

THE PHYSICS OF FLUIDS

VOLUME 3, NUMBER 3

MAY-JUNE, 1960

Nonequilibrium Distribution Functions in a Fluid

J. L. LEBOWITZ

Graduate School of Mathematical Sciences, Yeshiva University, New York

AND

H. L. FRISCH AND E. HELFAND

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received February 8, 1960)

The behavior of a nonequilibrium fluid is analyzed on a level intermediate between that of hydrodynamics, where microstructure is totally ignored, and a phase space description, where the complete N -body problem must be solved. The study of the fluid at this level generally involves solving an appropriate transport equation. For liquids, the primary subject of this investigation, the Fokker-Planck equation of Kirkwood is accepted as a working model and solutions are found by the methods of Chapman and Enskog and of Grad to terms linear in deviations from local equilibrium. (It is argued, however, for a different form of the pair space force than that suggested by Kirkwood and co-workers.) The results are similar in form to distributions found with other kinetic models. Variational principles are also considered. It is shown that the one- and two-particle distribution functions have the property of maximizing the entropy subject to the constraints of given densities and fluxes. Alternatively, these distributions maximize the entropy plus entropy productions in appropriate characteristic times. These variational principles do not depend on the use of the Fokker-Planck equation but appear to possess general validity.

1. INTRODUCTION

OUR aim is to discuss the behavior of nonequilibrium fluids by means of transport equations. This topic has been the subject of extensive study by Kirkwood and co-workers. The approach taken in this paper differs from previous ones in that we solve explicitly for the singlet and pair distribution functions in both positions and momenta. Furthermore, we argue for a different form of the pair space force. Lastly, we consider the use of variational principles which appear to apply to these systems. Before proceeding we shall briefly discuss the kind of assumptions which underlie this type of description of a fluid.

The systems behavior is specified by the N -particle Hamiltonian

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^N \varphi(r_{ij}) + \sum_{i=1}^N U(\mathbf{r}_i), \quad (1.1)$$

where \mathbf{r}_i and \mathbf{p}_i are the Cartesian coordinates and momenta ($i = 1, \dots, N$), $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, U and φ are the external and interparticle potentials, respec-

tively, and m is the mass of each particle. For large N we assume it suffices to replace the description of the actual system by that of a representative system chosen from an appropriately constructed Γ -space ensemble of systems. A point in this space is specified by the configurational coordinates $\mathbf{r}_1, \dots, \mathbf{r}_N$, and the velocities ξ_1, \dots, ξ_N . (If other than Cartesian coordinates are employed the specification must be, of course, in terms of conjugate position and momentum coordinates.) The Γ -space ensemble is described by the distribution function $f_N(\mathbf{r}_1, \dots, \mathbf{r}_N, \xi_1, \dots, \xi_N, t)$ which is symmetric in particle indices and satisfies the Liouville equation. The normalization of f_N is taken to be

$$\int f_N d\mathbf{r}_1 \cdots d\xi_N = N!$$

For many purposes it is not necessary to know f_N but only the lower-order distribution functions $f_n(\mathbf{r}_1, \dots, \mathbf{r}_n, \xi_1, \dots, \xi_n, t)$, $n \ll N$, which represent the probability density for the simultaneous existence of fluid particles at $\mathbf{r}_1, \dots, \mathbf{r}_n$ with velocities

ξ_1, \dots, ξ_n . These are given by

$$f_n = \frac{1}{(N-n)!} \int f_N(\mathbf{r}_1, \dots, \xi_N, t) \cdot d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N d\xi_{n+1} \cdots d\xi_N. \quad (1.2)$$

Because of the nature of the Hamiltonian the hydrodynamic quantities characterizing a fluid, such as the particle and energy densities $n(\mathbf{r})$, $E(\mathbf{r})$, etc., are determined by the one- and two-particle distribution functions f_1 and f_2 ; e.g.,

$$n(\mathbf{r}_1) = \int f_1(\mathbf{r}_1, \xi_1) d\xi_1, \quad (1.3)$$

$$n(\mathbf{r}_1)E(\mathbf{r}_1) = \int \left[\frac{1}{2} m \xi_1^2 + U(\mathbf{r}_1) \right] f_1(\mathbf{r}_1, \xi_1) d\xi_1 + \frac{1}{2} \int \varphi(r_{12}) f_2(\mathbf{r}_1, \mathbf{r}_2, \xi_1, \xi_2) d\xi_1 d\xi_2 d\mathbf{r}_2, \quad (1.4)$$

The integrals involving f_2 always contribute terms proportional to quadratic and higher powers of the density and so are negligible for dilute gases. The properties of such gases are therefore determined by f_1 alone.

It might appear from our discussion so far that we could dispense with f_N altogether and just consider f_1 and f_2 . The difficulty here lies in the fact that the f_n do not determine their own evolution for $n < N$. The f_n obey a continuity equation in the $6n$ dimensional space, Γ_n , of the same form as Liouville's equation,

$$\frac{\partial f_n}{\partial t} + \sum_{i=1}^n \left\{ \xi_i \frac{\partial f_n}{\partial \mathbf{r}_i} + \frac{\partial}{\partial \xi_i} \cdot \left(\frac{1}{m} \mathbf{Y}_i^{(n)} f_n \right) \right\} = 0. \quad (1.5)$$

The force $\mathbf{Y}_i^{(n)}$, however, depends not only on the configuration of the n molecules but also on the rest of the fluid. It is given by

$$\mathbf{Y}_i^{(n)} = - \sum_{\substack{j=1 \\ j \neq i}}^n \frac{\partial}{\partial \mathbf{r}_i} \varphi(r_{ij}) - \frac{\partial U(\mathbf{r}_i)}{\partial \mathbf{r}_i} + \boldsymbol{\Omega}_i^{(n)}. \quad (1.6)$$

The first two terms on the right of Eq. (1.6) are clearly the force on the i th molecule produced by the other $(n-1)$ molecules and external sources, and

$$\boldsymbol{\Omega}_i^{(n)} = - \int \frac{\partial \varphi(r_{i,n+1})}{\partial \mathbf{r}_i} \cdot \left[\frac{f_{n+1}(\mathbf{r}_1, \dots, \xi_{n+1}, t)}{f_n(\mathbf{r}_1, \dots, \xi_n, t)} \right] d\mathbf{r}_{n+1} d\xi_{n+1} \quad (1.7)$$

is the force due to the rest of the fluid. This interpretation of Eq. (1.7) is evident since the ratio (f_{n+1}/f_n) represents the conditional probability den-

sity for the presence of a particle at \mathbf{r}_{n+1} with velocity ξ_{n+1} when the positions and velocities of n particles are known to be $\mathbf{r}_1, \dots, \mathbf{r}_n, \xi_1, \dots, \xi_n$.

Equations (1.5)–(1.7) are the well-known Bogolubov-Yvon-Born-Green-Kirkwood¹ hierarchy of equations. As a special case, for $n = N$, Eq. (1.5) reduces to the full Liouville equation since $\boldsymbol{\Omega}_i^{(N)} \equiv 0$. For all smaller n the evolution of f_n depends on f_{n+1} . In order to obtain a closed set of equations for a set f_m , $m = 1, \dots, n < N$, and eventually the irreversible transport equations of the Boltzmann or Fokker-Planck type, some way has to be found to express f_{n+1} , or at least $\boldsymbol{\Omega}_i^{(n)}$, in terms of f_n , and/or introduce other assumptions, usually of a statistical nature, which insure the appearance of the desired irreversible behavior.^{2,3} We shall not discuss further the general nature of these steps but make reference to the recent comprehensive article by Grad.²

The remainder of this section and the next two sections will be devoted to the one-particle distribution f_1 . The form of this function might be amenable to experimental investigation so that a theoretical prediction of its nature is of importance. The techniques and results of this analysis will also prove useful for the subsequent investigation of f_2 .

Historically the first nonequilibrium situation to be investigated extensively, and the only one which may be regarded as understood in principle, is that of transport in dilute gases. For a dilute gas the hierarchy is broken at $n = 1$, and irreversibility introduced by: (1) assuming that only binary collisions occur, and (2) making the molecular chaos assumption on f_2 , by means of which f_2 before each "collision" may be written as a product of f_1 . If, furthermore, f_1 varies slowly on a molecular scale with position, there results the Boltzmann integro-differential equation for $f(\mathbf{r}, \xi, t)$ (subscript 1 will be omitted when obvious from here on).

The mathematical difficulties of solving the Boltzmann equation have made it worthwhile to look for alternatives or modifications which convey essentially an equivalent amount of physical information. Such an equation has been suggested by Bhatnager, Gross, and Krook⁴ in which the collision term has been modified.

¹ J. G. Kirkwood, *J. Chem. Phys.* **14**, 180 (1946).

² H. Grad, *Encyclopedia of Physics*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1958), Vol. XII, p. 205.

³ H. L. Frisch, *J. Chem. Phys.* **22**, 1713 (1954).

⁴ P. L. Bhatnager, E. P. Gross, and M. Krook, *Phys. Rev.* **94**, 511 (1954).

$$\frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}}{m} \cdot \frac{\partial f}{\partial \xi} = \nu(f^{(0)} - f). \quad (1.8)$$

$f^0(\mathbf{r}, \xi)$ is the locally Maxwellian distribution function

$$f^{(0)} = n(\mathbf{r}, t) \left[\frac{m}{2\pi kT(\mathbf{r}, t)} \right]^{\frac{3}{2}} \cdot \exp \left\{ -\frac{m[\xi - \mathbf{u}(\mathbf{r}, t)]^2}{2kT(\mathbf{r}, t)} \right\}, \quad (1.9)$$

where n is the number density [cf. Eq. (1.3)], \mathbf{u} is the mean velocity

$$\mathbf{u}(\mathbf{r}, t) = \int \xi f(\mathbf{r}, \xi, t) d\xi / n(\mathbf{r}, t), \quad (1.10)$$

and $T(\mathbf{r}, t)$ is the local temperature defined by

$$kT(\mathbf{r}, t) = \frac{1}{2} \int m(\xi - \mathbf{u})^2 f(\mathbf{r}, \xi, t) d\xi / n(\mathbf{r}, t). \quad (1.11)$$

The parameter ν , the collision frequency, is taken to be a function of n , \mathbf{u} , and T and plays the role of the reciprocal of the relaxation time in this theory. The basic physical assumption which underlies the modified Boltzmann equation [Eq. (1.8)], that the collision frequency is independent of the relative speed of the colliding molecules, is strictly justifiable, even in a linearized theory, only in the case of Maxwellian molecules.

In a different approach, specifically adapted to liquids, Kirkwood¹ approximates $\Omega_i^{(n)}$, for $n \ll N$, in Eq. (1.7) in a manner similar to that employed in the theory of Brownian motion. This leads to Fokker-Planck type equations for the lower-order distributions, f_n , particularly f_1 and f_2 . The equations derived by Kirkwood actually refer not to the f_n themselves but rather to the \bar{f}_n which are the average values of the f_n over a time interval τ . This interval is supposedly arbitrary, within certain limits, and is physically determined by the resolution of the instruments employed in the measurement of the macroscopic variables. In our discussion of the Fokker-Planck equation we shall not distinguish explicitly in notation between f_n and \bar{f}_n , but, if we choose, we could consider that all the distribution functions we work with are time smoothed ones since f_n and \bar{f}_n obey the same rigorous equations, Eq. (1.5). The difference between f_n and \bar{f}_n lies in their analytic properties and initial conditions which make certain operations and approximations more feasible (in the sense of almost all distributions nearly satisfying them) for the \bar{f} than for the f .

The Fokker-Planck equation appears in many different contexts. It was originally derived for the distribution function of a Brownian particle in a

fluid⁵ and is applicable in a more general form to a plasma.⁶ Recently Brout,⁷ Prigogine and Brout,⁸ and Zwanzig⁹ have shown that a Fokker-Planck equation in action-angle variables results from the classical limit of van Hove's theory¹⁰ of quantum-mechanical perturbations giving rise to a transport equation.

The Fokker-Planck equation for the one-particle distribution function, $f(\mathbf{r}, \xi, t)$, whose solution we seek has the form^{1,11,12}

$$\begin{aligned} \frac{\partial f}{\partial t} + \xi \cdot \frac{\partial f}{\partial \mathbf{r}} + \frac{\mathbf{F}(\mathbf{r})}{m} \cdot \frac{\partial f}{\partial \xi} &= \zeta \alpha(f) \\ &= \zeta \left\{ \frac{\partial}{\partial \xi} \cdot \left[\mathbf{c} f + \frac{kT}{m} \frac{\partial f}{\partial \xi} \right] \right\}, \end{aligned} \quad (1.12)$$

where $\mathbf{c} = \xi - \mathbf{u}$ is the velocity of the molecules relative to the mean velocity (the peculiar velocity). The (one-particle) friction constant $\zeta(\mathbf{r})$ is independent of velocity and is presumed, in what follows, to be known. Equation (1.12) formally divides $\mathbf{Y}_1^{(1)}$ of Eq. (1.5) into two parts

$$\begin{aligned} \mathbf{Y}_1^{(1)} &= - \int \frac{\partial \varphi(r_{12})}{\partial \mathbf{r}_1} \frac{f_2(\mathbf{r}_1, \mathbf{r}_2, \xi_1, \xi_2)}{f_1(\mathbf{r}_1, \xi_1)} d\mathbf{r}_2 d\xi_2 - \frac{\partial U(\mathbf{r}_1)}{\partial \mathbf{r}_1}, \\ &= \mathbf{F}(\mathbf{r}_1) - \zeta \left[\mathbf{c}_1 + \frac{kT(\mathbf{r}_1)}{m} \frac{\partial}{\partial \xi_1} \ln f_1 \right], \end{aligned} \quad (1.13)$$

with $\mathbf{F}(\mathbf{r}_1)$ independent of the velocity ξ_1 . We shall discuss this breakup and the form of $\mathbf{F}(\mathbf{r})$ in Sec. 5.

The collision term in the three models we have considered has the physical property of conserving the number density, particle momentum, and kinetic energy. Thus, denoting by $J(f)$ the collision term [the right-hand side of either the Boltzmann equation, Eq. (1.8) or Eq. (1.12)], we can write

$$\int J(f) \psi_r d\xi = 0, \quad r = 0, \dots, 4; \quad (1.14)$$

where $\psi_0 = 1$; ψ_1, ψ_2, ψ_3 are the three components of the vector ξ ; and $\psi_4 = \xi^2$. These five quantities are the collision invariants. We denote their expectation values by ρ_r ,

$$\rho_r = \int \psi_r f d\xi. \quad (1.15)$$

⁵ S. Chandrasekhar, *Rev. Modern Phys.* **15**, 1 (1943).
⁶ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1958).
⁷ R. Brout, *Physica* **23**, 953 (1957).
⁸ R. Brout and I. Prigogine, *Physica* **22**, 621 (1956).
⁹ R. W. Zwanzig, *Phys. Fluids* **2**, 12 (1959).
¹⁰ L. van Hove, *Physica* **21**, 518 (1955).
¹¹ J. G. Kirkwood, F. P. Buff, and M. S. Green, *J. Chem. Phys.* **17**, 988 (1949); R. W. Zwanzig, J. G. Kirkwood, K. F. Stripp, and I. Oppenheim, *ibid.* **21**, 2050 (1953).
¹² R. W. Zwanzig, J. G. Kirkwood, I. Oppenheim, and B. J. Alder, *J. Chem. Phys.* **22**, 783 (1954).

Since we wish to compare our results directly with certain equations given by Grad,^{1,13} we adopt his notation for the velocity moments of f , the "flows." By using the Einstein summation convention, the kinetic stress tensor P_{ij} , kinetic heat flow vector q_i , kinetic energy/unit mass e , and kinetic pressure p are defined by

$$\begin{aligned} P_{ij} &= m \int c_i c_j f d\xi = P_{ij}, \\ q_i &= \frac{1}{2} m \int c_i c^2 f d\xi, \\ e &= \frac{m}{n} \int \frac{1}{2} c^2 f d\xi, \\ p &= \frac{1}{3} P_{kk} = nkT. \end{aligned} \quad (1.16)$$

The reduced kinetic stress tensor (stress deviator) p_{ij} is defined by

$$p_{ij} = P_{ij} - p\delta_{ij}. \quad (1.17)$$

Multiplying the Boltzmann equation, Eq. (1.8), or Eq. (1.12) by ψ_r , and integrating over ξ , one obtains, after some manipulation, the hydrodynamic conservation equations

$$\begin{aligned} \frac{\partial n}{\partial t} + \frac{\partial}{\partial x_i} (nu_i) &= 0, \\ \frac{\partial u_i}{\partial t} + u_i \frac{\partial u_i}{\partial x_i} + \frac{1}{mn} \frac{\partial P_{ij}}{\partial x_j} - \frac{F_i}{m} &= 0, \\ \frac{\partial e}{\partial t} + u_i \frac{\partial e}{\partial x_i} + \frac{P_{ij}}{mn} \frac{\partial u_i}{\partial x_j} + \frac{1}{mn} \frac{\partial q_i}{\partial x_i} &= 0, \end{aligned} \quad (1.18)$$

where we have introduced the notation $\mathbf{r} = (x_1, x_2, x_3)$.

We have here a set of five equations in 13 variables which is very general, being independent of the model and applying also to dense fluids when the molecular interactions are taken into account in the definition of P_{ij} , q_i , and e . The equations are clearly incomplete, but the situation may be remedied in one of two obvious fashions: (1) Reduce the number of variables by expressing \mathbf{q} and \mathbf{P} as functionals of the ρ_r , or (2), increase the number of equations to 13 without introducing new unknowns.

In the phenomenological form of fluid dynamics the first method is applied through use of the empirical linear laws for \mathbf{q} and \mathbf{P} in terms of gradients of the ρ_r and the experimental, ρ_r dependent, coefficients of thermal conductivity and viscosity. From the kinetic theory viewpoint the first method

finds its expression for dilute gases in terms of the assumption of "normal" distributions, wherein the time dependence of $f(\mathbf{r}, \xi, \rho_r, t)$ and thus of \mathbf{q} and \mathbf{P} is assumed to reside fully in the time dependence of $\rho_r(\mathbf{r}, t)$. Normal distributions are determined from the Boltzmann equation by the Chapman-Enskog method^{1,6} of successive approximations starting with a locally Maxwellian distribution. In addition to molecular expressions for the transport coefficients the distribution function is determined. Clearly, this does not represent the most general solution since an initial value of f may be chosen arbitrarily. The assumption is that nearly all solutions tend to normal distributions in a very short time.

The second method, increasing the number of equations to 13, was developed by Grad.^{13,14} The distribution function is expressed in terms 13 moments which turn out to be the 13 unknowns of Eqs. (1.18). This distribution is found to satisfy the Boltzmann equation to a certain degree of approximation.

For dense fluids, where the Fokker-Planck equation is claimed to possess validity, Kirkwood and co-workers^{11,12} find expressions for the transport coefficients by considering appropriate moments of this equation. The coefficients may be used to reduce the number of variables in Eq. (1.18) as in the phenomenological approach. This method does not furnish the entire distribution function. We shall remedy this situation in Secs. 2 and 4 where Chapman-Enskog and Grad techniques will be employed to find solutions of the one- and two-particle Fokker-Planck equations.

2. THE ONE-PARTICLE DISTRIBUTION FUNCTION

In this section we will find solutions to the kinetic transport equations for f

$$\mathcal{D}f \equiv \frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial x_i} + \frac{F_i}{m} \frac{\partial f}{\partial \xi_i} = J(f), \quad (2.1)$$

correct to terms linear in the gradients of n , \mathbf{u} , and T . We will then demonstrate that when these solutions are expressed in terms of the flows q_i and p_{ij} , instead of the gradients of ρ_r , they assume a simple form which is identical for all models; viz.,

$$\tilde{f} = f^{(0)} \left\{ 1 + \frac{m}{2pkT} (c_i c_j - \frac{1}{3} c^2 \delta_{ij}) p_{ij} \right.$$

¹³ H. Grad, *Comm. Pure and Appl. Math.* 2, 331 (1949).

¹⁴ H. Grad, *Comm. Pure and Appl. Math.* 2, 325 (1949).

$$+ \frac{2}{5p(kT)^2} \left(\frac{mc^2}{2} - \frac{5}{2} kT \right) c_i q_i \}, \quad (2.2)$$

with $f^{(0)}$ given by Eq. (1.9).

The form of f in terms of the ρ_r , when f is a normal solution, is

$$f = f^{(0)} \{ 1 - \tau_2 C_2 - \tau_3 C_3 \}, \quad (2.3)$$

where C_2 and C_3 are defined by

$$C_2 = \frac{m}{kT} (c_i c_i - \frac{1}{3} c^2 \delta_{ii}) \frac{\partial u_i}{\partial x_i}$$

$$C_3 = \left(\frac{mc^2}{2kT} - \frac{5}{2} \right) c_i \frac{\partial \ln T}{\partial x_i}, \quad (2.4)$$

and the relaxation time for stress τ_2 and relaxation time for heat conduction τ_3 are given by

$$\tau_2 = \begin{cases} 1/6B_1^{(2)}n & \text{for the Boltzmann equation} \\ 1/\nu & \text{for the modified Boltzmann equation} \\ 1/2\zeta & \text{for the Fokker-Planck equation,} \end{cases} \quad (2.5)$$

$$\tau_3 = \begin{cases} 1/4B_1^{(2)}n & \text{for the Boltzmann equation} \\ 1/\nu & \text{for the modified Boltzmann equation} \\ 1/3\zeta & \text{for the Fokker-Planck equation.} \end{cases} \quad (2.6)$$

The relaxation times for the Boltzmann equation are strictly valid only for Maxwellian molecules. For the justification of using these with other molecular models, to the stated approximation, the reader is referred to Grad.^{2,13} $B_1^{(2)}$ is a quantity depending on the molecular parameters and the temperature, and is explicitly defined by Eq. (A3.46) of reference 13.

To apply the Chapman-Enskog method⁶ to the Fokker-Planck equation write the equation as

$$\mathfrak{D}f = (1/\epsilon)\zeta\mathcal{A}(f), \quad (2.7)$$

and the distribution function, in a form compatible with "normal" solutions, as

$$f(\mathbf{r}, \boldsymbol{\xi}, \epsilon) = f(r, \boldsymbol{\xi}, \rho_r, \epsilon) = \sum_{l=0}^{\infty} \epsilon^l f^{(l)}(\boldsymbol{\xi}, \rho_r), \quad (2.8)$$

where ϵ has been introduced as a formal expansion parameter which later will be set equal to unity. Physically the small quantity in which the expansion is made is the fractional variation of the hydrodynamical quantities like T and \mathbf{u} over a characteristic mean relaxation distance defined by τc_0 , with $\tau \approx \zeta^{-1}$ and c_0 a characteristic molecular speed. The operator \mathcal{A} is given by

$$\mathcal{A}(f) = \frac{\partial}{\partial \boldsymbol{\xi}} \cdot \left[\boldsymbol{\xi} - \frac{\int \boldsymbol{\xi}' f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}'}{\int f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}'} \right] f$$

$$+ \frac{1}{3} \left[\frac{\int \boldsymbol{\xi}'^2 f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}'}{\int f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}'} - \frac{\left[\int \boldsymbol{\xi}' f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}' \right]^2}{\left[\int f(\mathbf{r}, \boldsymbol{\xi}') d\boldsymbol{\xi}' \right]^2} \right] \frac{\partial}{\partial \boldsymbol{\xi}} f, \quad (2.9)$$

which corresponds with Eq. (1.12) when the ρ_r appearing there are expressed explicitly as functionals of f . These functionals may also be written as

$$\rho_r = \sum_{l=0}^{\infty} \epsilon^l \rho_r^{(l)}, \quad (2.10)$$

$$\rho_r^{(l)} = \int \boldsymbol{\psi}_r f^{(l)}(\mathbf{r}, \boldsymbol{\xi}) d\boldsymbol{\xi}. \quad (2.11)$$

Substituting Eqs. (2.8)–(2.11) into Eq. (2.9) and equating equal powers of ϵ , we find

$$0 = \zeta(r) \frac{\partial}{\partial \boldsymbol{\xi}} \cdot \left[(\boldsymbol{\xi} - \mathbf{u}^{(0)}) f^{(0)} + \frac{kT^{(0)}}{m} \frac{\partial f^{(0)}}{\partial \boldsymbol{\xi}} \right], \quad (2.12)$$

$$\mathfrak{D}f^{(0)} = \zeta(r) \frac{\partial}{\partial \boldsymbol{\xi}} \cdot \left[\mathbf{E} - \mathbf{u}^{(0)} \right] f^{(1)} + \frac{kT^{(0)}}{m} \frac{\partial f^{(1)}}{\partial \boldsymbol{\xi}}$$

$$+ \frac{\partial}{\partial \boldsymbol{\xi}} \cdot \left[-\mathbf{u}^{(1)} f^{(0)} + \frac{kT^{(1)}}{m} \frac{\partial f^{(0)}}{\partial \boldsymbol{\xi}} \right], \quad (2.13)$$

etc., where

$$n^{(0)} = \int f^{(0)} d\boldsymbol{\xi}, \quad (2.14)$$

$$\mathbf{u}^{(0)} = \int \boldsymbol{\xi} f^{(0)} d\boldsymbol{\xi} / n^{(0)}, \quad (2.15)$$

$$kT^{(0)} = \frac{1}{3} \int m(\boldsymbol{\xi} - \mathbf{u}^{(0)})^2 f^{(0)} d\boldsymbol{\xi} / n^{(0)}, \quad (2.16)$$

$$n^{(1)} = \int f^{(1)} d\boldsymbol{\xi}, \quad (2.17)$$

$$\mathbf{u}^{(1)} = \int (\boldsymbol{\xi} - \mathbf{u}^{(0)}) f^{(1)} d\boldsymbol{\xi} / n^{(0)}, \quad (2.18)$$

$$kT^{(1)} = \left[\frac{1}{3} \int m(\boldsymbol{\xi} - \mathbf{u}^{(0)})^2 f^{(1)} d\boldsymbol{\xi} - n^{(1)} kT^{(0)} \right] / n^{(0)}. \quad (2.19)$$

The zeroth-order equation (2.12) is highly non-linear, but a solution to it, in terms of five parametric functions of r and t , is

$$f^{(0)}(\mathbf{r}, \boldsymbol{\xi}) = n^{(0)}(\mathbf{r}, t) [m/2\pi kT^{(0)}(\mathbf{r}, t)]^3 \cdot \exp \{ -m[\boldsymbol{\xi} - \mathbf{u}^{(0)}(\mathbf{r}, t)]^2 / 2kT^{(0)}(\mathbf{r}, t) \}. \quad (2.20)$$

The higher-order equations now are linear. They determine $f^{(l)}$, however, only up to a linear combination of those quantities conserved by $\alpha(f)$; i.e., if $f^{(l)}$ is a solution then so is

$$f^{(l)*} = f^{(l)} + f^{(0)} [A(\mathbf{r}) + \mathbf{B}(\mathbf{r}) \cdot \boldsymbol{\xi} + C(\mathbf{r})\xi^2]. \quad (2.21)$$

This flexibility may be used to require that

$$\rho_r^{(0)} = \rho_r; \quad \rho_r^{(l)} = 0, \quad l > 0, \quad (2.22)$$

so that Eq. (2.20) becomes the local equilibrium distribution, Eq. (1.9). The insertion of $f^{(0)}$ into Eq. (2.13) completes the equation for $f^{(1)}$. As in the Enskog solution of the Boltzmann equation^{2,7} the time derivatives of n , \mathbf{u} , T which occur in the term $\mathfrak{D}f^{(l)}$ have to be expressed, using Eq. (1.18), in terms of the kinetic stress tensor and the kinetic heat flow vector whose values are computed from the distribution $f^{(l)}$ according to Eq. (1.16). This is necessary for the existence of a solution for $f^{(l+1)}$, $l > 0$. The equation for $f^{(l)}$ now assumes the form

$$(C_2 + C_3)f^{(0)} = \frac{kT\zeta}{m} \frac{\partial}{\partial \mathbf{c}} \cdot \left[f^{(0)} \frac{\partial}{\partial \mathbf{c}} (f^{(1)}/f^{(0)}) \right]. \quad (2.23)$$

This has a solution, satisfying Eq. (2.22),

$$f^{(1)} = -[C_2/2\zeta + C_3/3\zeta]f^{(0)}, \quad (2.24)$$

which has the form \tilde{f} of Eq. (2.3). Substituting Eq. (2.24) into the definition of the kinetic heat flow vector q_i and the kinetic stress tensor P_{ij} , given by Eq. (1.16), one finds

$$q_i = -5n \frac{k^2 T}{m} \frac{\partial T}{\partial x_i} / 6\zeta \quad (2.25)$$

$$P_{ij} = nkT \left\{ \delta_{ij} - \left[2\epsilon_{ij} - \frac{2}{3} \frac{\partial u_l}{\partial x_l} \delta_{ij} \right] / 2\zeta \right\},$$

where

$$\epsilon_{ij} = \frac{1}{2}[(\partial u_i / \partial x_j) + (\partial u_j / \partial x_i)],$$

is the deformation velocity tensor. From Eq. (2.15) the kinetic heat conductivity λ and the kinetic shear viscosity μ can be identified as

$$\begin{aligned} \lambda &= 5nk^2T/6m\zeta \\ \mu &= nkT/2\zeta, \end{aligned} \quad (2.26)$$

while the kinetic bulk viscosity is zero. Substituting Eq. (2.25) into Eq. (2.24), we obtain a solution in terms of the fluxes, i.e., one corresponding to \tilde{f} of Eq. (2.2).

The application of Enskog's method to the Boltzmann equation has been previously discussed^{2,13} and the result, on truncation of an

infinite determinant, agrees with Eqs. (2.2) and (2.3). For the modified Boltzmann equation, Enskog's method yields immediately, instead of Eq. (2.12)–(2.13),

$$\begin{aligned} f^{(0)} &= f^{(0)}, \\ f^{(1)} &= -(1/\nu)(C_2 + C_3)f^{(0)}, \text{ etc.} \end{aligned} \quad (2.27)$$

The computation of q_i and P_{ij} may be performed by inspection on comparison with Eq. (2.25), and Eqs. (2.2)–(2.6) are thus demonstrated also for the modified Boltzmann equation.

An alternative scheme for solving the transport equation (2.1) by successive approximations is to expand f in Hermite polynomials in the reduced velocity \mathbf{v} defined as $\mathbf{v} = m^{1/2}(\boldsymbol{\xi} - \mathbf{u})/(kT)^{1/2}$. The properties of these generalized Hermite polynomial tensors have been studied by Grad¹⁴ and applied by him to the solution of the Boltzmann equation.¹³ If we set

$$\omega(\mathbf{v}) = (2\pi)^{-3/2} e^{-\frac{1}{2}\mathbf{v}^2}, \quad (2.28)$$

the n th Hermite polynomial is defined as the tensor

$$\mathfrak{H}_{i_1, \dots, i_n}^{(n)} = \frac{(-1)^n}{\omega(\mathbf{v})} \frac{\partial}{\partial v_{i_1}} \dots \frac{\partial}{\partial v_{i_n}} \omega(\mathbf{v}) = \mathfrak{H}^{(n)}. \quad (2.29)$$

Using the completeness property of these polynomials, we write

$$\begin{aligned} f &= f^{(0)} \sum_{n=0}^{\infty} \frac{1}{n!} a^{(n)}(\mathbf{r}, t) \mathfrak{H}^{(n)}, \\ &= n(\mathbf{r}, t) [m/kT(r, t)]^{3/2} \omega(\mathbf{v}) \sum_{n=0}^{\infty} \frac{1}{n!} a^{(n)} \mathfrak{H}^{(n)}, \end{aligned} \quad (2.30)$$

where the coefficient tensors $a^{(n)}$ are given by¹³

$$a^{(n)} = \int f \mathfrak{H}^{(n)} d\boldsymbol{\xi} / n(\mathbf{r}, t), \quad (2.31)$$

and are either the desired velocity moments of f or linear combinations of them.

It is to be noted that the operator α of the Fokker-Planck equation may be expressed in the form

$$\alpha(f) = \frac{\partial}{\partial \mathbf{v}} \left[\omega(\mathbf{v}) \frac{\partial}{\partial \mathbf{v}} \frac{1}{\omega(\mathbf{v})} f \right].$$

The usefulness of expansion in Hermite polynomials arises from the fact that $\omega(\mathbf{v})\mathfrak{H}^{(n)}$ is the n th eigenfunction of the operator α with eigenvalue $-n$; i.e.,¹⁵

$$\alpha(\omega(\mathbf{v})\mathfrak{H}^{(n)}) = -n\omega(\mathbf{v})\mathfrak{H}^{(n)}. \quad (2.32)$$

This is the reason that $\tau_n = 1/n\zeta$ in Eqs. (2.5)–(2.6).

¹⁵ This fact should prove useful in a systematic discussion of the existence and uniqueness of solutions of the Fokker-Planck equation.

Equation (2.22) and a somewhat more general theorem are demonstrated in Appendix A. An advantage which this technique possesses, in principle at least, over Enskog's is that it is not restricted to yield only normal solutions of Eq. (2.1). In practice this method of solution is simply applied since one need only follow Grad,¹³ who has already carried out in his solution of the Boltzmann equation, certain basic, but tedious, calculations of which we shall make use.

Thus, substituting Eq. (2.30) into Eq. (2.1), eliminating time derivatives of n , \mathbf{u} , T by means of Eq. (1.20), multiplying the resulting equation by $\mathcal{H}^{(n)}$, and integrating over all values of \mathbf{v} , we obtain an infinite set of equations for the time derivatives of the $a^{(n)}$. These are Eqs. (4.20) of reference 13 to whose right-hand side the extra term (arising from the existence of the force \mathbf{F}) $-F_i a^{(n-1)}/(mkT)^{\frac{1}{2}}$ must be added. {The quantity $J^{(n)}$ in these equations, given explicitly¹³ for the Boltzmann equation, is equal to $-\nu a^{(n)}$ for the modified Boltzmann equation, and is $-\eta \zeta a^{(n)}$ for the Fokker-Planck equation [cf. Eq. (2.31)].}

This set of equations for $da^{(k)}/dt$, ($k=0, 1, \dots, n$), is made determinate for finite n by Grad's method of truncation;¹³ i.e., approximate f by the first n terms of its Hermite expansion and drop all terms involving $a^{(n+1)}$. (The neglected terms are given explicitly on page 361 of reference 13.) If, following Grad,¹³ the truncation is affected at $n = 3$, this leaves 20 equations for the 20 components of the symmetric tensors $a^{(0)}$, $a^{(1)}$, $a^{(2)}$, and $a^{(3)}$. These equations may be reduced to 13 equations for the 13 independent moments n , u_i , T , p_{ij} , and q_i by making the further approximation that [cf., Eq. (5.9) of reference 13],

$$a_{ijk}^{(3)} = \frac{1}{3}(a_i^{(3)} \delta_{jk} + a_j^{(3)} \delta_{ik} + a_k^{(3)} \delta_{ij}). \quad (2.33)$$

To this approximation f is given by Eq. (2.2) since

$$\begin{aligned} a^{(0)} &= 1, & a_i^{(1)} &= u_i, \\ a_{ij}^{(2)} &= p_{ij}/p, & a_i^{(3)} &= q_i(m/kT)^{\frac{1}{2}}/p. \end{aligned} \quad (2.34)$$

The eight independent quantities p_{ij} and q_i satisfy Eq. (5.18) (see Grad,¹³ where $\frac{1}{2}S_i$ replaces q_i) when τ_2 or τ_3 are introduced according to Eqs. (2.5)–(2.6) instead of $B_1^{(2)}$.¹⁶ By restricting these equations for p_{ij} and q_i to the problem of one-

dimensional heat conduction and plane Couette flow, λ and μ may be identified as

$$\lambda = 5pk\tau_3/2m, \quad (2.35)$$

and

$$\mu = p\tau_2, \quad (2.36)$$

for the Boltzmann equation, modified Boltzmann equation, and Fokker-Planck equation, with the τ given by Eqs. (2.5) and (2.6). We note that the ratio of $m\lambda$ to μ is

$$\frac{m\lambda}{\mu} = \frac{5}{2} k \frac{\tau_2}{\tau_3}, \quad (2.37)$$

and is independent of the nature of the particles.

Higher-order terms of f may be obtained by either method of solution but at least for the Fokker-Planck equation these are not of physical interest in view of the approximations made in deriving this equation from Eq. (1.5). These techniques may be extended to the treatment mixtures in order to study ordinary and thermal diffusion. We are now doing this.

3. VARIATIONAL PRINCIPLES

The fact that the different transport equations, arising from different kinetic models, are satisfied approximately by the same distribution \tilde{f} [cf. Eqs. (2.2) or (2.3)], for small deviations from local equilibrium, reminds one of the ubiquity of the Maxwell-Boltzmann distribution in equilibrium systems. The equilibrium distribution may be deduced, without any reference to kinetics, as a consequence of maximizing the entropy s

$$s = -k \int f \ln f d\xi, \quad (3.1)$$

for a given mean density, kinetic energy, and velocity (i.e., five moments of f). The question arises as to whether the nonequilibrium distribution \tilde{f} may be similarly derived. From an inspection of Eq. (2.2) the answer is evidently yes. The distribution \tilde{f} is such that it maximizes the entropy s for a given value of the 13 moments which appear in the hydrodynamic description of a fluid for small deviations from local equilibrium.

This result is suggestive, and it is of interest that it can be demonstrated to be a consequence (approximately at least) of the kinetic transport equations. We emphasize however that no explicit use has been made of the kinetic equations as yet and as a consequence there is no necessary relation between the fluxes appearing in \tilde{f} given by Eq. (2.2) and the

¹⁶ In the 20 moment approximation the presence of the force \mathbf{F} modifies Eq. (5.14) of reference 13 for S_{ijk} by introducing the extra term $-F_i p_{jk}/m$ to the right-hand side. Clearly this contribution must vanish in the 13 moment approximation since $p_{kk} = 0$.

gradients. Such a relationship can only arise from kinetic considerations, and, as Eqs. (2.35)–(2.36) show, the different models lead to different results for the transport coefficients.

The distribution \hat{f} , given by Eq. (2.3), which is expressed in terms of the gradients, and which satisfies the kinetic transport equations to a given order with the appropriate τ_2 and τ_3 , may also be derived directly from a variational principle. The quantity which is maximized by \hat{f} is a combination of the entropy s and entropy productions. It was shown by Ono¹⁷ that the quasi-thermodynamic entropy production σ_{II} is given by

$$\sigma_{II} = -k \int [C_2 + C_3] f d\xi = \sigma_2 + \sigma_3, \quad (3.2)$$

where C_2 and C_3 are defined by Eq. (2.4) and σ_2 , σ_3 are the entropy productions arising from momentum flow and heat flow, respectively. The distribution \hat{f} is now seen to maximize the quantity R ,

$$R = s + \tau_2 \sigma_2 + \tau_3 \sigma_3 \\ = -k \int f [\ln f + \tau_2 C_2 + \tau_3 C_3] d\xi \quad (3.3)$$

for a given local density, velocity and kinetic energy to terms linear in the deviations from local equilibrium. While s is a maximum when $f = f^{(0)}$, σ_2 and σ_3 are zero for this distribution; the entropy production achieved by the deviation of \hat{f} from $f^{(0)}$ more than compensates for the decrease of s from its maximum value. The values of τ_2 and τ_3 which appear in R as the characteristic times for entropy production due to momentum and energy transfer have to be taken from kinetic theory. The local equilibrium distribution in the presence of gradients, and consequently the Euler equations, correspond to the τ being zero, i.e., instantaneous relaxations. The quantity R appears as a natural generalization of the entropy and reduces to it when the system is uniform. An extension of these concepts to include entropy beyond the kinetic terms is presented in Sec. 6.

The entropy production may also be calculated directly from the transport equation, Eq. (2.1). The time rate of change of s is given by

$$\frac{\partial s(\mathbf{r})}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot \left[-k \int \xi f \ln f d\xi \right] \\ - k \int J(f) \ln f d\xi. \quad (3.4)$$

The first term represents the change in the entropy density due to the entropy flux and the second term is the collisional entropy production σ_I . When f is expanded in the deviations from local equilibrium,

$$f = f^{(0)} [1 + \varphi],$$

and only linear terms are kept, we get from the Fokker-Planck equation

$$\sigma_I = \frac{k^2 T \xi}{m} \int f^{(0)} \left[\frac{\partial \varphi}{\partial \xi} \right]^2 d\xi. \quad (3.5)$$

It was shown by Ono¹⁷ that the maximization of σ_I appropriate to the Boltzmann equation, subject to the subsidiary condition $\sigma_I = \sigma_{II}$, is equivalent to the first-order Chapman-Enskog approximation. We see that this is true also for the Fokker-Planck equation since the foregoing procedure yields again Eq. (2.13). Actually Ono's result will hold for any collision operator $J(f)$ as long as the operator K , defined by

$$J[f^{(0)}(1 + \varphi)] = \mathbf{X}(\varphi) + O(\varphi^2), \quad (3.6)$$

is Hermitian and linear.

We consider now the relation between the maximization of R and the usual "minimum entropy production principle"¹⁸ of the thermodynamics of irreversible processes.¹⁹ In the later, there is assumed to be a given (not derived) relation between the fluxes J_i and the forces X_i , which is linear for small deviations from equilibrium

$$J_i = \sum_{j=1}^n L_{ij} X_j \quad (3.7)$$

and the J and X are so chosen that

$$\sigma_{II} = \sum_{i=1}^n J_i X_i. \quad (3.8)$$

It is then shown²⁰ that if some of the forces (or fluxes) are constrained to have given definite values (e.g., $X_l = X_l^0$ for $l = 1, \dots, k$) then the other X_i , $i = k + 1, \dots, n$, adjust themselves in such a way as to make σ_{II} a minimum; i.e., $J_i = 0$ for $i > k$. In our formulation this would correspond to saying, for instance, that if $\mathbf{u}(\mathbf{r})$ is not specified then the distribution will be such that $p_{ii} = 0$, or if $T(\mathbf{r})$ is not specified (but only the total energy

¹⁸ I. Prigogine, *Étude Thermodynamique des Phénomènes Irréversibles* (Desoer, Liège, 1947), Chap. V.

¹⁹ See also papers and references cited by M. J. Klein, H. Wergeland, and H. B. Callen in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958).

²⁰ S. R. de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951).

¹⁷ S. Ono, *Sci. Papers Coll. Gen. Educ. Univ. Tokyo*, 5, 87 (1955).

is) then the distribution is such that $\mathbf{q} = 0$. This is indeed a consequence of our variational principle for R . Our principle, however, goes further in that it states that the distribution function corresponding to existence of fixed X is such as to make R a maximum; i.e., the L matrix will be such as to maximize R . This permits us to compute the $L_{i,j}$ in terms of relaxation times which the thermodynamics of irreversible processes is incapable of doing.

4. TWO-PARTICLE DISTRIBUTION FUNCTION

The time evolution of the two-particle distribution function f_2 , which plays a central role in the theory of liquids, is, according to Kirkwood,¹ also governed by a Fokker-Planck type equation with a six-dimensional friction tensor. When it is assumed further that the friction tensor in the six-dimensional pair space is a direct product of the velocity independent one-particle friction constants $\zeta(\mathbf{r}_1)_1$ and $\zeta(\mathbf{r}_2)_2$ then the Fokker-Planck equation for f_2 has the form^{1,11,12}

$$\begin{aligned} \mathcal{D}_2 f_2 &\equiv \frac{\partial f_2}{\partial t} + \xi_1 \cdot \frac{\partial f_2}{\partial \mathbf{r}_1} + \xi_2 \cdot \frac{\partial f_2}{\partial \mathbf{r}_2} \\ &+ \frac{\mathbf{F}_1^{(2)}}{m} \cdot \frac{\partial f_2}{\partial \xi} + \frac{\mathbf{F}_2^{(2)}}{m} \cdot \frac{\partial f_2}{\partial \xi_2} \\ &= \zeta(\mathbf{r}_1) \frac{\partial}{\partial \xi_1} \cdot \left\{ \mathbf{c}_1 f_2 + \frac{kT(\mathbf{r}_1)}{m} \frac{\partial f_2}{\partial \xi_1} \right\} \\ &+ \zeta(\mathbf{r}_2) \frac{\partial}{\partial \xi_2} \cdot \left\{ \mathbf{c}_2 f_2 + \frac{kT(\mathbf{r}_2)}{m} \frac{\partial f_2}{\partial \xi_2} \right\} \\ &= J(f_2). \end{aligned} \tag{4.1}$$

Here $\mathbf{F}_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ is the "equilibrium" part of the force $\mathbf{Y}_1^{(2)}$, defined by Eq. (1.6), which we shall discuss in detail in the next section. The requirements of symmetry lead to the relation

$$\mathbf{F}_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{F}_2^{(2)}(\mathbf{r}_2, \mathbf{r}_1). \tag{4.2}$$

Consider first the Chapman-Enskog approach to the determination of solutions of Eq. (4.1). The application of this method to f_2 is very similar to the procedure used in Sec. 2 when solving for f_1 . The main difference encountered here is that the pair space density $n_2(\mathbf{r}_1, \mathbf{r}_2)$,

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = \int f_2 d\xi_1 d\xi_2, \tag{4.3}$$

which is not a hydrodynamical variable, is also left invariant by the collision operator on the right-hand side of Eq. (4.1); i.e.,

$$\int J(f_2) d\xi_1 d\xi_2 = 0. \tag{4.4}$$

The other collision invariants, \mathbf{u} and T , may be taken either at \mathbf{r}_1 or \mathbf{r}_2 . We again call all these quantities ρ ,

$$\rho = \{n_2, \mathbf{u}(\mathbf{r}_1), \mathbf{u}(\mathbf{r}_2), T(\mathbf{r}_1), T(\mathbf{r}_2)\}. \tag{4.5}$$

The expansion parameter ϵ is introduced into Eq. (4.1) by writing

$$\mathcal{D}_2 f_2 = \frac{1}{\epsilon} J(f_2); \tag{4.6}$$

we assume, since "normal" solutions are sought, that f_2 has the form

$$f_2(\xi_1, \xi_2, \mathbf{r}, \rho, \epsilon) = \sum_{l=0}^{\infty} \epsilon^l f_2^{(l)}(\xi_1, \xi_2, \mathbf{r}, \rho), \tag{4.7}$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. The dependence of f_2 on the ρ is of a functional nature and may involve spatial gradients. As in the case of f_1 , the time dependence of f_2 is assumed to reside solely in the ρ . By an argument similar to that presented in Sec 2 we may take $\rho^{(0)} = \rho$, and $\rho^{(l)} = 0$, $l > 0$. With this short cut the equations for $f_2^{(l)}$ become

$$0 = J(f^{(0)}), \tag{4.8}$$

$$\mathcal{D}_2 f_2^{(l-1)} = J(f^{(l)}). \tag{4.9}$$

The zeroth-order equation has as a solution the locally Maxwellian distribution

$$\begin{aligned} f_2^{(0)} &= n_2 m^3 (2\pi k)^{-3} [T(\mathbf{r}_1) T(\mathbf{r}_2)]^{-\frac{1}{2}} \\ &\cdot \exp \left\{ -\frac{m}{2k} \left[\frac{(\xi_1 - \mathbf{u}(\mathbf{r}_1))^2}{T(\mathbf{r}_1)} \right. \right. \\ &\left. \left. + \frac{(\xi_2 - \mathbf{u}(\mathbf{r}_2))^2}{T(\mathbf{r}_2)} \right] \right\}. \end{aligned} \tag{4.10}$$

To complete the first-order equation [Eq. (4.9)], we insert Eq. (4.10) on the left-hand side. The time derivatives of the ρ may be written in the form²

$$\frac{\partial \rho}{\partial t} = \sum_{n=0}^{\infty} \epsilon^n \frac{\partial^{(n)} \rho}{\partial t}, \tag{4.11}$$

where $\partial^{(n)} \rho / \partial t$ is to be chosen in such a way that it insures the existence of solutions to the inhomogeneous equations [Eq. (4.9)]. The equations for \mathbf{u} and T are the same as those obtained from f_1 while n_2 satisfies a pair space equation of continuity

$$\frac{\partial^{(l)} n_2}{\partial t} = - \left[\frac{\partial}{\partial \mathbf{r}_1} \cdot \mathbf{j}_1^{(l)} + \frac{\partial}{\partial \mathbf{r}_2} \cdot \mathbf{j}_2^{(l)} \right], \tag{4.12}$$

with \mathbf{j}_i the (average) pair space velocity of the i th particle, $i = 1, 2$,

$$\mathbf{j}_i = \int \xi_i f_2 d\xi_1 d\xi_2, \tag{4.13}$$

$$\mathbf{j}_i^{(1)} = \int \xi_i f_2^{(1)} d\xi_1 d\xi_2, \tag{4.14}$$

and, in particular,

$$\mathbf{j}_i^{(0)} = n_2 \mathbf{u}(\mathbf{r}_i). \tag{4.15}$$

We can now solve for the $f_2^{(1)}$ in terms of the ρ and their spatial gradients. The first-order distribution $f_2^{(1)}$ is completely determined in terms of the radial distribution function

$$g = n_2/n(\mathbf{r}_1)n(\mathbf{r}_2), \tag{4.16}$$

n , \mathbf{u} , and T . We find on solving Eq. (4.12) that

$$f_2^{(1)} = f_2^{(0)} \left\{ \sum_{i=1}^2 \left[\tau_2(\mathbf{r}_i) C_2(\xi_i, \mathbf{r}_i) + \tau_3(\mathbf{r}_i) C_3(\xi_i, \mathbf{r}_i) + \tau_1(\mathbf{r}_i) (\xi_i - \mathbf{u}(\mathbf{r}_i)) \left(\frac{\tilde{\mathbf{F}}_i^{(2)}}{kT(\mathbf{r}_i)} - \frac{\partial \ln g}{\partial \mathbf{r}_i} \right) \right] \right\}, \tag{4.17}$$

where $\tilde{\mathbf{F}}_i^{(2)} = \mathbf{F}_i^{(2)} - \mathbf{F}_i^{(1)}$, $\tau_i(\mathbf{r}_i) = [l\zeta(\mathbf{r}_i)]^{-1}$ [cf. Eqs. (2.5)–(2.6)], and the C_i were defined by Eq. (2.4). From $f_2^{(1)}$ we obtain, in agreement with Zwanzig, Kirkwood, Oppenheim, and Alder,¹²

$$\mathbf{j}_i^{(1)} = -\frac{n_2}{\zeta(\mathbf{r}_i)} \frac{kT(\mathbf{r}_i)}{m} \cdot \left[\frac{\partial}{\partial \mathbf{r}_i} \ln g - \tilde{\mathbf{F}}_i^{(2)}/kT(\mathbf{r}_i) \right]. \tag{4.18}$$

This, in turn, gives the improved approximation to $\partial n_2/\partial t$, when ϵ is set equal to one,

$$\frac{\partial n_2}{\partial t} + \sum_{i=1}^2 \frac{\partial}{\partial \mathbf{r}_i} \cdot [n_2 \mathbf{u}(\mathbf{r}_i) + \mathbf{j}_i^{(1)}] = 0. \tag{4.19}$$

The distribution f_2 which we have obtained contains besides the so far unspecified $\tilde{\mathbf{F}}_i^{(2)}$, which we discuss in the next section, the nonhydrodynamic entity g . In order to obtain true “normal” distributions, and thus expressions for the transport coefficients, we assume that each small region of the system is close to local equilibrium and write g as

$$g = g_0[\mathbf{r}, T(\mathbf{R}, t), n(\mathbf{R}, t)] \cdot \left\{ 1 + \frac{m\zeta(\mathbf{R})}{kT(\mathbf{R})} \left[\frac{\mathbf{r}}{r} \cdot \frac{\partial \mathbf{u}(\mathbf{R})}{\partial \mathbf{R}} \cdot \frac{\mathbf{r}}{r} - \frac{1}{3} \frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{u}(\mathbf{R}) \right] \psi_2(r) + \frac{m\zeta(\mathbf{R})}{6kT(\mathbf{R})} \left[\frac{\partial}{\partial \mathbf{R}} \cdot \mathbf{u}(\mathbf{R}) \right] \psi_0(r) \right\}, \tag{4.20}$$

where $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, and $\rho(\mathbf{R}) = \frac{1}{2}[\rho(\mathbf{r}_1) + \rho(\mathbf{r}_2)]$ to first order in the gradients. This form of g is substantially the same as that of Kirkwood *et al.*

when account is taken not only of the dependence of n on time (see Zwanzig *et al.*¹¹) but also of the time dependence of T . We see further that in the absence of velocity gradients (i.e., pure heat conduction) g is completely determined for a single component fluid to terms linear in the gradients, by equilibrium theory. This result follows by reason of symmetry.²¹ Such a consideration obviates the necessity for some of the computation in the paper of Zwanzig, *et al.*,¹² on thermal conductivity. When Eq. (4.20) is substituted into Eq. (4.19) and use is made of the hydrodynamic equations to eliminate time derivatives, differential equations, which are substantially those of Kirkwood, *et al.*,¹¹ are obtained for the ψ in terms of $\tilde{\mathbf{F}}_i^{(2)}$.

To find an approximate solution of Eq. (4.1) by Grad’s method, we develop f_2 in a series of generalized Hermite polynomials as

$$f_2 = f_2^{(0)} \left[1 + \sum_{i=1}^2 \sum_{n=1}^{\infty} a^{(n)}(i) \mathcal{H}^{(n)}(\mathbf{v}_i) \right], \tag{4.21}$$

where $f_2^{(0)}$ is the locally Maxwellian distribution given by Eq. (4.10), $\mathcal{H}^{(n)}(\mathbf{v}_i)$ is the n th three-dimensional Hermite polynomial tensor, and the coefficient tensors are given by

$$a^{(n)}(i, \mathbf{r}_1, \mathbf{r}_2, t) = \int \mathcal{H}^{(n)}(\mathbf{v}_i) f_2 d\xi_1 d\xi_2/n_2. \tag{4.22}$$

As in Sec. 2, where this method was applied to finding an approximate f_1 , we multiply Eq. (4.1) by $\mathcal{H}^{(n)}(\mathbf{v}_i)$, integrate over all values of ξ_1 and ξ_2 , and use Eq. (4.22), to derive equations for $da^{(n)}(i)/dt$. To obtain, again, a finite set of determinate equations for the $da^{(n)}(i)/dt$ we truncate at $n = 3$ by neglecting all terms involving $a^{(n)}(i)$, $n \geq 4$. If it is assumed, further, that $\mathcal{H}_{ijk}^{(3)}$ in Eq. (4.25) can be replaced, to a sufficient degree of approximation, by the contracted $\mathcal{H}_{ikk}^{(3)}$ we obtain the 16 moment approximation (the two-particle analog of the 13 moment approximation to f_1) for f_2, \tilde{f}_2

$$\tilde{f}_2 = f_2^{(0)} \left\{ 1 + \sum_{i=1}^2 \left[a_i^{(1)}(i) \mathcal{H}_i^{(1)}(\mathbf{v}_i) + \frac{a_{ijk}^{(2)}}{2} (i) \mathcal{H}_{ijk}^{(2)}(\mathbf{v}_i) + \frac{a_j^{(3)}}{10} (i) \mathcal{H}_i^{(3)}(\mathbf{v}_i) \right] \right\}. \tag{4.23}$$

The 16 moments are: one from n_2 ; three from the vector $a^{(1)}(i)$ related linearly to $\mathbf{j}_i - n_2 \mathbf{u}(\mathbf{r}_i)$; five from the symmetric divergenceless tensor $a^{(2)}(i)$ related to the kinetic part of the two-particle stress deviator; three from the vector $a^{(3)}(i)$ related to

²¹ H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishers, New York, 1952).

the kinetic part of the two-particle heat flow; three from the velocity $\mathbf{u}(\mathbf{r}_i)$; and one from the temperature T . We note that by virtue of Eq. (A8) of Appendix A

$$J(\tilde{f}_2) = - \sum_{i=1}^2 \zeta(\mathbf{r}_i) f_2^{(0)} \left[a_i^{(1)}(\tilde{v}) \mathcal{H}_i^{(1)}(\mathbf{v}_i) + \frac{2a_{jk}^{(2)}}{2} (\tilde{v}) \mathcal{H}_{jk}^{(2)}(\mathbf{v}_i) + \frac{3a_i^{(3)}}{10} (\tilde{v}) \mathcal{H}_i^{(3)}(\mathbf{v}_i) \right], \quad (4.24)$$

so that the relaxation times are again given by $\tau_n(\tilde{v}) = [n\zeta(r_i)]^{-1}$. While the form of the velocity dependence of Eq. (4.23) is identical with that given by the Enskog solution, Eq. (4.17), the \tilde{f}_2 is not a "normal" solution. The equations governing the time evolution of the coefficient tensors of Eq. (4.23), the fluxes, must be solved under certain special conditions to obtain the transport coefficients. The procedure is similar to that of Sec. 2 and of reference 13.

5. THE FORCES IN THE FOKKER-PLANCK EQUATION

In this section we consider the nature of the forces $\mathbf{F}_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ and $\mathbf{F}(\mathbf{r}_1)$ which appear in the Fokker-Planck equation and the solutions we have found. The relation between the singlet space and pair space force may be examined by integrating Eq. (4.1) over \mathbf{r}_2, ξ_2 to obtain

$$\frac{\partial f_1}{\partial t} + \xi_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}_1} + \frac{\partial}{\partial \xi_1} \cdot \left\{ f_1 \left[\frac{1}{m(N-1)} \int \tilde{\mathbf{F}}_1^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \cdot \frac{f_2}{f_1} d\mathbf{r}_2 \zeta \xi_2 \right] \right\} = \zeta(\mathbf{r}_1) \mathcal{G}_1(f_1), \quad (5.1)$$

where we have used the relation [cf. Eq. (1.2)]

$$f_1(\mathbf{r}_1, \xi_1, t) = \frac{1}{(N-1)} \int f_2(\mathbf{r}_1, \mathbf{r}_2, \xi_1, \xi_2, t) d\mathbf{r}_2 d\xi_2. \quad (5.2)$$

The difference between Eq. (5.1), with a force term possibly ξ_1 dependent, and the one-particle Fokker-Planck equation [Eq. (1.14)], with a velocity independent $\mathbf{F}(\mathbf{r}_1)$, is the term

$$\frac{1}{N-1} \int [\mathbf{F}_1^{(2)} - \mathbf{F}(\mathbf{r}_1)] (f_2/f_1) d\mathbf{r}_2 d\xi_2, \quad (5.3)$$

which is negligible for large N if $[\mathbf{F}_1^{(2)} - \mathbf{F}(\mathbf{r}_1)] = \tilde{\mathbf{F}}_1^{(2)}$ vanishes with sufficient rapidity as $r_{12} \rightarrow \infty$. The same condition also assures that f_2 , given by Eq. (4.21), reduces to the f_1 of Eq. (2.3) upon integration or to a product of f_1 as $r_{12} \rightarrow \infty$.

The force $\tilde{\mathbf{F}}^{(2)}$ must have the further property that

$$\tilde{\mathbf{F}}_1^{(2)} = kT(\mathbf{r}_1) \left[\frac{\partial}{\partial \mathbf{r}_1} \ln g_0[\mathbf{r}, n(\mathbf{r}_1), T(\mathbf{r}_1)] \right]_{T,n} + O(\nabla \rho) \quad (5.4)$$

to insure that the equilibrium distribution be a stationary solution of the Fokker-Planck equation. The radial distribution function g_0 is calculated by integrating a canonical distribution, representing an equilibrium system whose constant T and n is given by the argument of g_0 , over the positions of $N - 2$ particles,²¹ and for simplicity it is assumed that there are no external forces. When the system is not in equilibrium Kirkwood and co-workers^{11,12} use just the first term of Eq. (5.4),²² an assumption which is not fully justified. Reference to Eqs. (4.17)–(4.18) reveals that it is the quantity

$$[\partial \ln g / \partial \mathbf{r}_1 - \tilde{\mathbf{F}}_1^{(2)} / kT(\mathbf{r}_1)]$$

which is needed to find the correction to local equilibrium so that it behooves us to consider carefully the $O(\nabla \rho)$ terms of Eq. (5.4).

We recall that the Kirkwood form of $\tilde{\mathbf{F}}_1^{(2)}$ is based on the assumption that the environs of particle 1 and 2 are in equilibrium with uniform thermodynamic conditions corresponding to those at r_1 . We believe that in keeping with the iterative nature of the solution of the Fokker-Planck equation which we have previously employed, it is proper, rather, to compute this force with the assumption the environs are in a local equilibrium condition. The N -particle distribution functions for a system in a state of local equilibrium have been discussed previously by one of us²³ for the case of nonuniform temperature. When the fluid is also in motion we must replace ξ_i by $[\xi_i - \mathbf{u}(\mathbf{r}_i)]$; thus,²⁴

$$f_N^{(0)} = (N! / Z^{(0)}) \exp \left\{ - \sum_{i=1}^N \left[\left(\frac{1}{2} m [\xi_i - u(\mathbf{r}_i)]^2 + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^N \varphi(r_{ij}) \right) / kT(\mathbf{r}_i) \right] - \sum_{j=1}^N \mu(\mathbf{r}_j) / kT(\mathbf{r}_j) \right\}, \quad (5.5)$$

where $Z^{(0)}$ is a constant chosen to normalize $f_N^{(0)}$ to $N!$, and $\mu(\mathbf{r}_i)$ is the chemical potential at r_i . [We may think of this, in the spirit of the grand canonical ensemble, so that $\mu(\mathbf{r}_i)$ insures that the average density at \mathbf{r} , is the specified $n(\mathbf{r}_i)$.]

According to these ideas the force $\tilde{\mathbf{F}}_1^{(2)}$ is given by [cf. Eq. (1.7)]

²² Actually, in the calculation of heat conductivity by Zwang *et al.* cited in footnote 11, g_0 is considered to be a function of temperature and pressure and consideration is limited to stationary states of uniform pressure.

²³ J. L. Lebowitz, Phys. Rev. **114**, 1192 (1959).

²⁴ This agrees with Lebowitz's Eq. (5.5) when use is made of his Eq. (5.15) to identify η as $-\mu/kT$.

$$\mathbf{F}_1^{(2)} = -\frac{1}{(N-3)!} \int \frac{\partial \varphi(r_{13})}{\partial \mathbf{r}_1} [f_N^{(0)}/f_2^{(0)}] \cdot d\mathbf{r}_3 \cdots d\mathbf{r}_N d\xi_3 \cdots d\xi_N - \frac{\partial \varphi(r_{12})}{\partial \mathbf{r}_1}, \quad (5.6)$$

where

$$f_2^{(0)} = \frac{1}{(N-2)!} \int f_N^{(0)} d\mathbf{r}_3 \cdots d\xi_N, \quad (5.7)$$

$$n_2^{(0)} = \int f_2^{(0)} d\xi_1 d\xi_2 = n(\mathbf{r}_1)n(\mathbf{r}_2)g_0 + O(|\nabla \rho|^2).$$

By considering the quantity $\partial[\ln kT(\mathbf{r}_1)n_{2,0}]/\partial \mathbf{r}_1$, we find

$$\begin{aligned} \mathbf{F}_1^{(2)} &= kT(\mathbf{r}_1) \frac{\partial}{\partial \mathbf{r}_1} \ln [kT(\mathbf{r}_1)n_2^{(0)}] \\ &+ \left(\frac{\partial}{\partial \mathbf{r}_1} \ln T \right) \cdot [h(\mathbf{r}_1)l - h_2(\mathbf{r}_1, \mathbf{r}_2)] \\ &- \left[\frac{\partial}{\partial \mathbf{r}_1} p(\mathbf{r}_1) \right] / n(\mathbf{r}_1) \end{aligned} \quad (5.8)$$

where $p(\mathbf{r}_1)$ is now the thermodynamic pressure at \mathbf{r}_1 , $h(\mathbf{r}_1)$ is the enthalpy/molecule given by $\{\partial[\mu/T]/\partial[1/T]\}_v$, and h_2 is a pair space tensor "enthalpy" at \mathbf{r}_1 when a molecule is fixed at \mathbf{r}_2 ,

$$\begin{aligned} h_2 &= \frac{5}{2} kT(\mathbf{r}_1)l + \frac{1}{2} [\varphi(r_{12})l - (\mathbf{r}_{12}\mathbf{r}_{12}/r_{12})\varphi'(r_{12})] \\ &+ \frac{1}{2} \int [\varphi(r_{13})l \\ &- (\mathbf{r}_{13}\mathbf{r}_{13}/r_{13})\varphi'(r_{13})][n_3^{(0)}/n_2^{(0)}] d\mathbf{r}_3. \end{aligned} \quad (5.9)$$

Under the stationary condition of uniform pressure the last term in Eq. (5.8) may be dropped. In an isothermal system (pure viscous flow) the second term vanishes and the force reduces to the Kirkwood form. For the case of pure heat flow we find that the distribution f_2 given by Eq. (4.17) with the force of Eq. (5.8) may be obtained from a variational principle, which we feel lends credence to our findings.

The singlet space force may be obtained by either a repetition of the procedure which leads to Eq. (5.8) or by taking the limit of $\mathbf{F}_1^{(2)}$ as $r_{12} \rightarrow \infty$. Either method yields

$$\begin{aligned} \mathbf{F}(\mathbf{r}_1) &= kT(\mathbf{r}_1) \frac{\partial}{\partial \mathbf{r}_1} \ln [kT(\mathbf{r}_1)n(\mathbf{r}_1)] \\ &- \left[\frac{\partial}{\partial \mathbf{r}_1} p(\mathbf{r}_1) \right] / n(\mathbf{r}_1). \end{aligned} \quad (5.10)$$

Note that this vanishes for the perfect gas. The gradient of pressure term cancels in the difference force $\tilde{\mathbf{F}}_1^{(2)}$ which enters into f_2 .

6. VARIATIONAL PRINCIPLE FOR f_N

In Sec. 5 of reference 23 one of us (J. L. L.) considered the problem of finding a stationary phase space ensemble, i.e., some f_N which would represent a stationary heat conducting system. Not being able to solve this problem in a rigorous fashion the assumption was made that the system relaxes exponentially with a single relaxation time towards the local equilibrium distribution, which lead to the distribution

$$\begin{aligned} f_N &= f_N^{(0)} \left[1 - \sum_{i=1}^N \frac{\tau(\mathbf{r}_i)}{kT(\mathbf{r}_i)} \frac{\partial \ln T(\mathbf{r}_i)}{\partial \mathbf{r}_i} \right. \\ &\cdot \left. \left\{ \frac{1}{2} m\xi_i^2 l + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^N \left[\varphi(r_{ij})l \right. \right. \right. \\ &\left. \left. \left. - \frac{\mathbf{r}_{ij}\mathbf{r}_{ij}}{r_{ij}} \varphi'(r_{ij}) \right] \cdot \xi_i \right\} \right], \end{aligned} \quad (6.1)$$

where, we recall, h is the enthalpy/particle. When integrated this lead to a pair distribution function [Eq. (5.20) of reference 23] which agrees in form with the f_2 of our Eq. (4.17), with the forces of our Sec. 5, when consideration is limited to pure heat conduction (no mass flow and hence uniform pressure).²⁵ We shall concentrate henceforth on this state which is one of the simplest and one for which the solution of the Fokker-Planck equation may be written out explicitly. An equivalent form for f_N , which is somewhat suggestive, is

$$\begin{aligned} f_N &= (N!/Z^{(0)}) \exp \left\{ \int \left[-\frac{E_N(\mathbf{x}, \mathbf{X}) + \mu(\mathbf{x})n_N(\mathbf{x}, \mathbf{X})}{kT(x)} \right. \right. \\ &\left. \left. - \frac{\tau(\mathbf{x})}{kT(\mathbf{x})} \frac{\partial \ln T(\mathbf{x})}{\partial \mathbf{x}} \cdot \mathbf{Q}_N(\mathbf{x}, \mathbf{X}) \right] d\mathbf{x} \right\}, \end{aligned} \quad (6.2)$$

where the dynamical variables, with an N subscript, are functions of the systems six N -dimensional phase point $\mathbf{X} = r_1, \dots, r_N, \xi_1, \dots, \xi_N$, and a three-dimensional position variable x . They are defined as

$$\begin{aligned} E_N(\mathbf{x}, \mathbf{X}) &= \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{r}_i) \left[\frac{1}{2} m\xi_i^2 \right. \\ &\left. + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^N \varphi(r_{ij}) \right], \end{aligned} \quad (6.3)$$

$$n_N(\mathbf{x}, \mathbf{X}) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{r}_i), \quad (6.4)$$

²⁵ We note, however, that the Fokker-Planck equation associates different relaxation times with the kinetic and the potential parts of the heat flux; i.e., the relaxation times are $\tau_i = 1/l_i^2$ where l is the order of the Hermite polynomial in velocity. On the other hand, in reference 23 and in this section only a single relaxation for heat flow is assumed.

$$Q_N(\mathbf{x}, \mathbf{X}) = \sum_{i=1}^N \delta(\mathbf{x} - \mathbf{r}_i) \left\{ \frac{1}{2} m \xi_i^2 + \frac{1}{2} \sum_{\substack{j=1 \\ j \neq i}}^N [\varphi(r_{ij}) + (\mathbf{r}_i \mathbf{r}_j / r_{ij}) \varphi'(r_{ij})] - h(\mathbf{x}) \right\} \cdot \xi_i. \quad (6.5)$$

The ensemble average value of the variables are, respectively, the energy density, $n(\mathbf{x})E(\mathbf{x})$, the particle density $n(\mathbf{x})$, and the heat current density, $Q(\mathbf{x})$.

We will now show that the N -particle distribution f_N is such that it maximizes the entropy plus entropy production in the characteristic time τ . The entropy of a system represented by a Γ -space ensemble with a probability f_N is given by S ,

$$S = -k \int f_N \ln f_N d\mathbf{X}. \quad (6.6)$$

The distribution function which maximizes the entropy subject only to the constraint of a given total (mean) energy and normalization is, of course, the canonical distribution of Gibbs. The reciprocal of the temperature and Helmholtz free energy play the role of Lagrange multipliers for the constraints. It is now to be observed that: (1) The local equilibrium distribution $f_N^{(0)}$ maximizes S subject to the constraints of given mean energy density $n(\mathbf{x})E(\mathbf{x})$, particle density $n(\mathbf{x})$, and normalization. Lagrange multipliers must be introduced at each point of space. (2) Subject to constraints on $n(\mathbf{x})E(\mathbf{x})$, $n(\mathbf{x})$, and normalization the distribution f_N maximizes the quantity

$$R = -k \int f_N(\mathbf{X}) \ln f_N(\mathbf{X}) d\mathbf{X} + \int f_N(\mathbf{X}) [\tau \sigma_N(\mathbf{X})] d\mathbf{X}, \quad (6.7)$$

where

$$\tau \sigma_N(\mathbf{X}) = \int \tau(\mathbf{x}) \sigma_N(\mathbf{x}, \mathbf{X}) d\mathbf{x} \quad (6.8)$$

and

$$\sigma_N(\mathbf{x}, \mathbf{X}) = -\frac{1}{T(\mathbf{x})} \frac{\partial \ln T(\mathbf{x})}{\partial \mathbf{x}} \cdot Q_N(\mathbf{x}, \mathbf{X}). \quad (6.9)$$

The quantity $\sigma_N(\mathbf{x}, \mathbf{X})$ is clearly the entropy production at \mathbf{x} in a system whose state is represented by the point \mathbf{X} in Γ -space while $\tau \sigma_N(\mathbf{X})$ is the entropy production in this average time $\tau(\mathbf{X})$. (Extension to other forms of entropy production is obviously possible. Each will have its own characteristic time.) The quantity R which is maximized by the nonequilibrium distribution f_N is thus again the sum of the entropy and the entropy production

over a characteristic time. The time τ has to be determined from kinetic theory. This can, however, only be an approximation to the truth. We have some evidence to suggest that the correct quantity which is maximized for small deviations from equilibrium is R^* ,

$$R^* = -k \int f_N \ln f_N d\mathbf{X} + \int f_N(\mathbf{X}) \left\{ \int_{-\infty}^t \sigma_N(\mathbf{X}, t'; t) dt' \right\} d\mathbf{X}, \quad (6.10)$$

where $\sigma_N(\mathbf{X}, t', t)$ is the entropy production at a time t' in a system whose state at time t is specified by \mathbf{X} . Generally $\sigma_N(\mathbf{X}, t', t)$ will be a function only of $t' - t$, and the integral becomes independent of t . The quantity R is thus a relaxation type of approximation to R^* . From Eq. (6.10) we see that an improved approximation might be obtained by assigning different relaxation times, perhaps in the mode of the Fokker-Planck equation. We will analyze this whole conjecture in detail in a future publication.

There is an alternative variational principle for f_N which does not involve the introduction of any relaxation time. The result is analogous to the f_1 found in Sec. 2 which was independent of the model. If we maximize the entropy, Eq. (6.6) subject to the constraints of given energy density, particle density, normalization, and heat current density, we find to terms linear in deviations from equilibrium

$$\begin{aligned} \tilde{f}_N = & (N!/Z^{(0)}) \\ & \cdot \exp \left\{ \int \left[\frac{-E_N(\mathbf{x}, \mathbf{X}) + \mu(\mathbf{x})n_N(\mathbf{x}, \mathbf{X})}{kT(\mathbf{x})} \right. \right. \\ & \left. \left. + \mathbf{A}(\mathbf{x}) \cdot Q_N(\mathbf{x}, \mathbf{X}) \right] dx \right\} \end{aligned} \quad (6.11)$$

where we identify the Lagrange multipliers for the thermodynamic conditions as before, and $\mathbf{A}(\mathbf{x})$ is a Lagrange multiplier for the heat flow.

To evaluate $\mathbf{A}(\mathbf{x})$ to linear terms we write the heat flux

$$Q(\mathbf{x}) = \mathbf{A}(\mathbf{x}) \cdot \int Q_N(\mathbf{x}, \mathbf{X}) Q_N(\mathbf{x}', \mathbf{X}) f_N^{(0)}(\mathbf{X}) d\mathbf{X} d\mathbf{x}'. \quad (6.12)$$

To this order we can replace the distribution function $f_N^{(0)}$ by an equilibrium canonical ensemble. The evaluation of the integral is then a problem in equilibrium theory. We need note here only that $\mathbf{A}(\mathbf{x})$ is completely determined by the heat flow so that \tilde{f}_N is a generalization of the f_1 defined by

Eq. (2.2). Actually \tilde{f}_N involves implicitly a relaxation time assumption, as will be made clear in our future publication.

When \tilde{f}_N is integrated over $N - 2$ particles it yields a pair distribution function \tilde{f}_2 which has the same formal dependence on ξ_1, ξ_2 and \mathbf{r}_{12} as the f_2 found from the Fokker-Planck equation, for the case of no mass flows considered in this section.

The advantage of \tilde{f}_N , over f_N , is that no new parameter like τ needs to be explicitly introduced. It has, however, the obvious disadvantage that there is now no prescribed relation between \mathbf{Q} and the temperature gradient; rather, each is specified separately, and we get the distribution function in terms of these. It is only when the \tilde{f}_2 coming from this distribution is put into some kinetic equation, like the Fokker-Planck equation, that a relation between \mathbf{Q} and $\partial T/\partial \mathbf{r}$ may be found, at least for "normal" distribution. We might have hoped to avoid using any kinetic equation but rather employ directly the Liouville equation, to find relations between \mathbf{Q} and $\partial T/\partial \mathbf{r}$. We have not succeeded, however, in doing this; it appears that irreversibility must be introduced somewhere before one can obtain transport coefficients.

ACKNOWLEDGMENTS

We would like to mention that several years ago Dr. Peter J. Price brought up the idea, during a discussion, with one of us (J. L. L.) that a quantity like $s + \sigma\tau$ might serve as a generalization of the entropy in nonequilibrium processes.

This work was supported by the Air Force Office of Scientific Research of the Air Research and Development Command.

APPENDIX A

Eigenfunctions of the Fokker-Planck Operator

In Sec. 2 we employed the theorem that the weighted N -dimensional Hermite polynomials, $\omega\mathcal{H}^{(n)}$, are the eigenfunctions of the three-dimensional Fokker-Planck operator, \mathcal{A} , with eigenvalues $(-n)$. This result follows from a theorem which we consider in this appendix concerning a more general Fokker-Planck operator, e.g., one of the type designated by J_2 in Sec. 4.

The N -dimensional Hermite polynomial of order n is a n th order tensor having N^n components. A typical component may be designated by $\mathcal{H}_{\alpha_1 \dots \alpha_n}^{(n)}(v_{\alpha_1}, \dots, v_{\alpha_n})$ where the v_α are elements of an N -space vector \mathbf{v} . We are concerned with the generalized N -dimensional Fokker-Planck operator

$$J_N(\varphi) = \sum_{i,j=1}^N \zeta_{ij} \frac{\partial}{\partial v_j} \left[\omega \frac{\partial}{\partial v_i} \omega^{-1} \varphi \right], \quad (\text{A1})$$

where

$$\omega = (2\pi)^{-\frac{1}{2}N} \exp \left\{ -\frac{1}{2} \sum_i v_i^2 \right\}. \quad (\text{A2})$$

It is easily verified that

$$J_N(\omega\mathcal{H}_{\alpha_1 \dots \alpha_n}^{(n)}) = - \sum_{i,j=1}^N \sum_{k=1}^n \zeta_{ij} \delta_{i\alpha_k} \omega\mathcal{H}_{\alpha_1 \dots \alpha_n}^{(n)} \cdot (v_{\alpha_1}, \dots, v_{\alpha_{k-1}}, v_j, v_{\alpha_{k+1}}, \dots, v_{\alpha_n}). \quad (\text{A3})$$

A proof involves the differential and recurrence properties of the Hermite functions.¹⁴ In the special case that ζ is diagonal $J_N(\)$ reduces to $\zeta\mathcal{A}(\)$ in N -dimensions and (A3) becomes

$$\mathcal{A}(\omega\mathcal{H}^{(n)}) = -n\omega\mathcal{H}^{(n)}. \quad (\text{A4})$$