta^2} \sum_{k=6}^{\infty} B_{5k, \alpha} \left(\frac{1}{(\bar{\lambda}_k)^2} \frac{\partial_0}{\partial t} \tilde{F}_k(\mathbf{r}, t) + \frac{1}{\bar{\lambda}_k} \sum_{i=6}^{\infty} B_{ki, \gamma} \frac{\partial}{\partial x_\gamma} \frac{1}{\bar{\lambda}_i} \tilde{F}_i(\mathbf{r}, t) \right),$$

one obtains for the second-order time derivatives of the hydrodynamical variables:

$$\frac{\partial_2}{\partial t} \Delta n(\mathbf{r}, t) = 0,$$

$$mn_{\text{eq}} \frac{\partial_2}{\partial t} u_\alpha(\mathbf{r}, t) = -\theta^2 \frac{\partial}{\partial x_\beta} (P_{\alpha\beta}^{(2)} + \tilde{P}_{\alpha\beta}^{(2)}), \quad (44)$$

$$\frac{3}{2} n_{\text{eq}} k_B \frac{\partial_2}{\partial t} \Delta T(\mathbf{r}, t) = -\theta^2 \frac{\partial}{\partial x_\alpha} (q_\alpha^{(2)} + \tilde{q}_\alpha^{(2)}).$$

Added to the zeroth- and first-order results (30) and (38) this leads to the linearized Burnett equations with fluctuations. For the second-order fluctuation terms (43) one finds the correlation formula

$$\langle \tilde{P}_{\alpha\beta}^{(2)}(\mathbf{r}, t) \tilde{q}_\gamma^{(1)}(\mathbf{r}', t') \rangle$$

$$= -2k_B T_{\text{eq}} \delta(t - t') Q_{\alpha\beta, \nu\gamma} \frac{\partial}{\partial x_\nu} \delta(\mathbf{r} - \mathbf{r}'),$$

$$\langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}, t) \tilde{q}_\gamma^{(2)}(\mathbf{r}', t') \rangle$$

$$= -2k_B T_{\text{eq}} \delta(t - t') Q_{\alpha\beta, \nu\gamma} \frac{\partial}{\partial x_\nu} \delta(\mathbf{r} - \mathbf{r}'), \quad (45)$$

$$\langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}, t) \tilde{P}_{\mu\nu}^{(2)}(\mathbf{r}', t') \rangle$$

$$= -2k_B T_{\text{eq}} \delta(\mathbf{r} - \mathbf{r}') D_{\alpha\beta, \mu\nu} \frac{\partial_0}{\partial t'} \delta(t - t'),$$

$$\langle \tilde{q}_\alpha^{(1)}(\mathbf{r}, t) \tilde{q}_\beta^{(2)}(\mathbf{r}', t') \rangle$$

$$= -2k_B T_{\text{eq}}^2 \delta(\mathbf{r} - \mathbf{r}') D'_{\alpha\beta} \frac{\partial_0}{\partial t'} \delta(t - t').$$

Note that in the definitions (42) and (43) of the second-order quantities and in (45) the zeroth-order time derivative $\partial_0/\partial t$ appears. Where it acts on the hydrodynamical variables directly as in (42), one can express the results in space derivatives by using the definitions (30). In the fluctuation terms, which are fluctuating *forces*, (30) should be used after their effect on the hydrodynamical variables has been made explicit.¹²

Finally one should point out that, while the first-order or Navier-Stokes equations with fluctuations are an example of a stationary Gaussian Markov process as shown in Ref. 1, the second-order or Burnett equations with fluctuations do *not* fit into the same general framework. This is most readily observed by noting that for instance $\langle q_\alpha^{(2)}(\mathbf{r}, t) q_\beta^{(2)}(\mathbf{r}', t') \rangle$ does not correspond to any dissipative constant of the average Burnett equations since it must contribute to the equations of the next order in $1/\theta$.

IV. FURTHER SIMPLIFICATIONS FOR SPHERICALLY SYMMETRIC POTENTIALS

Since for a spherically symmetric intermolecular potential the kernel $K(\mathbf{p}, \mathbf{p}')$ is isotropic, one knows that the eigenfunctions $\phi_k(\mathbf{p})$ are the product of a radial function of p and a spherical harmonic in the angles defining the direction of $\mathbf{p}$. Instead of spherical harmonics it is more convenient to use spherical tensors in $\mathbf{p}$ since these exhibit more clearly the tensorial properties of the quantities $\Pi_{\mu\nu, \alpha\beta}$, $Q_{\alpha\beta}$ which we want to calculate. We, therefore, make the replacement

$$\phi_k(\mathbf{p}) \rightarrow R_{r,l}(p) p^{-l} \langle p_{\mu_1} p_{\mu_2} \cdots p_{\mu_l} \rangle, \quad (46)$$

where r, l depend on k and $\langle p_{\mu_1} \cdots p_{\mu_l} \rangle$ is a completely symmetric and homogeneous polynomial

of degree l in the p_μ for which, in addition, all possible traces are zero. Examples are

$$\langle p_\mu p_\nu \rangle = p_\mu p_\nu - \frac{1}{3} p^2 \delta_{\mu\nu}, \quad (47)$$

$$\langle p_\alpha p_\beta p_\gamma \rangle = p_\alpha p_\beta p_\gamma - \frac{1}{5} p^2 (p_\alpha \delta_{\beta\gamma} + p_\beta \delta_{\alpha\gamma} + p_\gamma \delta_{\alpha\beta}).$$

In the notation of (46) the five zero-eigenvalue eigenfunctions become

$$\phi_1(\mathbf{p}) \rightarrow R_{00}(p) = 1,$$

$$\phi_\alpha(\mathbf{p}) \rightarrow R_{01}(p) p^{-1} p_\alpha, \quad R_{01}(p) = p(mk_B T_{eq})^{-1/2}, \quad (48)$$

$$\phi_5(\mathbf{p}) \rightarrow R_{10}(p) = \left(\frac{2}{3}\right)^{1/2} (k_B T_{eq})^{-1} \left(\frac{p^2}{2m} - \frac{3}{2} k_B T_{eq} \right).$$

One now must compute the $B_{\mu i, \alpha}$, $B_{5j, \alpha}$, and $B_{ik, \alpha}$ for $j, k > 6$. From the definition (17), using (47) and (48) one can write

$$B_{\mu i, \alpha} = \frac{(mk_B T_{eq})^{-1/2}}{mn_{eq}} \int d\mathbf{p} f_{eq}(p) [\langle p_\mu p_\alpha \rangle + \frac{1}{3} p^2 \delta_{\mu\alpha}] \phi_i(\mathbf{p}).$$

Since $p^2 \delta_{\mu\alpha}/3$ is a linear combination of $\phi_1(\mathbf{p})$ and $\phi_5(\mathbf{p})$, it makes no contribution to the integral if $j \geq 6$. Also if one writes $\phi_i(\mathbf{p})$ in the form (46), only $l = 2$ contributes, so that one obtains

$$B_{\mu i, \alpha} = \frac{(mk_B T_{eq})^{-1/2}}{mn_{eq}} \int d\mathbf{p} f_{eq}(p) R_{r2}(p) p^{-2} \langle p_\mu p_\alpha \rangle \langle p_\mu p_\alpha \rangle, \quad (49)$$

where the index j corresponds to r, μ_1, μ_2 .

Similarly, one finds for $j \geq 6$

$$B_{5j, \alpha} = \left(\frac{2}{3}\right)^{1/2} (2m^2 n_{eq} k_B T_{eq})^{-1} \int d\mathbf{p} f_{eq}(p) R_{r1}(p) p p_\alpha p_\mu, \quad (50)$$

where the index j now corresponds to r, μ . The general $B_{ik, \alpha}$ term for $j, k \geq 6$ is only needed for the computation of $Q_{\mu\alpha, \beta\gamma}$ and from the definition (41) it may be seen that this requires only the spherical tensor of order 2 in $\phi_i(\mathbf{p})$ and of order 1 in $\phi_k(\mathbf{p})$ because of (49) and (50). For these values one can write

$$B_{ik, \alpha} = \frac{1}{mn_{eq}} \int d\mathbf{p} f_{eq}(p) R_{r2}(p) R_{s1}(p) p^{-1} p_\nu \langle p_\mu p_\alpha \rangle, \quad (51)$$

where the indices j, k correspond to r, μ_1, μ_2 and s, ν , respectively.

Using the following integral theorems:

$$\begin{aligned} \int d\mathbf{p} f_{eq}(p) F(p) \langle p_i p_j \rangle \langle p_\alpha p_\beta \rangle \\ = \frac{1}{15} (\delta_{i\alpha} \delta_{j\beta} + \delta_{i\beta} \delta_{j\alpha} - \frac{2}{3} \delta_{ij} \delta_{\alpha\beta}) \\ \cdot \int d\mathbf{p} f_{eq}(p) p^4 F(p), \end{aligned}$$

$$\int d\mathbf{p} f_{eq}(p) F(p) p_i p_j = \frac{1}{3} \delta_{ij} \int d\mathbf{p} f_{eq}(p) p^2 F(p)$$

which hold for any scalar function $F(p)$, the integrals (49), (50), and (51) become

$$\begin{aligned} B_{\mu i, \alpha} &= \frac{(mk_B T_{eq})^{-1/2}}{15mn_{eq}} \int d\mathbf{p} f_{eq}(p) p^2 R_{r2}(p) \\ &\quad \cdot (\delta_{\mu\mu_1} \delta_{\alpha\mu_2} + \delta_{\mu\mu_2} \delta_{\alpha\mu_1} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\mu_1\mu_2}), \\ B_{5j, \alpha} &= \left(\frac{2}{3}\right)^{1/2} (6m^2 n_{eq} k_B T_{eq})^{-1} \int d\mathbf{p} f_{eq}(p) p^3 R_{r1}(p) \delta_{\alpha\mu}, \\ B_{ik, \alpha} &= \frac{1}{15mn_{eq}} \int d\mathbf{p} f_{eq}(p) p R_{r2}(p) R_{s1}(p) \\ &\quad \cdot (\delta_{\alpha\mu_1} \delta_{\nu\mu_2} + \delta_{\alpha\mu_2} \delta_{\nu\mu_1} - \frac{2}{3} \delta_{\alpha\nu} \delta_{\mu_1\mu_2}). \end{aligned}$$

Using these expressions and the following abbreviations:

$$N_{r2} = \frac{(mk_B T_{eq})^{-1/2}}{15mn_{eq}} \int d\mathbf{p} f_{eq}(p) p^2 R_{r2}(p),$$

$$N_{r1} = \left(\frac{2}{3}\right)^{1/2} (6m^2 n_{eq} k_B T_{eq})^{-1} \int d\mathbf{p} f_{eq}(p) p^3 R_{r1}(p),$$

$$N_{r2, s1} = \frac{1}{15mn_{eq}} \int d\mathbf{p} f_{eq}(p) p R_{r2}(p) R_{s1}(p) \quad (52)$$

the basic tensors (35) and (41) can be written in the form

$$\begin{aligned} \Pi_{\mu\alpha, \nu\beta} &= 2m \sum_{r=0}^{\infty} \frac{1}{\lambda_{r2}} (N_{r2})^2 \\ &\quad \cdot (\delta_{\mu\nu} \delta_{\alpha\beta} + \delta_{\mu\beta} \delta_{\nu\alpha} - \frac{2}{3} \delta_{\mu\alpha} \delta_{\nu\beta}), \end{aligned} \quad (53)$$

$$Q_{\alpha\beta} = \frac{3}{2} k_B \sum_{r=1}^{\infty} \frac{1}{\lambda_{r1}} (N_{r1})^2 \delta_{\alpha\beta}, \quad (54)$$

$$\begin{aligned} D_{\mu\alpha, \nu\beta} &= \frac{2m}{n_{eq}} \sum_{r=0}^{\infty} \left(\frac{1}{\lambda_{r2}} N_{r2} \right)^2 \\ &\quad \cdot (\delta_{\mu\nu} \delta_{\alpha\beta} + \delta_{\mu\beta} \delta_{\nu\alpha} - \frac{2}{3} \delta_{\mu\alpha} \delta_{\nu\beta}), \end{aligned} \quad (55)$$

$$D'_{\alpha\beta} = \frac{3k_B}{2n_{eq}} \sum_{r=1}^{\infty} \left(\frac{1}{\lambda_{r1}} N_{r1} \right)^2 \delta_{\alpha\beta}, \quad (56)$$

$$\begin{aligned} Q_{\mu\alpha, \beta\gamma} &= \frac{2}{n_{eq}} \left(\frac{3}{2} m k_B T_{eq} \right)^{1/2} \sum_{r=0}^{\infty} \sum_{s=1}^{\infty} \frac{1}{\lambda_{r2} \lambda_{s1}} N_{r2} N_{s1} N_{r2, s1} \\ &\quad \cdot (\delta_{\alpha\beta} \delta_{\mu\gamma} + \delta_{\alpha\gamma} \delta_{\mu\beta} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\gamma}), \end{aligned} \quad (57)$$

where we have put in evidence the dependence of the eigenvalues λ_k on the indices r and l of the

eigenfunctions in the form (46). Note that (53) and (54) have precisely the same tensor form obtained for fluctuating hydrodynamics as in Ref. 1.

For the special case of the Maxwell model (intermolecular potential k/r^4) the results can be simplified further since all the eigenvalues $\lambda_{r,l}$ and eigenfunctions are known. In this case the radial part of the eigenfunctions will be denoted by $M_{r,l}(p)$ instead of $R_{r,l}(p)$. They are polynomials in p of degree $2r + l$; those corresponding to the zero eigenvalues are, of course, the same as in the general case [see (48)]; the explicit form for the first two positive eigenvalues λ_{11} and λ_{02} are

$$M_{11}(p) = \left(\frac{4}{3}\right)^{1/2} (2mk_B T_{eq})^{-3/2} p(p^2 - 5mk_B T_{eq}), \quad (58)$$

$$M_{02}(p) = 2^{1/2} (2mk_B T_{eq})^{-1} p^2.$$

For the same value of l the $M_{r,l}$ are an orthogonal set in r . Using (58), this gives, for the quantities N in (52),

$$N_{r2} = \left(\frac{k_B T_{eq}}{2m}\right)^{1/2} \delta_{r0}; \quad N_{r1} = \left(\frac{5k_B T_{eq}}{3m}\right)^{1/2} \delta_{r1},$$

$$N_{r2,s1} = \left(\frac{k_B T_{eq}}{5m}\right)^{1/2} \delta_{r0} \delta_{s1}.$$

Substituting in Eqs. (53)–(57) and replacing $\lambda_{r,l}$ by $(2k/m)^{1/2} \lambda_{r,l}$ in order to connect with the dimensionless eigenvalues given in the literature,⁶ one obtains, for the numerical coefficients in the tensors (53)–(57), the values

$$\eta = k_B T_{eq} \left(\frac{m}{2k}\right)^{1/2} \frac{1}{\lambda_{02}}; \quad \kappa = \frac{5}{2} \frac{k_B^2 T_{eq}}{m} \left(\frac{m}{2k}\right)^{1/2} \frac{1}{\lambda_{11}},$$

$$D = \frac{k_B T_{eq}}{n_{eq}} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{02}^2}; \quad D' = \frac{5}{2} \frac{k_B^2 T_{eq}}{mn_{eq}} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{11}^2}$$

and

$$Q = \frac{(k_B T_{eq})^2}{mn_{eq}} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{02} \lambda_{11}}.$$

Note that since for Maxwell molecules $\lambda_{11} = \frac{2}{3} \lambda_{02}$ all the coefficients can be expressed in η . As a result one can write, using the definitions (36) and (42), the average stress tensor and heat flux up to the Burnett approximation in the form

$$P_{\alpha\beta} = p \delta_{\alpha\beta} - \eta \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \frac{\partial u_\mu}{\partial x_\mu} \right)$$

$$+ \frac{3\eta^2}{mn_{eq} T_{eq}} \left(\frac{\partial^2}{\partial x_\alpha \partial x_\beta} - \frac{1}{3} \delta_{\alpha\beta} \Delta \right) \Delta T(\mathbf{r}, t)$$

$$- \frac{2\eta^2}{mn_{eq} p_{eq}} \left(\frac{\partial^2}{\partial x_\alpha \partial x_\beta} - \frac{1}{3} \delta_{\alpha\beta} \Delta \right) \Delta p(\mathbf{r}, t), \quad (59)$$

$$q_\alpha = -\frac{15k_B}{4m} \eta \frac{\partial T}{\partial x_\alpha} + \frac{3}{2} \frac{\eta^2}{mn_{eq}} \left(\Delta u_\alpha + \frac{1}{3} \frac{\partial}{\partial x_\alpha} \frac{\partial u_\mu}{\partial x_\mu} \right)$$

$$- \frac{15}{4} \frac{\eta^2}{mn_{eq}} \frac{\partial}{\partial x_\alpha} \frac{\partial u_\mu}{\partial x_\mu}, \quad (60)$$

where Eqs. (30) have been used to eliminate the terms containing $\partial_0/\partial t$. These results agree with those obtained by Wang Chang.¹³

V. AN INTERNAL CONSISTENCY THEOREM

In Ref. 1 the general mathematical formalism for stationary Gaussian Markov processes was presented and it was shown that the linearized Navier–Stokes equations with fluctuations is an example of such a process. In this paper the linearized Boltzmann equation with fluctuations was shown to be another example. Moreover, an adaptation of the Enskog contraction procedure up to second order in the scaling parameter θ , permitted a derivation of the fluctuating hydrodynamical equations from the fluctuating Boltzmann equation. An entirely analogous contraction may be performed on the fluctuating hydrodynamical equations and to second order the result is a diffusion equation for the density $n(\mathbf{r}, t)$ with fluctuations, which is again a stationary Gaussian Markov process. This suggests a general theorem to the effect that the second-order approximation obtained through application of the Enskog contraction procedure always results in a stationary Gaussian Markov process when the initial process is also such a process.

To prove this theorem we will adopt the discrete formalization of stationary Gaussian Markov processes as presented in Ref. 1. It was shown there that, in general, such processes are described by the generalized Langevin equation

$$\frac{da_i}{dt} + A_{ij} a_j = -S_{ij} a_j + \tilde{F}_i,$$

where A_{ij} is antisymmetric, S_{ij} is symmetric with nonnegative eigenvalues, and the $\tilde{F}_i$ have mean value zero and are purely random with correlations

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = (G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{jk}) \delta(t - s),$$

where $G_{ij} = A_{ij} + S_{ij}$ and E_{ij} is a real, symmetric, and positive definite matrix, which is determined by the first probability distribution function for the process

$$W_1(a) = W_0 \exp \left(-\frac{1}{2} a_i E_{ij} a_j \right).$$

In the examples already presented E_{ij} is the entropy matrix.

From the properties of E_{ij} it is easy to show that one can find linear combinations a'_i of the a_i for which the first distribution function becomes

$$W_1(a') = W_0 \exp(-\frac{1}{2}a'_i a'_i)$$

and the Langevin equations

$$\frac{da'_i}{dt} = G'_{ij}a'_j + \tilde{F}'_i,$$

where the matrix G'_{ij} has the same eigenvalues as G_{ij} , so that it may also be written as $G' = A' + S'$ where A' is antisymmetric and S' symmetric with nonnegative eigenvalues. Furthermore, the $\tilde{F}'_i$ are linear combinations of the original $\tilde{F}_i$ with the correlations

$$\langle \tilde{F}'_i(t) \tilde{F}'_j(s) \rangle = 2S'_{ij} \delta(t-s).$$

Finally, the matrix S' may be diagonalized by a unitary transformation and this leads to the following form for the Langevin equation:

$$\frac{da''_i}{dt} + A''_{ij}a''_j = -\lambda''_i a''_i + \tilde{F}''_i, \quad (61)$$

where A''_{ij} is antisymmetric and the $\lambda''_i \geq 0$. The $\tilde{F}''_i$ are again purely random with mean value zero and with the correlations

$$\langle \tilde{F}''_i(t) \tilde{F}''_j(s) \rangle = 2\lambda''_i \delta_{ij} \delta(t-s). \quad (62)$$

Equations (61) and (62) are taken as the canonical form for an arbitrary stationary Gaussian Markov process. In the following the double primes will be omitted.

When some of the λ_i are zero, a contraction of the stationary Gaussian Markov process (61) becomes possible. Suppose the first n of the λ_i are zero. Greek indices will be used to indicate the special values of the Latin indices which are $\leq n$. We again adopt the Enskog contraction procedure by introducing a scaling parameter θ . The a_i are expanded as

$$a_i = a_i^{(0)} + \frac{1}{\theta} a_i^{(1)} + \frac{1}{\theta^2} a_i^{(2)} + \dots \quad (63)$$

Let $\lambda_i = \theta \bar{\lambda}_i$ and assume $\bar{\lambda}_i$ to be of order zero in θ . The $\tilde{F}_i$ are also taken to be of order zero. The time derivative is formally expanded as

$$\frac{d}{dt} = \frac{d_0}{dt} + \frac{1}{\theta} \frac{d_1}{dt} + \frac{1}{\theta^2} \frac{d_2}{dt} + \dots \quad (64)$$

Substituting (63) and (64) in (61) and equating equal powers of θ leads to the series of equations

$$\bar{\lambda}_i a_i^{(0)} = 0, \quad (65)$$

$$\frac{d_0}{dt} a_i^{(0)} + A_{ij} a_j^{(0)} = -\bar{\lambda}_i a_i^{(1)} + \tilde{F}_i, \quad (66)$$

$$\frac{d_0}{dt} a_i^{(1)} + \frac{d_1}{dt} a_i^{(0)} + A_{ij} a_j^{(1)} = -\bar{\lambda}_i a_i^{(2)}, \quad (67)$$

and so on. The solution of (65) is $a_\alpha^{(0)}$ for $\alpha = 1, 2 \dots n$ since $\bar{\lambda}_\alpha = 0$ and $a_i^{(0)} = 0$ for $i > n$ since $\bar{\lambda}_i \neq 0$ for $i > n$. From (62) it is seen that $\tilde{F}_\alpha = 0$ for $\alpha = 1, 2 \dots n$. Therefore, the solubility conditions for (66) are

$$\frac{d_0}{dt} a_\alpha^{(0)} + A_{\alpha\beta} a_\beta^{(0)} = 0. \quad (68)$$

The solution of (66) is unique if we impose the condition $a_\alpha^{(1)} = 0$ for $\alpha = 1, 2 \dots n$, and one obtains

$$a_i^{(1)} = -\frac{1}{\bar{\lambda}_i} (A_{i\alpha} a_\alpha^{(0)} - \tilde{F}_i) \quad (69)$$

for all $i > n$.

The solubility conditions for (67) are

$$\frac{d_1}{dt} a_\alpha^{(0)} + A_{\alpha i} a_i^{(1)} = 0$$

which becomes, by substituting (69),

$$\frac{d_1}{dt} a_\alpha^{(0)} = A_{\alpha i} \frac{1}{\bar{\lambda}_i} A_{i\beta} a_\beta^{(0)} - A_{\alpha i} \frac{1}{\bar{\lambda}_i} \tilde{F}_i. \quad (70)$$

Combining (68) and (70), one obtains, up to order $1/\theta$ in the time derivative, the contracted Langevin equation

$$\frac{d}{dt} a_\alpha^{(0)} + A_{\alpha\beta} a_\beta^{(0)} = -A_{i\alpha} \frac{1}{\bar{\lambda}_i} A_{i\beta} a_\beta^{(0)} + A_{i\alpha} \frac{1}{\bar{\lambda}_i} \tilde{F}_i \quad (71)$$

for the variables $a_\alpha^{(0)}$. It is easy to show that the matrix

$$S_{\alpha\beta} = A_{i\alpha} \frac{1}{\bar{\lambda}_i} A_{i\beta} \quad (72)$$

is symmetric and has nonnegative eigenvalues because A is antisymmetric. Note that the sums over j indicated by the repeated indices in (71) and (72) always go from $j = n+1$ to $j = \infty$ for which $\bar{\lambda}_j > 0$. Note also that the new fluctuating forces $\tilde{F}'_\alpha$ defined by

$$\tilde{F}'_\alpha = A_{i\alpha} \frac{1}{\bar{\lambda}_i} \tilde{F}_i \quad (73)$$

have mean value zero, are purely random, and satisfy

$$\langle \tilde{F}'_\alpha(t) \tilde{F}'_\beta(s) \rangle = 2S_{\alpha\beta} \delta(t-s), \quad (74)$$

where (62) was used. Consequently, the contracted equations (71) and (74) again describe a stationary Gaussian Markov process, as was suggested in the beginning of this section.

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

† Miller Institute for Basic Research in Science Post-doctoral Fellow.

¹ R. F. Fox and G. E. Uhlenbeck, *Phys. Fluids* **13**, 1893 (1970).

² M. Bixon and R. Zwanzig, *Phys. Rev.* **187**, 267 (1969) have independently derived the fluctuation terms in the Boltzmann equation and have also shown that they lead to the Landau-Lifshitz formula for the fluctuating stress tensor and heat flux vector in hydrodynamics. Since these authors use a different method and do not put the theory in the general framework of the stationary Gaussian Markov processes, it did not seem superfluous to present our derivation. Compare also F. L. Hinton, *Phys. Fluids* **13**, 857 (1970).

³ For a short review of the Boltzmann equation see G. E. Uhlenbeck and G. W. Ford, in *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, Rhode Island, 1963), Chap. IV.

⁴ D. Hilbert, *Theorie der Integralgleichungen* (Teubner Verlag, Leipzig, 1912), Chap. 22.

⁵ D. Enskog, Doctoral dissertation, University of Uppsala

(1917), p. 140. Also compare L. Waldmann, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 366.

⁶ C. S. Wang Chang and G. E. Uhlenbeck, Engineering Research Institute, University of Michigan (1952). This report will be reprinted in the *Studies of Statistical Mechanics* (North-Holland, Amsterdam, 1970), Vol. 5. Also compare L. Waldmann, Ref. 5, Sec. 38.

⁷ L. Kuscer and M. M. R. Williams, *Phys. Fluids* **10**, 1922 (1967).

⁸ See also S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1961).

⁹ We use Greek letters for vector or tensor indices. In the numbering of the eigenfunctions φ_l we therefore write α for $l = 2, 3, 4$.

¹⁰ No summation over k is intended. The integrand of the double integral over $\mathbf{p}$ and $\mathbf{p}'$, which one obtains by writing out the left-hand side of (34), is odd under the reflection $\mathbf{p} \rightarrow -\mathbf{p}$, $\mathbf{p}' \rightarrow -\mathbf{p}'$ if φ_i and φ_j have opposite parity.

¹¹ See the discussion in the book by S. Chapman and T. G. Cowling, Ref. 8, Chap. 15.

¹² Note that in (42) the same matrix Q appears in $P_{\alpha\beta}^{(2)}$ and $q_{\alpha}^{(2)}$. Such a symmetry relationship, which also remains in higher approximations, is reminiscent of the Onsager reciprocity relations.

¹³ C. S. Wang Chang, Engineering Research Institute, University of Michigan (1948). This report will be reprinted in Vol. 5 of the *Studies in Statistical Mechanics* (North-Holland Amsterdam, 1970).