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Theory of the Dynamics of Simple Fluids for Large Spatial Gradients and Long Memory

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A generalization of the classical fluid dynamics which describes noninstantaneous, nonlocal, and nonlinear responses of flows to the thermodynamic forces (gradients) is derived by statistical-mechanical methods. The conservation equations determining the mass, momentum, and energy densities are unchanged in form, but new expressions are given for the pressure tensor and heat current vector. The new expressions are specified functionals of the temperature, flow velocity, and Helmholtz free energy density, are determined by microscopic quantities (e.g., interparticle potential), and consist of a reversible and an irreversible part. The reversible parts are the expected fluxes in a local-equilibrium ensemble that includes nonlocal effects. The reversible contribution to the heat current is nonvanishing for large enough gradients. The expressions for the irreversible parts are the analog of the classical transport relations, and are linear combinations of integrals over space and time of correlation-function kernels convoluted with the thermodynamic forces. The kernels, which are specified functionals of the fluid densities and are a kind of local-equilibrium correlation of subtracted fluxes, are natural generalizations of the autocorrelation expressions for the classical transport coefficients.

I. INTRODUCTION

Fluids in bulk display a complexity of behavior which classical fluid dynamics cannot fully describe; namely, they exhibit noninstantaneous, nonlocal, and nonlinear responses of the flows of momentum and energy to the thermodynamic forces. Our objective here is to derive by statistical-mechanical methods a generalization of the classical dynamical equations for one-component simple fluids[1,2] which is capable of describing such effects. The new equations which are derived are exact because they are essentially a transcription of Liouville's equation, and we expect that they are indeed sufficiently rich in content so that they are capable of modeling the most complex behavior of such fluids. The most important new result is that the irreversible parts of the pressure tensor and heat current are linear combinations of integrals over space and time of correlation function kernels convoluted with the thermodynamic forces. These kernels are completely defined in terms of microscopic quantities; they are correlations averaged with a local-equilibrium distribution of subtracted fluxes, which are shifted in time by a new dynamical evolution operator. Each factor of the viscosity kernel generalizes in a natural way an analogous factor in the classical autocorrelation function (the space-time integral of which is the viscosity), and similarly for the thermal conductivity kernel. This result is established only under the circumstance that the fluid is initially in constrained equilibrium.

The conservation equations of the classical theory, in which the momentum and energy currents are expressed in terms of the pressure tensor and heat current, are generally valid. Thus the only issue for molecular theory is the derivation of expressions for the pressure tensor and heat current in terms of the densities of mass, momentum, and energy. M. S. Green found the current autocorrelation expressions for the transport coefficients appearing in the irreversible parts of the pressure tensor and heat current in 1954.[3,4] Since then many workers have sought to improve upon the derivation of his results; this work has been reviewed by Zwanzig.[5] All these derivations have contained a variety of heuristic elements, however, so that improved derivations based on the mechanical model for an isolated system of many particles are not superfluous. Work has also been directed toward finding more general expressions for the irreversible currents. Some of it gives an account of noninstantaneous and nonlocal effects, but only near absolute equilibrium.[6-10] Other work aimed at including nonlinear effects[11-13] has considered the steady state only, and has immediately sought an expansion in powers of the thermodynamic forces.

The present work is most closely related to the general theory presented by Richardson.[14] The expressions for the irreversible currents given in the present paper have precisely the structure proposed by him. Although he used a statistical-mechanical method, Richardson gave only the structure of a general dynamical theory. It is precisely our objective here to give the molecular expressions for all the quantities in his theory.

Very general formalisms for nonequilibrium statistical-mechanical theory have been given by Zwanzig[15] and by Robertson.[16] Our goals could be achieved by a direct application of Robertson's work and, in fact, he has already applied his method to pure energy transport.[17] We have considered it a *desideratum*, however, to take an approach which flows as naturally as possible from the Bogolubov-Chapman-Enskog[18-20] point of view familiar in the kinetic theory of gases while incorporating the use of projection techniques introduced by Zwanzig and Robertson. Therefore, while relying heavily on the work of these authors, a modified approach will be presented which can be viewed as a direct extension of the work of Kirkwood, H. S. Green, and others.[21-23] Our approach also has features in common with the work of Nakajima and Mori.[24,25] Moreover, it complements McLennan's work on the steady states of systems in thermomechanical baths.[26,27]

The present work is intended to provide a natural way of seeing that the pressure tensor and heat current are approximately proportional to the gradients of velocity and temperature (i.e., of deriving the whole transport relations rather than just deriving expressions for the coefficients). It is also intended to provide a theoretical framework within which the limits of applicability of the classical theory can be assessed. Moreover, it is felt that the approach to be presented contributes to our understanding of several issues, namely: Why is there an initial value problem for the usual fluid densities which are known to be an incomplete description of the microscopic state? In what sense (if any) do these densities have to be coarse-grained analogs of mechanical variables? Can such closed irreversible equations be derived for a completely isolated mechanical system?

The experimental motivation for this work is based mainly on data for fluids which require more complex microscopic models for their description than the one contemplated here. For example, more complicated materials exhibit a non-Newtonian dependence of the shear stress on the velocity gradient and this can be viewed as nonlinear behavior of the shear viscosity.[28] Although such effects do not seem to occur in simple fluids, the theoretical expectations have not yet been explored. It is known that the classical theory cannot predict the frequency dependence of the velocity and absorption of sound for many gases and liquids.[29] In some cases, such as in glycerol,[30] near critical points,[31,32] and in Greenspan's experiments on sound propagation in low-density gases,[33] relaxation effects occur which cannot be accounted for by the slow exchange of energy between internal and translational degrees of freedom. Near critical points the usual equation of state for the pressure becomes inadequate because of nonlocal effects, and a theoretical interpretation is being developed.[34-36] There is evidence from neutron scattering data[37] that the classical transport relations also eventually become inadequate at high wave numbers. Also, one can argue, by supposing that length and time scales are co-determined in simple fluids, that Greenspan's experiments exhibit nonlocal effects. Although the present theory has direct implications only for data in the rare gases, it can serve as the first step toward similar theories for more complicated models.

This paper has the following plan: For orientation, the second section recapitulates the classical theory and gives the structure of Richardson's proposed generalization. Then molecular expressions for the pressure tensor and heat current are derived in the third section. In the fourth section the currents are transformed so that one can identify a reversible part and an irreversible part. The irreversible part consists of terms proportional to the thermodynamic forces and a term due to the memory of the initial distribution. The expressions for the irreversible currents are further developed in the fifth section. There it is shown that these expressions have a form which is strikingly analogous to the subtracted flux autocorrelations of classical theory. Also, it is argued that the initial value terms should vanish.

II. THE CLASSICAL THEORY AND ITS GENERALIZATION

After a brief recapitulation of some of the classical theory of fluids, the kind of generalization which we are seeking is displayed.

Consider only one-component fluids comprised of neutral particles in nonelectromagnetic external fields. The classical theory of the dynamics of such fluids is embodied in a closed system of equations which determine a set of variables characterizing the macroscopic fluid state conditional on the initial and boundary values of these variables.[1,2] The macroscopic state is fully described by five variables defined as point functions of position and time $(\vec{r}, t)$, and as usual we take these to be the momentum density $\vec{j}(\vec{r}t)$, the mass density $\rho(\vec{r}t)$, and the total energy density of the system $e(\vec{r}t)$.[38,39] Since only those fluids for which internal structure of the particles plays no role will be considered, the angular momentum density is determined by the momentum density $\vec{j}$ and need not be separately included. It is accepted that this set of fluid densities provides a complete causal description in the sense that the set of initial values determines the values at any later time.

The classical system of equations which determines these functions consists of the conservation equations, equations of state, and a set of constitutive equations relating currents to the gradients of variables. The conservation equations are

$$\partial_t \vec{j} + \vec{\nabla}\cdot(\vec{v}\vec{j} + \overleftrightarrow{P}) + \rho\vec{\nabla} V_0 = 0, \tag{1}$$

$$\partial_t \rho + \vec{\nabla}\cdot\vec{j} = 0, \tag{2}$$

and

$$\partial_t e + \vec{\nabla}\cdot(\vec{v}e + \vec{q} + \overleftrightarrow{P}\cdot\vec{v}) = 0. \tag{3}$$

The vector $\vec{v}$ is the flow velocity defined by

$$\vec{v} \equiv \vec{j}/\rho, \tag{4}$$

and $\vec{\nabla}$ is the gradient operator. The potential of the external force per unit mass is denoted by V_0. In Eqs. (1)-(4) and in the sequel, the independent variables $(\vec{r}, t)$ are suppressed.

The nonconvective parts of the currents are expressed in terms of the pressure tensor $\overleftrightarrow{P}$ and the heat current $\vec{q}$. The fluid densities are not determined by Eqs. (1)-(4) until the relationship of $\overleftrightarrow{P}$ and $\vec{q}$ to the variables is specified. To do this, one first separates a local-equilibrium[40] part of the pressure tensor by writing

$$\overleftrightarrow{\mathrm{P}} \equiv \overleftrightarrow{\mathrm{P}}_0 + \Delta\overleftrightarrow{\mathrm{P}}. \tag{5}$$

Then $\overleftrightarrow{\mathrm{P}}_0$ is taken to be the local-equilibrium value in the sense that it is equal to the *thermodynamic* pressure for the local state multiplied by the unit tensor $\overleftrightarrow{\mathrm{U}}$; that is,

$$\overleftrightarrow{\mathrm{P}}_0(\vec{\mathrm{r}}t) = \overleftrightarrow{\mathrm{U}}p^0[\rho(\vec{\mathrm{r}}t), \beta(\vec{\mathrm{r}}t)], \tag{6}$$

where β is the inverse temperature $(kT)^{-1}$. The inverse temperature is defined in terms of $\vec{\mathrm{j}}$, ρ, and e by the caloric equation of state expressing the internal energy density $u(\vec{\mathrm{r}}t)$ as the *thermodynamic* internal energy for the local density and inverse temperature; that is,

$$u(\vec{\mathrm{r}}t) = u^0[\rho(\vec{\mathrm{r}}t), \beta(\vec{\mathrm{r}}t)]. \tag{7}$$

In terms of the fluid densities, the internal energy density is given by

$$u \equiv e - \tfrac{1}{2}\rho\vec{\mathrm{v}}^2 - \rho V_0. \tag{8}$$

Equations (6) and (7) mean that p^0 and u^0 are the *same functions* of $\rho(\vec{\mathrm{r}}t)$ and $\beta(\vec{\mathrm{r}}t)$ as the equilibrium pressure and internal energy density are of ρ and β.

The classical transport relations can now be given as

$$\Delta\overleftrightarrow{\mathrm{P}} = -2\eta_S[\tfrac{1}{2}[\vec{\nabla}\vec{\mathrm{v}} + (\vec{\nabla}\vec{\mathrm{v}})^T] - \tfrac{1}{3}\overleftrightarrow{\mathrm{U}}\vec{\nabla}\cdot\vec{\mathrm{v}}] - \eta_B\overleftrightarrow{\mathrm{U}}\vec{\nabla}\cdot\vec{\mathrm{v}} \equiv -\overleftrightarrow{\kappa}^{(4)} : \vec{\nabla}\vec{\mathrm{v}}, \tag{9}$$

where $(\vec{\nabla}\vec{\mathrm{v}})^T$ means the transpose of $\vec{\nabla}\vec{\mathrm{v}}$, and

$$\vec{\mathrm{q}} = -\lambda\vec{\nabla}T \equiv -\overleftrightarrow{\kappa}^{(2)}\cdot\vec{\nabla}\ln\beta. \tag{10}$$

The coefficients of shear and bulk viscosity have been denoted by η_S and η_B, and λ denotes the thermal conductivity.[41] The coefficients $\overleftrightarrow{\kappa}^{(4)}$ and $\overleftrightarrow{\kappa}^{(2)}$ are defined by these equations to be symmetric numeric tensors, their simplicity being due to the isotropy of fluids.[42] The tensor $\overleftrightarrow{\kappa}^{(4)}$ is of fourth rank, while $\overleftrightarrow{\kappa}^{(2)}$ which is the unit tensor multiplied by $(k\lambda/\beta)$ is second rank. These transport coefficients are themselves functions of ρ and β which are usually determined empirically. The autocorrelation expressions for them are well known.[4,15]

If we imagine the result of eliminating $\overleftrightarrow{\mathrm{P}}$ and $\vec{\mathrm{q}}$ from the conservation equations in favor of expressions involving $\vec{\mathrm{j}}$, ρ, and e, we can say that the classical theory represented here consists of a *closed* set of differential equations which are first-order in time so that the *initial values* of the densities (and boundary conditions) determine the *future values*. All of the equations are also *local in space and time*; that is, they contain only differential operations on the densities evaluated at the same point. Finally, although the system is nonlinear in the fluid densities, the transport relations state that the local flux of momentum $\overleftrightarrow{\mathrm{P}}$ and the local flux of energy $\vec{\mathrm{q}}$ are *linear functions* of the thermodynamic forces; that is, they are proportional to the negative of $\vec{\nabla}\vec{\mathrm{v}}$ and $\vec{\nabla}\ln\beta$. Note that this system of equations may be expected to apply even when the constituent particles have internal degrees of freedom as long as they do not possess a significant amount of internal angular momentum.[2]

Phenomenological generalizations which adequately represent various features of the data have already been developed to a certain extent by the methods of continuum mechanics (e.g., viscoelastic theory). Richardson, however, has presented in a statistical-mechanical context a formal generalization which is probably entirely adequate for all simple fluids.[14]

The first feature of his proposal is that the local equilibrium pressure tensor becomes a time-independent but nonlocal functional of the fluid densities; $\overleftrightarrow{\mathrm{P}}_0$ depends on the time t only implicitly through the fluid densities at t, but it depends on their values everywhere in the fluid. The caloric equation of state, Eq. (7), is similarly generalized. In addition, an analogous local equilibrium part of the heat current appears so that

$$\vec{\mathrm{q}} \equiv \vec{\mathrm{q}}_0 + \Delta\vec{\mathrm{q}}. \tag{11}$$

There is no classical analog of $\vec{\mathrm{q}}_0$. Because neither $\overleftrightarrow{\mathrm{P}}_0$ nor $\vec{\mathrm{q}}_0$ contribute to the time rate of change of total entropy,[43] this aspect of the proposal constitutes a generalization of the perfect fluid.

A second feature of his proposal is a generalization of the transport relations to forms reminiscent of Boltzmann's elastic aftereffect principle; namely,

$$\Delta\overleftrightarrow{\mathrm{P}}(\vec{\mathrm{r}}t) = -\int_0^t dt' \int d\vec{\mathrm{r}}' [\overleftrightarrow{\mathrm{K}}^{(4)}(\vec{\mathrm{r}}t;\vec{\mathrm{r}}'t') : \vec{\nabla}\vec{\mathrm{v}}(\vec{\mathrm{r}}'t') + \overleftrightarrow{\mathrm{K}}^{(3)}(\vec{\mathrm{r}}t;\vec{\mathrm{r}}'t')\cdot\vec{\nabla}\ln\beta(\vec{\mathrm{r}}'t')], \tag{12}$$

and

$$\Delta\vec{\mathrm{q}}(\vec{\mathrm{r}}t) = -\int_0^t dt' \int d\vec{\mathrm{r}}' [\tilde{\overleftrightarrow{\mathrm{K}}}^{(3)}(\vec{\mathrm{r}}t;\vec{\mathrm{r}}'t') : \vec{\nabla}\vec{\mathrm{v}}(\vec{\mathrm{r}}'t') + \overleftrightarrow{\mathrm{K}}^{(2)}(\vec{\mathrm{r}}t;\vec{\mathrm{r}}'t')\cdot\vec{\nabla}\ln\beta(\vec{\mathrm{r}}'t')]. \tag{13}$$

These generalize Eqs. (9) and (10) in two ways. Clearly, the currents now depend nonlocally and noninstantaneously on the thermodynamic forces. But also the transport kernels $\overleftrightarrow{\mathrm{K}}^{(l)}$, unlike the $\overleftrightarrow{\kappa}^{(l)}$, now are *functionals* of the fluid densities and depend on the values of these densities everywhere in space and for all times in the interval $[0, t]$. This implies, in fact, an additional nonlinear dependence on the thermodynamic forces.

Somewhat less sweeping generalizations have also been suggested in which the transport kernel (like the classical coefficients) depends only on the local values of the densities, and is a function only of space and time differences.[44] Such expressions should be valid near absolute thermodynamic equilibrium. Molecular expressions for the kernels have essentially been given but further development is needed.[6-10]

Although Richardson gives molecular expressions for $\overleftrightarrow{P}_0$ and $\vec{q}_0$, he does not do so for the transport kernels $\overleftrightarrow{K}^{(l)}$. Thus, our primary objectives are to establish from first principles that $\Delta\overleftrightarrow{P}$ and $\Delta\vec{q}$ do indeed have the form given by Eqs. (12) and (13), and to give molecular expressions for the kernels.

III. MOLECULAR EXPRESSIONS FOR THE AVERAGE FLUXES

Although other viewpoints can be taken, it is sufficient for our purposes to consider statistical mechanics as an application of probability theory to mechanical systems. The fundamental sample space is the $6N$-dimensional space of phase points Γ, each of which is a set of one-particle phases $\{X_1, X_2, \ldots, X_N\}$, where $X_i \equiv (\vec{R}_i, \vec{P}_i)$ is the position and momentum of the ith particle. A probability density over phase points is considered to be given at some initial time.[45] The quantities of interest are a set of random densities $A_\nu(\vec{r}; \Gamma_t)$ which are defined for all positions $\vec{r}$. The phase point Γ_t is the mechanical state into which a system initially at the point Γ evolves in t seconds, according to the classical dynamics of an isolated system of N point particles constrained to remain in a volume V. The Hamiltonian $H(\Gamma)$ of the system is considered to contain, in addition to two-particle interparticle potentials, appropriate wall potentials (corresponding, for example, to specular reflection) and also a scalar external potential.[46]

The densities are random variables precisely because the initial phase point of the system is random. The basic idea for generating a correspondence with observed values is that for appropriate variables the values observed for a given system in a given trial are essentially the expectation values of these random variables.[47] Thus the observed densities which are to satisfy the equations of fluid dynamics are equal to the expectation values of the set of phase functions $A_\nu(\vec{r}, \Gamma_t)$; that is,

$$a_\nu(\vec{r}t) \equiv \int d\Gamma\, A_\nu(\vec{r}; \Gamma_t) D(\Gamma; 0), \tag{14}$$

where $D(\Gamma; 0)$ is the given initial probability density. To be definite, the region of integration is taken to be all of phase space, and distributions $D(\Gamma; 0)$ are admitted in the theory only if they vanish for phases such that not all the particles are in the volume. In fact, just as in the statistical-mechanical theory of thermodynamics, one wants to consider the *observed* densities to be the asymptotic values of these expectations when the number of particles is very large. This is not just a calculational device; real systems of interest do contain enormous numbers of particles, and therefore exhibit small fluctuations. In the present nonequilibrium theory there is an additional reason. While one has every reason to expect that the integrals over phase space which occur in the definitions of $\overleftrightarrow{P}_0$, $\vec{q}_0$ and the transport kernels are well defined, one also wants the time integral of the transport kernels over the infinite interval to exist. Such an integral (of an approximation to these kernels) will appear in deriving the Markoffian limit of these currents.

The precise nature of the limiting process depends somewhat on the use to be made of the theory. For example, to derive the classical results one might want to let the size of the system increase with N such that the integrals of the densities remain fixed and the gradients of the variables vanish. For other purposes one might want a continuum limit similar to Grad's "Boltzmann gas"[48] in which some approximation to the currents becomes exact while the effect of finite numbers of finite-sized particles disappears. While further specification of the limiting process is not given here, it will be clear if one reviews the derivation to be given, that the *structure* of the results remains the same when a large-N limit of expectation values is introduced from the beginning. Therefore, in the sequel all the quantities will be considered as taken in some large-N limit.

The functions $A_\nu(\vec{r})$ which we observe are the momentum, mass, and energy densities defined as functions of the phase (i.e., microscopically) in the following way:

$$\vec{J}(\vec{r}; \Gamma) \equiv \sum_i \vec{P}_i \delta(\vec{r} - \vec{R}_i) \tag{15}$$

defines the momentum density;

$$\mathfrak{M}(\vec{r}; \Gamma) \equiv \sum_i m\delta(\vec{r} - \vec{R}_i) \tag{16}$$

defines the mass density; and

$$\mathcal{E}(\vec{r}; \Gamma) \equiv \sum_i H_i(\Gamma)\delta(\vec{r} - \vec{R}_i) \tag{17}$$

defines the energy density, where

$$H_i(\Gamma) \equiv \vec{P}_i^{\,2}/2m + mV_0(\vec{R}_i) + \tfrac{1}{2}\sum_k{}' V(\vec{R}_{ik}). \tag{18}$$

All the particles have the same mass m and the prime on the summation over k indicates that one excludes the term for which $k = i$. The potential per unit mass $V_0(\vec{R}_i)$ includes the wall potential as well as any external one-particle potential while $V(\vec{R}_{ik})$ is the interparticle potential between any two particles. The interparticle distance $\vec{R}_{ik}$ is equal to $\vec{R}_k - \vec{R}_i$. Except for the definition of the energy density, which rather arbitrarily assigns half of the potential energy of a pair of particles to each of them, the intuitive basis of these definitions is obvious: A particle contributes to the density of the given quantity at a point only if it is exactly at that point.[49] Notice that these equations define the densities for all of configuration space so that this is also true of the expectations given by Eqs. (15)–(18). Because Γ_t always corresponds to the case where every particle is inside a given volume, however, the expectations are found to vanish outside this volume as they should.

Of course, we not only cannot measure these quantities exactly, but we cannot measure exactly these quantities. The definitions represent idealizations of the more coarse-grained ones we actually measure but the idealization is sufficient for our purpose. The singular character of our definition never hurts us because we are always interested only in their expectations over smooth distributions. Moreover, to show that the fluid-dynamic laws apply to the expectations of such variables is to show that coarse graining is not necessary to such conclusions.

Identifying the quantities which are to correspond to measurements on a single system as the expectation values of certain phase functions is still not a complete prescription for comparison with experiment, however, because we cannot *directly* prepare distributions in phase space (since this would require measurements of phase). Clearly, we want to require that $D(\Gamma;0)$ implies the same initial expectation values $a_\nu(\vec{r};0)$ as those imposed by the experiment. In addition, although one does not typically prepare the initial *distribution* of the values of the A_ν,[50] there is some requirement that the initial dispersion about the average be small initially so that the predictions will be useful. It would appear, however, that the Gibbsian approach does not contain any further principles bearing on the determination of the initial distribution in phase. An heuristic choice will be made in this paper but we will defer making it until necessary so as to increase the force of *a posteriori* arguments for our choice.

If we were interested only in predicting the values of the densities at time t, given particular initial values, Eqs. (14)–(18) together with a choice of $D(t=0)$ would be a sufficient algorithm. The computation of Γ_t required by such an approach is not only difficult but would yield an enormous amount of highly specialized information of no intrinsic interest. More importantly, it would yield no insight into the general structure of the behavior of the densities; namely, into those aspects which are common to all systems regardless of the detailed nature of intermolecular forces (e.g., the existence of the transport relations). Such an insight is provided by finding the differential or quasidifferential (i.e., integrodifferential with short-ranged kernels) equations for the densities. To be sure, the parameters of such equations are expressed in terms of molecular objects like Γ_t. With such equations, however, one is able to determine these parameters empirically, thereby enabling prediction in particular cases without calculating Γ_t every time. This suggests that we calculate instead the time rates of change of the fluid densities.

To do this recall that the densities $a_\nu(\vec{r}t)$ can be given as the expectation of the corresponding phase functions in the ensemble at time t; that is, instead of Eq. (14) we can write that[51]

$$a_\nu = \int d\Gamma A_\nu(\Gamma) D(\Gamma;t), \tag{19}$$

where the independent variables are $\vec{r}$ and t. The function $D(\Gamma;t)$ is the probability density into which $D(\Gamma;0)$ evolves in time t; that is, it is the solution of Liouville's equation:

$$\partial_t D + LD = 0, \tag{20}$$

where the dependence on t is suppressed. The Liouville operator L is defined by

$$L(\Gamma) \equiv \textstyle\sum_i \{ m^{-1} \vec{P}_i \cdot \vec{\nabla}_{\vec{R}_i} - [m \vec{\nabla}_{\vec{R}_i} V_0(\vec{R}_i) - \sum_k{}' \vec{F}_{ik}] \cdot \vec{\nabla}_{\vec{P}_i} \}, \tag{21}$$

where the interparticle force is given by

$$\vec{F}_{ik} \equiv -\vec{\nabla}_{\vec{R}_i} V(\vec{R}_{ik}) \equiv \vec{F}(\vec{R}_{ik}). \tag{22}$$

The gradients with respect to positions and momenta are distinguished by subscripts. From Eq. (19) it follows by using Liouville's equation for $\partial_t D$ and integrating by parts that

$$\partial_t a_\nu = \int d\Gamma A_\nu(\Gamma) \partial_t D(\Gamma) = \int d\Gamma \dot{A}_\nu(\Gamma) D(\Gamma). \tag{23}$$

The function $\dot{A}_\nu(\Gamma)$ defined by

$$\dot{A}(\Gamma) \equiv L(\Gamma) A(\Gamma) \tag{24}$$

is the time rate of change of A_ν (its Poisson bracket with the Hamiltonian). The functions $\dot{A}_\nu$ corresponding to the quantities given by Eqs. (15)–(17) can be given as follows:

$$\dot{\vec{J}} = -\vec{\nabla} \cdot \overleftrightarrow{\Pi} - \mathfrak{M} \vec{\nabla} V_0, \tag{25}$$

$$\dot{\mathfrak{M}} = -\vec{\nabla} \cdot \vec{J}, \tag{26}$$

and

$$\dot{\mathcal{E}} = -\vec{\nabla} \cdot \vec{Q}. \tag{27}$$

The total mass current $\vec{J}$ has already been defined by Eq. (15). The total momentum current $\overleftrightarrow{\Pi}$ is defined by

$$\overleftrightarrow{\Pi}(\vec{r};\Gamma) \equiv \frac{1}{m} \sum_i \vec{P}_i \vec{P}_i \delta(\vec{r} - \vec{R}_i) + \frac{1}{2} \sum_{i \neq k} \int_0^1 d\epsilon\, \vec{R}_{ik} \vec{F}_{ik} \delta(\vec{r} + \epsilon \vec{R}_{ik} - \vec{R}_k). \tag{28}$$

The total energy current $\vec{Q}$ is the vector defined by

$$\vec{Q}(\vec{r};\Gamma) \equiv \frac{1}{m} \sum_i \vec{P}_i H_i(\Gamma) \delta(\vec{r} - \vec{R}_i) + \frac{1}{4m} \sum_{i \neq k} \int_0^1 d\epsilon\, \vec{R}_{ik} \vec{F}_{ik} \cdot (\vec{P}_i + \vec{P}_k) \delta(\vec{r} + \epsilon \vec{R}_{ik} - \vec{R}_k). \tag{29}$$

Although these results have been derived before,[14,49] a sketch of the derivation is given in Appendix A for completeness.[52] The integral terms in $\overleftrightarrow{\Pi}$ and $\vec{Q}$ will not be expanded about $(\vec{r}-\vec{R}_i)$[49] until it becomes necessary so as to preserve the possibility of a full description of nonlocal effects.

Notice that these terms do not vanish for points $\vec{r}$ lying outside the system but on the line joining $\vec{R}_i$ and $\vec{R}_k$. Although this becomes important only near walls, expressions which do vanish whenever $\vec{r}$ is outside are given in Appendix A.

According to Eq. (23), if we average the microscopic conservation equations [Eqs. (25)–(27)] at time t, we have derived the macroscopic conservation laws in the form given by Eqs. (1)–(3) and we can identify explicit molecular expressions for the currents.[53] One finds that

$$\int d\Gamma \overleftrightarrow{\Pi}(\Gamma)D(\Gamma)=\vec{v}\vec{j}+\overleftrightarrow{P}, \tag{30}$$

and

$$\int d\Gamma \vec{Q}(\Gamma)D(\Gamma)=\vec{v}e+\vec{q}+\overleftrightarrow{P}\cdot\vec{v}, \tag{31}$$

where the suppressed independent variables are $\vec{r}$ and t.[54] These equations give us molecular expressions for the *total* currents rather than directly for $\overleftrightarrow{P}$ and $\vec{q}$ alone.

To obtain expressions for $\overleftrightarrow{P}$ and $\vec{q}$ themselves, one has to extract the convective part of $\overleftrightarrow{\Pi}$ and $\vec{Q}$ by referring the momentum of a particle to the local velocity at the position of the particle. Thus, we want to express $\overleftrightarrow{\Pi}$ and $\vec{Q}$ in terms of the phase point Γ^+ that is the set of N local one-particle points $(\vec{R}_i, \vec{P}_i{}^+)$. The local momenta $\vec{P}_i{}^+$ are defined by

$$\vec{P}_i{}^+\equiv\vec{P}_i-m\vec{v}(\vec{R}_i,t). \tag{32}$$

It is not difficult to verify by substitution of the definition of $\vec{P}_i{}^+$ that

$$\overleftrightarrow{\Pi}=\vec{v}\vec{J}+\vec{J}\vec{v}-\vec{v}\vec{v}\mathfrak{M}+\overleftrightarrow{\Pi}^+, \tag{33}$$

where $\overleftrightarrow{\Pi}^+(\Gamma)\equiv\overleftrightarrow{\Pi}(\Gamma^+)$, (34)

and also that[55]

$$\vec{Q}=\tfrac{1}{2}\vec{v}^2\vec{J}-\tfrac{1}{2}\vec{v}^2\vec{v}\mathfrak{M}+\vec{v}\mathscr{E}+\vec{Q}^++\overleftrightarrow{\Pi}^+\cdot\vec{v}, \tag{35}$$

where

$$\vec{Q}^+(\Gamma)\equiv\vec{Q}(\Gamma^+)+\vec{Q}_0(\Gamma^+). \tag{36}$$

As indicated in Appendix A, the additional part of the heat current $\vec{Q}_0$ is defined by

$$\vec{Q}_0(\vec{r};\Gamma)\equiv-\tfrac{1}{2}\int d\vec{R}\int_0^1 d\epsilon\int_0^\epsilon d\epsilon'\vec{R}\vec{R}\cdot\vec{\nabla}\vec{v}(\vec{r}-\epsilon'\vec{R})\cdot\vec{F}(\vec{R})\mathfrak{N}^{(2)}(\vec{r}-\epsilon\vec{R};\vec{R};\Gamma), \tag{37}$$

where

$$\mathfrak{N}^{(2)}(\vec{r}_1,\vec{r}_{12};\Gamma)\equiv\sum_{i\neq k}\delta(\vec{r}_1-\vec{R}_i)\delta(\vec{r}_1+\vec{r}_{12}-\vec{R}_k) \tag{38}$$

defines the density in pair space. Substituting these expressions for $\overleftrightarrow{\Pi}$ and $\vec{Q}$ into Eqs. (30) and (31), one immediately sees that

$$\overleftrightarrow{P}(\vec{r}t)=\int d\Gamma\overleftrightarrow{\Pi}^+(\vec{r};\Gamma)D(\Gamma;t), \tag{39}$$

and $\vec{q}(\vec{r}t)\equiv\int d\Gamma\vec{Q}^+(\vec{r};\Gamma)D(\Gamma;t)$. (40)

These are the molecular expressions for the pressure tensor and heat flux which we have been seeking. Our view is that these fluxes are the appropriate objects for calculation rather than the densities themselves.

In parallel to Eq. (19) for the densities, these expressions are algorithms for the calculation of $\overleftrightarrow{P}$ and $\vec{q}$ for the initial-value problem. Because $D(\Gamma;0)$ must be some functional of the initial fluid densities, however, these expressions give the fluxes as functionals of the initial densities. What we really want is to eliminate this dependence on the initial values in favor of a dependence on the values of the densities at time t, or at least near it. This is just what the phenomenological laws (i.e., the transport relations) achieve, and therefore by this process we expect to arrive at molecular expressions for the transport coefficients. Since the microscopic fluxes have no dependence on the a_ν, we now want to find a way of expressing $D(\Gamma;t)$ itself as a functional of the a_ν.

IV. EXPRESSIONS FOR THE FLUXES IN TERMS OF FLUID DENSITIES

If we succeed in finding expressions for the pressure tensor and heat current which are functionals only of the densities at and near t and not depending explicitly on the initial values, we will have arrived at a set of equations for the densities which is closed, that is, not involving any arbitrary functions (such as the initial probability density). Such closure means that one has achieved in common with classical theory a "contraction of the description" for which the initial values of the densities suffice to determine the future values, but for which, unlike classical theory, the description is not local in time (i.e., not all terms in the equations of the theory involve the densities only at time t).

It seems natural to try to achieve our goal along lines suggested by the Bogolubov and Chapman-Enskog (B-C-E) procedure for solving the Boltzmann equation which determines the one-particle probability density in dilute gases.[56] The essential idea of this method[18-20] is that asymptotically for long times the solutions of this equation approach "normal" solutions; that is, solutions which are *time-independent functionals* of special variables which are slow in the sense that they have rates proportional to some small parameter. In this case the slow variables are the fluid densities and the small parameter is the uniformity parameter; i.e., the size of the corresponding gradients. This functional is determined by a functional differential equation, which is the equation a time-independent functional must satisfy in order that it be a solution of Boltzmann's equation.[57] A further essential feature is that the local-equilibrium probability density, with its parameters determined so as to yield the correct expected densities, is the first approximation to the functional. In fact, if one expresses the one-particle density as the sum of the local-equilibrium density plus a deviation, one can prove that the deviation is at least first order in the gradients. A third feature of the method is that this deviation is determined as a power series in the uniformity parameter (or a functional power series in the gradients).

A treatment analogous to this might be attempted for the solutions of the Liouville equation.[58] But, since the method assumes the existence of the time-independent functional and then proceeds to determine it, it does not provide any insight into the *approach* to the normal solution, that is, into relaxation effects.

This can be achieved (at least for the linearized equation) with a somewhat more general method essentially given by McLennan.[27] Suppose one preserves the idea that the solution is a functional of the densities but that it is a *time-independent* functional only in lowest order. Then one can still show from the Boltzmann equation itself that the deviations from the appropriate local-equilibrium distribution are at least first order in the gradients. Thus one should again take the lowest-order term in the functional to be the appropriate local-equilibrium distribution. Now (at least for the linear equation) one can proceed to determine formally the deviation from this using the Boltzmann equation itself but without assuming that this deviation is a time-independent functional and without immediately developing it as a series.

To have a suggestive context which provides motivation, we will proceed by analogy to the B-C-E method. For our purposes, however, one must use the generalization of this method just described. Thus we will write for D

$$D(\Gamma;t) \equiv D_0(\Gamma|a(t)) + \Delta D(\Gamma;t), \tag{41}$$

where $D_0(\Gamma|a(t))$ denotes a time-independent functional of the densities alone; it depends on the fluid densities a_ν only at a single time t while it depends on their values at every point in space. This equation is intended as a definition of the deviation ΔD consequent upon explicit definition of D_0.[59] The analogy clearly suggests that we take for D_0 a generalized local-equilibrium probability density, the parameters of which are so determined as to yield the expected fluid densities at time t. Then we can expect to be able to show that ΔD is at least first order in the gradients so that D_0 in fact corresponds to the zero-order approximation to Bogolubov's asymptotic functional.

A. The Local-Equilibrium Distribution

Thus it is proposed that

$$D_0(\Gamma|a(t)) \equiv \exp\{-\int d\vec{r}\,\beta(\vec{r})[\mathcal{E}(\vec{r}) - \vec{v}(\vec{r})\cdot\vec{J}(\vec{r}) - \phi(\vec{r})\mathfrak{M}(\vec{r})]\}, \tag{42}$$

which is an explicit functional of the quantities $\vec{v}$, ϕ, and β.[60] The integral here is over all space; and $\vec{v}$, ϕ, and β are defined by the requirement that D_0 yield the correct densities:

$$a_\nu(\vec{r}) = \int d\Gamma\, A_\nu(\vec{r};\Gamma) \exp\{-\int d\vec{r}\,\beta(\vec{r})[\mathcal{E}(\vec{r}) - \vec{v}(\vec{r})\cdot\vec{J}(\vec{r}) - \phi(\vec{r})\mathfrak{M}(\vec{r})]\}, \tag{43}$$

where all quantities are taken at time t. Equation (43) determines the quantities $\vec{v}$, ϕ, and β to be time-independent functionals of the densities a_ν; that is, they depend on time only implicitly through the $a_\nu(t)$.

To elucidate this definition of D_0 we will first give it a more familiar form and then discuss the interpretation of the quantities $\vec{v}$, ϕ, and β.

The distribution D_0 can be given a more useful form by introducing local values of the momenta defined by Eq. (32). As shown in Appendix B, one has that

$$D_0(\Gamma|a(t)) = \exp\{-\int d\vec{r}\,\beta(\vec{r})[\mathcal{E}^+(\vec{r}) - f(\vec{r})\mathfrak{M}^+(\vec{r})]\} \equiv D_0^{\,+}(\Gamma^+|f(t),\beta(t)), \tag{44}$$

where $\mathcal{E}^+(\vec{r};\Gamma) \equiv \mathcal{E}(\vec{r};\Gamma^+)$, (45)

and $\mathfrak{M}^+(\vec{r};\Gamma) \equiv \mathfrak{M}(\vec{r};\Gamma^+) = \mathfrak{M}(\vec{r};\Gamma)$. (46)

We have also introduced

$$f \equiv \phi + \tfrac{1}{2}\vec{v}^2. \tag{47}$$

Other workers have introduced this distribution in related contexts.[14,16,22,23,61,62]

Second, in Eq. (43) which determines the quantities $\vec{v}$, ϕ, and β, the momentum integrals can be performed if one uses Eq. (44) for D_0. As shown in Appendix B, one finds that $\vec{j}$ is equal to $\rho\vec{v}$ so that the quantity $\vec{v}$ appearing in D_0 is indeed the flow velocity. Furthermore, one finds that

$$\rho(\vec{r}) = (N/V)\rho_0^{(1)}(\vec{r}|f,\beta) \equiv \langle\mathfrak{M}\rangle^+, \tag{48}$$

and $u(\vec{r}) = \dfrac{3}{2}\left(\dfrac{\rho}{m\beta}\right) + \dfrac{1}{2}\,\dfrac{N(N-1)}{V^2}\int d\vec{R}\,V(\vec{R})\rho_0^{(2)}(\vec{r};\vec{R}|f\beta)$. (49)

Equation (48) defines $\rho_0^{(1)}$ while $\rho_0^{(2)}$ is defined by

$$\frac{N(N-1)}{V^2}\rho_0^{(2)}(\vec{r};\vec{r}_{12}\,|f\beta) \equiv \int d\Gamma\, \mathfrak{N}^{(2)}(\vec{r},\vec{r}_{12};\Gamma)D_0^{+}(\Gamma\,|f\beta). \tag{50}$$

Thus $\rho_0^{(1)}$ and $\rho_0^{(2)}$ are the generic probability densities marginal to $D_0^{+}(\Gamma\,|f\beta)$ and both are time-independent functionals of f and β. It is worth observing that Eqs. (48) and (49) imply that f and β are functionals of $\vec{j}$, ρ, and e only through ρ and u (which is therefore not true of ϕ). Eliminating f from Eq. (49) yields the analog of the classical caloric equation of state, Eq. (7).

Third, consider the dimensionless functional defined by

$$S'\{a(t)\} \equiv -\int d\Gamma\, D_0(\Gamma\,|a(t))\ln[D_0(\Gamma\,|a(t))/\Gamma_0], \tag{51}$$

where Γ_0 is the unit volume in phase space. It is not difficult to see that this quantity is the inverse of Boltzmann's constant k_B^{-1} times the maximum value of the Gibbs definition of the entropy, subject to the constraints that the distribution gives the correct averages, that is, subject to Eq. (43).[63] The idea that the distribution which maximizes the Gibbs entropy for fixed constraints plays a central role in a theory for the dynamics of macroscopic variables has been realized and pursued by others.[61,62,64,65] The present work, while consistent with this, follows the spirit of the B-C-E method and also considers the deviation ΔD.

Using the form for D_0 given by Eq. (44) to evaluate this functional, one finds that

$$S'\{a(t)\} = \int d\vec{r}\,\beta[u-(f-V_0)\rho]+\ln\Gamma_0. \tag{52}$$

It is natural to try to interpret $S'\{a(t)\}$ (times k_B^{-1}) as the entropy of arbitrary nonequilibrium states specified by the a_ν, and the integrand of Eq. (52) as the corresponding density. Others have already made and supported this point.[14,16,27,62] Clearly, with this interpretation the *formal structure* of the relations between the pair (ρ,u) and the pair (f,β) embodied in Eqs. (48), (49), and (52) is the same as in equilibrium thermodynamics.

The formal similarity to the usual equilibrium theory has been put sufficiently in evidence to suggest the conclusion that β should be interpreted as the local inverse temperature (multiplied by k_B) and f as the local Helmholtz free energy per unit mass. Both of these are defined as nonlocal functionals of ρ and u (and therefore of $\vec{j}$, ρ, and e) by Eqs. (48) and (49). A full demonstration that $\beta(\vec{r}t)$ and $f(\vec{r}t)$ (related in this nonlocal way to the densities) are what would be measured by appropriate test probes, however, requires an analysis of how such test probes interact with a fluid system.[66]

From these results, it is clear that D_0 is a generalized local-equilibrium distribution for a system of particles which is microcanonical in the number of particles but is canonical in the total momentum $\int d\vec{r}\,\vec{j}(\vec{r}t)$, and in the total energy $\int d\vec{r}\,e(\vec{r}t)$ (i.e., both of these have a dispersion).[67] It is clear from Eq. (42) that this distribution corresponds to a local equilibrium in small cells moving with the local flow velocity.[68]

This choice of D_0 will be justified by its consequences. In the following we will show that its contribution to the expected current yields a natural generalization of the perfect fluid and, more importantly, that it implies that the deviation ΔD is at least of first order in the gradients of $\vec{v}$ and β (i.e., the thermodynamic forces). The basic physical idea underlying the choice of zero-order solution for solving the Boltzmann equation[69] remains relevant: One expects that a system equilibrates very rapidly in little cells moving with the flow velocity and that then the differences between the equilibrium parameters f and β for each cell slowly approach final values.[25] Although this remark is probably more relevant for the limiting forms of the marginal probability densities for large N, it indicates that the present choice of D_0 is a sensible zero-order approximation.[70]

B. Local-Equilibrium Contribution to Currents and Change of Entropy

The separation of the distribution D into a local-equilibrium part and the deviation implies a corresponding separation for all averages. Thus if $Z(\Gamma)$ is any phase function and z is its expectation taken over the distribution D, then

$$z \equiv z_0 + \Delta z, \tag{53}$$

where the local-equilibrium part z_0 is defined by

$$z_0 \equiv \int d\Gamma\, Z(\Gamma)D_0(\Gamma) \equiv \langle Z\rangle_0. \tag{54}$$

Thus the deviation is

$$\Delta z \equiv \int d\Gamma\, Z(\Gamma)\Delta D(\Gamma). \tag{55}$$

We see, referring to definitions of $\overleftrightarrow{P}$ and $\vec{q}$ [Eqs. (39) and (40)], that the local-equilibrium part of the pressure tensor $\overleftrightarrow{P}_0$ is equal to $\langle\overleftrightarrow{\Pi}^{+}\rangle_0$ while $\vec{q}_0$ is equal to $\langle\vec{Q}^{+}\rangle_0$. Just as we did to compute ρ and u in terms of the marginal densities, we perform the momentum integrals by transforming the integration variables to Γ^{+} which is determined by the local momenta [see Eq. (32)]. For the pressure tensor, one finds directly that

$$\overleftrightarrow{P}_0(\vec{r}) = \overleftrightarrow{U}(\rho/m\beta)+[N(N-1)/V^2]\int d\vec{R}\int_0^1 d\epsilon\, \vec{R}\vec{F}(\vec{R})\rho_0^{(2)}(\vec{r}-\epsilon\vec{R},\vec{R}\,|f\beta), \tag{56}$$

where $\rho_0^{(2)}$ is defined by Eq. (50). Because of the nonlocal terms, this is not proportional to the unit tensor $\overleftrightarrow{U}$. For the heat current there is no contribution from the term $\vec{Q}(\Gamma^{+})$ which is odd in momenta, and the remaining contribution $\langle \vec{Q}_0{}^+ \rangle_0$ is given by

$$\vec{q}_0(\vec{r}) = -[N(N-1)/2V^2]\int d\vec{R}\int_0^1 d\epsilon \int_0^\epsilon d\epsilon' \vec{R}\vec{R}\cdot\vec{\nabla}\vec{v}(\vec{r}-\epsilon'\vec{R})\cdot\vec{F}(\vec{R})\rho_0{}^{(2)}(\vec{r}-\epsilon\vec{R},\vec{R}\,|f\beta). \tag{57}$$

Both of these expressions which were already given by Richardson[14] are time-independent but nonlocal functions of $\vec{v}$, f, and β (and therefore of the fluid densities).

There is a strong similarity between Eq. (56) and the expression for the classical local-equilibrium pressure. In fact, it can be shown[71] that the classical expression is the leading term in an expansion of Eq. (56) in powers of the gradients. The present expression should be sufficient for arbitrary gradients and therefore useful for interpreting neutron scattering, for example. For later use, one should observe that $\overleftrightarrow{P}_0$ is independent of $\vec{v}$ because it depends on $\vec{j}$, ρ, and e only through f and β. The expression for the heat current $\vec{q}_0$ is perhaps more surprising. Notice that it is already first order in the thermodynamic force $(-\vec{\nabla}\vec{v})$ and that this dependence on $\vec{v}$ which is explicit is the only dependence on it.

In spite of the more complicated dependence of $\overleftrightarrow{P}_0$ on the variables and the nonvanishing of the analogous current $\vec{q}_0$, these local-equilibrium currents are like the classical quantity $\overleftrightarrow{U}p^0$ in that, along with the convective terms in the total current, they do not contribute to the time rate of change of the total entropy. In Appendix C it is shown that, in fact, for the entropy defined by Eq. (51), one has that

$$dS'/dt = -\int d\vec{r}\,\beta[(\Delta\overleftrightarrow{P})^T:\vec{\nabla}\vec{v} + \Delta\vec{q}\cdot\vec{\nabla}\ln\beta], \tag{58}$$

where $(\Delta\overleftrightarrow{P})^T$ is the transpose of the deviation of $\overleftrightarrow{P}$ from $\overleftrightarrow{P}_0$ and $\Delta\vec{q}$ is the deviation of $\vec{q}$ from $\vec{q}_0$. From this result we can identify $-\vec{\nabla}\vec{v}$ and $-\vec{\nabla}\ln\beta$ as the thermodynamic forces, just as they are in the classical case, and justify calling $\Delta\overleftrightarrow{P}$ and $\Delta\vec{q}$ the irreversible momentum and energy currents or the irreversible parts of the pressure tensor and heat current.

C. Irreversible Currents in Terms of Fluid Densities

The central problem is to obtain expressions for the irreversible currents in terms of the fluid densities. To do this we want to find such expressions for the deviation ΔD defined by Eq. (41).

Because D obeys Liouville's equation, the equation for the deviation is clearly

$$(\partial_t + L)\Delta D(t) = -(\partial_t + L)D_0(t). \tag{59}$$

Although D_0 is only implicitly dependent on time, the symbol $D_0(t)$ is used for brevity here and in the following. Just as in the B-C-E procedure, one wants to evaluate the time derivative of D_0 by using the equations of motion. To do this we follow other workers,[21-23] and use the fact that D_0 is a time-independent functional of the conjugate variables $(-\beta\vec{v})$, $(-\beta\phi)$, and β. Let v_ν denote the νth component of the velocity $\vec{v}$. Then consider for convenience $(-\beta v_\nu)$, $(-\beta\phi)$, and β as the elements b_ν of a row matrix b, and also consider the A_ν as the elements of a corresponding column matrix A.[72] With this notation, the exponent of D_0 is expressed as $b * A(\Gamma)$, the asterisk denoting the matrix product. Now we simply use the chain rule for functional differentiation of a time-independent functional to obtain

$$\partial_t D_0 = -\int d\vec{r}d\vec{r}'D_0A(\vec{r}) * \frac{\delta b(\vec{r})}{\delta a(\vec{r}')} * \int d\Gamma'\mathring{A}(\vec{r}';\Gamma)D(\Gamma'). \tag{60}$$

The factor D_0A is the negative of the functional derivative of D_0 with respect to $b(\vec{r})$, while the integral over phase space, according to Eq. (23), is just the time derivative of $a(\vec{r}')$.

The contribution of the local-equilibrium part of D to this expression is the contribution of the reversible part of the currents. If we were interested only in terms of first order in the gradients, we could follow others by retaining only these terms in the sequel.[73] This approximation is not, however, sufficient for all purposes. More importantly, it is not at all clear at this point why the contribution of the deviation ΔD should be neglected in using this expression for $\partial_t D_0$ to determine ΔD while other similar terms in Eq. (59) are kept.

Fortunately, it is not *necessary* to neglect this term in order to proceed. For, if an integration by parts is performed in the integral over phase space, one can re-express Eq. (60) as

$$\partial_t D_0 = -\int d\Gamma'\mathcal{P}(\Gamma;\Gamma'\,|D_0)L(\Gamma')[D_0(\Gamma') + \Delta D(\Gamma')] = \mathcal{P}\partial_t D. \tag{61}$$

The matrix $\mathcal{P}$ in phase space is defined by

$$\mathcal{P}(\Gamma;\Gamma'\,|D_0) \equiv -D_0(\Gamma)\int d\vec{r}d\vec{r}'A(\vec{r};\Gamma) * \frac{\delta b(\vec{r})}{\delta a(\vec{r}')} * A(\vec{r}';\Gamma'). \tag{62}$$

We shall refer to it as the projector because, as the second equality in Eq. (61) (implied by Liouville's equation) indicates, one of its roles is precisely to project the time rate of change of D onto the time rate of change of D_0. Since it is a time-independent functional of D_0 (and therefore of a or b), it is completely defined by Eq. (62).[74]

Instead of pausing to examine other properties of this projector (see Appendix D) let us continue to evaluate ΔD. Using the expression for $\partial_t D_0$ given by Eq. (61) in Eq. (59) yields an exact equation for the determination of ΔD:

$$[\partial_t + (1-\mathcal{P})L]\Delta D = -(1-\mathcal{P})LD_0, \tag{63}$$

where $\mathcal{P}$ operating on a phase function $Z(\Gamma')$ means to multiply it by $\mathcal{P}(\Gamma;\Gamma')$ and integrate over Γ', and where time dependence has been suppressed.[75] From this equation we see that the order in the gradients of ΔD is determined by the order of the inhomogeneous term. The inhomogeneous term of Eq. (63) can immediately be evaluated from the definition of D_0, and the result is that

$$LD_0 = -D_0 \int d\vec{r}\, b(\vec{r}) * \dot{A}(\vec{r}) = +D_0 \int d\vec{r}\, [\vec{\nabla} \cdot \overleftrightarrow{\Pi} \cdot (-\beta\vec{v}) - \beta\phi\vec{\nabla} \cdot \vec{J} + \beta\vec{\nabla} \cdot \vec{Q} - \beta\vec{v} \cdot (\vec{\nabla} V_0)\, \mathfrak{M}], \tag{64}$$

the more explicit form being obtained by writing out the matrix product and using Eqs. (25)–(27). Integrating by parts yields that

$$LD_0 = -D_0 \int d\vec{r}\, [\tilde{\overleftrightarrow{\Pi}} : \vec{\nabla}(-\beta\vec{v}) + \vec{J} \cdot \vec{\nabla}(-\beta\phi) + \vec{Q} \cdot \vec{\nabla}\beta + \beta\vec{v} \cdot (\vec{\nabla} V_0)\mathfrak{M}] + (\textit{surface term}), \tag{65}$$

where $\tilde{\overleftrightarrow{\Pi}}$ is the transpose of $\overleftrightarrow{\Pi}$. The integrand of the surface term is just

$$-\vec{n} \cdot [\overleftrightarrow{\Pi}(\vec{r}_S) \cdot \vec{v}(\vec{r}_S) + \vec{J}(\vec{r}_S)\phi(\vec{r}_S) - \vec{Q}(\vec{r}_S)]\beta(\vec{r}_S)$$

in which the surface is to be taken at infinity, $\vec{n}$ is the outward unit normal vector, and $\vec{r}_S$ denotes a point on the surface. One sees that the surface term vanishes by recalling that $D_0(\Gamma)$ vanishes (because of the wall potential) except for phases corresponding to all particles being contained in the volume V. For such phases, however, $\overleftrightarrow{\Pi}$, $\vec{J}$, and $\vec{Q}$ vanish unless $\vec{r}$ is also contained in the volume,[76] and none of the points $\vec{r}_S$ are so contained.

The external force term in Eq. (65) does not vanish in general, but we notice that it is proportional to $\mathfrak{M}$. To find ΔD, however, the object we want to compute is not LD_0 but $(1-\mathcal{P})LD_0$. Now, as is shown in Appendix D, precisely because the operator $\mathcal{P}$ is the projector for the densities A_ν, one has that

$$(1-\mathcal{P})A_\nu D_0 = 0. \tag{66}$$

Since $\mathfrak{M}(\vec{r})$ is one of the $A_\nu(\vec{r})$, this external force term does not contribute to $(1-\mathcal{P})LD_0$. For the same reason, the term proportional to $\vec{J}$ does not contribute, so that one has for the inhomogeneous term of Eq. (63) that

$$(1-\mathcal{P})LD_0 = -(1-\mathcal{P})D_0 \int d\vec{r}\, [\tilde{\overleftrightarrow{\Pi}} : \vec{\nabla}(-\beta\vec{v}) + \vec{Q} \cdot \vec{\nabla}\beta], \tag{67}$$

which is of first order in the gradients of the conjugate variables $-\beta\vec{v}$ and β. We conclude that the deviation ΔD is also at least of first order in the gradients. This property, which is expected physically, is seen to be a direct consequence of the choice of D_0. Other normalized functions of the same linear combination of the $A_\nu(\vec{r})$ as appears in D_0 will lead to the same result, of course, so that taken by itself this result is not a sufficient reason for our choice.

To express ΔD in a form which is almost closed, we formally solve Eq. (63) by introducing the Green function $\mathcal{K}(t;t')$ defined as a solution of

$$\{\partial_t + [1-\mathcal{P}(t)]L\}\mathcal{K}(\Gamma t; \Gamma' t') = -\delta(\Gamma - \Gamma')\delta(t-t'). \tag{68}$$

In particular, it is that solution which vanishes when $t < t'$ and has the value $\delta(\Gamma - \Gamma')$ at $t = t'$. Notice that the operator $[1-\mathcal{P}(t)]$ is *time-dependent* so that this Green function is more complicated than that for Liouville's equation. In terms of $\mathcal{K}$, a formal solution of Eq. (63) is that

$$\Delta D(\Gamma;t) = \int d\Gamma' \mathcal{K}(\Gamma, t; \Gamma', 0)\Delta D(\Gamma'; 0) - \int_0^t dt' \int d\Gamma' \mathcal{K}(\Gamma t; \Gamma' t')[1-\mathcal{P}(t')]LD_0(\Gamma' | a(t)). \tag{69}$$

With this expression for the deviation, the irreversible parts of the expected pressure tensor and heat current defined by Eqs. (39) and (40) can be expressed in a suggestive form: Introduce, for convenience, for any matrix $O(\Gamma;\Gamma')$ in phase space and any two phase functions V and W, a kind of matrix element defined by

$$(V|O|W) \equiv \int d\Gamma_1 d\Gamma_2 V(\Gamma_1) O(\Gamma_1; \Gamma_2) W(\Gamma_2). \tag{70}$$

Then the irreversible momentum current which is the expectation of $\overleftrightarrow{\Pi}^+$ with ΔD can be written according to Eq. (69) as

$$\Delta\overleftrightarrow{P}(\vec{r}t) = -\int_0^t dt' (\overleftrightarrow{\Pi}^+(\vec{r}) | \mathcal{K}(t;t')[1-\mathcal{P}(t')] | LD_0(t')) + \overleftrightarrow{R}_{\vec{j}}(\vec{r}t), \tag{71}$$

where $D_0(t)$ denotes only implicit time dependence. The remainder $\overleftrightarrow{R}_{\vec{j}}$, which is a second-rank tensor, is defined by

$$\overleftrightarrow{R}_{\vec{j}}(\vec{r}t | \Delta D(0)) \equiv (\overleftrightarrow{\Pi}^+(\vec{r}) | \mathcal{K}(t;0) | \Delta D(0)). \tag{72}$$

Similarly, the irreversible energy current, which is the expectation of $\vec{Q}^+$ with ΔD, can be given as

$$\Delta\vec{q}(\vec{r}t) = -\int_0^t dt' (\vec{Q}^+(\vec{r}) | \mathcal{K}(t;t')[1-\mathcal{P}(t')] | LD_0(t')) + \vec{R}_e(\vec{r}t), \tag{73}$$

where the remainder $\vec{R}_e$ is defined

$$\vec{R}_e(\vec{r}t) \equiv (\vec{Q}^+(\vec{r}) | \mathcal{K}(t;0) | \Delta D(0)). \tag{74}$$

One should also recall that the factor $(1-\mathcal{P})LD_0$ in these equations has the expression given in Eq. (67). Since $\mathcal{K}$ and $\mathcal{P}$ depend on D_0 in a well-defined way and on no other arbitrary functions (such as initial values), these expressions are almost closed; that is, they are composed of a term determined entirely by the fluid densities and the remainder terms $\overleftrightarrow{R}_{\vec{j}}$ and $\vec{R}_e$ which contain all the dependence on the initial values. The first terms in Eqs. (71) and (73) are memory terms which in fact depend on the value of the fluid densities for positions near $\vec{r}$ and for times near t.[77] Since we know empirically that initial conditions are forgotten, we expect either that $\Delta D(t=0)$ vanishes identically or else the remainder terms become negligible very rapidly. Then Eqs. (71) and (73) would be fully closed expressions for the irreversible currents.

Since these almost closed expressions for the irreversible currents are central to the present work, the following remarks should be made. The expressions are almost closed only because we have assumed that $D(\Gamma, t)$ is split into a differentiable time-independent functional D_0 of the densities and a remainder and not because of the particular form of D_0. The forms given in Eqs. (71) and (73) where LD_0 is left unevaluated can be obtained without any other assumptions on D_0. To see this, one has only to notice that simply assuming D_0 to be a time-independent functional of the densities immediately yields that the time rate of change of D_0 is a projection of the time rate of change of D as in Eq. (61), but now with $\mathcal{P}$ defined only as

$$\mathcal{P}(\Gamma; \Gamma' | D_0) \equiv \int d\vec{r}\, \frac{\delta D_0(\Gamma | a(t))}{\delta a \vec{r}'} * A(\vec{r}'; \Gamma'). \tag{75}$$

Thus one can proceed to Eqs. (71) and (73) as before. Of course, when D_0 is the local-equilibrium distribution, the projector defined by Eq. (75) is the same as that defined by Eq. (62).

From this point of view, our choice of D_0 would appear to be arbitrary; any of a whole class of choices will yield almost closed expressions for the currents. One should notice concerning this point: First, that a certain arbitrariness over various generalized equilibrium distributions is desirable to reflect differences in experimental circumstances. It will be argued in the concluding section that the final results are invariant to such choices. Second, we have just seen that the use of generalized equilibrium distributions for D_0 introduces the conjugate variables and their gradients in a very natural way. As will emerge presently, this yields a structural form of the equations which has a very strong and complete analogy to the classical ones which must be their limiting form. Finally, there is no reason to expect that arbitrary choices of D_0 will lead by any route to the classical limit, and in particular, one cannot expect the initial value terms to have the proper behavior for arbitrary choices of D_0 which may not correspond to physically realizable initial preparations (see Sec. V.C).

The present derivation intends to emphasize the similarities to the B-C-E procedure and to focus on the expectation value of the currents as the objects of calculation.[78] But consider the logical status of Eqs. (71)–(74). In spite of the references to the B-C-E procedure which are intended to motivate our procedure, *no assumptions* of a physical nature have been made other than a particular choice of variables and the basic one of statistical mechanics. A number of definitions have been stated and subsequently some exact manipulations have been made. It is by now no longer surprising that with no assumptions one can derive equations for averages which are closed except for initial value terms, but we believe that it is useful to develop the theory this way so that the assumptions which do have physical content are made to stand out.

V. FURTHER EVALUATION OF THE IRREVERSIBLE CURRENTS

The analogy between the expressions given in Eqs. (71) and (73) and the well-known expressions corresponding to the classical transport relations can be made much more obvious. In particular, we will see that analogs of the subtracted fluxes arise naturally. Also, we will argue that the remainder terms vanish for physically interesting circumstances so that one indeed gets fully closed expressions for the currents.

A. The Transport Kernels

First notice that $(1-\mathcal{P})LD_0$ can be written as a linear combination of the thermodynamic forces $-\vec{\nabla}\vec{v}$ and $-\vec{\nabla}\ln\beta$. From Eq. (67) one obtains by calculating the gradients that

$$(1-\mathcal{P})LD_0 = (1-\mathcal{P})D_0 \int d\vec{r}'\beta[\tilde{\overleftrightarrow{\Pi}} : \vec{\nabla}\vec{v} + (\vec{Q} - \vec{v}\cdot\tilde{\overleftrightarrow{\Pi}})\cdot\vec{\nabla}\ln\beta], \tag{76}$$

where the independent variables $\vec{r}'$, t', and Γ' are suppressed. Using this result to evaluate $\Delta\overleftrightarrow{P}$ and $\Delta\vec{q}$ given in Eqs. (71) and (73), one obtains

$$\Delta\overleftrightarrow{P}(1) = -\int_0^{t_1} dt_2 \int d\vec{r}_2 [\overleftrightarrow{K}^{(4)}(1;2) : \vec{\nabla}\vec{v}(2) + \overleftrightarrow{K}^{(3)}(1;2)\cdot\vec{\nabla}\ln\beta(2)] + \overleftrightarrow{R}_{\vec{j}}(1), \tag{77}$$

and $$\Delta\vec{q}(1) = -\int_0^{t_1} dt_2 \int d\vec{r}_2 [\tilde{\overleftrightarrow{K}}^{(3)}(1;2) : \vec{\nabla}\vec{v}(2) + \overleftrightarrow{K}^{(2)}(1;2)\cdot\vec{\nabla}\ln\beta(2)] + \vec{R}_e(1), \tag{78}$$

where for brevity the index i used as the argument of a quantity means $x_i \equiv (\vec{r}_i, t_i)$. The remainder terms are as defined by Eqs. (71) and (73), while the transport kernels are defined in the notation of Eq. (70) as follows:

$$\overleftrightarrow{K}^{(4)}(1;2) \equiv (\overleftrightarrow{\Pi}^{+}(\vec{r}_1) | \mathcal{K}(t_1;t_2)(1-\mathcal{P}) | \tilde{\overleftrightarrow{\Pi}}(\vec{r}_2) D_0(t_2))\beta(2), \tag{79}$$

$$\overleftrightarrow{K}^{(3)}(1;2) \equiv (\overleftrightarrow{\Pi}^{+}(\vec{r}_1) | \mathcal{K}(t_1;t_2)(1-\mathcal{P}) | [\vec{Q}(\vec{r}_2) - \vec{v}(2)\cdot\tilde{\overleftrightarrow{\Pi}}(\vec{r}_2)] D_0(t_2))\beta(2), \tag{80}$$

$$\tilde{\overleftrightarrow{K}}^{(3)}(1;2) \equiv (\vec{Q}^{+}(\vec{r}_1) | \mathcal{K}(t_1;t_2)(1-\mathcal{P}) | \tilde{\overleftrightarrow{\Pi}}(\vec{r}_2) D_0(t_2))\beta(2), \tag{81}$$

$$\overleftrightarrow{K}^{(2)}(1;2) \equiv (\vec{Q}^{+}(\vec{r}_1) | \mathcal{K}(t_1;t_2)(1-\mathcal{P}) | [\vec{Q}(\vec{r}_2) - \vec{v}(2)\cdot\tilde{\overleftrightarrow{\Pi}}(\vec{r}_2)] D_0(t_2))\beta(2). \tag{82}$$

The superscript denotes the tensorial rank, and in all of these expressions $\mathcal{P}$ is taken at time t_2. Notice that $\overleftrightarrow{K}^{(4)}$, $\overleftrightarrow{K}^{(3)}$, and $\tilde{\overleftrightarrow{K}}^{(3)}$ have obvious symmetry properties because the tensor $\overleftrightarrow{\Pi}$ is symmetric.[79] It will emerge that $\tilde{\overleftrightarrow{K}}^{(3)}$ is in an obvious sense the transpose of $\overleftrightarrow{K}^{(3)}$. Except for the initial value terms, the form announced in the introduction for the irreversible parts of the pressure tensor and heat current has been achieved. The first term of Eq. (77) leads to a generalization of Newton's law of viscosity so that $\overleftrightarrow{K}^{(4)}$ *is the viscosity kernel* while the last term of Eq. (78) generalizes Fourier's law so that $\overleftrightarrow{K}^{(2)}$ *is the thermal conductivity kernel.* The second term of Eq. (77) and first term of Eq. (78) are cross-effect terms which are not present in the classical theory. These kernels are all functionals of D_0 and therefore of either the densities or the conjugate variables.

The important observation can be made that in Eqs. (77) and (78) no term appears convoluting a kernel with $\vec{\nabla}\phi$. This means that the gradient of ϕ (and therefore $\vec{\nabla}\rho$) contributes to the irreversible currents only in higher orders in the gradients of the conjugate variables (e.g., in terms proportional to $\vec{\nabla}\phi\vec{\nabla}\vec{v}$). This is to be expected in the present case of a one-component fluid, and it has emerged as a general result precisely because the $\mathcal{P}$ projects out the corresponding current $\vec{J}$.[80]

At this stage the primary objective of giving molecular expressions for Richardson's kernels has been achieved. As they are presented in Eqs. (79)–(82), however, the kernels have an awkward form and in particular $\overleftrightarrow{K}^{(4)}$ and $\overleftrightarrow{K}^{(2)}$ are not autocorrelations. To derive improved forms we want to make the operation by $(1-\mathcal{P})$ more explicit.

B. Subtracted Fluxes

The relationship of these kernels to the correlation expressions, the space-time integrals of which are the classical coefficients, can be made even more apparent. When M. S. Green first derived the autocorrelation expressions for the classical transport coefficients,[4] he found that they involved not autocorrelations just of $\overleftrightarrow{\Pi}$ and $\vec{Q}$ but of the fluctuations of these fluxes in a microcanonical ensemble. It was later realized that, for any ensemble, a transport coefficient is an integral of an autocorrelation of a "subtracted flux"; namely, the flux minus a certain linear combination of the fluctuations of the densities of mass, momentum, and energy.[5,9,81]

We want to show that $(1-\mathcal{P})\overleftrightarrow{\Pi}D_0$ and $(1-\mathcal{P})(\vec{Q}-\vec{v}\cdot\tilde{\overleftrightarrow{\Pi}})D_0$ are natural generalizations of these subtracted fluxes appropriate to the present theory.

In Appendix D it is shown that for any phase function $Z(\vec{r};\Gamma)$ which is independent of $\vec{j}$, ρ, and e:

$$(1-\mathcal{P})Z(\vec{r})D_0=\left\{\Delta Z(\vec{r})-\int d\vec{r}'\left[\frac{\vec{J}^+}{\rho}\cdot\frac{\delta}{\delta\vec{v}}+\Delta\mathfrak{M}^+\frac{\delta}{\delta\rho}+\Delta\mathfrak{U}^+\frac{\delta}{\delta u}\right]\langle Z\rangle_0\right\}D_0. \tag{83}$$

The argument of quantities in the integrand is $\vec{r}'$ and $\langle Z\rangle_0$ is to be considered as a function of $\vec{v}$, ρ, and u.[82] The fluctuation ΔZ of Z is defined by

$$\Delta Z\equiv Z-\langle Z\rangle_0, \tag{84}$$

where $\langle Z\rangle_0$ is given in Eq. (54). The fluctuations in the local frame are defined by

$$\vec{J}^+(\Gamma)\equiv\vec{J}(\Gamma^+), \tag{85}$$

$$\Delta\mathfrak{U}^+\equiv\mathcal{E}^+-V_0\mathfrak{M}^+-u, \tag{86}$$

and $$\Delta\mathfrak{M}^+\equiv\mathfrak{M}^+-\rho. \tag{87}$$

Observe that according to Eq. (83) the integral of $(1-\mathcal{P})ZD_0$ over phase space vanishes by definition of the fluctuations.

To use this result for the case where Z is identical with $\tilde{\overleftrightarrow{\Pi}}$, notice that

$$\langle\tilde{\overleftrightarrow{\Pi}}\rangle_0=\rho\vec{v}\vec{v}+\tilde{\overleftrightarrow{P}}_0, \tag{88}$$

which is, in fact, all of the reversible momentum current. This equation follows immediately from the definition of $\overleftrightarrow{P}_0$ as the expectation of $\overleftrightarrow{\Pi}^+$ over D_0 [see Eqs. (39) and (54)] and Eq. (33), if one observes that D_0 gives the exact expectations for the A_ν. From Eq. (88) the derivatives appearing in Eq. (83) can be computed, and one should recall that $\overleftrightarrow{P}_0$ is independent of $\vec{v}$. If one then expresses $\overleftrightarrow{\Pi}$ in terms of $\overleftrightarrow{\Pi}^+$ and the $A_\nu{}^+$ by using Eq. (33) and the equations relating A_ν and $A_\nu{}^+$ (given in Appendix B), one obtains

$$(1-\mathcal{P})\tilde{\overleftrightarrow{\Pi}}(\vec{r};\Gamma)D_0(\Gamma)=\tilde{\overleftrightarrow{I}}_{\vec{j}}(\vec{r};\Gamma^+)D_0(\Gamma), \tag{89}$$

where Γ^+ is again the phase in terms of the local momenta. The subtracted momentum flux $\tilde{\overleftrightarrow{I}}_{\vec{j}}(\vec{r};\Gamma)$ is the transpose of

$$\overleftrightarrow{I}_{\vec{j}}(\vec{r};\Gamma)\equiv\overleftrightarrow{\Pi}(\vec{r})-P_0(\vec{r})-\int d\vec{r}'\left[\Delta\mathfrak{M}(\vec{r}')\frac{\delta\overleftrightarrow{P}_0(\vec{r})}{\delta\rho(\vec{r}')}+\Delta\mathfrak{U}(\vec{r}')\frac{\delta\overleftrightarrow{P}_0(\vec{r})}{\delta u(\vec{r}')}\right], \tag{90}$$

and this quantity evaluated at Γ^+ is what appears in Eq. (89).

In a similar way, one can calculate the effect of $(1-\mathcal{P})$ operating on $(\vec{Q}-\vec{v}\cdot\tilde{\overleftrightarrow{\Pi}})D_0$.[83] One computes the functional derivatives of the expectation of Q over D_0 from the equation

$$\langle\vec{Q}\rangle_0=\vec{v}e+\overleftrightarrow{P}_0\cdot\vec{v}+\vec{q}_0, \tag{91}$$

which is, in fact, all of the reversible heat current. Also, one re-expresses $\vec{Q}$ in terms of $\vec{Q}^+$, $\overleftrightarrow{\Pi}^+$, and the $A_\nu{}^+$. In the calculation of $(1-\mathcal{P})\vec{Q}D_0$, one must recognize the terms belonging to $(1-\mathcal{P})\vec{v}\cdot\tilde{\overleftrightarrow{\Pi}}D_0$ by referring to Eq. (89). Then one derives that

$$(1-\mathcal{P})[\vec{Q}(\vec{r};\Gamma)-\vec{v}(\vec{r})\cdot\tilde{\overleftrightarrow{\Pi}}(\vec{r};\Gamma)]D_0(\Gamma)=\vec{I}_e(\vec{r};\Gamma^+)D_0(\Gamma), \tag{92}$$

where the subtracted heat flux is defined by

$$\vec{I}_e(\vec{r};\Gamma) \equiv \vec{Q}(\vec{r}) - \frac{\vec{J}(\vec{r})}{\rho}\cdot[\overleftrightarrow{P}_0 + \overleftrightarrow{U}(u+\rho V_0)] + \vec{Q}_0(r) - \vec{q}_0 - \int d\vec{r}'\left[\frac{\vec{J}(\vec{r}')}{\rho}\cdot\frac{\delta\vec{q}_0(\vec{r})}{\delta\vec{v}(\vec{r}')} + \Delta\mathfrak{M}(\vec{r}')\frac{\delta\vec{q}_0(\vec{r})}{\delta\rho(\vec{r}')} + \Delta\mathfrak{U}(\vec{r}')\frac{\delta\vec{q}_0(\vec{r})}{\delta u(\vec{r}')}\right]. \tag{93}$$

The subtracted fluxes $\overleftrightarrow{I}_{\vec{j}}$ and $\vec{I}_e$ are natural generalizations of their classical counterparts which appear in the autocorrelation expressions for the viscosity and heat conductivity. The classical subtracted fluxes[5,27,84] are the integral over all space of the near-equilibrium local approximations to Eqs. (90) and (93). In this approximation $\overleftrightarrow{\Pi}(\vec{r})$ and $\vec{Q}(\vec{r})$ are replaced by their corresponding expressions in which the nonlocal contributions from the terms proportional to the forces are dropped. The functional derivatives of $\overleftrightarrow{P}_0$ become δ-functions multiplied by the ordinary thermodynamic derivatives of the pressure p^0 defined by Eq. (6). The tensor enthalpy density $\overleftrightarrow{P}_0 + \overleftrightarrow{U}u$ is replaced by the unit tensor times $h^0 \equiv p^0 + u$, and all terms in $\vec{Q}_0$ or $\vec{q}_0$ are neglected because they are proportional to gradients. Just as the equilibrium average of the classical subtracted fluxes vanishes, so $\overleftrightarrow{I}_{\vec{j}}$ and $\vec{I}_e$ have vanishing averages over the distribution D_0.

It is noteworthy that the subtracted fluxes remain linear combinations of the fluctuations even when nonlocal and nonlinear effects may be important. Moreover, we want to remark that it has been verified that the same form for the subtracted flux is valid when a D_0 of grand canonical type is used.[85] This supports the idea that, like the result for the classical limiting case, this form of the flux is covariant for all ensembles which are appropriate generalizations of the usual equilibrium ones.

Even using Eqs. (89) and (92) to express the transport kernels $\overleftrightarrow{K}^{(l)}$ does not yet give $\overleftrightarrow{K}^{(4)}$ and $\vec{K}^{(2)}$ the autocorrelation form. This would be so, however, if we could legitimately replace $\overleftrightarrow{\Pi}^+$ by $\overleftrightarrow{I}_{\vec{j}}(\Gamma^+)$ and $\vec{Q}^+$ by $\vec{I}_e(\Gamma^+)$. To see that this can indeed be done, notice that[17,86]

$$\mathcal{K}(1-\mathcal{P}) = (1-\mathcal{P})\mathcal{K}(1-\mathcal{P}) \tag{94}$$

One can also easily verify that for any phase functions V and W

$$\int d\Gamma\, V(\Gamma)(1-\mathcal{P})W(\Gamma) = \int d\Gamma\,[(1-\tilde{\mathcal{P}})V(\Gamma)]W(\Gamma), \tag{95}$$

where $\tilde{\mathcal{P}}$ is the transpose of $\mathcal{P}$. (An explicit form is given in Appendix D.) Moreover, it can be seen that

$$(1-\tilde{\mathcal{P}})\overleftrightarrow{\Pi}^+(\vec{r}) = \overleftrightarrow{I}_{\vec{j}}(\vec{r};\Gamma^+) \equiv \overleftrightarrow{I}_{\vec{j}}^{\,+}(\vec{r};\Gamma), \tag{96}$$

$$\text{and}\quad (1-\tilde{\mathcal{P}})\vec{Q}^+(\vec{r}) = \vec{I}_e(\vec{r};\Gamma^+) \equiv \vec{I}_e^{\,+}(\vec{r};\Gamma). \tag{97}$$

To verify these equations, first express $\overleftrightarrow{\Pi}^+$ and $\vec{Q}^+$ in terms of the $\overleftrightarrow{\Pi}$, $\vec{Q}$, and the A, then make use of the fact that $(1-\tilde{\mathcal{P}})A$ vanishes (as indicated in Appendix D), and finally apply the relation that $(1-\tilde{\mathcal{P}})Z$ is equal to the bracketed expression of Eq. (83) [see Eq. (D.17) of Appendix D].

The autocorrelation form emerges using these results; for example, one has for $\overleftrightarrow{K}^{(4)}$, that

$$\begin{aligned}\overleftrightarrow{K}^{(4)}(1;2) &= \int d\Gamma_1 d\Gamma_2 \overleftrightarrow{I}_{\vec{j}}(1;\Gamma_1^{\,+})\mathcal{K}(\Gamma_1 t_1;\Gamma_2 t_2)\tilde{\overleftrightarrow{I}}_{\vec{j}}(2;\Gamma_2^{\,+})D_0(\Gamma_2 t_2)\beta(2)\\ &= \int d\Gamma_1 d\Gamma_2 \overleftrightarrow{I}_{\vec{j}}(1;\Gamma_1)\bar{\mathcal{K}}(\Gamma_1 t_1;\Gamma_2 t_2)\tilde{\overleftrightarrow{I}}_{\vec{j}}(2;\Gamma_2)D_0^{\,+}(\Gamma_2 t_2)\beta(2),\end{aligned} \tag{98}$$

where we have defined

$$\bar{\mathcal{K}}(\Gamma_1 t_1;\Gamma_2 t_2) \equiv \mathcal{K}(\Gamma_1^- t_1;\ \Gamma_2^- t_2). \tag{99}$$

The subscript on the phase point $\Gamma_{\bar{\alpha}}$ indicates the time with which the point is associated, while the superscript minus sign indicates that $\vec{P}_i$ is obtained from the component momenta $\vec{P}_i^-$ by subtracting $m\vec{v}$ rather than adding it as with the $\vec{P}_i^{\,+}$ previously defined; that is,

$$\vec{P}_{\alpha i}^{\,-} \equiv \vec{P}_{\alpha i} + m\vec{v}(\vec{R}_{\alpha i}, t_2). \tag{100}$$

Clearly all the kernels $\overleftrightarrow{K}^{(l)}$ can now be expressed in an analogous way, so that using the notation introduced by Eq. (70), we can write

$$\overleftrightarrow{K}^{(4)}(1;2\,|\,\vec{v}f\beta) = (\overleftrightarrow{I}_{\vec{j}}(1)\,|\,\bar{\mathcal{K}}(t_1;t_2)\,|\,\tilde{\overleftrightarrow{I}}_{\vec{j}}(2)D_0^{\,+}(t_2))\beta(2), \tag{101}$$

$$\vec{K}^{(3)}(1;2\,|\,\vec{v}f\beta) = (\overleftrightarrow{I}_{\vec{j}}(1)\,|\,\bar{\mathcal{K}}(t_1;t_2)\,|\,\vec{I}_e(2)D_0^{\,+}(t_2))\beta(2), \tag{102}$$

$$\tilde{\vec{K}}^{(3)}(1;2\,|\,\vec{v}f\beta) = (\vec{I}_e(1)\,|\,\bar{\mathcal{K}}(t_1;t_2)\,|\,\tilde{\overleftrightarrow{I}}_{\vec{j}}(2)D_0^{\,+}(t_2))\beta(2), \tag{103}$$

$$\text{and}\quad \vec{K}^{(2)}(1;2\,|\,\vec{v}f\beta) = (\vec{I}_e(1)\,|\,\bar{\mathcal{K}}(t_1;t_2)\,|\,\vec{I}_e(2)D_0^{\,+}(t_2))\beta(2). \tag{104}$$

These expressions are *the central result of this paper*.

Observe first that the viscosity kernel $\overleftrightarrow{K}^{(4)}$ and the heat conductivity kernel $\vec{K}^{(2)}$ are autocorrelations, and that $\tilde{\vec{K}}^{(3)}$ is in an obvious sense the transpose of the coupling kernel $\vec{K}^{(3)}$. Also notice that since $D_0^{\,+}$ is independent of the velocity $\vec{v}$, all the dependence on $\vec{v}$ (except for the explicit linear dependence of heat fluxes on $\nabla\vec{v}$) is contained in the dynamical kernel $\bar{\mathcal{K}}(t_1;t_2)$. The kernels for the classical theory (the integrals of which over all space and time are the transport coefficients) of course do not depend on velocity at all.

These results differ from the kernels of the classical theory in other ways: Classically $\vec{K}^{(3)}$ and $\tilde{\vec{K}}^{(3)}$ do not appear at all and the factor β is taken at the space-time point $(\vec{r}_1 t_1)$ instead of $(\vec{r}_2 t_2)$. Also, in Eqs.

(101)–(104), D_0^+ replaces the usual canonical distribution (containing no nonlocal effects), and the subtracted fluxes $\overleftrightarrow{\mathrm{I}}_{\mathrm{j}}$ and $\vec{\mathrm{I}}_e$ replace the near-equilibrium, long-wavelength forms, which have just been described. But the most important difference is the appearance here of the time-evolution kernel $\mathcal{K}$ instead of the usual one which is the Green function corresponding to Liouville's operator. Not only does $\mathcal{K}$ depend on $\vec{v}$ as well as on f and β, but it is a time-dependent nonlocal functional of all three of these variables.

C. The Initial Value Terms

The preceding discussion has led to expressions for the pressure tensor, namely Eqs. (77) and (72), and the heat current, namely Eqs. (78) and (74). Moreover, even though these expressions are exact, the local-equilibrium terms and the terms proportional to the thermodynamic forces have been shown to be natural generalizations of the expressions appropriate to the classical theory. All the effects of the initial distribution are embodied in the initial value terms $\overleftrightarrow{\mathrm{R}}_{\mathrm{j}}$ and $\vec{\mathrm{R}}_e$ defined by Eqs. (72) and (74). To proceed further, a physical assumption is required so that the terms vanish identically or at least become small.

Two remarks will be made.[87] First, if one wants to use this formal expression for the currents to discuss the approach to a Markoffian limit and thereby the approach to equilibrium, one can hope to show that for a sufficiently large class of initial distributions this term vanishes quickly enough. This conjecture is supported *a posteriori*. Suppose one accepts on the basis of the very strong similarities between the present currents and the currents in the Markoff limit that this classical Markoff limit follows asymptotically in the time for the reversible and irreversible parts of the current for sufficiently small gradients. (This can be shown.) Then one can conclude from the fact that this Markoffian limit is supported by experiment that the initial value term vanishes for experimentally attained initial distributions. More than that, it must vanish at least as rapidly as the small wave-number limit of the transport kernels. If this conjecture can be validated it would provide a theory of the approach to equilibrium.

This argument gives no indication, however, that the initial value terms vanish any faster than the transport kernels. Indeed, since both terms involve the same time-evolution function $\mathcal{K}$, it is difficult to see any way for the initial-value term and the term linear in the thermodynamic forces belonging to the same current to decay at radically different rates. Thus, the second point is the following: If one wants to have a valid theory for very high frequencies and wave numbers (so that essentially the full generality of the thermodynamic force term in the currents is required), then one must either include the initial-value terms or consider only cases for which they vanish identically; namely, those cases for which $\Delta D(t=0)$ vanishes.

The difficulties of the first alternative are obvious, especially since we do not *in general* determine initial distributions. Thus we adopt the second alternative and *consider only cases for which* $\Delta D(t=0)$ *vanishes*; namely, those for which $D(t=0)$ is equal to the initial value $D_0(t=0)$ of the distribution defined by Eq. (42). In principle, one can set up many past histories all of which will arrive at the desired distribution $D_0(t=0)$ at $t=0$, but we cannot do this in practice. In practice, probably the only experimental circumstances for which we can argue that we know $D(t=0)$ are those in which we prepare states of *constrained* equilibrium corresponding to the initial expectation values $a_\nu(\vec{r};0)$.[88] In such experiments the system is in an equilibrium with the expectation values of the a_ν fixed in some way for at least a relaxation time before $t=0$. The appropriate distribution in phase space is the one which maximizes the Gibbs entropy [given in Eq. (51)] under these constraints. Operationally, the idea is to randomly take samples from an equilibrium ensemble by a particular prescription which is kept fixed in the sampling.

By adopting this alternative, one is giving up other initial conditions (for example, catching the system during the course of relaxation from some constrained equilibrium), but this does not appear to be an important restriction from an experimental point of view. In fact, as a third point one can argue that the choice of $D_0(t=0)$ as the initial value of D should be made precisely because it corresponds to possible laboratory practice.[14,16,89]

Perhaps, for emphasis, one should point out that the present assumption is wholly different from assuming that $D(t)$ is equal to $D_0(t)$ for times t later than the initial time. This equality cannot be true and indeed we have just calculated the difference $\Delta D(t)$. What is true as has been shown is that $\Delta D(t)$ is first order in the gradients and may therefore be small in physically interesting cases.

VI. CONCLUSIONS AND DISCUSSIONS

The expectation values of a set of mechanical quantities A_ν corresponding to mass, momentum, and energy density have been shown to satisfy the usual conservation laws. For the given mechanical model initially in constrained equilibrium corresponding to given initial densities $a_\nu(\vec{r};0)$, it has been shown that the pressure tensor is given by

$$\overleftrightarrow{\mathrm{P}}(\vec{r}_1 t_1)=\overleftrightarrow{\mathrm{P}}_0(\vec{r}_1\,|\,f(t_1)\beta(t_1))-\int_0^t dt_2\int d\vec{r}_2[\overleftrightarrow{\mathrm{K}}^{(4)}(1;2\,|\,\vec{v}f\beta):\vec{\nabla}\vec{v}(2)+\overleftrightarrow{\mathrm{K}}^{(3)}(1;2\,|\,\vec{v}f\beta)\cdot\vec{\nabla}\ln\beta(2)], \tag{105}$$

while the heat current is given by

$$\vec{q}(\vec{r}_1 t_1)=\vec{q}_0(\vec{r}_1\,|\,\vec{v}(t_1)f(t_1)\beta(t_1))-\int_0^{t_1} dt_2\int d\vec{r}_2[\overset{\approx}{\overleftrightarrow{\mathrm{K}}}{}^{(3)}(1;2\,|\,\vec{v}f\beta):\vec{\nabla}\vec{v}(2)+\overleftrightarrow{\mathrm{K}}^{(2)}(1;2\,|\,\vec{v}f\beta)\cdot\vec{\nabla}\ln\beta(2)].$$

The local-equilibrium values $\overleftrightarrow{\mathrm{P}}_0$ and $\vec{q}_0$ of the pressure tensor and heat current are the expectations in a local-equilibrium ensemble D_0 for appropriate phase functions defined by Eqs. (34) and (36). In the expressions for $\overleftrightarrow{\mathrm{P}}_0$ and $\vec{q}_0$ given in Eqs. (56) and (57), all orders in gradients are included so as to account for nonlocal effects. The local-equilibrium ensemble D_0 is defined to be the exponential function of a linear combination of the mechanical quantities corresponding to the observed densities [Eq. (42)]. The coefficients of this linear combination $-\beta\vec{v}$, $-\beta\phi$, and β, called conjugate variables, are entirely determined as functionals of these densities. Averaging with such a distribution has the effect that there are contributions from terms of all orders in the gradients of both the Helmholtz free energy density f and the inverse temperature β. While $\overleftrightarrow{P}_0$ generalizes the classical local-equilibrium pressure, $\vec{q}_0$, which is linear in the velocity gradient, has no classical counterpart.[90] Such expressions are not new, but they do not seem to have been fully exploited, for example, in discussing nonlocal effects near the critical point or neutron scattering.

The molecular expressions for the *transport kernels* $\overleftrightarrow{K}^{(l)}$ *were the main goal and are the fundamental results of this paper.* These are explicitly given by Eqs. (101)-(104), by Eqs. (90) and (93), which define the subtracted fluxes $\overleftrightarrow{I}_{\vec{j}}$ and $\vec{I}_e$, by Eq. (68), which defines the time-evolution operator $\mathcal{K}$, and by Eq. (44), which defines the local-equilibrium ensemble in the local frame. Each factor in the viscosity kernel $\overleftrightarrow{K}^{(4)}$ and the thermal conductivity kernel $\overleftrightarrow{K}^{(2)}$ generalizes an analogous factor in the corresponding autocorrelation function of the classical theory. It is noteworthy that the subtracted fluxes remain linear combinations of the fluctuations. In addition to the fact that the subtracted fluxes and the distribution over which the correlations are averaged are time-independent but nonlocal functionals of the velocity, Helmholtz free energy density, and the inverse temperature, the time-evolution operator $\mathcal{K}$ is the one appropriate not to the Liouville operator but to $(1-\mathcal{P})L$.

The projector $\mathcal{P}$ is the operator which projects the time rate of change of the solution of Liouville's equation into the time rate of change of the generalized canonical ensemble, and is defined in terms of D_0 by Eq. (62). Because $\mathcal{P}$ is itself a time-independent but nonlocal functional of $\vec{v}$, f, and β, the Green function $\mathcal{K}$ is a *time-dependent* as well as nonlocal functional of these variables [i.e., the corresponding operator is not just the exponential function of the negative of $(t-t')(1-\mathcal{P})L$].

It was also shown that the free energy f and inverse temperature β are determined as nonlocal functionals of the mass density and internal energy density by equations of state which are nonlocal generalizations of the usual ones.

Thus, we conclude that the conservation equations, the molecular expressions for $\overleftrightarrow{P}$ and $\vec{q}$, and these equations of state *achieve the goal of a closed integrodifferential description of the fluid variables for which initial values determine the future ones.*

We emphasize that the only assumptions necessary for the validity of this system of equations within the context of the statistical-mechanical method are the choice of a particular set of variables and the special initial distribution in phase space. Furthermore, since this system of equations is an exact consequence of Liouville's equation for the initial condition chosen, one expects them to give a complete theory of the expected dynamical behavior of isolated simple fluids for all experiments corresponding to such an initial condition. The theory is complete because the equations are a closed system for a finite number of variables: There is no infinite hierarchy which must be truncated by uncontrolled approximations. The variables themselves are also complete in the sense that for small enough gradients they are determined by a description which is local in both space and time (i.e., the classical theory). If our variables did not have this property we could not expect the kernels to be quasilocal (i.e., short ranged) in space and time.

The present derivation of these results, however, is based on a formal solution of the initial value problem for an isolated system while the classical-fluid dynamic equations are known to apply for subsystems of thermomechanical baths. McLennan has developed a theory for the steady states of such systems.[27] In the present context, one would want to deduce the behavior of a small subsystem of a large system to which the present theory applies. But McLennan's work strongly suggests that such a study will yield essentially the same set of equations with the same molecular expressions. The only difference will be the presence of source terms to be taken as given. In other words, the equations and parameters are characteristic of the given system and not of its surroundings. This would be in complete analogy to the situation for the classical dynamics linearized about absolute equilibrium: The same Green function which determines the solution to the initial-value problem for the source-free equations also determines the solution in the presence of sources at the boundaries. Therefore, our opinion is that the present theory provides exactly the appropriate system of equations and molecular expressions for open systems if one simply introduces the given sources in the usual way.

We have already noted that our choice of the local-equilibrium distribution D_0 is not unique; there are other possible ones which are appropriate to different experimental situations. Although it has not been shown, one expects that the molecular expressions are invariant to such choices. The expected reversible part of the stress and heat current would be the same even though the fluctuations of them would be different. Also, although the transport kernels are fluctuations, they should remain invariant in the way found by M. S. Green[91] for the correlations of the classical theory; namely, the subtracted fluxes change *value* in just such a way as to compensate for the change in the distribution. The *form* of the subtracted fluxes, however, would remain the same just as it does in the classical case (i.e., they are covariant). If one assumes the validity of this invariance property, the nonuniqueness to which we have referred is an asset of the theory.

The fact that the present expressions for the expected fluxes are in close formal analogy to the classical forms and to the molecular expressions of them is in itself noteworthy. Within a statistical-mechanical context, such a form for general fluid dynamics was first given by Richardson.[14] Our primary result is to have completed his work by exhibiting the detailed molecular expressions for the transport kernels in the general case. We can display the connection with Richardson's work in a very direct way. If one takes Eq. (69) for ΔD and evaluates $(1-\mathcal{P})LD_0$ with the first equality of Eq. (64), one derives exactly his nonlinear, quasidifferential equation [Eq. (25) in Ref. 14], but now with the kernel

$$(\dot{A}(\vec{r})|\mathcal{K}(t;t')(1-\mathcal{P})|\dot{A}(\vec{r}\,')D_0(t'))$$

where $\mathcal{K}$ and $\mathcal{P}$ are again defined by Eqs. (68) and (62). Notice that it is not necessary to specify the functions A_ν in order to arrive at this result.[16]

The present results also extend and complement other work. For example, it goes further than Mori's generalized Langevin-equation approach[8] in that it is not limited to near-equilibrium situations and it introduces the conjugate variables in a natural way. In another place, we hope to show how such a small fluctuation theory can be elaborated from the present structure. In his earlier work on deriving the molecular expressions for the classical equations[25] Mori uses the same $D_0(t)$ used here. The expected currents are calculated, however, by use of a successive coarse-graining in which $D(t)$ is repeatedly set equal to $D_0(t)$ after each small interval of time. The present theory relieves us of the necessity of this assumption. We have already remarked that the present work complements McLennan's for the steady state. Moreover, for the problem it treats, the present work includes not only the nonlinear effects arising from evaluating the autocorrelation with the local-equilibrium distribution, but includes the contributions from all higher powers of the thermodynamic forces in a way quite different from his.

The theory embodies a number of concepts in common with other work. The primary one which originates from the Chapman-Enskog solution of Boltzmann's equation and Bogolubov's work is that, at least for special initial conditions, distribution functions are in some sense functionals of certain kinds of variables. Here, for a special initial condition, we have expressed $D(t)$ exactly as a functional of the fluid densities. This functional is not Bogolubov's time-independent functional for our problem, however, and the expression given in Eq. (69) allows the possibility of studying the approach to the time-independent form (if one exists in general). The other feature of this idea is that the variables should be in some sense special; for example, that they be approximate integrals of the motion. This is embodied in somewhat disguised form by the fact that the present choice of D_0 is physically sensible. This property will be strongly used, however, only when one continues the theory by investigating approximations for small departures from equilibrium. Another broad feature in common with other work is the existence for special initial conditions of closed exact equations which are in a sense projections of Liouville's equation.[15,92,93]

The method we have used is suggested by the Bogolubov-Chapman-Enskog technique for solving the Boltzmann equation. Among the advantages of this approach are: the possibility of making the assumptions fully explicit; the possibility of framing the problem as the calculation of the mean currents; the lack of necessity for introducing fictitious forces in the Hamiltonian; the natural occurrence of the subtracted fluxes; and the lack of necessity for any coarse-graining.

Because of this method, the present work is most closely related in spirit to that of Kirkwood and Fitts,[22] and H. S. Green.[23] Because they neglected certain terms in the evaluation of D_0 at an early stage, however they became committed to a sequential approach to higher-order effects. But more importantly, this had the effect that some general features of the theory were obscured. For example, one does not easily see by their method that the appropriate subtracted fluxes can arise in complete generality because of the occurrence of a projector, or that one still gets an autocorrelation of these exact subtracted fluxes. Thus the introduction of the projector $\mathcal{P}$, which projects the time rate of change of D onto that of the time rate of change of D_0, has extended and clarified this work.

Of course, the present results are not directly useful as they stand. One might say that they have only transformed the full mathematical problem into a form which is exact but for which physical insight immediately suggests a number of approximation schemes corresponding to various limiting cases. Because of this, these results are particularly suitable as starting points for further approximations. For example, we know physically that the densities will change more slowly as the departures either from absolute equilibrium or from some local equilibrium become smaller. In the first case, the departure of the conjugate variables b_ν from the equilibrium values is small for all points at any time and therefore these departures may be suitable expansion parameters. The second case may be of more fundamental interest. Here although the departures from absolute equilibrium may be very large, the gradients of the conjugate variables at any time are small everywhere, so that in the neighborhood of any given point the deviations from the value appropriate to the point are small.[94] Thus the gradients of the conjugate variables which are a linear combination of the thermodynamic forces may be useful expansion parameters in this case.[95] Notice, however, that neither one of these expansions demands that we go to the low-frequency, long-wavelength limit.

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APPENDIX A. DERIVATION OF CURRENTS

Our purpose is to describe the calculation leading to Eqs. (25)–(27). First notice that all the densities $A_\nu(\vec{r})$ are a sum over all particles of a coefficient $A_{\nu i}(\Gamma)$ depending on Γ but not on $\vec{r}$, multiplied by $\delta(\vec{r}-\vec{R}_i)$. Since the Liouville operator is a partial-differential operator, LA_ν will be the sum over particles of $A_{\nu i}L\delta(\vec{r}-\vec{R}_i)$ added to $\delta(\vec{r}-\vec{R}_i)LA_{\nu i}(\Gamma)$. But by evaluating derivatives we see that

$$L\delta(\vec{r}-\vec{R}_i) = -\vec{\nabla}\cdot(\vec{P}_i/m)\delta(\vec{r}-\vec{R}_i), \qquad \text{(A.1)}$$

and also that

$$L\vec{P}_i = -m\vec{\nabla}_{\vec{R}_i} V_0(\vec{R}_i) + \textstyle\sum_k' \vec{F}_{ik}, \tag{A.2}$$

and $$LH_i = (2m)^{-1}\textstyle\sum_k' \vec{F}_{ik}\cdot(\vec{P}_i + \vec{P}_k), \tag{A.3}$$

where the symbols are defined in the text. Thus since we assume $\vec{F}_{ik} = -\vec{F}_{ki}$ we find that

$$\dot{\vec{J}} = -\vec{\nabla}\cdot\sum_i \frac{\vec{P}_i\vec{P}_i}{m}\delta(\vec{r}-\vec{R}_i) + \tfrac{1}{2}\sum_{i\neq k}\vec{F}_{ik}[\delta(\vec{r}-\vec{R}_i)-\delta(\vec{r}-\vec{R}_k)] - \mathfrak{M}\vec{\nabla}V/m, \tag{A.4}$$

and

$$\dot{\mathcal{E}} = -\vec{\nabla}\cdot\sum_i \frac{\vec{P}_i}{m}H_i\delta(\vec{r}-\vec{R}_i) + \frac{1}{4m}\sum_{i\neq k}\vec{F}_{ik}\cdot(\vec{P}_i+\vec{P}_k)[\delta(\vec{r}-\vec{R}_i)-\delta(\vec{r}-\vec{R}_k)]. \tag{A.5}$$

The only trick necessary is to express the second sum as a divergence of a quantity which preserves the property of the original expression of vanishing for $\vec{r}$ outside the volume (for all Γ of interest). We accomplish this (not uniquely) by using the identity

$$\delta(\vec{r}-\vec{R}_i)-\delta(\vec{r}-\vec{R}_k) = -\vec{\nabla}\cdot\int_0^1 d\epsilon\,\vec{l}'(\epsilon,\vec{R}_i,\vec{R}_{ik})\delta[\vec{r}+l(\epsilon,\vec{R}_i,\vec{R}_{ik})-\vec{R}_k] \cong -\vec{\nabla}\cdot\int_0^1 d\epsilon\,\vec{R}_{ik}\delta(\vec{r}+\epsilon\vec{R}_{ik}-\vec{R}_k). \tag{A.6}$$

The vector $\vec{l}(\epsilon,\vec{R}_i\vec{R}_{ik})$ is defined in the following way: It vanishes when $\epsilon = 0$, it equals $\vec{R}_{ik}$ when $\epsilon = 1$, and otherwise it lies on the shortest line between $\vec{R}_i$ and $\vec{R}_k$ which lies entirely inside the system. The quantity $\vec{l}'(\epsilon,\vec{R}_i,\vec{R}_{ik})$ is the derivative with respect to ϵ of $\vec{l}(\epsilon,\vec{R}_i,\vec{R}_{ik})$. Except in the unusual circumstance, when $\vec{R}_i$ and $\vec{R}_k$ are on opposite sides of a small inward protrusion of the surface, $\vec{l}(\epsilon,\vec{R}_i,\vec{R}_{ik})$ equals $\vec{R}_{ik}$ and one has the second equality in Eq. (A.6). For large systems, this second form suffices for most purposes, and we adhere to it in the text. For the discussion about surface terms in LD_0, however, one uses the exact form which vanishes as it should.

For the heat-current expression of the text, the transformation to the local frame gives rise to the term

$$\vec{Q}_0 = \tfrac{1}{2}\int_0^1 d\epsilon\int d\vec{R}\,\vec{R}\vec{F}(\vec{R})\cdot\sum_{i\neq k}[\vec{v}(\vec{R}_i)-\vec{v}(\vec{r})]\delta(\vec{R}_{ik}-\vec{R})\delta(\vec{r}+\epsilon\vec{R}_{ik}-\vec{R}_k) \tag{A.7}$$

as well as to terms in which $\vec{v}$ can be taken at $\vec{r}$ because of the factor $\delta(\vec{r}-\vec{R}_i)$. Because of the δ functions in Eq. (A.7), however, the sum over particle pairs is equal to

$$\{\vec{v}[\vec{r}-(1-\epsilon)\vec{R}]-\vec{v}(\vec{r})\}\sum_{i\neq k}\delta[\vec{r}-(1-\epsilon)\vec{R}-\vec{R}_i]\delta(\vec{r}+\epsilon\vec{R}-\vec{R}_k),$$

and this yields the expression for $\vec{Q}_0$ in the text. If one starts with the more exact heat current derived by using the first equality of Eq. (A.6), one can still derive an expression in terms of $\mathfrak{N}^{(2)}$; namely,

$$\vec{Q}_0 = -\tfrac{1}{2}\int d\vec{R}d\vec{R}'\int_0^1 d\epsilon\int_0^1 d\epsilon'\,\vec{l}'(\epsilon,\vec{r}-\vec{R}',\vec{R})\vec{R}'\cdot\vec{\nabla}\vec{v}(\vec{r}-\epsilon\vec{R}')\cdot\vec{F}(\vec{R})\mathfrak{N}^{(2)}(\vec{r}-\vec{R}',\vec{r}-\vec{R}'+\vec{R};\Gamma)\delta[\vec{R}'-\vec{R}+\vec{l}(\epsilon,\vec{r}-\vec{R}',\vec{R})]. \tag{A.8}$$

APPENDIX B. FORM OF D_0 AND CALCULATION OF THE CONJUGATE VARIABLES

To exhibit D_0 in the more familiar form given in Eq. (44) and to advance the calculation of the conjugate variables by deriving Eqs. (48) and (49), one wants to convert the momentum integrals to Gaussian form.

One can easily verify by substituting the definition of Γ^+ that

$$\vec{J}(\vec{r}) = \vec{J}^+(\vec{r}) + \vec{v}(\vec{r})\mathfrak{M}^+(\vec{r}), \tag{B.1}$$

(B.2)

and $$\mathcal{E}(\vec{r}) = \mathcal{E}^+(\vec{r}) + \vec{v}(\vec{r})\cdot\vec{J}^+(\vec{r}) + \tfrac{1}{2}\vec{v}(\vec{r})\cdot\vec{v}(\vec{r})\mathfrak{M}^+(\vec{r}), \tag{B.3}$$

where $\mathfrak{M}^+$ and $\mathcal{E}^+$ are defined by Eqs. (45) and (46) and $\vec{J}^+$ is similarly defined. It is clear by substituting these expressions that Eq. (42) is equivalent to the more familiar form in Eq. (44).

Moreover, the expected densities according to Eqs. (B.1)–(B.3) are a linear combination of the expectations computed with D_0^+. For, if we define

$$\langle A\rangle^+ \equiv \int d\Gamma A(\Gamma)D_0^+(\Gamma), \tag{B.4}$$

then by taking the expectation of Eqs. (B.1)–(B.3) over $D_0(\Gamma)$, we find that

$$\vec{j} = \langle\vec{J}\rangle^+ + \vec{v}\langle\mathfrak{M}\rangle^+, \tag{B.5}$$

$$\rho = \langle\mathfrak{M}\rangle^+ = \langle\mathfrak{M}\rangle_0, \tag{B.6}$$

and $$e = \langle\mathcal{E}\rangle^+ + \vec{v}\cdot\langle\vec{J}\rangle^+ + \tfrac{1}{2}\vec{v}^2\langle\mathfrak{M}\rangle^+. \tag{B.7}$$

To obtain Eqs. (B.5)–(B.7), we replaced D_0 with D_0^+ according to Eq. (44) and then transformed the variables of integration to Γ^+. One can verify that although this transformation is not canonical it nevertheless has unit Jacobian. Clearly, $\langle\vec{J}^+\rangle$ vanishes.

The expected energy can be written, by noticing that the term in $e(\vec{r};\Gamma)$ due to the external potential is just $\mathfrak{M}(\vec{r};\Gamma)V_0(\vec{r})$, as

$$e(\vec{r}) = \vec{j}^2/2\rho + \rho V_0 + \langle \mathcal{E}_K(\vec{r})\rangle^+ + [N(N-1)/2V^2]\int d\vec{R}\, V(\vec{R})\rho_0^{(2)}(\vec{r};\vec{R}\,|f,\beta). \tag{B.8}$$

The quantity $\mathcal{E}_K(\vec{r};\Gamma)$ is the kinetic-energy term in $e(\vec{r};\Gamma)$ [see Eqs. (17) and (18)], and the two-particle probability density $\rho_0^{(2)}(\vec{r};\vec{R})$ is defined by Eq. (50). Now the momentum integrals can be done explicitly with the result that

$$\langle \mathcal{E}_K(\vec{r})\rangle^+ = \tfrac{3}{2}(\rho/m\beta). \tag{B.9}$$

Equations (B.8) and (B.9) together imply Eq. (49).

APPENDIX C. TIME RATE OF CHANGE OF TOTAL ENTROPY

We will show here that the time rate of change of total entropy defined by Eq. (51) is equal to a linear combination of the irreversible currents $\Delta\overleftrightarrow{P}$ and $\Delta\vec{q}$ times the corresponding thermodynamic forces. Thus, using the notation described in the text that the exponent of D_0 is equal to $b*A$, one can write

$$dS'/dt = \int d\vec{r}\, b*\partial_t a + \int d\vec{r}(\partial_t b)*a. \tag{C.1}$$

The second term vanishes because it is just equal to the negative of the time rate of change of the integral over all Γ space of D_0, and this vanishes because normalization is a constant. Thus one finds, by rewriting the first term according to Eq. (23), that

$$dS'/dt = \int d\vec{r}\, b*\int d\Gamma \dot{A}(\Gamma)D(\Gamma). \tag{C.2}$$

The contribution of D_0 to this, however, is just equal to the negative of the integral over Γ space of LD_0 which vanishes. The remaining contribution from ΔD can be written

$$dS'/dt = -\int d\vec{r}[\vec{\nabla}\cdot\Delta\mathcal{P}\cdot(-\beta\vec{v}) + \beta\vec{\nabla}\cdot(\Delta\vec{q} + \Delta\overleftrightarrow{P}\cdot\vec{v})], \tag{C.3}$$

where Eqs. (25)–(27) have been used to express the $\dot{A}_\nu$ and the matrix product has been made explicit. As they appear here, $\Delta\overleftrightarrow{P}$ and $\Delta\vec{q}$ are simply defined by

$$\int d\Gamma\, \overleftrightarrow{\Pi}\Delta D \equiv \Delta\overleftrightarrow{P}, \tag{C.4}$$

and $$\int d\Gamma\, \vec{Q}\Delta D \equiv \Delta\vec{q} + \Delta\overleftrightarrow{P}\cdot\vec{v}. \tag{C.5}$$

No term in $\vec{J}$ or $\mathfrak{M}$ appears in Eq. (C.3) because its expectation over ΔD vanishes. Now if one integrates by parts and writes the result in terms of $\vec{\nabla}\vec{v}$ instead of $\vec{\nabla}\beta\vec{v}$, one finds Eq. (58). The form of Eq. (58) suggests that it is appropriate to identify the integrand with the entropy production. One should also observe that this result depends only on the definition of the entropy functional and on the form of D_0. Thus Eq. (58) is generally valid without any assumption concerning the initial distribution $D(t=0)$.

APPENDIX D. PROPERTIES OF THE PROJECTOR

Some relations used in the text involving the projector $\mathcal{P}(\Gamma;\Gamma')$ are proved.

First, notice that the negative of the functional derivative of the conjugate variables with respect to the fluid densities is the matrix inverse to the autocorrelation matrix of the densities over D_0. The autocorrelation G is defined by

$$G_{\nu\mu}(\vec{r}';\vec{r}) \equiv \langle A_\nu(\vec{r}')A_\mu(\vec{r})\rangle_0. \tag{D.1}$$

If we also define a matrix g by

$$g_{\mu\nu}(\vec{r};\vec{r}') \equiv -\frac{\delta b_\mu(\vec{r})}{\delta a_\nu(\vec{r}')} \tag{D.2}$$

then $$\int d\vec{r}''[g(\vec{r};\vec{r}'')*G(\vec{r}'';\vec{r}')]_{\mu\nu} = \delta_{\mu\nu}\delta(\vec{r}-\vec{r}'). \tag{D.3}$$

The proof is simply to observe that the negative of the autocorrelation matrix is the functional derivative of the densities with respect to the conjugate variables, and that this derivative is by definition the inverse of the negative of g. Also observe that

$$g_{\mu\nu}(\vec{r};\vec{r}') = g_{\nu\mu}(\vec{r}';\vec{r}), \tag{D.4}$$

because G has just such a symmetry property.

Second, $\mathcal{P}$ is the projector of the A_ν, which means that

$$\mathcal{P}A_\nu(\vec{r})D_0 = A_\nu(\vec{r})D_0. \tag{D.5}$$

Furthermore the transpose of $\mathcal{P}$, given by

$$\tilde{\mathcal{P}}(\Gamma;\Gamma') \equiv \int d\vec{r}d\vec{r}'A(\vec{r};\Gamma)*g*A(\vec{r}';\Gamma')D_0(\Gamma'), \tag{D.6}$$

also projects out the A_ν, so that

$$\tilde{\mathcal{P}}A_\nu(\vec{r}) = A_\nu(\vec{r}). \tag{D.7}$$

Both of these equations are easily established from the definitions of $\mathcal{P}$ [see Eq. (62)] and $\tilde{\mathcal{P}}$ by using Eq. (D.3).

Third, $\mathcal{P}$ is idempotent and one can directly verify from its definition, Eq. (62), that

$$\mathcal{P}(t_1)\mathcal{P}(t_2)=\mathcal{P}(t_1), \tag{D.8}$$

where t_1 and t_2 are *any* pair of finite times.

Fourth, $\mathcal{P}$ projects D_0 from the distribution D; that is,

$$\mathcal{P}D=D_0=\mathcal{P}D_0. \tag{D.9}$$

Thus, although it is not so important here, this projector has the same property as the time-independent ones used by Zwanzig. To prove Eq. (D.9), one begins with the fact that D_0 is a homogeneous functional of first degree of $\vec{j}$, ρ, and e. This fact has been established by Robertson[17] for the quantum analog of D_0 and an analogous proof works here. This means that[96]

$$D_0(\Gamma\,|\,\epsilon a(t))=\epsilon D_0(\Gamma\,|\,a(t)). \tag{D.10}$$

If we compute the partial derivative of $D_0(\Gamma\,|\,\epsilon a(t))$ with respect to ϵ from Eq. (D.10) and evaluate it at $\epsilon=1$, we find

$$\int d\vec{r}\;\frac{\delta D_0(\Gamma\,|\,a(t))}{\delta a(\vec{r})}*a(\vec{r})=D_0(\Gamma\,|\,a(t)). \tag{D.11}$$

Since a_ν is the expectation of A_ν over either D or D_0, Eq. (D.11) implies both equalities in Eq. (D.9).

Fifth, if we use the chain rule to express the functional derivative in Eq. (D.11), we immediately see that

$$\int d\vec{r}\,'d\vec{r}\,''A(\vec{r}\,')*g(\vec{r}\,';\vec{r}\,'')*a(\vec{r}\,'')=1, \tag{D.12}$$

which will be useful in the following.

The sixth property of $\mathcal{P}$ we wish to establish is the expression for $(1-\mathcal{P})ZD_0$ given as Eq. (83) in the text. We clearly have that

$$(1-\mathcal{P})Z(\vec{r})D_0=(1-\mathcal{P})\Delta Z(\vec{r})D_0 \tag{D.13}$$

just because of the second equality in Eq. (D.9). From the definition of $\mathcal{P}$ we see that

$$\mathcal{P}\Delta ZD_0=D_0\int d\vec{r}\,'d\vec{r}\,''A(\vec{r}\,')*g(\vec{r}\,';\vec{r}\,'')*\langle A(\vec{r}\,'')\Delta Z\rangle_0=D_0\int d\vec{r}\,'d\vec{r}\,''\Delta A(\vec{r}\,')*g(\vec{r}\,';\vec{r}\,'')*\langle A(\vec{r}\,'')Z\rangle_0. \tag{D.14}$$

The second equality follows because Eq. (D.12) is valid. Now one notices that the factor $\langle A(\vec{r}\,'')Z\rangle_0$ is just the negative of the functional derivative of $\langle Z\rangle_0$ with respect to $b(\vec{r}\,'')$. Furthermore, because of the symmetry of g displayed in Eq. (D.4), the integral over $\vec{r}\,''$ of the matrix product of $g(\vec{r}\,',\vec{r}\,'')$ with this derivative is identical with the derivative of $\langle Z\rangle_0$ with respect to $a(\vec{r}\,')$. Thus, by rewriting Eq. (D.14) in terms of this functional derivative of $\langle Z\rangle_0$ with respect to $a(\vec{r}\,')$ and using it to express the right-hand side of Eq. (D.13), we arrive at

$$(1-\mathcal{P})Z(\vec{r})D_0=\Big\{\Delta Z-\int d\vec{r}\,'\Delta A(\vec{r}\,')*\frac{\delta\langle Z\rangle_0}{\delta a(\vec{r}\,')}\Big\}D_0\,. \tag{D.15}$$

One can now consider $\langle Z\rangle_0$ to be a functional not of $\vec{j}$, ρ, and e, but of $\vec{v}$, ρ, and u. But if this functional is, say, $z_0\{\vec{v},\rho,u\}$, it must be such that $\langle Z\rangle_0$ is equal to $z_0\{\vec{j}/\rho,\rho,e-\tfrac{1}{2}\vec{j}^2\rho-\rho V_0\}$. From this one can relate the functional derivatives with respect to $\vec{j}$, ρ, and e to those with respect to $\vec{v}$, ρ, and u, and find that

$$\Delta A*\frac{\delta\langle Z\rangle_0}{\delta a}=\left(\frac{\Delta\vec{J}-\vec{v}\Delta\mathfrak{M}}{\rho}\cdot\frac{\delta}{\delta\vec{v}}+\Delta\mathfrak{M}\frac{\delta}{\delta\rho}+[\Delta\mathcal{E}-\vec{v}\cdot\Delta\vec{J}+(\tfrac{1}{2}\vec{v}^2-V_0)]\frac{\delta}{\delta u}\right)\langle Z\rangle_0. \tag{D.16}$$

If one re-expresses this with the quantities J^+, $\mathfrak{M}^+$, and $\mathcal{E}^+$ defined by Eqs. (B.15), one arrives at the desired relation, namely Eq. (83).

By a procedure similar to that just used to establish Eq. (83), we can derive for the transpose of $\mathcal{P}$ that

$$(1-\tilde{\mathcal{P}})Z(\vec{r})=\Delta Z(\vec{r})-\int d\vec{r}\,'\left[\frac{\vec{J}^+}{\rho}\cdot\frac{\delta}{\delta\vec{v}}+\Delta\mathfrak{M}^+\frac{\delta}{\delta\rho}+\Delta\mathcal{U}^+\frac{\delta}{\delta u}\right]\langle Z\rangle_0. \tag{D.17}$$

Just as Eqs. (89) and (92) are established by using Eq. (D.16), so Eqs. (96) and (97) are established by using Eq. (D.17).

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[38] One might use temperature instead of energy density, and velocity or velocity potential instead of momentum density. Such choices are equivalent to the present one which is theoretically more suitable because the variables are directly related to purely mechanical quantities.

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[40] Note that $\overleftrightarrow{\mathrm{P}}_0$ is not the diagonal part of $\overleftrightarrow{\mathrm{P}}$ which, in fact, contains both reversible and irreversible parts.

[41] These transport relations are given, for example, in Ref. (2) .

[42] The tensor $\overleftrightarrow{\kappa}^{(4)}$ has the elements $\eta_S(\delta_{ac}\delta_{bd}+\delta_{ad}\delta_{bc}-\frac{2}{3}\delta_{ab}\delta_{cd})+\eta_B\delta_{ab}\delta_{cd}$.

[43] See Appendix C for the proof.

[44] See G. V. Chester, in Rept. Progr. Phys. 26, 411 (1963), and Ref. 10. Such integral forms are used for the dielectric response in solids. Both of these proposals are in some sense equivalent to proposals which introduce more variables or higher derivatives in space and time, and both avoid some of the disadvantages of these alternatives.

[45] This Gibbsian viewpoint is perhaps most natural as a context for the initial value problem, but it is sufficient to describe steady states as well.

[46] The system is still to be considered isolated because these potentials are fixed, nonstatistical quantities so that no system quantities can be exchanged to the outside because of them.

[47] The proposition that observed quantities have values equal to the expectations of these A_ν means the following: In an experiment one should actually determine values for a large number of suitably prepared repeated trials on the same system, or for a given trial on an ensemble of systems with suitable initial preparation, and then compute the mean. For the densities of mechanical quantities to be defined, however, the number of terms in the A_ν is proportional to the total number of particles. Thus, when the number of particles is large, the fluctuations due to the uncertainty of initial phase are expected to be small even away from equilibrium, so that in any trial we will observe the average with overwhelming probability. Put another way, almost every representative of the process will be an approximate solution of the equations satisfied by the average.

[48] H. Grad, in Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 205.

[49] J. H. Irving and J. G. Kirkwood, in J. Chem. Phys. 18, 817 (1950), use these definitions.

[50] Even the full distribution of the A_ν does not fix $D(\Gamma;0)$.

[51] This well-known result follows from the fact that $D(\Gamma;t)$ is equal to $D(\Gamma_{-t};0)$ and that the transformation to Γ_{-t} as a new variable is canonical with unit Jacobian.

[52] As has been remarked by McLennan [Progr. Theoret. Phys. (Kyoto) 30, 408 (1963)] and Robertson (Ref. 17), there is some arbitrariness in the definition of the currents. We have taken essentially the expression proposed by Richardson which has the Taylor series proposed by Irving and Kirkwood. The present expressions do not quite vanish outside the system for all relevant values of Γ (i.e., particles inside) and improved expressions are given in Appendix A.

[53] See Irving and Kirkwood (Ref. 49) who also argue that $\overleftrightarrow{\Pi}(\vec{\mathrm{r}};\Gamma)$ is consistent with the macroscopic concept of pressure.

[54] This procedure is clearly equivalent to finding "equations of change" by multiplying Liouville's equation by A_ν and integrating over phases. Such a procedure emphasizes that the macroscopic conservation laws are "contractions" of the Liouville equation while the present procedure emphasizes the existence of the microscopic analog of the conservation laws.

[55] To make the verification, substitute $\vec{\mathrm{P}}_i=\vec{\mathrm{P}}_i^{\,+}+m\vec{\mathrm{v}}(\vec{\mathrm{R}}_i)$ into the expressions for $\overleftrightarrow{\Pi}$ and $\vec{\mathrm{Q}}$ and make use of the presence of the factor $\delta(\vec{\mathrm{r}}-\vec{\mathrm{R}}_i)$ in all but one term of $\vec{\mathrm{Q}}$. One can then identify the terms which are a linear combination of the A_ν. See Appendix A for remarks on deriving Eq. (37).

[56] Another way of proceeding would be to derive equations for the time rates of change of the momentum and energy currents which would contain expectations of still more complicated quantities (e.g., of higher tensorial rank). Such a process can be continued to an infinite hierarchy of equations. Whether one truncates this hierarchy in the spirit of the "13-moment approximation" [H. Grad, Commun. Pure Appl. Math. 2, 331 (1949)], or tries to find some approximate solution of the whole sys-

tem, one ultimately wants to eliminate all the "higher" variables in favor of the fluid densities. It seems unsatisfactory to introduce a large number of variables which are not and probably cannot be measured and then, in addition, to have to explain why their initial values do not influence the outcome.

[57] In this equation the time derivative is replaced by its value for a time-independent functional of the fluid densities in which the time rates of change of the densities are evaluated from the fluid dynamic equations.

[58] Born and Green (Ref. 21) do essentially this for the hierarchy of distribution functions.

[59] As we will show in a moment, this splitting alone (assuming D_0 is functionally differentiable) is enough to enable us to derive almost closed equations which have a very suggestive form.

[60] This expression is sometimes given in a more symmetrical form in which the potential energy part of the term containing $\beta\mathcal{E}$ is written

$$\tfrac{1}{2}\sum_{i\neq k}[\beta(\vec{R}_i)V_{ik}+\beta(\vec{R}_k)V_{ki}]$$

where $V_{ik}=V(\vec{R}_{ik})$.

[61] J. L. Lebowitz, H. L. Frisch, and E. Helfand, Phys. Fluids 3, 325 (1960).

[62] J. E. Mayer, J. Chem. Phys. 34, 1207 (1961).

[63] See, for example, the discussion in Refs. 62 and 64.

[64] E. T. Jaynes, in Lectures in Theoretical Physics, edited by K. W. Ford (Brandeis University Press, Waltham, Mass., 1962), Vol. 3, p. 181.

[65] R. M. Lewis, J. Math. Phys. 8, 1448 (1967).

[66] For further relevant remarks see Ref. 20.

[67] We could introduce other distributions corresponding to dispersion-free values of total energy and momentum, or, on the other hand, to the case in which N also has a dispersion. Indeed, physical circumstances may dictate such a choice but the present choice is convenient for our purposes.

[68] For example, replace the integration by a sum over cells of suitable size. In spite of this obvious interpretation we refer to it as "generalized" to distinguish it from the distribution proportional to $\exp[-\beta(\vec{r})H(\Gamma^+)]$, where H is the total Hamiltonian, which is the distribution which would yield the usual local-equilibrium value of the pressure. Such a distribution is, in fact, the zero-order term in the expansion of D_0 itself in gradients.

[69] In solving Boltzmann's equation the zero-order solution is dictated by the structure of the collision operator, and there is no direct parallel here.

[70] The fact that D_0 maximizes Gibbs's entropy functional leads to the following additional consideration. If one simply observes the system at a given time and has no further information, the theory of statistical inference indicates that the distribution which best embodies this information is just this $D_0(t)$; see Ref. 64. Then it can be argued that, although information about the initial values requires one to use a more appropriate distribution, the former best estimate remains a sensible first approximation.

[71] To be discussed elsewhere.

[72] This notation has been introduced by several authors. See, for example, Refs. 8 and 14.

[73] Others also neglect nonlocal contributions from the first term.

[74] This projector first appears in general form (for any quantum variables) in Ref. 16.

[75] One may note that the term proportional to $\mathcal{P}$ on the left-hand side of Eq. (62) comes from keeping all the terms arising from the evaluation of $\partial_t D_0$.

[76] This is generally true only for the more exact expressions given in Appendix A.

[77] The original expression also depends only on $D(t=0)$ but there is no indication whatsoever of a dependence on the densities which is *almost* local in space and time.

[78] An alternate way of arriving at Eqs. (70) and (72) is the following: One adopts the spirit of Zwanzig's work to compute $\partial_t a_\nu$. One does not really need $\partial_t D$ in Eq. (24) to compute $\partial_t a_\nu$ but only, say, $\mathcal{P}'\partial_t D$ where $\mathcal{P}'$ projects out the "relevant part" of $\partial_t D$. But according to Eq. (43), $\partial_t D_0$ is just the quantity with which to average A_ν to give $\partial_t a_\nu$. Since $\mathcal{P}$ defined by Eq. (62) is precisely the projector which guarantees the equality of these two expressions for $\partial_t a_\nu$, take $\mathcal{P}'$ to be identical with $\mathcal{P}$. Then one can derive the almost-closed equation for D_0 from Liouville's equation [i.e., substitute Eq. (69) into Eq. (61)], and use the resulting expression for $\partial_t D_0$ to again derive the equation for $\partial_t a_\nu$ with the expressions for the currents given in Eqs. (70) and (72).

[79] This symmetry requires central forces.

[80] There is no irreversible term in the continuity equation precisely because the total mass current is itself one of the variables.

[81] J. M. Luttinger, Phys. Rev. 135, A1505 (1964), gives their Fourier transforms.

[82] Also note that one must first calculate the expectation of the flux as a functional of $\vec{v}$, ρ, and u, and evaluate the derivative before evaluating this expression for some particular functions.

[83] One must not try to calculate by applying Eq. (83) to $(\vec{Q}-\vec{v}\cdot\overset{\sim}{\overleftrightarrow{\Pi}})$ directly because this phase function depends on $\vec{v}$.

[84] See Ref. 9 for the form of the subtracted momentum current most closely related to the present one.

[85] If one is dealing with an explicitly normalized D_0, then $\overleftrightarrow{K}^{(l)}$ will still be given in terms of the same subtracted fluxes, but this result must be derived somewhat differently.

[86] Consider the power series for $\mathcal{K}$ or notice that, since $\Delta D=(1-\mathcal{P})\Delta D$, one could have used $(1-\mathcal{P})\mathcal{K}$ from the beginning.

[87] I would like to acknowledge discussions of these points with M. S. Green and B. Robertson.

[88] An independent discussion is necessary to establish that distributions corresponding to the experimental situation of constrained equilibrium are the ones which maximize the entropy.

[89] E. T. Jaynes, Phys. Rev. 106, 620 (1957); and 108, 171 (1957).

[90] The question arises whether this term, although it does not directly change the entropy, should be incorporated with the term in the irreversible energy current, which is also proportional to $\nabla\vec{v}$. For the moment, we only remark that in the linear and local approximation this term vanishes (along with the cross term) so that there is no conflict with the classical result.

[91] M. S. Green, Phys. Rev. 119, 829 (1960).

[92] I. Progogine, Non-Equilibrium Statistical Mechanics (Interscience Publishers, Inc., New York, 1962).

[93] As already noted by B. Robertson, because $\mathcal{P}$ projects D into D_0, except for the fact that it is time-dependent, this theory may be looked upon as an application of Zwanzig's approach. His general theory, however, contains much more information than the present one because it yields the complete probability distribution of the A_ν.

[94] Higher-order gradients might still be large.

[95] In fact, we conjecture that the situation is as follows: Unless the physical circumstances can be described by keeping only the first few terms in the expansion of the transport kernels in powers either of the thermodynamic forces (near local equilibrium) or of the fluctuations in the densities (near global equilibrium), this quasidifferential description will have limited utility.

[96] These properties were pointed out to me by B. Robertson.

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Metastable Atoms and Molecules. III. Metastable Impacts on Surfaces with Various Work Functions*

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Surfaces of atomically clean tungsten, with work function 4.5 eV, tungsten oxidized with a monolayer of oxide and having a work function 6.6 eV, and tungsten coated with BaO with a work function probably under 2 eV were hit by metastable atoms or molecules of Ar, Xe, N_2, and H_2. The emission of secondary electrons by metastable atoms and the surface ionization of the atomic metastables were shown to follow the expected dependency on the work function. The N_2 molecular metastables were weakly surface ionized as N_2^+ on the oxidized tungsten but not on the surfaces of lower work function. Secondary electron emission either did not occur at all or was obscured by the large emission of CN^- negative ions. No CN^- emission nor electron emission was observed on the W-O surface. Metastables of H_2 dissociated on the clean and the oxidized surfaces. On the clean surface, one atom became H(2*p*) and gave out Lyman alpha radiation. On the W-O surface, one of the H atoms became a proton and no Lyman alpha radiation was produced. No other ion emission than H^+ occurred.

I. INTRODUCTION

The procedure described in Paper I of this sequence[1] has been used to produce beams of excited neutral particles of Ar, Xe, H_2, and N_2 with kinetic energies in the range of 25 to 200 eV. Their interactions with surfaces have been examined as described in Paper II.[2] The primary change in apparatus structure relative to the earlier work has been to replace the molybdenum target with a tungsten ribbon approximately 0.000 75-in. thick and connected so that it could be heated to high temperature by an electric current. This target was used in various states including coated with BaO to provide a low work-function surface, flash cleaned to give a normal work function for heterogeneous tungsten, and oxidized with approximately a monomolecular layer of oxide to give an elevated work function. In addition, studies were made of the behavior of the target under "dirty" conditions, obtained simply by letting the target stand at room temperature for hours or days in either a controlled, low pressure of oxygen or in the residual gases of a high-vacuum system.

II. PREPARATION OF TARGET SURFACE

The tungsten ribbon could be flash heated by the conduction current for purposes of cleaning. Flash temperatures were not measured, but the heating current which was around 25 A, was closely observed, and ultimately every target was burned out by only a slight excess of current above the normal flash-current used. Hence, it is believed that flashing was surely at temperatures above 2000°C and probably above 2500°C. On flash heating of a new target, or of an old target after several days of idleness even in the vacuum of 10^{-9} Torr or better, a burst of emitted gas was observable on ionization gauges. After several successive flashes, the gas evolution was negligible. In ensuing work, it is assumed without further measurement that the work function of the surface was then 4.5 eV.

For lowered work-function studies, the target was coated with $BaCO_3$ which in turn was reduced by heating the target to approximately 950°C in high vacuum until gas evolution was negligible. It is assumed that the work function was then of the order of 1.6 eV, but no results are presented which depend on any assumption other than that the work function was lower than for the clean tungsten. This surface was essentially a dirty one by contrast with others of the present paper so that only minor observations about its behavior are offered.

To oxidize the surface, oxygen was admitted to the closed-off system at 0.5×10^{-3}-Torr pressure, and the freshly cleaned tungsten was then heated to 900°C until the pressure dropped to 0.4×10^{-3}