Definition of Temperature in the Kinetic Theory of Dense Gases*

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(Received 20 May 1966)

The question of the appropriate definition of temperature in the kinetic theory of dense gases is discussed. An apparent contradiction in the value of the bulk viscosity between two methods of making the transition from the kinetic to the hydrodynamic stage is resolved. It is shown that the definitions of temperature through the kinetic energy and through the total energy are equivalent. The general question of the appropriate choice of macroscopic variables in nonequilibrium statistical mechanics is discussed. It is pointed out that the form of the equations of hydrodynamics is covariant with the definition of the macroscopic variables, but the molecular-distribution functions are invariant to this choice. In spite of the equivalence of temperature definition between a quantity which is a local integral of motion and one which is not, the the principle that macroscopic observables are properly chosen to be "approximate single-valued integrals of motion" can still be maintained. The question of which temperature or bulk viscosity is measured is discussed in the context of specific experimental situations.

I. INTRODUCTION

AS the program for a kinetic theory of dense gases proposed by Bogolyubov[1] becomes realized in specific formulas and algorithms, a number of ambiguities and internal inconsistencies have become apparent. The best known of these is the fact, almost certainly established, that no power-series expansion of transport properties is possible beyond the term linear in the density. Less well known, but equally disturbing, is the fact that two different ways of carrying out the transition from the kinetic to the hydrodynamic stage, each reasonable in itself, lead to different results for the bulk viscosity. Thus an apparently well-defined fluid property seems to have a value which depends on the means of calculating it.

The first of these two difficulties, of course, opens up the possibility that the whole Bogolyubov program is invalid. It is possible, however, on the basis of the established facts to take the more conservative position that the Bogolyubov functional expressions for the distribution functions exist, but have no density expansion beyond the first few terms. In this paper we will be concerned, not with the first difficulty, but with the second. In doing so we will provisionally take the conservative position with respect to the first.

The transition from the kinetic stage to the hydrodynamic stage, taking triple collision into account, i.e., the Chapman-Enskog solution of the generalized Boltzmann equation, was first carried out by Choh and Uhlenbeck.[2] An essential feature of their procedure was

their choice of a microscopic expression to represent the temperature valid both in the presence of gradients of the macroscopic variables and in the presence of intermolecular interactions. Noting that the kinetic energy per particle is still $\frac{3}{2}kT$, even in the presence of intermolecular interactions, they chose this dynamical variable as the appropriate measure of the temperature. This choice has an obvious advantage of simplicity. Recently, Green, Garcia-Colin, and Chaos[3] in the context of a Chapman-Enskog solution of the generalized Boltzmann equation, and Ernst[4] in the context of the autocorrelation expressions for transport properties, have used another microscopic definition of temperature based on the local *total*-energy density, including the potential energy. The temperature is defined by the same relationship to the local densities of particles, energy, and momentum as obtained in equilibrium. This definition, while more complicated than that used by Choh and Uhlenbeck, is based on the five local integrals of motion: the two scalars, energy and number of particles, and the vector, momentum. The importance of choosing as macroscopic variables approximate dynamical integrals of motion has been emphasized elsewhere by one of us.[5]

Although these two definitions yield the same result in equilibrium, they apparently yield different results for the bulk viscosity and other aspects of the hydrodynamic stage. It is clear that the ambiguity in the definition goes beyond the specific Bogolyubov program and is nothing else than the question: what is the appropriate definition of temperature in a nonequilibrium interacting system? Indeed, the question is one

[1] N. N. Bogolyubov, *Problems of a Dynamical Theory in Statistical Mechanics* (Moscow, 1946) [English transl.—*Studies in Statistical Mechanics*, edited by J. De Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 1].

[2] S. T. Choh and G. E. Uhlenbeck, University of Michigan Report, 1958 (unpublished). See also L. S. Garcia-Colin and A. Flores, Physica **32**, 289, 444 (1966).

[3] M. S. Green, L. S. Garcia-Colin, and F. Chaos, Physica **32**, 450 (1966).

[4] M. H. Ernst, thesis, University of Amsterdam, 1964 (unpublished); Physica **32**, 209 (1966).

[5] M. S. Green, J. Chem. Phys. **20**, 1281 (1952).

aspect of the even broader question: how are macroscopic variables describing nonequilibrium systems to be chosen? The ambiguity in the definition of temperature has also been considered by Wang Chang, Uhlenbeck, and De Boer,[6] by Ernst,[7] and by McLennan.[8]

We shall denote by method I the Chapman-Enskog solution of the generalized Boltzmann equation using the total-energy definition of temperature, and by method II, the solution using the kinetic-energy definition of temperature. Both of these methods have been carried out in a form[3,9] which defers the density expansion to the last step in the calculation. This procedure has the advantage that general questions, such as that of the present paper, can be seen through more easily. At the same time it permits the conservative position about the validity of the Bogolyubov program to be taken.

The following features are characteristic of these two methods.[10]

(a) The results for shear viscosity and thermal conductivity are identical in both cases.

(b) The bulk viscosities are the same in the zeroth and first order in the density and indeed are both equal to zero. They are both nonzero and different in higher order.

(c) In method I, the energy-conservation equation in lowest order (i.e., the first) in gradients involves only equilibrium thermodynamic quantities. In method II the kinetic-energy equation to the same order *apparently* involves the first-order deviations from the Maxwell distribution.

Since the bulk viscosity enters into the phenomenological equations only in a term which is second order in the gradients, (b) implies that the equation of momentum conservation differs for the two cases only in the second order in the gradients. This is true also for the equation for the rate of change of temperature in the two methods. They are identical in the first order, but differ in the second order. In spite of these fundamental differences in the results of the two methods, it is the primary purpose of this paper to show that they are entirely equivalent. We will show that there is an equivalence relationship between the two macroscopic descriptions such that equivalent macroscopic states will be predicted to develop in exactly the same way by both methods. A more precise statement of this equivalence is given in Sec. II below. In Sec. III we express the equations of method I and method II in parallel form. In Sec. IV we give the explicit relationship between the two macroscopic descriptions, while in Sec.

V we demonstrate identical time development of equivalent macroscopic states. In Sec. VI we attempt to draw some inferences of the equivalence theorem proved in Secs. II, III, IV, and V for the general question of the appropriate choice of macroscopic variables in a nonequilibrium system.

II. THE STATEMENT OF THE EQUIVALENCE THEOREM

In method I we seek a solution of the generalized Boltzmann equation which is a functional of the local density of particles $n(q)$, the local velocity $\mathbf{u}(q)$, and the local *total*-energy density $\mathscr{E}(q)$

$$f_{\mathrm{I}}(x/n,\mathbf{u},\mathscr{E}),$$

where $x \equiv (\mathbf{q},\mathbf{p})$, the position and momentum of a particle. In method II we seek a solution of the generalized Boltzmann equation which is a functional of the local particle, the local velocity and the local kinetic-energy density

$$f_{\mathrm{II}}(x/n,\mathbf{u},\theta),$$

where $n(q)$ and $\mathbf{u}(q)$ are as before and $\frac{3}{2}n\theta(q)$ $+n(q)\frac{1}{2}mu^2$ (q) is the total kinetic-energy density. m is the mass of a particle. The second part of the kinetic energy may be called the kinetic energy of the convective motion, the first part, the kinetic energy of the peculiar motion. θ has been called the kinetic temperature.

n, $\mathbf{u}$, $\mathscr{E}$, and θ are functions of position and f_{I} and f_{II} depend in principle on the values of these functions throughout the fluid. Actually the value of $f_{\mathrm{I,II}}(\mathbf{q},\mathbf{p})$ depends only on the values of n, $\mathbf{u}$, $\mathscr{E}$, and θ in the immediate neighborhood of $\mathbf{q}$. In the Chapman-Enskog procedure, an expansion in a uniformity parameter is made in which the dependence on the macroscopic variables for other points than $\mathbf{q}$ is expressed through their first and higher order spatial derivatives.

It has been pointed out by Ernst[7] by direct comparison of the solutions, that f_{I} and f_{II} differ in first order in the gradients by a term proportional to the divergence of the velocity field, but that the local temperature corresponds to the same macroscopic state also differs in the two methods by a term proportional to the divergence of the velocity field. Ernst points out also that the effect of these two differences exactly compensate each other. Thus to the first order in the gradients the two methods lead to exactly the same single-particle distribution for the same macroscopic state. In this paper we will show that this compensation is a consequence of the general formulation of the two methods, independent of an expansion in the uniformity parameter. There is only one Chapman-Enskog solution of the Boltzmann equation independent of the choice of macroscopic variables.

We may express the theorem to be proved in the following more mathematical terms. There exists a

[6] C. S. Wang Chang, G. E. Uhlenbeck, and J. De Boer, *Studies in Statistical Mechanics*, edited by J. De Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1964), Vol. II. p. 243.

[7] M. H. Ernst, Physica **32**, 252 (1966).

[8] J. A. McLennan, Advan. Chem. Phys. **5**, 261 (1963).

[9] L. S. Garcia-Colin and Asdrúbal Flores, J. Math. Phys. **7**, 254 (1966).

[10] F. Chaos and L. S. Garcia-Colin, Phys. Fluids **9**, 382 (1966).

one-to-one relationship between the macroscopic variables of method I and those of method II.

$$\theta(\mathbf{q}) = \theta(\mathbf{q}\,|\,n(\mathbf{q}'), \mathbf{u}(\mathbf{q}'), \mathscr{E}(\mathbf{q}')), \qquad (1)$$

$\mathbf{u}$ and n identical in both methods, such that

$$f_{II}(x\,|\,n,\mathbf{u},\theta) = f_I(x\,|\,n,\mathbf{u},\mathscr{E}). \qquad (2)$$

The relationship (1) is nonlocal in the same sense that the dependence of $f_{I,II}$ on n, $\mathbf{u}$, θ, $\mathscr{E}$ is nonlocal, i.e., $\theta(\mathbf{q})$ is determined in principle by the values of n, $\mathbf{u}$ and $\mathscr{E}$ at all points of the fluid. Actually, only the values of n, $\mathbf{u}$, $\mathscr{E}$ for points $\mathbf{q}'$ near $\mathbf{q}$ will be significant in determining the values of $\theta(\mathbf{q})$. Equation (1) makes precise the meaning of equivalent macroscopic states, while Eq. (2) expresses the identity of the single-particle distribution function for equivalent macroscopic states. Equation (1) has an inverse:

$$\mathscr{E}(\mathbf{q}) = \mathscr{E}(\mathbf{q}\,|\,n(\mathbf{q}'), u(\mathbf{q}'), \theta(\mathbf{q}')), \qquad (3)$$

so that the relationship between methods I and II is symmetric.

III. THE TWO METHODS

Let us consider those equations which determine f_I. These are first of all the equations which define the macroscopic variables n, $\mathbf{u}$, and $\mathscr{E}$. These are

$$n(\mathbf{q}) = \int f_I(x\,|\,n,\mathbf{u},\mathscr{E})d\mathbf{p}, \qquad (4)$$

$$mn(\mathbf{q})\mathbf{u}(\mathbf{q}) = \int \mathbf{p}f_I(x\,|\,n,\mathbf{u},\mathscr{E})d\mathbf{p}, \qquad (5)$$

$$\mathscr{E}(\mathbf{q}) = \int \frac{p^2}{2m}f_I(x\,|\,n,\mathbf{u},\mathscr{E})d\mathbf{u}$$
$$+\frac{1}{2}\int \phi(r)f_2(x_1,x_2\,|\,f_I(x_1\,|\,n,\mathbf{u},\mathscr{E}))d\mathbf{p}dx_2. \qquad (6)$$

In Eq. (6), $\phi(r)$ is the intermolecular pair potential, $r = |\mathbf{q} - \mathbf{q}_2|$, $x_1 \equiv (\mathbf{p},\mathbf{q})$, and $f_2(x_1,x_2\,|\,f_I)$ is the pair-distribution function given in the Bogolyubov theory as a functional of the single-particle distribution function. In its turn, this is a functional of n, $\mathbf{u}$, $\mathscr{E}$ in the Chapman-Enskog procedure. Note that Eqs. (4), (5), and (6) are in fact identities which f_I must satisfy. f_I also satisfies the generalized Boltzmann equation, which we write in the form given in Ref. 3:

$$\frac{\partial f_I}{\partial t} + \frac{\mathbf{p}}{m}\cdot\frac{\partial}{\partial \mathbf{q}}f_I = -\frac{\partial}{\partial \mathbf{p}}\cdot\int \frac{\partial}{\partial \mathbf{q}}\phi(r)$$
$$\times f_2(x_1,x_2\,|\,f_I)dx, \quad d\mathbf{p} = \Phi(x_1\,|\,f_I). \qquad (7)$$

The Chapman-Enskog approach requires that f_I be a *time-independent* functional of n, $\mathbf{u}$, and ξ, and therefore, that f_I changes with time only through changes in these quantities. Their time-rate-of-change is given by

the equations

$$Dn/Dt + n\ \mathrm{div}\mathbf{u} = 0, \qquad (8)$$

$$D\mathbf{u}/Dt + (1/nm)\mathrm{div}\mathbf{P} = 0, \qquad (9)$$

$$(D\mathscr{E}/Dt) + \mathrm{div}\mathbf{J} + \mathscr{E}\ \mathrm{div}u + \mathbf{P}:\mathbf{D} = -\mathbf{u}\cdot\mathrm{div}\mathbf{P}, \qquad (10)$$

where $D/Dt = \partial/\partial t + \mathbf{u}\ \mathrm{grad}$. $\mathbf{D}$ is the symmetric part of the rate-of-strain tensor,

$$\mathbf{D} = (\nabla\mathbf{u})_{sym}, \qquad (11)$$

$\mathbf{P}$ is the stress tensor, and $\mathbf{J}$ is the total heat-current vector. These are expressed in terms of f_1 and $f_2(x_1x_2\,|\,f_1)$ though well-known formulas given for example in Ref. 3.

This system of equations is solved in the Chapman-Enskog method by expansion in powers of a uniformity parameter, or what is the same thing, in powers of the the gradients. The zeroth-order solution is, of course, a local Maxwellian distribution

$$f_1{}^0(x/n,\mathbf{u},\mathscr{E}) = \frac{n(\mathbf{q})}{(2\pi m\theta'(\mathbf{q}))^{3/2}}\exp\left[-\frac{(\mathbf{p}-m\mathbf{u}(\mathbf{q}))^2}{2m\theta'(\mathbf{q})}\right], \qquad (12)$$

where θ' is a parameter which is to be determined by requiring that $f_1{}^0$ satisfy the identities, Eqs. (4), (5), and (6), to zeroth order in the gradients. Since $f_1{}^0$ is of the Maxwellian form, this is nothing else than the statement that $\theta'(q)$ is determined by the values of n, $\mathbf{u}$, and $\mathscr{E}$ at $\mathbf{q}$ by the *equilibrium* thermodynamic relationship. θ' is the quantity which plays the role of temperature in method I.

In the first order, the substitution of Eqs. (8–10) into the Boltzmann equation (7) yields an inhomogeneous integral equation whose general solution has five undetermined constants, corresponding to the five conserved quantities: particles, energy, and the total-momentum vector. These are uniquely determined by the requirement that the five identities, Eqs. (4), (5), (6) are satisfied in the first order. The same situation holds formally in all higher orders. Thus we may say that a solution to Eqs. (4–11), which is expandable in powers of the gradients, is unique.

In method II the Boltzmann equation [Eq. (7)], the defining identities [Eqs. (4), (5)], and the macroscopic equations of motion [Eqs. (8), (9)] for n and $\mathbf{u}$ are identical to those of method I. Instead of Eq. (6) we have the defining identity for the kinetic temperature

$$\tfrac{3}{2}n\theta(\mathbf{q}) + \frac{nmu^2}{2} = \int \frac{p^2}{2m}f_{II}(x\,|\,n,\mathbf{u},\theta)d\mathbf{p}, \qquad (13)$$

and instead of Eq. (10), we have the macroscopic equation of motion for θ

$$\tfrac{3}{2}n(D\theta/Dt) + \mathrm{div}(\mathbf{J}^K + \mathbf{J}^{\phi_1}) + \mathbf{P}:\mathbf{D} = R(\mathbf{q}\,|\,f_{II}), \qquad (14)$$

where

$$R(\mathbf{q}/f) = \int dx_2 d\mathbf{p}_1\frac{\partial\phi(r)}{\partial\mathbf{q}}\cdot\frac{\mathbf{p}_2-\mathbf{p}_1}{m}f(x_1,x_2\,|\,f), \qquad (15)$$

and $\mathbf{J}^K$ and $\mathbf{J}^{\phi 1}$ are the kinetic and first-potential part of the heat current, respectively, as given in Ref. 3.

Equations (4), (5), (7–9), (13–15) have been solved as an expansion in powers of the uniformity parameter by Garcia-Colin and Flores[10] and by Ernst.[7] In zeroth order

$$f_{II}{}^0(x\,|\,nu\theta) = \frac{n(\mathbf{q})}{(2\pi m\theta(\mathbf{q}))^{3/2}}\exp\left[-\frac{(\mathbf{p}-m\mathbf{u}(\mathbf{q}))^2}{m\theta(\mathbf{q})}\right]. \quad (16)$$

Substitution of $f_I{}^0$ in the identities, Eqs. (4), (5) and (13), identifies the parameter θ with the kinetic temperature. In the next order, an inhomogeneous integral equation is obtained whose general solution has five undetermined constants which are determined uniquely by the requirement that the defining identities are satisfied also in the first order. This procedure can be carried through formally in all orders, yielding a unique solution expandable in powers of the gradients.

IV. THE RELATIONSHIP BETWEEN THE TWO MACROSCOPIC DESCRIPTIONS

It is easy to see what the explicit form of the relationship between the macroscopic descriptions of methods I and II must be. If Eq. (2) is valid, we may substitute f_I for f_{II} in the defining identity for θ [Eq. (13)]. This equation becomes

$$\tfrac{3}{2}n\theta(\mathbf{q}) + \tfrac{1}{2}nmu^2(\mathbf{q}) = \int \frac{p^2}{2m}f_I(x\,|\,n,\mathbf{u},\mathcal{E})d\mathbf{p}. \quad (17)$$

Since the right-hand side of Eq. (17) is a functional of n, $\mathbf{u}$, $\mathcal{E}$, this equation implies a relationship of the form of Eq. (1). Equation (17) becomes an explicit relationship as soon as we know f_I explicitly, i.e., as soon as we have solved the Boltzmann equation by method I.

Similarly, we may obtain the inverse-relationship equation (13) by substituting f_{II} for f_I in the defining identity for $\mathcal{E}$ [Eq. (6)]. We have

$$\mathcal{E}(q) = \tfrac{3}{2}n(\mathbf{q})\theta(\mathbf{q}) + \tfrac{1}{2}n(\mathbf{q})mu^2(\mathbf{q})$$
$$+ \frac{1}{2}\int \phi(r)f_2(x_1x_2\,|\,f_{II}(x\,|\,n,\mathbf{u},\theta))dx_2d\mathbf{p}. \quad (18)$$

Equation (18) becomes explicit as soon as we have the solution of the Boltzmann equation by method II. Needless to say, in writing Eq. (17) as the explicit form of equation (1), [or Eq. (18), as the explicit form of Eq. (3)], we have not *assumed* the equality of f_I and f_{II} but merely use the supposed equality to motivate our choice.

V. THE PROOF OF THE THEOREM

In order to prove the theorem stated in Sec. II we construct a functional of n, $\mathbf{u}$, $\mathcal{E}$:

$$f_I{}'(x\,|\,n,\mathbf{u},\mathcal{E}) = f_{II}[x\,|\,n,\mathbf{u},\theta(q'\,|\,n,\mathbf{u},\mathcal{E})]. \quad (19)$$

By substituting for θ in f_{II} its values in terms of n, $\mathbf{u}$, $\mathcal{E}$, we will show that $f_I{}'$ satisfies all the equations [Eqs. (4–11)] which determine f_I. Since a solution of these equations expandable in powers of the gradients is unique, we have

$$f_I{}' = f_I, \quad (20)$$

which is the theorem to be proved. Making use of the fact that f_I depends on time only through n, $\mathbf{u}$, $\mathcal{E}$, we write the Boltzmann equation [Eq. (7)] in the form

$$\frac{Df_I}{Dt} = \int dq'\left\{\left(\frac{\delta f_I}{\delta n(q')}\right)_{u,\mathcal{E}}\frac{Dn(\mathbf{q}')}{Dt}\right.$$
$$\left. + \left(\frac{\delta f_I}{\delta \mathbf{u}(q')}\right)_{n,\mathcal{E}}\cdot\frac{D\mathbf{u}(\mathbf{q}')}{Dt} + \left(\frac{\delta f_I}{\delta\mathcal{E}(q')}\right)_{n,\mathbf{u}}\frac{D\mathcal{E}(\mathbf{q}')}{Dt}\right\}$$
$$= -(\mathbf{p}/m)\cdot(\partial f_I/\partial\mathbf{q}) + \Phi(x\,|\,f_I). \quad (21)$$

In Eq. (21), the time derivatives of the macroscopic variables are to be taken from Eqs. (8–11).

Similarly we have

$$\frac{Df_{II}}{Dt} = \int dq'\left\{\left(\frac{\delta f_{II}}{\delta n(\mathbf{q}')}\right)_{u,\mathcal{E}}\frac{Dn(\mathbf{q}')}{Dt} + \left(\frac{\delta f_{II}}{\delta \mathbf{u}(q')}\right)_{n,\mathcal{E}}\frac{D\mathbf{u}(\mathbf{q}')}{Dt}\right.$$
$$\left. + \left(\frac{\delta f_{II}}{\delta\theta(\mathbf{q}')}\right)_{n,\mathbf{u}}\frac{D\theta(q')}{Dt}\right\} = -\frac{\mathbf{p}}{m}\cdot\frac{\partial f_{II}}{\partial\mathbf{q}} + \Phi(x\,|\,f_{II}), \quad (22)$$

where the time derivatives of the macroscopic variables are to be taken from Eqs. (8), (9), and (14). In Eqs. (21) and (22), the symbols $(\delta f/\delta n)$, etc. signify functional differentiation with respect to the indicated argument function at the point $\mathbf{q}'$. The subscripts $\mathbf{u}$, $\mathcal{E}$, etc. indicate which variables are held constant.

Let us show first of all that $f_I{}'$ satisfies Eq. (21). We substitute for f_{II} in Eq. (22) its expression in terms of $f_I{}'$, i.e.,

$$f_{II}(x\,|\,n,\mathbf{u},\theta) = f_I{}'[x\,|\,n,\mathbf{u},\mathcal{E}(n,\mathbf{u},\theta)], \quad (23)$$

and use the chain rule for functional differentiation.

$$\left(\frac{\delta f_{II}}{\delta n(q')}\right)_{u,\theta} = \left(\frac{\delta f_I{}'}{\delta n(\mathbf{q}')}\right)_{u,\mathcal{E}}$$
$$+ \int d\mathbf{q}''\left(\frac{\delta f_I{}'}{\delta\mathcal{E}(\mathbf{q}'')}\right)_{n,\mathbf{u}}\left(\frac{\delta\mathcal{E}(q'')}{\delta n(q')}\right)_{u,\theta}, \quad (24)$$

$$\left(\frac{\delta f_{II}}{\delta\mathbf{u}(\mathbf{q}')}\right)_{n,\theta} = \left(\frac{\delta f_I{}'}{\delta\mathbf{u}(q')}\right)_{n,\mathcal{E}}$$
$$+ \int d\mathbf{q}''\left(\frac{\delta f_I{}'}{\delta\mathcal{E}(\mathbf{q}'')}\right)_{n,\mathbf{u}}\left(\frac{\delta\mathcal{E}(q'')}{\delta\mathbf{u}(q')}\right)_{n,\theta}, \quad (25)$$

$$\left(\frac{\delta f_{II}}{\delta\theta(\mathbf{q}')}\right)_{n,\mathbf{u}} = \int d\mathbf{q}''\left(\frac{\delta f_I{}'}{\delta\mathcal{E}(\mathbf{q}'')}\right)_{n,\mathbf{u}}\left(\frac{\delta\mathcal{E}(q'')}{\delta\theta(\mathbf{q}')}\right)_{n,\mathbf{u}}. \quad (26)$$

Substituting these expressions in Eq. (22) and noting Eq. (21)

$$\frac{Df_{\mathrm{I}}}{Dt} = \frac{Df_{\mathrm{I}}'}{Dt} + \int d\mathbf{q}'' d\mathbf{q}' \left(\frac{\delta f_{\mathrm{I}}'}{\delta \mathcal{S}(\mathbf{q}'')}\right)_{n,\mathbf{u}} \left\{ \int d\mathbf{q}' \left[\left(\frac{\delta \mathcal{S}(\mathbf{q}'')}{\delta n(\mathbf{q}')}\right)_{\mathbf{u},\theta} \right. \right.$$

$$\times \frac{Dn(\mathbf{q}')}{Dt} + \left(\frac{\delta \mathcal{S}(\mathbf{q}'')}{\delta \mathbf{u}(\mathbf{q}')}\right)_{n,\theta} \frac{D\mathbf{u}(\mathbf{q}')}{Dt}$$

$$\left. \left. + \left(\frac{\delta \mathcal{S}(\mathbf{q}'')}{\delta \theta(\mathbf{q}')}\right)_{n,\mathbf{u}} \frac{D\theta(\mathbf{q}')}{Dt} \right] - \frac{D\mathcal{S}(\mathbf{q}'')}{Dt} \right\}. \quad (27)$$

The second term on the right in Eq. (27) is zero. That this is so may be seen immediately from the definition of $\mathcal{S}(q|n,\mathbf{u},\theta)$ [Eq. (18)]. On the one hand, since $\mathcal{S}$ is given in terms of single-particles distribution function f_{II} and a pair distribution function $f_2(x_1x_2|f_{\mathrm{II}})$ which satisfy the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy, $D\mathcal{S}/Dt$ must be given by Eq. (10) in which the heat current, stress, etc. are computed from f_{II} and $f_2(x_1x_2|f_{\mathrm{II}})$. On the other hand, since $\mathcal{S}$ is a time-independent functional of n, $\mathbf{u}$, and θ, $D\mathcal{S}/Dt$ must also be given by the integral expression in the curly brackets in Eq. (27), where Dn/Dt, $D\mathbf{u}/Dt$, $D\theta/Dt$ are given by Eqs. (8), (9), and (14). Since they are simply two different expressions for the rate of change of the same quantity, the two terms in the curly brackets must cancel identically. Thus we have

$$Df_{\mathrm{I}}'/Dt = Df_{\mathrm{II}}/Dt = -(\mathbf{p}/m)\cdot(\partial f_{\mathrm{II}}/\partial \mathbf{q}) + \phi(x|f_{\mathrm{II}})$$
$$= -(\mathbf{p}/m)\cdot(\partial f_{\mathrm{I}}'/\partial \mathbf{q}) + \Phi(x|f_{\mathrm{I}}'), \quad (28)$$

where the last step is justified by Eq. (23). We have shown that f_{I}' satisfies Eq. (22). Since we may also substitute f_{I}' for f_{II} in Eq. (18), f_{I}' also satisfies the defining identities for n, $\mathbf{u}$, $\mathcal{S}$. Since f_{I}' satisfies all the equations which determine f_{I}, we have

$$f_{\mathrm{I}}' = f_{\mathrm{I}}. \quad (29)$$

VI. CONCLUSION

The theorem proved in the last section brings several questions to the fore. The first question, of course, is the one with which we started. How can there be two valid theoretical values for the bulk viscosity and for the temperature, which are, after all, experimentally measurable quantities? A second question is: if the two methods for arriving at macroscopic hydrodynamics from generalized kinetic theory are equivalent in a mathematical sense, are there considerations of convenience or formal simplicity which would favor one method over the other? Finally there are questions which relate to the general problem of the choice of macroscopic variables in nonequilibrium statistical mechanics. How wide is the range of choice of appropriate macroscopic variables? Must we give up the principle that the macroscopic variables are properly

chosen to be the "approximate single-valued integrals of motion"?[11]

We consider the first question. When we substitute $f_{\mathrm{I}}(x|n,\mathbf{u},\mathcal{S})$ into Eqs. (8), (9), and (10) and $f_{\mathrm{II}}(x|n,\mathbf{u},\theta)$ into Eqs. (8), (9), and (14) we obtain two sets of five macroscopic equations of motion governing, in the first case, n, $\mathbf{u}$, and $\mathcal{S}$, and in the second, n, $\mathbf{u}$ and θ. These equations determine the development of the macroscopic variables in such a way that, if $n(q)$, $\mathbf{u}(q)$, $\theta(q)$, and $n(q)$, $\mathbf{u}(q)$ and $\mathcal{S}(q)$ are equivalent states at $t=0$, they are equivalent for all times. The phenomenological equations themselves, however, are covariant with respect to such a change. In particular, the coefficient of $\boldsymbol{\nabla}\boldsymbol{\nabla}:\mathbf{u}$ in the equation of motion for $\mathbf{u}$ changes in the transformation. This would also be true of the equation of motion for θ' in method I. The coefficients of various second spatial derivatives of the macroscopic variables would be different from those of corresponding derivatives in the equations of motion of θ in method II.

If we ask the question from the experimental point of view, i.e., which bulk viscosity do we measure, we note that every measurement of a transport property of matter must be interpreted through the appropriate macroscopic equations of motion. Thus in one of the most common ways of measuring bulk viscosity we measure the attenuation coefficient of a sound wave in passing through the fluid. This attenuation coefficient is related to the bulk viscosity (and the shear viscosity and thermal conductivity) by a formula obtained from a solution of the macroscopic equations of motion of a fluid for wave propagation. If we take for these equations those of method I, it will be the bulk viscosity of method I which will be derived from experiment. If we take the macroscopic equations of motion of method II, the bulk viscosity of method II will be obtained.

It should be noted that in both cases the bulk viscosity can be defined as a ratio of stress to rate of strain in the limit as the rate of strain goes to zero, i.e., in the limit in which the system approaches an equilibrium system. The temperature to be associated with each bulk viscosity is the limiting equilibrium temperature which is defined unambiguously. One may, how-

[11] The concept of "approximate single-valued integrals of motion" which was introduced in Ref. 5 in a heuristic way can be made more precise in the context of a uniformity-parameter expansion. Dynamical variables whose rate of change is zero in zeroth order in the uniformity parameter but not in higher order are "approximate single-valued integrals of motion." More generally, in a dynamical system whose description depends analytically on a small parameter, an "approximate single-valued integrals of motion" is any function of the phase which is a "single-valued integral of motion" in the ordinary sense when the small parameter is set equal to zero. Since the approximate single-valued integrals of motion are usually relatively few in number and since their rates of change are small, they follow a more comprehensible pattern than that of the other dynamical variables. These quantities are natural choices as macroscopic variables. If we have chosen a sufficient number of such quantities to determine a generalized microcanonical ensemble in phase space in which the zeroth-order dynamical system is ergodic, we can expect the macroscopic equations of motion to be differential equations of the first order in time, as are, for example, Eqs. (8), (9), and (10).

ever, legitimately ask, which temperature, θ or θ', does one measure when a finite velocity divergence is present? The answer to this question must be that a thermometer calibrated to read equilibrium temperatures correctly will not necessarily read either θ or θ' in the nonequilibrium situation.[8] What it does read will depend, in contrast to the equilibrium case, on its structure and on the nature of its interaction with the system. To determine either θ or θ' from its reading would require a knowledge of the effect of this structure and interaction.

As Ernst has pointed out[7] $\mathcal{S}$ and θ are not the only macroscopic variables which lead to a consistent Chapman-Enskog solution of the generalized Boltzmann equation. Indeed, he has shown that quite arbitrary moments of the distribution function lead to a solution of the Boltzmann equation. For instance, if one uses instead of $\mathcal{S}$ or θ, trace $\mathbf{P}$, where $\mathbf{P}$ is the stress tensor, one obtains a system of phenomenological equations in which the bulk viscosity is zero.

It is clear that nothing in the analysis in the previous sections of this paper depended on the specific choice of macroscopic variables. We might, indeed, have replaced n and $\mathbf{u}$ as well by other quantities. Whatever the choice, however, there is only one Chapman-Enskog solution to the Boltzmann equation. The state of the fluid as represented by the single-particle distribution is *invariant* under the choice of macroscopic variables. The macroscopic equations of motion, however, are *covariant* with this choice.

The variables n, $\mathbf{u}$ and $\mathcal{S}$ recommend themselves to us because they are "approximate single-valued integrals of motion"[5,12] of the system. The number of particles, the total momentum, the total energy in a region of space can only change through effects which take place across the boundaries of the region. In view of the equivalence theorem, is there then no advantage in using these as macroscopic variables?

Actually there is an obvious formal advantage. The macroscopic equations of motion for n, $\mathbf{u}$ and $\mathcal{S}$ to the first order in the gradients, i.e., the Euler equations, can be derived, and were in fact historically so derived, without a detailed knowledge of the deviation of the local state of the fluid from equilibrium. This is not so for the variables n, $\mathbf{u}$, and θ. When the Chapman-Enskog scheme is carried out for these variables, the first-order (in the gradients) deviation of f_{I} for equilibrium is required in order to determine the macroscopic equations of motion to the same order. Thus the variables n, $\mathbf{u}$ and $\mathcal{S}$ which are "approximate single-valued integrals of motion" have a formal advantage over the variables n, $\mathbf{u}$ and θ which are not. It is important to note that the Navier-Stokes equations, which are the commonly used form of the macroscopic equations of motion, are equations of motion for n, $\mathbf{u}$, and $\mathcal{S}$.[12] They were derived phenomenologically before

[12] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1959).

any statistical-mechanical treatment of nonequilibrium phenomena, no doubt because of this formal advantage.

There is, however, a much more important and pervasive role than the above for macroscopic variables which are approximate dynamical integrals of motion. To see this let us note that the variables $n(q)$, $\mathbf{u}(q)$, $\mathcal{S}(q)$ for all q are not the only approximate dynamical integrals of motion. Any function of these variables will also be such. Since they are parametrized by a continuous variable q, this means that any nonlocal *functional* of $n(q)$, $\mathbf{u}(q)$, $\mathcal{S}(q)$ considered as functions of q will be an approximate dynamical integral of motion. Now a little reflection on Eq. (17) shows that, so far as any state of the system which belongs to a Chapman-Enskog solution of the generalized Boltzmann equation is concerned, $\theta(q)$ is just such a nonlocal functional of $n(q)$, $\mathbf{u}(q)$, and $\mathcal{S}(q)$. This means that, insofar as such a state is concerned, $\theta(q)$ may also be considered to be an approximate dynamical integral of motion. The kinetic temperature is not, of course, a nonlocal functional of the local energy density for all states of the system, but only for Chapman-Enskog states. If, however, we had started with $\theta(q)$ defined by Eq. (17) with ξ defined through an arbitrary single-particle distribution, instead of the most general definition of kinetic temperature, we would have arrived at no different Chapman-Enskog solution. Thus the range of macroscopic variables which are appropriate to describe a Chapman-Enskog state need be taken to be no wider than all nonlocal functionals of $n(q)$, $\mathbf{u}(g)$, and $\mathcal{S}(q)$. Any more general variables will be projected by the manipulations of the method onto the set of variables which are functionals of $n(q)$, $\mathbf{u}(q)$, and $\mathcal{S}(q)$. Physically, the difference between the actual dynamical variable and the projected one will be manifest only during the short induction interval during which the Chapman-Enskog solution is being set up.

To summarize our conclusions: We have found that the two methods proposed for making the transition from the kinetic to the hydrodynamic stage in the kinetic theory of dense gases are equivalent. They lead, however, to different macroscopic equations of motion and one must be careful to use the transport properties of each theory with the equations of motion appropriate to the theory. There is a certain formal advantage to the same variables n, $\mathbf{u}$, $\mathcal{S}$ and the most commonly used equations of fluid motion are based on these variables. Finally, the equivalence theorem does not imply that there is no special role played by the "approximate dynamical integrals of motion" but rather that this class of dynamical variables is much wider than, perhaps, was hitherto appreciated.

ACKNOWLEDGMENTS