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Nonlinear Transport in the Boltzmann Limit

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Formal expressions for the irreversible fluxes of a simple fluid are obtained as functionals of the thermodynamic forces and local equilibrium time correlation functions. The Boltzmann limit of the correlation functions is shown to yield expressions for the irreversible fluxes equivalent to those obtained from the nonlinear Boltzmann kinetic equation. Specifically, for states near equilibrium, the fluxes may be formally expanded in powers of the thermodynamic gradients and the associated transport coefficients identified as integrals of time correlation functions. It is proved explicitly through nonlinear Burnett order that the time correlation function expressions for these transport coefficients agree with those of the Chapman–Enskog expansion of the nonlinear Boltzmann equation. For states far from equilibrium the local equilibrium time correlation functions are determined in the Boltzmann limit and a similar equivalence to the Boltzmann equation solution is established. Other formal representations of the fluxes are indicated; in particular, a projection operator form and its Boltzmann limit are discussed. As an example, the nonequilibrium correlation functions for steady shear flow are calculated exactly in the Boltzmann limit for Maxwell molecules.

KEY WORDS: Nonlinear transport; irreversible fluxes; time correlation function; kinetic theory.

1. INTRODUCTION

There are two common methods for describing transport in a solid or fluid. The first and oldest is by means of kinetic theory. An approximate kinetic equation for the reduced distribution function is obtained, and is solved to get the macroscopic equations of motion and associated constitutive equations. For example, the Boltzmann kinetic equation may be used to derive

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the hydrodynamic equations with Newton's viscosity law for the momentum flux and Fourier's law for the heat flux.(1) The second and somewhat more recent approach is the time correlation function method.(2) In this case an appropriate formally exact solution to Liouville's equation is used to derive the macroscopic equations of motion and constitutive equations for the irreversible fluxes. The latter are expressed in terms of time correlation functions whose evaluation requires approximation schemes similar to those necessary to obtain the above-mentioned kinetic equation. The difference between the two methods lies essentially in the stage at which approximations are introduced. In kinetic theory, approximations are required at the outset to get a closed kinetic equation; in the correlation function method, approximations are postponed until after the irreversible fluxes are identified, and are introduced only at the point of evaluating the correlation function. There is a certain advantage to the latter approach, in that some information is available from the general properties of the correlation functions (such as the Onsager reciprocal relations) before introducing approximations. Due to the different formulations, comparison of the results from these two methods is not always straightforward. Indeed, it is not a priori evident that identical approximations to the kinetic equation and to the correlation functions should yield the same irreversible fluxes. Nevertheless, equivalence of the time correlation function expressions for Navier–Stokes transport coefficients at low density with those of the Boltzmann kinetic equation has been established.(3) Similar correspondence has been made for solids(4) (Boltzmann–Peierls kinetic equation) and plasmas(5) (Balescu–Lénard kinetic equation). These studies have been limited to the linear relationship between the fluxes and thermodynamic gradients (Green–Kubo relations), with almost no study of the more general nonlinear transport processes.[3] The purpose here is to show the complete equivalence of the kinetic theory and time correlation function methods for the special case of a Boltzmann gas. In doing so the correlation functions characterizing states far from equilibrium are related to solutions to a set of coupled nonlinear equations, and equivalence with the nonlinear Boltzmann equation is established. Although strictly applicable only to gases, these expressions may aid in modeling correlation functions to gain a qualitative understanding of nonlinear transport of fluids in general. Additionally, the Boltzmann results have historically been a conceptual reference against which new results are measured. In this regard, it has been suggested recently that mode-coupling effects in the correlation functions are responsible for a nonanalytic dependence of the irreversible fluxes on the thermodynamic gradients,(7) and it may be useful in assessing such results

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[3] In addition to Refs. 2 and 9, some other treatments of nonlinear transport phenomena can be found in Refs. 6.

to have some understanding of the corresponding correlation functions in the Boltzmann limit where such effects are neglected.

The macroscopic fluid equations and formal expressions for the irreversible fluxes in terms of correlation functions are discussed briefly in the next section for completeness, although most results have been given elsewhere.(6,8) In Section 3 the Boltzmann limit is considered for two different cases, states near equilibrium and those far from equilibrium. For the former, a formal expansion of the irreversible fluxes through terms quadratic in the thermodynamic gradients (nonlinear Burnett order) has been given recently(8) to identify equilibrium time correlation function expressions for the transport coefficients. The Boltzmann limit of these expressions is shown here to give the results of the Chapman–Enskog solution to the nonlinear Boltzmann equation. For states far from equilibrium the local equilibrium time correlation functions are considered in the Boltzmann limit and shown to yield fluxes equal to those obtained from a formal solution to the nonlinear Boltzmann equation. A compact projection operator formulation (similar to that of Piccirelli(9) and Kawasaki and Gunton(7)) is described. It is also shown how the Boltzmann limit may be put in this form, generalizing previous projection operator solutions of the linearized Boltzmann equation.(10) Finally, to illustrate the form of the nonequilibrium correlation functions for conditions far from equilibrium, the stress tensor for uniform shearing flow is considered. Ikenberry and Truesdell have shown(11) that an exact solution to this problem may be obtained from the nonlinear Boltzmann equation for Maxwell molecules. The discussion here constitutes an analogous solution in the correlation function formalism.

2. FORMAL SOLUTION TO LIOUVILLE'S EQUATION

2.1. The Hydrodynamic Equations

The macroscopic equations of motion for a fluid are a reflection of the microscopic conservation laws characterizing the system. For a simple fluid the relevant conservation laws are those of mass, energy, and momentum. Their local form may be written

$$\frac{\partial \psi_\alpha}{\partial t} + \frac{\partial \gamma_{\alpha i}}{\partial r_i} = 0 \tag{2.1}$$

where $\psi_\alpha(\mathbf{r})$ denotes the mass density ρ, energy density ϵ, and momentum density g_i,

$$\psi_\alpha \leftrightarrow (\rho, \epsilon, g_i) \tag{2.2}$$

The corresponding fluxes $\gamma_{\alpha i}(\mathbf{r})$ are

$$\gamma_{\alpha i} \leftrightarrow (g_i, s_i, t_{ij}) \tag{2.3}$$

where s_i is the energy flux, and t_{ij} is the momentum flux. The microscopic state of the system F at some time t is specified, for given initial conditions, by the solution to Liouville's equation

$$\partial F/\partial t + LF = 0 \tag{2.4}$$

Here L is the Liouville operator, defined for arbitrary phase function A by

$$LA = \{A, H\}$$

with $\{.,.\}$ denoting Poisson brackets and H the Hamiltonian. The macroscopic conservation laws follow by averaging (2.1) over the solution to Liouville's equation

$$\frac{\partial}{\partial t}\langle\psi_\alpha; t\rangle + \frac{\partial}{\partial r_i}\langle\gamma_{\alpha i}; t\rangle = 0 \tag{2.5}$$

with the notation

$$\langle A; t\rangle \equiv \sum_N \frac{1}{h^{3N}N!}\int d\Gamma\, AF(t) \tag{2.6}$$

and Γ represents a point in the phase space of the N-particle system. The quantities $\langle\psi_\alpha; t\rangle$ denote the macroscopic nonequilibrium mass density, energy density, and momentum density. It is more common, however, to describe the system in terms of other variables, such as temperature, flow velocity, etc. To introduce such variables it is usual to define them in such a way that they are related in a manner similar to that of the equilibrium state. A suitable definition is obtained by requiring that the nonequilibrium average of ψ_α be the same as the corresponding local equilibrium average,

$$\langle\psi_\alpha; t\rangle \equiv \langle\psi_\alpha; t\rangle_L \tag{2.7}$$

Here $\langle\psi_\alpha; t\rangle_L$ is the average of ψ_α over a local equilibrium distribution at time t,

$$\langle A; t\rangle_L \equiv \sum_N \frac{1}{h^{3N}N!}\int d\Gamma\, AF_L(t) \tag{2.8}$$

and

$$F_L(t) \equiv \exp\left\{-Q(t) - \int d\mathbf{r}\, y_\alpha(\mathbf{r}, t)\psi_\alpha(\mathbf{r})\right\} \tag{2.9}$$

The local thermodynamic variables $y_\alpha(\mathbf{r}, t)$ are

$$y_\alpha \leftrightarrow (-\zeta + \tfrac{1}{2}\beta U^2, \beta, -\beta U_i) \tag{2.10}$$

where $\beta^{-1}\zeta$ is the chemical potential per unit mass; $\beta = 1/kT$, where T is the Kelvin temperature and k is Boltzmann's constant; and U_i is the flow velocity. Finally, $Q(t)$ is determined by the requirement that $F_L(t)$ be normalized to one. The space and time variation of the $y_\alpha(\mathbf{r}, t)$ is therefore defined through Eq. (2.7). The macroscopic conservation law may now be written

$$\frac{\partial}{\partial t}\langle\psi_\alpha; t\rangle_L + \frac{\partial}{\partial r_i}\langle\gamma_{\alpha i}; t\rangle_L = \frac{-\partial\gamma^*_{\alpha i}}{\partial r_i} \tag{2.11}$$

where the irreversible flux $\gamma^*_{\alpha i}(\mathbf{r}, t)$ has been defined by

$$\gamma^*_{\alpha i} \equiv \langle\gamma_{\alpha i}; t\rangle - \langle\gamma_{\alpha i}; t\rangle_L \tag{2.12}$$

and represents the irreversible part of the flux $\langle\gamma_{\alpha i}; t\rangle$. For a simple fluid the local equilibrium averages in (2.11) are found to be

$$\langle\psi_\alpha; t\rangle_L \leftrightarrow (\bar{\rho}, \bar{u} + \tfrac{1}{2}\bar{\rho}U^2, \bar{\rho}U_i)$$
$$\langle\gamma_{\alpha i}; t\rangle_L \leftrightarrow (\bar{\rho}U_i, (h + \tfrac{1}{2}\bar{\rho}U^2)U_i, P\delta_{ij} + \bar{\rho}U_iU_j)$$

where $\bar{\rho}$ and $\bar{u}$ are the macroscopic mass and internal energy densities, P is the pressure, and $h = \bar{u} + P$ is the enthalpy density. The left side of Eq. (2.11) represents the contribution from the Euler equations for a perfect fluid. Since the left side is an explicit functional of the $y_\alpha(\mathbf{r}, t)$, Eqs. (2.11) may be written as equations for y_α,

$$\frac{\partial y_\alpha(\mathbf{r}, t)}{\partial t} + \int d\mathbf{r}'\, K^i_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\,\frac{\partial y_\beta(\mathbf{r}', t)}{\partial \mathbf{r}_i{}'} = \int d\mathbf{r}'\, g^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\,\frac{\partial\gamma^*_{\beta i}(\mathbf{r}', t)}{\partial r_i{}'} \tag{2.13}$$

with

$$\begin{aligned} g_{\alpha\beta}(\mathbf{r}, \mathbf{r}') &\equiv \langle\tilde{\psi}_\alpha(\mathbf{r})\tilde{\psi}_\beta(\mathbf{r}'); t\rangle_L \\ K^i_{\alpha\beta}(\mathbf{r}, \mathbf{r}') &\equiv \int d\mathbf{r}''\, g^{-1}_{\alpha\sigma}(\mathbf{r}, \mathbf{r}'')h^i_{\sigma\beta}(\mathbf{r}'', \mathbf{r}') \\ h^i_{\alpha\beta}(\mathbf{r}, \mathbf{r}') &\equiv \langle\tilde{\psi}_\alpha(\mathbf{r})\tilde{\gamma}_{\beta i}(\mathbf{r}'); t\rangle_L \end{aligned} \tag{2.14}$$

The time dependence of g, K, and h has been left implicit. Also, the tilde over a phase function A denotes the deviation from its local equilibrium average,

$$\tilde{A}(t) \equiv A - \langle A; t\rangle_L \tag{2.15}$$

Although $K^i_{\alpha\beta}$ and $g_{\alpha\beta}$ are explicit functionals of the y_α, Eqs. (2.13) still require constitutive equations for $\gamma^*_{\alpha i}$ as functionals of the y_α before a closed set of equations for the y_α are obtained. Equations (2.13) together with such constitutive equations form the hydrodynamic equations for the system.

2.2. Irreversible Fluxes

To obtain an expression for $\gamma^*_{\alpha i}(\mathbf{r}, t)$ as a functional of the $y_\alpha(\mathbf{r}, t)$, an appropriate formal solution to the Liouville equation may be used. Any solution requires specification of initial data, and for simplicity the interesting but special case of initial local equilibrium will be used. Several equivalent forms of the solution are obtained in Ref. 8, a convenient one of which is

$$F(t) = F_L(t) + \int_0^t d\tau\, e^{-L(t-\tau)} \int d\mathbf{r} \left[\frac{\partial y_\alpha(\mathbf{r}, \tau)}{\partial r_i} \tilde{\phi}_{\alpha i}(\mathbf{r}, \tau) + \frac{\partial \gamma^*_{\alpha i}(\mathbf{r}, \tau)}{\partial r_i} \tilde{\xi}_\alpha(\mathbf{r}, \tau) \right] F_L(\tau) \tag{2.16}$$

with

$$\begin{aligned} \tilde{\phi}_{\alpha i}(\mathbf{r}, t) &\equiv \tilde{\gamma}_{\alpha i}(\mathbf{r}, t) - \int d\mathbf{r}'\, \tilde{\psi}_\beta(\mathbf{r}', t) K^i_{\beta\alpha}(\mathbf{r}', \mathbf{r}; t) \\ \tilde{\xi}_\alpha(\mathbf{r}, t) &\equiv \int d\mathbf{r}'\, \tilde{\psi}_\beta(\mathbf{r}') g^{-1}_{\beta\alpha}(\mathbf{r}', \mathbf{r}) \end{aligned} \tag{2.17}$$

The phase functions $\tilde{\psi}_\alpha$ and $\tilde{\xi}_\alpha$ form a biorthogonal set with respect to the local equilibrium average,

$$\langle \tilde{\psi}_\alpha(\mathbf{r}, t) \tilde{\xi}_\beta(\mathbf{r}', t); t \rangle_L = \delta_{\alpha\beta}\, \delta(\mathbf{r} - \mathbf{r}') \tag{2.18}$$

Also, the $\tilde{\phi}_{\alpha i}$ are orthogonal to this set,

$$\langle \tilde{\phi}_{\alpha i}(\mathbf{r}, t) \tilde{\psi}_\beta(\mathbf{r}', t); t \rangle_L = 0 = \langle \tilde{\phi}_{\alpha i}(\mathbf{r}, t) \tilde{\xi}_\beta(\mathbf{r}', t); t \rangle_L \tag{2.19}$$

Substitution of the formal solution (2.16) into the definition (2.12) gives $\gamma^*_{\alpha i}$ as a functional of the thermodynamic variables y_α as desired,

$$\gamma^*_{\alpha i}(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}' \left[G_{\alpha i, \beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \frac{\partial y_\beta(\mathbf{r}', \tau)}{\partial r_j'} + H_{\alpha i, \beta}(\mathbf{r}, \mathbf{r}'; t, \tau) \frac{\partial \gamma^*_{\beta j}(\mathbf{r}', \tau)}{\partial r_j'} \right] \tag{2.20}$$

with

$$G_{\alpha i, \beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \equiv \langle [e^{L(t-\tau)} \tilde{\phi}_{\alpha i}(\mathbf{r}, t)] \tilde{\phi}_{\beta j}(\mathbf{r}', \tau); \tau \rangle_L \tag{2.21}$$

$$H_{\alpha i, \beta}(\mathbf{r}, \mathbf{r}'; t, \tau) \equiv \langle [e^{L(t-\tau)} \tilde{\phi}_{\alpha i}(\mathbf{r}, t)] \tilde{\xi}_\beta(\mathbf{r}', \tau); \tau \rangle_L \tag{2.22}$$

Use has been made of the fact that

$$\gamma^*_{\alpha i}(\mathbf{r}, t) = \langle \tilde{\gamma}_{\alpha i}(\mathbf{r}, t); t \rangle = \langle \tilde{\phi}_{\alpha i}(\mathbf{r}, t); t \rangle \tag{2.23}$$

The correlation functions G and H are generalizations of those occurring for linear transport. The latter are obtained by replacing F_L everywhere by the strict equilibrium distribution F_0:

$$G_{\alpha i, \beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \xrightarrow[\text{linear}]{} \langle [e^{L(t-\tau)} \tilde{\phi}_{\alpha i}(\mathbf{r})] \tilde{\phi}_{\beta j}(\mathbf{r}') \rangle_0 \tag{2.24}$$

$$H_{\alpha i, \beta}(\mathbf{r}, \mathbf{r}'; t, \tau) \xrightarrow[\text{linear}]{} \langle [e^{L(t-\tau)} \tilde{\phi}_{\alpha i}(\mathbf{r})] \tilde{\xi}_\beta(\mathbf{r}') \rangle_0 \tag{2.25}$$

where $\langle \ldots \rangle_0$ denotes an equilibrium average. Even for this linear case, there does not appear to have been a complete study of the relationship to results from kinetic theory, beyond linear Navier–Stokes and Burnett orders.(12) Such a study is possible in the linear case without restriction to the Boltzmann limit; however, the following sections will be concerned as well with the nonlinear case, for which less is known about the general kinetic theory, and attention will be restricted to the Boltzmann limit. First, however, an alternative formulation of $\gamma^*_{\alpha i}$ will be noted.

2.3. Projection Operator Formulation

The formal expression for $\gamma^*_{\alpha i}(\mathbf{r}, t)$ given by Eq. (2.20) is only an implicit expression for $\gamma^*_{\alpha i}$ because of its occurrence also on the right side of the equation. The latter may be removed by the introduction of a suitable projection operator. The projection operator P_t is defined by

$$P_t A = \int d\mathbf{r}\, \xi_\alpha(\mathbf{r}, t) \langle \tilde{\psi}_\alpha(\mathbf{r}, t) A; t \rangle_L \tag{2.26}$$

(recall that ξ_α and $\tilde{\psi}_\alpha$ form a biorthogonal set). Then it is readily shown that

$$\int d\mathbf{r}\, \frac{\partial \gamma^*_{\alpha i}(\mathbf{r}, \tau)}{\partial r_i}\, \xi_\alpha(\mathbf{r}, \tau) = F_L^{-1}(\tau) P_\tau{}^* L[F(\tau) - F_L(\tau)] \tag{2.27}$$

$$P_\tau{}^* \equiv F_L(\tau) P_\tau F_L^{-1}(\tau) \tag{2.28}$$

With Eq. (2.27), the formal solution to Liouville's equation (2.16) may be rewritten as

$$\begin{aligned} F(t) - F_L(t) = {} & \int_0^t d\tau\, e^{-L(t-\tau)} F_L(\tau) \int d\mathbf{r}\, \tilde{\phi}_{\alpha i}(\mathbf{r}, \tau) \frac{\partial y_\alpha(\mathbf{r}, \tau)}{\partial r_i} \\ & + \int_0^t d\tau\, e^{-L(t-\tau)} P_\tau{}^* L[F(\tau) - F_L(\tau)] \end{aligned}$$

or

$$F(t) = F_L(t) + \int_0^t d\tau \int d\mathbf{r}\, \frac{\partial y_\alpha(\mathbf{r}, \tau)}{\partial r_i}\, U^*(t, \tau)(\tilde{\phi}_{\alpha i}(\mathbf{r}, \tau) F_L(\tau)) \tag{2.29}$$

with the operator U^* defined by

$$U^*(t, \tau) \equiv T_+ \exp\left\{ -\int_\tau^t d\tau' \,(1 - P^*_{\tau'}) L \right\} \tag{2.30}$$

and T_+ is the chronological time ordering operator.

Returning to the determination of $\gamma^*_{\alpha i}$, substitution of (2.29) into (2.23) leads to

$$\gamma^*_{\alpha i}(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}'\, C_{\alpha i, \beta j}(\mathbf{r}, \mathbf{r}'; t, \tau)\, \frac{\partial y_\beta(\mathbf{r}', \tau)}{\partial r_j{}'} \tag{2.31}$$

with

$$\begin{aligned} C_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) &= \langle [U(t, \tau)\tilde{\phi}_{\alpha i}(\mathbf{r}, t)]\tilde{\phi}_{\beta j}(\mathbf{r}', \tau); \tau\rangle_L \\ U(t, \tau) &= T_- \exp\left\{\int_\tau^t d\tau'\, L(1 - P_{\tau'})\right\} \end{aligned} \tag{2.32}$$

These equations, (2.31) and (2.32), are equivalent to Eqs. (2.20)–(2.22). The form of Eq. (2.31) differs from that of (2.20) in that there is no explicit dependence on $\gamma^*_{\alpha i}$ in the former. However, a price has been paid since the time evolution of the system is modified by the projection operator P^* (or P), and is no longer straightforward to interpret or analyze. The relationship of the kernel C in (2.31) to those of (2.20) is easily found to be

$$\begin{aligned} C_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) &= G_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \\ &\quad + \int_\tau^t d\tau' \int d\mathbf{r}''\, H_{\alpha i,\sigma}(\mathbf{r}, \mathbf{r}''; t, \tau') \frac{\partial}{\partial r_k''} C_{\sigma k,\beta j}(\mathbf{r}'', \mathbf{r}'; \tau', \tau) \end{aligned} \tag{2.33}$$

The form of the general hydrodynamic equations (2.13) and the fluxes (2.20) and (2.31) is given more explicitly in terms of β, ζ, and $\mathbf{U}$ in Appendix D.

3. THE BOLTZMANN LIMIT

The irreversible fluxes $\gamma^*_{\alpha i}$ are governed by the local equilibrium correlation functions G and H of Eqs. (2.21) and (2.22). For the linear case these become *equilibrium* time correlation functions whose properties may be related, in the low-density limit, to the solution of a corresponding *linear* Boltzmann equation.(3) The equations determining the local equilibrium correlation functions are nonlinear, however, and their connection with Boltzmann kinetic theory is somewhat more remote. The Boltzmann limit of the time correlation function formulation will be studied in two stages. First, for states near equilibrium, the gradients $\partial y_\alpha/\partial r$ are small and an expansion of the irreversible fluxes in these gradients leads to constitutive equations characterized by transport coefficients. The latter are defined as time integrals of certain equilibrium correlation functions, and it is verified that the Boltzmann limits of these correlation function expressions for the transport coefficients agree with those of the Chapman–Enskog solution to the nonlinear Boltzmann kinetic equation. When the fluid is far from equilibrium not all of the thermodynamic gradients are small, so that a Chapman–Enskog expansion of the fluxes is not possible. In this case the Boltzmann limits of the *local equilibrium* correlation functions $G_{\alpha i,\beta j}$ and $H_{\alpha i,\beta}$ of Eqs. (2.21) and (2.22) must be studied directly; a formal equivalence with Boltzmann kinetic theory is again established.

3.1. Near Equilibrium

The most commonly studied experimental and theoretical situation corresponds to a system disturbed only slightly from equilibrium. Then, with the thermodynamic gradients as a small parameter, the exact expression (2.20) for the irreversible fluxes may be expanded formally to give

$$\gamma^{*}_{\alpha i}(\mathbf{r}, t) = \gamma^{(1)}_{\alpha i,\beta j} \frac{\partial y_\beta}{\partial r_j} + \gamma^{(2,1)}_{\alpha i,\beta jk} \frac{\partial^2 y_\beta}{\partial r_j\, \partial r_k} + \gamma^{(2,2)}_{\alpha i,\beta j,\mu k} \frac{\partial y_\beta}{\partial r_j} \frac{\partial y_\mu}{\partial r_k} + \cdots \tag{3.1}$$

The first term on the right of Eq. (3.1) corresponds to Navier–Stokes-order irreversible fluxes, while the second and third terms correspond to linear(12) and nonlinear Burnett-order fluxes, respectively. The constants $\gamma^{(p,q)}$ are the associated transport coefficients. This Chapman–Enskog type of expansion for γ^* has been discussed in detail recently, and the transport coefficients identified as(8)

$$\gamma^{(1)}_{\alpha i,\beta j} = \lim_{t\to\infty} \int_0^t d\tau\, \langle [e^{L\tau}\tilde{\phi}_{\alpha i}(0, t)]\tilde{\Phi}_{\beta j}\rangle_0 \tag{3.2}$$

$$\gamma^{(2,1)}_{\alpha i;\beta jk} = \lim_{t\to\infty} \int_0^t d\tau \int d\mathbf{r}'\, [r_k{}'\, \delta_{\lambda\beta} + \tau c^k_{\lambda\beta}]\langle [e^{L\tau}\tilde{\phi}_{\alpha i}(0, t)]\tilde{\phi}_{\lambda j}(\mathbf{r}', t)\rangle_0 \tag{3.3}$$

$$\begin{aligned}\gamma^{(2,2)}_{\alpha i,\beta j,\mu k} = \lim_{t\to\infty} \Bigg\{ & \int_0^t d\tau\; \tau\langle [e^{L\tau}\tilde{\phi}_{\alpha i}(0, t)]\tilde{\Phi}_{\lambda k}\rangle_0 \frac{\partial c^j_{\lambda\beta}}{\partial y_\mu} \\ & + \int_0^t d\tau \int d\mathbf{r}'\, [r_k{}'\, \delta_{\lambda\mu} + \tau c^k_{\lambda\mu}] \\ & \times \left\langle [e^{L\tau}\tilde{\phi}_{\alpha i}(0, t)]\left[\frac{\partial \tilde{\phi}_{\beta j}(\mathbf{r}', t)}{\partial y_\lambda} - \tilde{\Phi}_{\beta j}\tilde{\psi}_\lambda(\mathbf{r}')\right]\right\rangle_0 \Bigg\}\end{aligned} \tag{3.4}$$

Here

$$\Phi \equiv \int d\mathbf{r}\, \phi(\mathbf{r}), \qquad c^i_{\alpha\beta} \equiv \int d\mathbf{r}'\, K^i_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$$

where $K^i_{\alpha\beta}$ is defined by Eq. (2.14).

The Boltzmann limits of (3.2) and (3.3) are known from the study of equilibrium time correlation functions composed of two phase functions, each being sums of single-particle functions.[4] The nonlinear Burnett coefficient (3.4), however, depends on correlation functions with three such phase functions at two times, for which the usual theory does not apply. Furthermore, if the projection operator formulation for the fluxes were used, an

[4] The literature on kinetic theory of two-time correlation functions is extensive. For recent reviews and references see Refs. 13.

equivalent expression for $\gamma^{(2,2)}$ would be obtained, although expressed in terms of correlation functions with three phase functions at three different times. The Boltzmann limit of these more general multitime correlation functions has been determined and the above may be obtained from the results,$^{(14)}$

$$\langle A_1(t_1)A_2(t_2)\rangle_0 = \int dx_1\, f_0(p_1)a_1(x_1)T_{t_1-t_2}a_2(x_1), \qquad t_1 \geqslant t_2 \tag{3.5}$$

$$\begin{aligned}
&\langle A_1(t_1)A_2(t_2)A_3(t_3)\rangle_0 \\
&\quad = \int dx_1\, f_0(p_1)a_1(x_1)T_{t_1-t_2}[a_2(x_1)T_{t_2-t_3}a_3(x_1)] \\
&\qquad + \int_0^{t_1-t_2} d\tau \int dx_1\, f_0(p_1)a_1(x_1)T_{t_1-t_2-\tau}J_s[T_\tau a_2, T_{\tau+t_2-t_3}a_3] \\
&\qquad + \int_0^{t_2-t_3} d\tau \int dx_1\, f_0(p_1)a_3(x_1)T^*_{t_2-t_3-\tau}J_s[T_\tau{}^*\bar{a}_2, T^*_{\tau+t_1-t_2}\bar{a}_1] \\
&\qquad\qquad t_1 \geqslant t_2 \geqslant t_3
\end{aligned} \tag{3.6}$$

Here the A_α are arbitrary sums of single-particle phase functions with vanishing average,

$$A_\alpha = \sum_{i=1}^{N} [a_\alpha(x_i) - \langle a_\alpha(x_i)\rangle_0] \tag{3.7}$$

and $\bar{a}(p) \equiv a(-p)$. Also, T_t is the time development operator for the linearized Boltzmann equation

$$T_t \equiv \exp -[(\mathbf{v}\cdot\nabla + I)t] \tag{3.8}$$

and $T_t{}^*$ is the adjoint operator. The operators I and J_s are the linearized and symmetric bilinear Boltzmann operators, respectively,

$$\begin{aligned}
I[h] &= f_0^{-1}(p_1)\int\cdots\int f_0(p_1)f_0(p_2)[h(\mathbf{p}_1) + h(\mathbf{p}_2) - h(\tilde{\mathbf{p}}_1) - h(\tilde{\mathbf{p}}_2)] \\
&\qquad \times \left|\frac{\mathbf{p}_1 - \mathbf{p}_2}{m}\right| b\, db\, d\epsilon\, d\mathbf{p}_2 \\
J_s[h, g] &\equiv -f_0^{-1}(p_1)\int\cdots\int f_0(p_1)f_0(p_2)[h(\mathbf{p}_1)g(\mathbf{p}_2) + h(\mathbf{p}_2)g(\mathbf{p}_1) \\
&\qquad - h(\tilde{\mathbf{p}}_1)g(\tilde{\mathbf{p}}_2) - h(\tilde{\mathbf{p}}_2)g(\tilde{\mathbf{p}}_1)]\left|\frac{\mathbf{p}_1 - \mathbf{p}_2}{m}\right| b\, db\, d\epsilon\, d\mathbf{p}_2
\end{aligned} \tag{3.9}$$

Finally, $f_0(p_1)$ is the Maxwell–Boltzmann distribution normalized to the number density n; x_i denotes the position and momentum of the ith particle;

and $\tilde{\mathbf{p}}_i$ denotes the scattered momentum. Equations (3.5) and (3.6) may now be used to evaluate the expressions (3.2)–(3.4) for the transport coefficients. To do so first note that the fluxes $\tilde{\phi}_{\alpha i}(\mathbf{r}, t)$ are of the form

$$\tilde{\phi}_{\alpha i}(\mathbf{r}, t) = \sum_{\sigma} \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_\sigma) + \sum_{\sigma \neq \sigma'}\sum \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_\sigma, x_{\sigma'}) \tag{3.10}$$

where $\tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_\sigma)$ is a single-particle function and $\tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_\sigma, x_{\sigma'})$ is a two-particle function. A similar form holds for the functions $\tilde{\psi}$ and $\tilde{\xi}$. It is easily shown that the two-particle functions do not contribute to lowest order in the density, and so the fluxes reduce to phase functions of the type (3.7). The correlation functions defining the transport coefficients $\gamma^{(p,q)}$ may then be evaluated using the results (3.5) and (3.6).

Navier–Stokes coefficients: Substitution of (3.5) into (3.2) gives

$$\gamma^{(1)}_{\alpha i,\beta j} = \lim_{t\to\infty} \int_0^t d\tau \int dx_1\, f_0(p_1)\phi_{\alpha i}(\mathbf{p}_1)\, \delta(\mathbf{r} - \mathbf{q}_1) T_\tau \phi_{\beta j}(\mathbf{p}_1) \tag{3.11}$$

where use has been made of the fact that the q dependence of the single-particle function occurs through a delta function,

$$\tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1) = \phi_{\alpha i}(\mathbf{p}_1)\, \delta(\mathbf{r} - \mathbf{q}_1), \qquad \tilde{\psi}_\alpha(\mathbf{r}, t|x_1) = \psi_\alpha(\mathbf{p}_1)\, \delta(\mathbf{r} - \mathbf{q}_1) \tag{3.12}$$

and the residual dependence of $\phi_{\alpha i}(\mathbf{p}_1)$ and $\psi_\alpha(\mathbf{p}_1)$ on $\mathbf{r}$, t through the y_α has been left implicit. Then, carrying out the time integral and integral over $\mathbf{q}_1$ in (3.11) gives

$$\gamma^{(1)}_{\alpha i,\beta j} = (\phi_{\alpha i}, I^{-1}\phi_{\beta j}) \tag{3.13}$$

where a scalar product notation has been introduced,

$$(h, g) \equiv \int d\mathbf{p}\, f_0(p) h^*(\mathbf{p}) g(\mathbf{p}) \tag{3.14}$$

Linear Burnett coefficients: Equation (3.3) may be written with the use of (3.5) as

$$\gamma^{(2,1)}_{\alpha i,\beta jk} = \lim_{z\to 0+} \int_0^\infty d\tau\, e^{-z\tau} \int d\mathbf{p}_1 \int d\mathbf{q}_1\, f_0(p_1)\phi_{\alpha i}(\mathbf{p}_1)\, \delta(\mathbf{q}_1) \times T_\tau({q_1}^k\, \delta_{\lambda\beta} + \tau c^k_{\lambda\beta})\phi_{\lambda j}(\mathbf{p}_1)$$

Performing the time integral and expanding the resolvent as

$$(z + \mathbf{v}_1\cdot\nabla_1 + I)^{-1} = (z + I)^{-1} - (z + \mathbf{v}_1\cdot\nabla_1 + I)^{-1}\mathbf{v}_1\cdot\nabla_1(z + I)^{-1}$$

leads to

$$\gamma^{(2,1)}_{\alpha i,\beta jk} = (I^{-1}\phi_{\alpha i}, (c^k_{\lambda\beta} - v_k\, \delta_{\lambda\beta})I^{-1}\phi_{\lambda j}) \tag{3.15}$$

Nonlinear Burnett coefficients: In a manner similar to that for the linear Burnett coefficients, Eq. (3.4) may be written

$$\begin{aligned}\gamma^{(2,2)}_{\alpha i,\beta j,\mu k} = \lim_{z\to 0+}\Bigg\{&\int_0^\infty d\tau\ \tau e^{-z\tau}\int d\mathbf{p}_1\int d\mathbf{q}_1\, f_0(p_1)\phi_{\alpha i}(\mathbf{p}_1)\\ &\times\ \delta(\mathbf{q}_1)T_\tau\phi_{\lambda k}(\mathbf{p}_1)\,\frac{\partial c^j_{\lambda\beta}}{\partial y_\mu}\\ &+\int_0^\infty d\tau\ e^{-z\tau}\int d\mathbf{p}_1\int d\mathbf{q}_1\, f_0(p_1)\phi_{\alpha i}(\mathbf{p}_1)\ \delta(\mathbf{q}_1)\\ &\times\ T_\tau({q_1}^k\,\delta_{\lambda\mu}+\tau c^k_{\lambda\mu})\left[\frac{\partial}{\partial y_\lambda}\,\phi_{\beta j}(\mathbf{p}_1)-\phi_{\beta j}(\mathbf{p}_1)\psi_\lambda(\mathbf{p}_1)\right]\\ &+\int_0^\infty d\tau\ e^{-z\tau}\int_0^\tau d\tau_1\int d\mathbf{p}_1\int d\mathbf{q}_1\, f_0(p_1)\phi_{\alpha i}(\mathbf{p}_1)\ \delta(\mathbf{q}_1)\\ &\times\ T_{\tau-\tau_1}J_s[T_{\tau_1}\phi_{\beta j},\, T_{\tau_1}({q_1}^k\,\delta_{\lambda\mu}+\tau c^k_{\lambda\mu})\psi_\lambda]\Bigg\}\end{aligned}\tag{3.16}$$

The low-density time development of the space moment of the conservation laws (2.1) is

$$\int d\mathbf{q}_1\ T_\tau {q_1}^k\psi_\lambda = \int d\mathbf{q}_1\ {q_1}^k\psi_\lambda - \int_0^\tau d\tau_1\ T_{\tau_1}\Phi_{\lambda k} - \tau\psi_\sigma c^k_{\sigma\lambda}\tag{3.17}$$

where the time independence of the conserved variables has been used. After substitution of (3.17) into (3.16), the time integrals are done with the identities

$$\int_0^\infty d\tau\int_0^\tau d\tau'\ \tau' e^{-z\tau}e^{a(\tau-\tau')}e^{b\tau'} = (z-a)^{-1}(z-b)^{-2}$$

$$\int_0^\infty d\tau\ \tau\int_0^\tau d\tau'\ e^{-z\tau}e^{a(\tau-\tau')}e^{b\tau'} = (z-a)^{-1}(z-b)^{-2}+(z-a)^{-2}(z-b)^{-1}$$

$$\begin{aligned}&\lim_{z\to 0+}\int_0^\infty d\tau\ e^{-z\tau}\int_0^\tau d\tau_1\ e^{a(\tau-\tau_1)}\left[e^{b\tau_1}\int_0^{\tau_1} d\tau_2\ e^{c\tau_2}+\int_0^{\tau_1} d\tau_2\ e^{b\tau_2}e^{c\tau_1}\right]\\ &\quad=\frac{1}{2}\lim_{z\to 0+}(z-a)^{-1}\int_0^\infty d\tau_1\ e^{-z\tau_1}\,\frac{\partial}{\partial\tau_1}\left[\int_0^{\tau_1} d\tau_2\ e^{b\tau_2}\int_0^{\tau_1} d\tau_3\ {}^{c\tau_3}\right]\\ &\quad\ \frac{1}{2}\lim_{z\to 0+}(z-a)^{-1}b^{-1}c^{-1}\end{aligned}\tag{3.18}$$

where a, b, and c may be operators. Equation (3.18) is useful for the symmetrized form of the last term of (3.16). The application of (3.18) to (3.16) results in

$$\begin{aligned}\gamma^{(2,2)}_{\alpha i,\beta j,\mu k} = {} & (I^{-1}\phi_{\alpha i}, I^{-1}\phi_{\lambda k})\,\partial c^{j}_{\lambda\beta}/\partial y_{\mu} \\ & + \lim_{z\to 0+} (I^{-1}\phi_{\alpha i}, (c^{k}_{\lambda\mu} - v_k\,\delta_{\lambda\mu})(z+I)^{-1} \\ & \times \{(\partial/\partial y_\lambda)\phi_{\beta j} - \phi_{\beta j}\psi_\lambda + J_s[I^{-1}\phi_{\beta j}, \psi_\lambda]\}) \\ & + \tfrac{1}{2}(I^{-1}\phi_{\alpha i}, J_s[I^{-1}\phi_{\beta j}, I^{-1}\phi_{\mu k}])\end{aligned} \tag{3.19}$$

Using the identity

$$\begin{aligned}&(z+I)^{-1}J_s[(z+I)^{-1}h, \psi_\lambda] \\ &\quad = f_0^{-1}\frac{\partial}{\partial y_\lambda} f_0 (z+I)^{-1}h - (z+I)^{-1}\frac{\partial h}{\partial y_\lambda} + (z+I)^{-1}\psi_\lambda h\end{aligned} \tag{3.20}$$

in the second term of (3.19) gives

$$\begin{aligned}\gamma^{(2,2)}_{\alpha i,\beta j,\mu k} = {} & (I^{-1}\phi_{\alpha i}, I^{-1}\phi_{\lambda k})\,\partial c^{j}_{\lambda\beta}/\partial y_{\mu} \\ & + (I^{-1}\phi_{\alpha i}, (c^{k}_{\lambda\mu} - v_k\,\delta_{\lambda\mu}) f_0^{-1}(\partial/\partial y_\lambda) f_0 I^{-1}\phi_{\beta j}) \\ & + \tfrac{1}{2}(I^{-1}\phi_{\alpha i}, J_s[I^{-1}\phi_{\beta j}, I^{-1}\phi_{\mu k}])\end{aligned} \tag{3.21}$$

The results (3.13), (3.15), and (3.21) are indeed identical to the expressions for the transport coefficients obtained from the Boltzmann equation, as is proved in Appendix A. In summary, evaluation of the time correlation function expressions for the transport coefficients in the Boltzmann limit yields agreement with Boltzmann kinetic theory, up to and including nonlinear Burnett order.

3.2. Far from Equilibrium

Returning to the exact result (2.20) for γ^*, we now consider the case where no restrictions are placed on the magnitudes of $\partial y_\alpha/\partial r$. The Boltzmann limit for γ^* will then be determined from the corresponding limits of $G_{\alpha i,\beta j}$ and $H_{\alpha i,\beta}$. The latter correlation functions involve only two phase functions, but they are averaged over a local rather than strict equilibrium ensemble so that, as with the nonlinear Burnett coefficients in (3.4), the usual time correlation function analysis does not apply.

To obtain the low-density (actually Boltzmann) limit for $G_{\alpha i,\beta j}$ and $H_{\alpha i,\beta}$, a procedure paralleling the cluster expansions of Green[15] and Cohen[16] will be used. As noted above [Eq. (3.10)], the fluxes $\tilde{\phi}_{\alpha i}(\mathbf{r}, t)$, $\tilde{\psi}_\alpha$, and $\tilde{\xi}_\alpha$ for a simple fluid are sums of single-particle or two-particle functions. Consider first $G_{\alpha i,\beta j}$. Substituting (3.10) into Eq. (2.21) gives

$$G_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) = n \int dx_1\, \tilde{\phi}_{\alpha i}(x_1)\tilde{\Phi}^{(1)}_{\beta j}(x_1; t, \tau) + n^2 \int dx_1\, dx_2\, \tilde{\phi}_{\alpha i}(x_1, x_2)\tilde{\Phi}^{(2)}_{\beta j}(x_1, x_2; t, \tau) \qquad (3.22)$$

where the $\mathbf{r}$, t dependence of $\tilde{\phi}(x_1)$, $\tilde{\phi}(x_1, x_2)$, and $\tilde{\Phi}^{(s)}$ has been suppressed, and $\tilde{\Phi}^{(s)}_{\beta j}(x_1,\dots, x_s; t, \tau)$ is defined by

$$n^s\tilde{\Phi}^{(s)}_{\beta j}(x_1,\dots, x_s; t, \tau) \equiv \sum_{N>s} \frac{1}{(N-s)!\, h^{3N}} \int dx_{s+1} \cdots dx_N\, e^{-L(t-\tau)}\tilde{\phi}_{\beta j}(\mathbf{r}, \tau)F_L(\tau) \qquad (3.23)$$

This expression is still exact. However, in the Boltzmann limit the second term on the right side of Eq. (3.22) contributes to higher order in the density than the first, and may be neglected. Similarly, the contributions from the pair function $\tilde{\phi}(x_\sigma, x_{\sigma'})$ to all $\tilde{\Phi}^{(s)}$ may also be neglected as contributing to higher order in the density [this may be seen by considering Eq. (3.23) at $t = \tau$]. Correlation functions of the type (3.22) therefore reduce in the low-density limit to the calculation of

$$G_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \to n \int dx_1\, \tilde{\phi}_{\alpha i}(x_1)\tilde{\Phi}^{(1)}_{\beta j}(x_1; t, \tau)$$

$$n^s\tilde{\Phi}^{(s)}_{\beta j}(x_1,\dots, x_s; t, \tau) \to \sum_{N>s} \frac{1}{(N-s)!\, h^{3N}} \int dx_{s+1} \cdots dx_N\, e^{-L(t-\tau)}F_L(\tau) \sum_\sigma \tilde{\phi}_{\beta j}(x_\sigma)$$

The set of functions $\tilde{\Phi}^{(s)}$ obey the BBGKY hierarchy with specified initial conditions. The first equation of the hierarchy may be used as the basis for obtaining a low-density kinetic equation for $\tilde{\Phi}^{(1)}$, whose solution would then determine the correlation functions. The determination of kinetic equations from the BBGKY hierarchy for conditions of low density is perhaps most easily accomplished through the cluster expansions of Green$^{(15)}$ and Cohen.$^{(16)}$ For the purpose of making a cluster expansion, it is useful to introduce a modified local equilibrium distribution function,

$$F_L(t|\lambda) \equiv \exp -\left\{Q(t|\lambda) - \int d\mathbf{r} \left[y_\alpha(\mathbf{r}, t)\psi_\alpha(\mathbf{r}) - \lambda_{\alpha i}(\mathbf{r}, t) \sum_\sigma \phi_{\alpha i}(x_\sigma)\right]\right\} \qquad (3.24)$$

$Q(t|\lambda)$ is again chosen to normalize $F_L(t|\lambda)$. The functions $\lambda_{\alpha i}(\mathbf{r}, t)$ are arbitrary, aside from providing the existence of the integrals indicated. A set of reduced distribution functions similar to the $\tilde{\Phi}_{\alpha i}^{(s)}$ may be defined,

$$f_\lambda^{(s)}(x_1,\ldots,x_s;\,t,\,\tau) \equiv \sum_{N>s} \frac{1}{(N-s)!\,h^{3N}} \int dx_{s+1}\cdots dx_N\, e^{-L(t-\tau)} F_L(\tau|\lambda) \tag{3.25}$$

The functions $\tilde{\Phi}^{(s)}$ and $f_\lambda^{(s)}$ are related by

$$n^s \tilde{\Phi}_{\beta j}^{(s)}(x_1,\ldots,x_s;\,t,\,\tau) = \left.\frac{\delta f_\lambda^{(s)}(x_1,\ldots,x_s;\,t,\,\tau)}{\delta\lambda_{\beta j}(\mathbf{r},\,\tau)}\right|_{\lambda=0} \tag{3.26}$$

Therefore, a kinetic equation for $f_\lambda^{(1)}$ may be used to generate one for $\tilde{\Phi}^{(1)}$. It may be noted at this point that aside from the dependence on λ the $f_\lambda^{(s)}$ are essentially the reduced distribution functions for the Liouville equation with local equilibrium at $t = \tau$. Thus $f_\lambda^{(1)}$ may be expected to satisfy a kinetic equation like the nonlinear Boltzmann equation, for low density.

Differentiating $f_\lambda^{(1)}$ with respect to time shows that it satisfies the first equation of the BBGKY hierarchy,$^{(16)}$

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) f_\lambda^{(1)} = \int dx_2\, \theta_{12} f_\lambda^{(2)} \tag{3.27}$$

where $\theta_{12} = -\mathbf{F}_{12}\cdot\nabla_{p_2}$ and $\mathbf{F}_{12}$ is the force on particle 1 due to particle 2. Also, the initial conditions are,

$$f_\lambda^{(s)}(t,\,\tau)|_{t=\tau} \equiv \sum_{N>s} \frac{1}{(N-s)!\,h^{3N}} \int dx_{s+1}\cdots dx_N\, F_L(\tau|\lambda) \tag{3.28}$$

This hierarchy is of the type considered by Green$^{(15)}$ and Cohen$^{(16)}$ using a cluster expansion; the kinetic equation for $f_\lambda^{(1)}$ is obtained from Eq. (3.27) by formally expressing $f_\lambda^{(2)}$ as a functional of $f_\lambda^{(1)}$ and expanding the functional in density holding $f_\lambda^{(1)}$ constant. In addition, the low-density form simplifies considerably in the Boltzmann limit of $t - \tau \gg \tau_c \equiv$ typical binary collision time, and neglect of variations of the space dependence of $f_\lambda^{(1)}$ over the force range. The details are carried out in Appendix B, with the result

$$\int dx_2\, \theta_{12} f_\lambda^{(2)} \rightarrow J[f_\lambda^{(1)}, f_\lambda^{(1)}] \tag{3.29}$$

where $J[f_\lambda^{(1)}, f_\lambda^{(1)}]$ is the usual nonlinear Boltzmann collision operator,

$$J[f_\lambda^{(1)}, f_\lambda^{(1)}] \equiv \int\cdots\int \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} [f_\lambda^{(1)}(\tilde{\mathbf{p}}_1) f_\lambda^{(1)}(\tilde{\mathbf{p}}_2) - f_\lambda^{(1)}(\mathbf{p}_1) f_\lambda^{(1)}(\mathbf{p}_2)]\, b\, db\, d\epsilon\, d\mathbf{p}_2$$

The tildes denote a dependence of the function on the restituting momenta. The kinetic equation for $f_\lambda^{(1)}$ is therefore, in the low-density limit,

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) f_\lambda^{(1)} = J[f_\lambda^{(1)}, f_\lambda^{(1)}] \tag{3.30}$$

The initial condition for Eq. (3.30) is obtained from the low-density limit of Eq. (3.25) for $s = 1$:

$$f_\lambda^{(1)}(t, \tau)|_{t=\tau} = f_L(\tau, \lambda) \tag{3.31}$$

i.e., the distribution function at time $t = \tau$ is the single-particle local equilibrium distribution function, aside from the dependence on λ:

$$f_L(\tau, \lambda) = \exp -\left\{q(\tau, \lambda) + \int d\mathbf{r}\,[y_\alpha(\mathbf{r}, \tau)\psi_\alpha(\mathbf{r}, \tau|x_1) - \lambda_{\alpha i}(\mathbf{r}, \tau)\phi_{\alpha i}(\mathbf{r}, \tau|x_1)]\right\} \tag{3.32}$$

Here $\psi_\alpha(\mathbf{r}, t|x_1)$ and $\phi_{\alpha i}(\mathbf{r}, t|x_1)$ are the single-particle functions associated with ψ_α and $\phi_{\alpha i}$, respectively, [see Eq. (3.12)] and $q(\tau, \lambda)$ is a normalization constant.

The kinetic equation for $\tilde{\Phi}_{\alpha i}^{(1)}(\mathbf{r}; t, \tau)$ now follows from Eqs. (3.30) and (3.31) using Eq. (3.26),

$$(\partial/\partial t + \mathbf{v}\cdot\nabla)\tilde{\Phi}_{\alpha i}^{(1)} = \bar{J}[\tilde{\Phi}_{\alpha i}^{(1)}, f] \tag{3.33}$$

where $\bar{J}$ is the symmetric form associated with J,

$$\bar{J}[A, B] \equiv J[A, B] + J[B, A] \tag{3.34}$$

and $f(t, \tau)$ satisfies the usual nonlinear Boltzmann equation,

$$(\partial/\partial t + \mathbf{v}\cdot\nabla)f = J[f, f] \tag{3.35}$$

The initial conditions for these equations are

$$\begin{aligned} \tilde{\Phi}_{\alpha i}^{(1)}(\mathbf{r}; t, \tau)|_{t=\tau} &= \tilde{\phi}_{\alpha i}(\mathbf{r}, \tau|x_1)f_L(\tau) \\ f(t, \tau)|_{t=\tau} &= f_L(\tau) \equiv f_L(\tau, \lambda)|_{\lambda=0} \end{aligned} \tag{3.36}$$

The correlation function $G_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau)$ is therefore given by

$$G_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) = n\int dx_1\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1)\tilde{\Phi}_{\beta j}^{(1)}(\mathbf{r}'; t, \tau|x_1) \tag{3.37}$$

with $\tilde{\Phi}_{\beta j}^{(1)}$ determined by the pair of equations (3.33) and (3.35).

The determination of the correlation function H is entirely analogous, with only the initial conditions changing,

$$H_{\alpha i,\beta}(\mathbf{r}, \mathbf{r}'; t, \tau) = \int dx_1\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1)\Xi_\beta^{(1)}(\mathbf{r}'; t, \tau|x_1) \tag{3.38}$$

where

$$\begin{aligned} (\partial/\partial t + \mathbf{v}\cdot\nabla)\Xi_\beta^{(1)} &= \bar{J}[\Xi_\beta^{(1)}, f] \\ \Xi_\beta^{(1)}(\mathbf{r}'; t, \tau|x_1)|_{t=\tau} &= \tilde{\xi}_\beta(\mathbf{r}', \tau|x_1)f_L(\tau) \end{aligned} \tag{3.39}$$

and f again satisfies Eq. (3.35). Also, $\tilde{\xi}_\alpha(\mathbf{r}', \tau|x_1)$ is the single-particle function corresponding to $\tilde{\xi}_\alpha(\mathbf{r}', \tau)$. In summary, the low-density Boltzmann limit for the general nonlinear irreversible fluxes is given by Eq. (2.20) with correlation functions replaced by Eqs. (3.37) and (3.38).

For linear transport $f(t, \tau)$ may be replaced by the equilibrium distribution f_0, and Eqs. (3.33) and (3.39) reduce to the linearized Boltzmann equation. The correlation functions then become special cases of Eq. (3.5). As mentioned above, the linearized Boltzmann equation has been used extensively to study linear response generally, in addition to the analysis of the Green–Kubo expressions for the transport coefficients discussed in Section 3.1. For the general nonlinear case it is difficult to reduce the results further. However, it is straightforward to show that these results are indeed equivalent to those obtained by the kinetic theory method based on the nonlinear Boltzmann equation. To do so, it is first convenient to rewrite the results (2.20), (3.37), and (3.38) in an abbreviated notation,

$$\gamma^*_{\alpha i}(\mathbf{r}, t) = n \int dx_1\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1) \int_0^t d\tau\, X(t, \tau|x_1) \tag{3.40}$$

where

$$X(t, \tau|x_1) \equiv \int d\mathbf{r} \left\{ \frac{\partial y_\alpha(\mathbf{r}, \tau)}{\partial r_i}\, \tilde{\Phi}^{(1)}_{\alpha i}(\mathbf{r}; t, \tau|x_1) + \frac{\partial \gamma^*_{\alpha i}}{\partial r_i}(\mathbf{r}, \tau)\Xi^{(1)}_\alpha(\mathbf{r}; t, \tau|x_1) \right\} \tag{3.41}$$

and Eqs. (3.33) and (3.39) imply

$$(\partial/\partial t + \mathbf{v}\cdot\boldsymbol{\nabla})X(t, \tau|x_1) = \bar{J}[f(t, \tau), X(t, \tau)] \tag{3.42}$$

$$X(t, t|x_1) = \int d\mathbf{r} \left\{ \frac{\partial y_\alpha}{\partial r_i}(\mathbf{r}, t)\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1) + \frac{\partial \gamma^*_{\alpha i}}{\partial r_i}(\mathbf{r}, t)\, \tilde{\xi}_\alpha(\mathbf{r}, t|x_1) \right\} f_L(t) \tag{3.43}$$

It is convenient to further simplify the expression (3.43) for the initial value of X. To do so, consider the material derivative of the local equilibrium distribution function [see Eq. (3.32) for $\lambda = 0$],

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\boldsymbol{\nabla}\right) f_L = -f_L(t)\left\{ \frac{\partial q(t)}{\partial t} + \int d\mathbf{r} \left[\frac{\partial y_\alpha(\mathbf{r}, t)}{\partial t}\, \psi_\alpha(\mathbf{r}, t|x_1) \right.\right.$$
$$\left.\left. + \frac{\partial y_\alpha(\mathbf{r}, t)}{\partial r_i}\, v_i \psi_\alpha(\mathbf{r}, t|x_1) \right] \right\} \tag{3.44}$$

The term $\partial q(t)/\partial t$ may be evaluated using the normalization condition

$$\exp q(t) = \int dx_1 \exp\left\{ -\int d\mathbf{r}\, y_\alpha(\mathbf{r}, t)\psi_\alpha(\mathbf{r}, t|x_1) \right\}$$

to give

$$\frac{\partial q(t)}{\partial t} = -\int d\mathbf{r}\, \frac{\partial y_\alpha(\mathbf{r}, t)}{\partial t} \langle \psi_\alpha; t \rangle_L \tag{3.45}$$

(we use the same notation for local equilibrium average here as in Section 2, although here it is understood to be the low-density limit). Furthermore, the time derivative $\partial y_\alpha/\partial t$ may be eliminated using the conservation laws (2.13) (with all averages being understood as their low-density limits),

$$\frac{\partial y_\alpha(\mathbf{r}, t)}{\partial t} + \int d\mathbf{r}'\, K^i_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \frac{\partial y_\beta(\mathbf{r}', t)}{\partial r_i{}'} = \int d\mathbf{r}'\, g^{-1}_{\alpha\beta}(\mathbf{r}, \mathbf{r}')\, \frac{\partial \gamma^*_{\beta i}(\mathbf{r}', t)}{\partial r_i{}'} \tag{3.46}$$

Finally, then, substitution of (3.45) and (3.46) into (3.44) gives

$$\begin{aligned}\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right) f_L(t) = -\int d\mathbf{r} \left\{ \frac{\partial y_\alpha(\mathbf{r}, t)}{\partial r_i}\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1) \right.\\ \left. + \frac{\partial \gamma^*_{\alpha i}(\mathbf{r}, t)}{\partial r_i}\, \tilde{\xi}_\alpha(\mathbf{r}, t|x_1) \right\} f_L(t)\end{aligned}$$

Comparison with Eq. (3.43) gives the desired result,

$$X(t, t|x_1) = -(\partial/\partial t + \mathbf{v}\cdot\nabla) f_L \tag{3.47}$$

This result will prove useful in comparing Eq. (3.40) with the corresponding expression based on the usual Boltzmann kinetic theory.

The object now is to show that the solution to the nonlinear Boltzmann equation for initial local equilibrium is equivalent to (3.40)–(3.43). Let $f(t, 0)$ be the single-particle phase-space probability density satisfying the Boltzmann equation with the local equilibrium distribution specified at $t = 0$,

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) f = J[f, f], \qquad f(0, 0) \equiv f_L(0) \tag{3.48}$$

Let $\Delta(t, 0)$ denote the deviation from local equilibrium at time t,

$$\Delta(t, 0) \equiv f(t, 0) - f_L(t) \tag{3.49}$$

Then the irreversible fluxes are given by

$$[\gamma^*_{\alpha i}(\mathbf{r}, t)]_{\text{kinetic}} = \int dx_1\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1)\Delta(t, 0) \tag{3.50}$$

Since $\Delta(t, 0)$ vanishes at $t = 0$, we may look for solutions of the form

$$\Delta(t, 0) = \int_0^t d\tau\, Y(t, \tau|x_1) \tag{3.51}$$

Substitution of (3.49) and (3.51) back into the Boltzmann equation requires

$$\int_0^t d\tau \left\{ \left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla \right) Y(t,\tau) - \bar{J}[f_L(t), Y(t,\tau)] - \int_0^t d\tau' \, J[Y(t,\tau'), Y(t,\tau)] \right\}$$
$$= X(t, t|x_1) - Y(t, t|x_1) \tag{3.52}$$

Here, Eq. (3.47) has been used to identify the right side of Eq. (3.52). The third term on the left side of (3.52) may be rewritten

$$\begin{aligned} -\int_0^t d\tau \int_0^t d\tau' \, J[Y(t,\tau'), Y(t,\tau)] &= -\tfrac{1}{2} \int_0^t d\tau \int_0^t d\tau' \, \bar{J}[Y(t,\tau'), Y(t,\tau)] \\ &= -\int_0^t d\tau \int_\tau^t d\tau' \, \bar{J}[Y(t,\tau'), Y(t,\tau)] \\ &= -\int_0^t d\tau \, \bar{J}[(f(t,\tau) - f_L(t)), Y(t,\tau)] \end{aligned} \tag{3.53}$$

where use has been made of (3.49) and (3.51) in the form

$$\Delta(t,\tau) \equiv f(t,\tau) - f_L(t) = \int_\tau^t d\tau' \; Y(t,\tau')$$

Substitution of (3.53) into (3.52) gives the conditions that Y must satisfy in order that (3.51) yield a solution to the Boltzmann equation

$$\int_0^t d\tau \, \{ (\partial/\partial t + \mathbf{v}\cdot\nabla) Y(t,\tau) - \bar{J}[f(t,\tau), Y(t,\tau)] \} = X(t, t|x_1) - Y(t, t|x_1) \tag{3.54}$$

Since Y is otherwise arbitrary, Eq. (3.54) is satisfied if Y is chosen to be the solution to

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) Y = \bar{J}[f(t,\tau), Y] \tag{3.55}$$

with

$$Y(t, t|x_1) = X(t, t|x_1) \tag{3.56}$$

But it is now clear that Eqs. (3.55) and (3.42) are the same first-order differential equations with the same initial conditions. Therefore the solutions are the same, i.e.,

$$Y(t, \tau|x_1) = X(t, \tau|x_1)$$

and consequently, through (3.40) and (3.50),

$$[\gamma^*_{\alpha i}(\mathbf{r}, t)]_{\text{kinetic}} = [\gamma^*_{\alpha i}(\mathbf{r}, t)]_{\text{correlation function}} \tag{3.57}$$

as was to be proved.

3.3. Projection Operator Formulation of the Boltzmann Limit

The corresponding low-density limit of the projection form for $\gamma_{\alpha i}^*$ in the correlation function method, Eq. (2.32), is not as easy to obtain directly. However, the Boltzmann limit obtained above [e.g., Eqs. (3.40)–(3.43)] may be put in the form of the projection operator result and the corresponding Boltzmann limit for $C_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau)$ identified. First, a single-particle projection operator, analogous to P_t, is defined by

$$P_t a(x_1) = \int d\mathbf{r}\, \tilde{\xi}_\alpha(\mathbf{r}, t|x_1) \int dx_1{}' f_L(t) \tilde{\psi}_\alpha(\mathbf{r}, t|x_1{}') a(x_1{}') \tag{3.58}$$

Use of (3.58) in (3.41) leads to

$$X(t, \tau|x_1) = T(t, \tau)\left[f_L^{-1}(\tau) P_\tau{}^* \mathbf{v}\cdot\nabla\Delta(\tau, 0) + \int d\mathbf{r}\, \frac{\partial y_\alpha}{\partial r_i}(\mathbf{r}, \tau) f_L(\tau) \tilde{\phi}_{\alpha i}(\mathbf{r}, \tau|x_1) \right] \tag{3.59}$$

where T is the linear solution operator to Eq. (3.42) (for fixed f)

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) T(t, \tau) = \bar{J}[f(t, \tau), T(t, \tau)], \qquad T(t, t) = 1 \tag{3.60}$$

and $P_\tau{}^* \equiv f_L(\tau) P_\tau f_L^{-1}(\tau)$. Integrating (3.59) gives

$$\begin{aligned}\Delta(t, 0) = \int_0^t d\tau\, T(t, \tau) \Big\{ & f_L^{-1}(\tau) P_\tau{}^* \mathbf{v}\cdot\nabla\Delta(\tau, 0) \\ & + \int d\mathbf{r}\, \frac{\partial y_\alpha}{\partial r_i}(\mathbf{r}, \tau) f_L(\tau) \tilde{\phi}_{\alpha i}(\mathbf{r}, \tau|x_1) \Big\}\end{aligned} \tag{3.61}$$

or

$$\begin{aligned}&\left[\frac{\partial}{\partial t} + (1 - P_t{}^*)\mathbf{v}\cdot\nabla\right]\Delta(t, 0) \\ &\quad = \bar{J}[f_L, \Delta(t, 0)] \\ &\qquad + \bar{J}[\Delta(t, 0), \Delta(t, 0)] + \int dr\, \frac{\partial y_\alpha(\mathbf{r}, t)}{\partial r_i} f_L(t) \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1)\end{aligned} \tag{3.62}$$

Since $\Delta(t, 0) = 0$ at $t = 0$, consider solutions of the form

$$\Delta(t, 0) = \int_0^t d\tau \int d\mathbf{r}\, \frac{\partial y_\alpha(\mathbf{r}, t)}{\partial r_i} \Phi'_{\alpha i}(\mathbf{r}, t, \tau|x_1) \tag{3.63}$$

Substitution of (3.63) into (3.62) and use of a property analogous to (3.53) leads to the requirement that $\Phi'_{\alpha i}$ satisfy

$$[\partial/\partial t + (1 - P_t{}^*)\mathbf{v}\cdot\nabla] \Phi'_{\alpha i}(\mathbf{r}, t, \tau|x_1) = \bar{J}[f(t, \tau), \Phi'_{\alpha i}(\mathbf{r}, t, \tau|x_1)] \tag{3.64}$$

with the initial condition

$$\Phi'_{\alpha i}(\mathbf{r}, t, t|x_1) = \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1) f_L(t) \tag{3.65}$$

and $f(t, \tau)$ again satisfies the nonlinear Boltzmann equation (3.35). The irreversible fluxes are now given by Eqs. (3.40) and (3.63),

$$\gamma^{*}_{\alpha i}(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}'\, C_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau)\, \frac{\partial y_\beta(\mathbf{r}', \tau)}{\partial r_j{}'} \tag{3.66}$$

with

$$C_{\alpha i,\beta j}(\mathbf{r}, \mathbf{r}'; t, \tau) \equiv \int dx_1\, \tilde{\phi}_{\alpha i}(\mathbf{r}, t|x_1)\Phi'_{\beta j}(\mathbf{r}', t, \tau|x_1) \tag{3.67}$$

and $\Phi'_{\beta j}$ satisfies the modified kinetic equation (3.64). The results (3.66) and (3.67) provide the desired Boltzmann limit of the correlation function formulation in projection operator form. For linear transport, Eq. (3.64) becomes the modified linearized Boltzmann equation,

$$[\partial/\partial t + (1 - P_t{}^{*})\mathbf{v}\cdot\nabla]\Phi'_{\alpha i} = J_s[\Phi'_{\alpha i}, f_0] = -I[\Phi'_{\alpha i}] \tag{3.68}$$

where $I[\cdots]$ denotes the linearized Boltzmann collision operator. This equation in conjunction with (3.61) and (3.62) reproduces the "generalized hydrodynamics" obtained by others$^{(10)}$ applying projection operator techniques to the *linearized* Boltzmann equation.

4. STEADY SHEARING FLOW

To illustrate the form of the correlation functions and irreversible fluxes for highly nonlinear processes the problem of steady shearing flow will be considered. The motivation arises from the fact that for Maxwell molecules the irreversible momentum flux may be determined exactly from the nonlinear Boltzmann equation. Additionally, this problem has been reconsidered recently both from molecular dynamics experiments$^{(17)}$ and from a more general theoretical point of view.$^{(7)}$ It appears from the theory that coupling of the linear hydrodynamic modes leads to a nonanalytic dependence of the flux on the shear rate. Such anomalous behavior is not predicted by the nonlinear Boltzmann equation and will not be discussed here. However, it should be useful to have the Boltzmann results for the correlation functions as a reference for discussion of the mode coupling results.[5]

To define the problem, consider the macroscopic conservation laws,

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[5] The mode coupling calculations of Ref. 7 yield only the lowest order corrections to the Navier–Stokes transport for asymptotically small shear rate. It may well be that for finite shear rate the regular (analytic) part of the stress tensor dominates the mode coupling anomalies. The computer experiments to study mode coupling effects would need to subtract out such Boltzmann-like results.

Eq. (2.11). For a simple one-component fluid, the local equilibrium averages of Eqs. (2.2) and (2.3) lead to

$$\langle\psi_\alpha; t\rangle_L \leftrightarrow (\bar{\rho}, \bar{u} + \tfrac{1}{2}\bar{\rho}U^2, \bar{\rho}U_i)$$

$$\langle\gamma_{\alpha i}; t\rangle_L \leftrightarrow (\bar{\rho}U_i, [h + \tfrac{1}{2}\bar{\rho}U^2]U_i, P\delta_{ij} + \bar{\rho}U_iU_j)$$

where $\bar{\rho}$ and $\bar{u}$ are the average mass and internal energy densities, P is the pressure, and $h \equiv \bar{u} + P$ is the enthalpy density. With these results, Eqs. (2.11) become

$$\frac{\partial\bar{\rho}}{\partial t} + \nabla\cdot(\bar{\rho}\mathbf{U}) = 0 \tag{4.1}$$

$$\frac{\partial\bar{u}}{\partial t} + \mathbf{U}\cdot\nabla\bar{u} + h\nabla\cdot\mathbf{U} = -\nabla\cdot\mathbf{q}^* - t_{ij}^*\frac{\partial U_i}{\partial r_j} \tag{4.2}$$

$$\frac{\partial U_i}{\partial t} + \mathbf{U}\cdot\nabla U_i + \frac{1}{\bar{\rho}}\frac{\partial P}{\partial r_i} = -\frac{1}{\bar{\rho}}\frac{\partial t_{ij}^*}{\partial r_j} \tag{4.3}$$

Here, $q_i^* \equiv s_i^* - U_j t_{ij}^*$ is the irreversible heat flux. The steady shear flow corresponds physically to a fluid in steady state between two parallel plates at a fixed distance apart and in relative motion. The flow field is expected to vary linearly between the plates (except perhaps near the surface) and be of the form

$$U_i(\mathbf{r}, t) = U_{0i} + a_{ij}r_j \tag{4.4}$$

The constant vector U_{0i} and constant tensor a_{ij} are the velocity of the lower plate and the shear rate tensor, respectively. In the following U_{0i} will be set equal to zero without loss of generality. The system is otherwise assumed to be spatially homogeneous, i.e.,

$$\begin{aligned} \bar{\rho}(\mathbf{r}, t) &= \bar{\rho}(t), \qquad & \mathbf{q}^*(\mathbf{r}, t) &= \mathbf{q}^*(t) \\ \bar{u}(\mathbf{r}, t) &= \bar{u}(t), \qquad & t_{ij}^*(\mathbf{r}, t) &= t_{ij}^*(t) \end{aligned} \tag{4.5}$$

With these conditions, the conservation laws (4.1)–(4.3) become

$$\partial\bar{\rho}/\partial t = 0, \qquad \partial\bar{u}/\partial t = -a_{ij}t_{ij}^*$$

and $\bar{\rho}$ is also a constant. It is consistent with the conservation laws, therefore, to look for the irreversible fluxes under the conditions,

$$\begin{gathered} U_i(\mathbf{r}, t) = a_{ij}r_j, \qquad \bar{\rho}(\mathbf{r}, t) = \bar{\rho}_0, \qquad \bar{u}(\mathbf{r}, t) = \bar{u}(t) \\ \mathbf{q}^*(\mathbf{r}, t) = \mathbf{q}^*(t), \qquad t_{ij}^*(\mathbf{r}, t) = t_{ij}^*(t) \end{gathered} \tag{4.6}$$

Since the energy density $\bar{u}$ may be considered a function of $\bar{\rho}$ and the temperature $T = 1/k\beta$, the only conservation law is

$$\partial\beta(t)/\partial t = -a_{ij}\alpha(t)t_{ij}^*(t) \tag{4.7}$$

where $\alpha \equiv (\partial\beta/\partial\bar{u})_{\bar{\rho}}$.

To prepare the system, let external forces and sources be present such as to maintain a steady shear rate but at fixed temperature. Consequently $t_{ij}^*(t < 0) = 0$. At $t = 0$ all sources are removed except those surface forces required to maintain the conditions (4.6) and (4.7), sufficiently far from the surfaces. The corresponding initial local equilibrium ensemble is then

$$F_L(0) = \exp[-Q(0) - \beta(0)H' + \zeta(0)N] \tag{4.8}$$

where $Q(0)$ is a normalization constant, and H' is

$$H' \equiv H(\{\mathbf{p}_\alpha - m\mathbf{U}(\mathbf{q}_\alpha)\}) = H(\{p_{\alpha i} - ma_{ij}q_{\alpha j}\}) \tag{4.9}$$

More generally, in the following any phase function with a prime is defined as the corresponding unprimed function with $\mathbf{p}_\alpha$ replaced by $\mathbf{p}_\alpha - m\mathbf{U}(\mathbf{q}_\alpha)$,

$$X' \equiv X(\{\mathbf{p}_\alpha - m\mathbf{U}(\mathbf{q}_\alpha)\}) \tag{4.10}$$

The formal solutions of Section 2 cannot be directly applied since they were derived for an isolated system, whereas here the surfaces forces are required for steady flows. However, if one repeats these derivations retaining the effects of surface forces, the solutions are similar to those of Section 2. The resulting irreversible fluxes $\gamma_{\alpha i}^*(\mathbf{r}, t)$ are again characterized by time correlation functions at two different space points. If the argument $\mathbf{r}$ of $\gamma_{\alpha i}^*(\mathbf{r}, t)$ is chosen well away from the boundaries, it is reasonable to expect that the correlation with the surfaces is negligibly small. This does not mean that the boundary conditions are unimportant, but instead that they are largely incorporated in the thermodynamic parameters, rather than explicitly through the correlation functions; it is plausible, then, that Eq. (2.20) should still hold, for points away from the surfaces. For the conditions (4.6) and (4.7) the irreversible momentum flux is (see Appendix D)

$$t_{ij}^*(t) = -a_{kl}\int_0^t d\tau\,[G_{ijkl}(t, \tau) + H_{ij}(t, \tau)t_{kl}^*(\tau)] \tag{4.11}$$

with

$$G_{ijkl}(t, \tau) \equiv \beta(\tau)\langle[e^{L(t-\tau)}t'_{ij}(\mathbf{r})]T'_{kl}(\tau);\, \tau\rangle_L$$

$$H_{ij}(t, \tau) \equiv \left\langle [e^{L(t-\tau)}t'_{ij}(\mathbf{r})]\,\frac{\partial\beta}{\partial\bar{u}}\bigg|_n \bigg[(H' - \langle H';\, \tau\rangle_L)\right.$$

$$\left. - m\,\frac{\partial\zeta}{\partial\beta}\bigg|_n (N - \langle N;\, \tau\rangle_L)\bigg];\, \tau\right\rangle_L \tag{4.12}$$

The phase functions in Eq. (4.12) are the local momentum flux $t_{ij}(\mathbf{r})$ and its volume integral T_{ij}. Also, n is the number density, $\bar{\rho}/m$. Equation (4.11) with (4.12) is still exact for the conditions specified above. For small shear rate the term with H_{ij} vanishes to order a^2, leaving

$$t_{ij}^*(t) = -a_{kl} \int_0^t d\tau \, G_{ijkl}(t, \tau) \tag{4.13}$$

A pseudo-Galilean transformation, introduced by Yamada and Kawasaki,(7)

$$\mathbf{p}_\alpha{}' = \mathbf{p}_\alpha - m\mathbf{U}(\mathbf{q}_\alpha) \tag{4.14}$$

may be used to reduce $G_{ijkl}(t, \tau)$ to an equilibrium-like correlation function,

$$G_{ijkl}(t, \tau) = \beta(\tau)\langle[\{\exp[\tilde{L}(t - \tau)]\}t_{ij}(\mathbf{r})]T_{kl}; \beta(\tau)\rangle \tag{4.15}$$

with

$$\tilde{L} \equiv L + L', \qquad L' = a_{ij} \sum_{\alpha=1}^N \left(q_{\alpha j} \frac{\partial}{\partial q_{\alpha i}} - p_{\alpha j} \frac{\partial}{\partial p_{\alpha i}} \right) \tag{4.16}$$

This result is similar to that defining the shear viscosity in linear transport, with the additional nonlinear dependence on shear rate occurring only through the modified L. Due to the neglect of the H_{ij} contribution, Eq. (4.13) is only reliable to order less than a^2, but is adequate for the investigation of a possible dependence of the stress tensor on fractional powers of the shear rate.(7) The correlation function (4.15) may be amenable to a molecular dynamics analysis to test the mode coupling predictions for small shear rate. However, as the concern here is with the Boltzmann limit, no further consideration of Eqs. (4.13) and (4.15) will be made.

Returning to the exact expression, Eqs. (4.11) and (4.12), the Boltzmann limit of G_{ijkl} and H_{ij} is defined by the results of Section 3. Consider first $G_{ijkl}(t, \tau)$. Using Eq. (3.37), G_{ijkl} is given by

$$G_{ijkl}(t, \tau) = nm \int dx_1 \, \delta(\mathbf{r} - \mathbf{q}_1) v'_{1i} v'_{1j} \tilde{\Phi}_{kl}^{(1)}(t, \tau | v_1{}') \tag{4.17}$$

where $v'_{1i} = v_{1i} - U_i(\mathbf{q}_1)$ and it has been observed that the q dependence of $\tilde{\Phi}_{kl}^{(1)}$ occurs through $\mathbf{U}$. Further, $\tilde{\Phi}_{kl}^{(1)}$ is determined from Eqs. (3.33) and (3.35),

$$(\partial/\partial t + \mathbf{v}\cdot\nabla)\tilde{\Phi}_{kl}^{(1)} = \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] \tag{4.18}$$

$$(\partial/\partial t + \mathbf{v}\cdot\nabla) f = J[f, f] \tag{4.19}$$

with the initial conditions, (3.36),

$$n\tilde{\Phi}_{kl}^{(1)}(t, \tau)|_{t=\tau} = m\beta(\tau)(v'_{1k} v'_{1l} - \tfrac{1}{3}\delta_{kl} v_1'^2) f_0(\beta(\tau), v_1{}') \tag{4.20}$$

Here $f_0(\beta(t), v')$ is the Maxwell–Boltzmann distribution as a function of $\beta(t)$ and v'. Equations (4.17)–(4.19) may be solved exactly to determine

G_{ijkl} for the special case of the Maxwell force law $[\mathbf{F}(r) \sim \hat{\mathbf{r}}/r^5]$. As noted above, the direct determination of t^*_{ij} from the nonlinear Boltzmann equation for this case has been given by Ikenberry and Truesdell.(11) The analysis of the correlation functions G_{ijkl} and H_{ij} follows essentially the analysis of Ikenberry and Truesdell, and is given in Appendix C, where it is shown that G_{ijkl} and H_{ij} are determined from

$$\left(\frac{\partial}{\partial t} + \nu\right)\begin{pmatrix} G_{ijkl} \\ H_{ij} \end{pmatrix} + a_{im}\begin{pmatrix} G_{mjkl} \\ H_{mj} \end{pmatrix} + a_{jm}\begin{pmatrix} G_{imkl} \\ H_{im} \end{pmatrix} = 0 \tag{4.21}$$

with the initial conditions

$$\begin{aligned} G_{ijkl}(t, \tau)\big|_{t=\tau} &= \beta \int d\mathbf{v}\, m^2 v_i v_j (v_k v_l - \tfrac{1}{3}\delta_{kl} v^2) f_0(\beta(\tau), v) \\ &= \frac{n}{\beta(\tau)}\left\{\delta_{il}\,\delta_{jk} + \delta_{ik}\,\delta_{jl} - \frac{2}{3}\,\delta_{ij}\,\delta_{kl}\right\} \end{aligned} \tag{4.22}$$

and

$$\begin{aligned} H_{ij}(t, \tau)\big|_{t=\tau} &= \frac{\partial \beta}{\partial \bar{u}}\bigg|_n \int d\mathbf{v}\, m v_i v_j \left(\frac{1}{2}\, m v^2 - \frac{3}{2}\, kT\right) f_0(\beta(\tau), v) \\ &= -\tfrac{2}{3}\delta_{ij} \end{aligned} \tag{4.23}$$

It is now straightforward to solve Eqs. (4.21); however, for illustration it is sufficient to limit attention to determination of t^*_{xy}, taking $a_{ij} = a\,\delta_{ix}\,\delta_{jy}$. The relevant equations are then

$$\left(\frac{\partial}{\partial t} + \nu\right)\begin{pmatrix} G_{xyxy} \\ H_{xy} \end{pmatrix} + a\begin{pmatrix} G_{yyxy} \\ H_{yy} \end{pmatrix} = 0$$

$$\left(\frac{\partial}{\partial t} + \nu\right)\begin{pmatrix} G_{yyxy} \\ H_{yy} \end{pmatrix} = 0$$

which give

$$H_{xy}(t, \tau) = \tfrac{2}{3} a(t - \tau) e^{-\nu(t-\tau)} \tag{4.24}$$

$$G_{xyxy}(t, \tau) = n\beta^{-1} e^{-\nu(t-\tau)} \tag{4.25}$$

Use of these results in (4.11) gives

$$t^*_{xy}(t) = -a \int_0^t d\tau\, e^{-\nu(t-\tau)} P(\tau) - \int_0^t d\tau\, (t - \tau) e^{-\nu(t-\tau)} \tfrac{2}{3} a^2 t^*_{xy}(\tau) \tag{4.26}$$

where $P(t)$ is the pressure. Alternatively, solving Eq. (3.64) gives the equivalent projection operator form,

$$t^*_{xy}(t) = -a \int_0^t d\tau\, \{e^{-\nu(t-\tau)} \cos[(\tfrac{2}{3})^{1/2} a(t - \tau)]\} P(\tau) \tag{4.27}$$

Although nonlocal in time, Eq. (4.26) or (4.27) gives the necessary constitutive equation to make the conservation law (4.7),

$$\partial P(t)/\partial t = -\tfrac{2}{3} a t_{xy}^{*}(t) \tag{4.28}$$

a closed deterministic equation in terms of the pressure,

$$\partial P(t)/\partial t = \tfrac{2}{3} a^{2} \int_{0}^{t} d\tau \, \{e^{-\nu(t-\tau)} \cos[(\tfrac{2}{3})^{1/2} a(t-\tau)]\} P(\tau) \tag{4.29}$$

Clearly, the pressure increases with time (due to viscous heating). The solution to this equation and the corresponding expression for t_{xy}^{*} have been discussed by Ikenberry and Truesdell and will not be repeated here. Newton's viscosity law is regained in the limits $t \gg \nu^{-1}$ and $a \ll \nu$,

$$t_{xy}^{*}(t) \rightarrow -\eta a \tag{4.30}$$

where the viscosity η is the familiar result for Maxwell molecules

$$\eta = \nu^{-1} P(t) \tag{4.31}$$

5. DISCUSSION

The correlation function expressions for the transport coefficients through nonlinear Burnett order have been shown to agree with those obtained from the Chapman–Enskog solution to the nonlinear Boltzmann kinetic equation, in the appropriate limit. This agreement was also shown to be quite general, independent of small gradient expansions, by indicating that the nonlocal correlation function expression for the irreversible fluxes also agrees with kinetic theory in the appropriate limit. This correspondence also provides some insight into the structure of the local equilibrium correlation functions characterizing states far from equilibrium, and may be of some use in modeling such correlation functions for more general fluids than dilute gases. In particular, the relationship of the equations for the correlation functions to the nonlinear Boltzmann equation permits application of the substantial literature from gas dynamics on states far from equilibrium.(18) One example of this is provided in Section 4, where the correlation functions for steady shear flow were evaluated directly from knowledge of the corresponding solution to the nonlinear Boltzmann equation. It is interesting to speculate on how the results of Section 4 might suggest modeling shear flow in, for example, liquid argon. The Maxwell molecules calculation reduces ultimately to a single relaxation time model for the correlation functions. It is not unreasonable to expect such a model of the time dependence to be approximately correct more generally, with perhaps a different value for the relaxation time ν^{-1}. In this case the correlation functions in (4.12) become

$$G_{xyxy}(t, \tau) = G_{xyxy}(\tau, \tau)e^{-\nu(t-\tau)} \tag{5.1}$$

$$H_{xy}(t, \tau) = H_{yy}(\tau, \tau)a(t - \tau)e^{-\nu(t-\tau)} \tag{5.2}$$

The functions $G_{xyxy}(\tau, \tau)$ and $H_{yy}(\tau, \tau)$ are equilibrium-like averages whose τ dependence arises only through $\beta(\tau)$. In particular,

$$G_{xyxy}(\tau, \tau) = (\beta/V)\langle T_{xy}^2; \beta(\tau)\rangle_0 = G_\infty(\beta(\tau)) \tag{5.3}$$

$$H_{yy}(\tau, \tau) = -(\partial P/\partial \bar{u})|_n(\beta(\tau)) \tag{5.4}$$

Here $G_\infty(\beta(\tau))$ is the high-frequency shear viscosity discussed by Zwanzig and Mountain,$^{(19)}$ and V is the volume. The irreversible stress tensor, generalizing Eq. (4.26), is therefore

$$t_{xy}^*(\beta(t)) = -a\int_0^t d\tau \left[e^{-\nu(t-\tau)}G_\infty(\beta(\tau)) + \left.\frac{\partial P}{\partial \bar{u}}\right|_n a(t - \tau)e^{-\nu(t-\tau)}t_{xy}^*(\beta(\tau))\right] \tag{5.5}$$

At low density $(\partial P/\partial \bar{u})|_n$ is independent of β; if more generally the τ dependence of $(\partial P/\partial \bar{u})|_n$ is weak compared to that of $t_{xy}^*(\beta(\tau))$, then the above equation may be solved by Laplace transformation to give

$$\tilde{t}_{xy}^*(z) = -a\frac{\tilde{G}_\infty(z)/(\nu + z)}{1 + (\partial P/\partial \bar{u})|_n[a/(\nu + z)]^2} \tag{5.6}$$

where the tilde denotes Laplace transformation. For small shear rate this reduces to

$$\tilde{t}_{xy}^*(z) \to -a\eta(z)/z \tag{5.7}$$

where $\eta(z)$ is the frequency-dependent shear viscosity, identified as

$$\eta(z) = G_\infty/(z + \nu) \tag{5.8}$$

Here $G_\infty \equiv G_\infty(\beta(0))$. This identification may be used to determine the relaxation time ν^{-1}, and t_{xy}^* rewritten

$$\tilde{t}_{xy}^*(z) = -a\frac{\tilde{G}_\infty(z)}{G_\infty}\frac{\eta(z)}{1 + (\partial P/\partial \bar{u})|_n[\eta(z)a/G_\infty]^2} \tag{5.9}$$

For small z (times large compared to ν^{-1}), $\eta(z)$ may be replaced by $\eta \equiv \eta(0)$ and the transform inverted to give

$$t_{xy}^*(t) \xrightarrow[t \gg \nu^{-1}]{} -a\frac{\eta(\beta(t))}{1 + (\partial P/\partial \bar{u})|_n(\eta a/G_\infty)^2} \tag{5.10}$$

with $\eta(\beta(t)) \equiv \eta[G_\infty(\beta(t))/G_\infty]$. For a Lennard-Jones fluid such as argon G_∞ is determined entirely from thermodynamic properties,(19)

$$G_\infty = 3P + (26/5)nkT - (24/5)n\bar{u} \tag{5.11}$$

so that the above model for $t^*_{xy}(t)$ has no adjustable parameters. Unfortunately, it is not possible to compare directly with the molecular dynamics results of Ashurst and Hoover,(17) since in the latter, heat is removed at the walls, whereas here $G_\infty(\beta(\tau))$ increases without bound due to the increasing temperature from viscous heating. A more general treatment of the kinetic theory incorporating heat loss at the boundaries, however, could presumably be modeled in the manner described above to permit a reasonable comparison with the molecular dynamics data.

As mentioned in the introduction and in Section 4, mode coupling effects are expected to contribute a nonanalytic dependence on the thermodynamic forces not incorporated in the above kinetic models. Such effects have been discussed recently from a kinetic theory generalizing the nonlinear Boltzmann equation to include mode coupling.(7) Although the situation is somewhat more complicated than in the Boltzmann case, it may be expected that the correspondence between such a kinetic theory and the correlation function formulation could be worked out along the lines described here.

APPENDIX A. CHAPMAN–ENSKOG SOLUTION TO THE BOLTZMANN EQUATION

In this appendix the usual Chapman–Enskog expansion for the normal solution to the Boltzmann equation is carried out to Burnett order in a form suitable for comparison with the correlation function results of Section 3. The nonlinear Boltzmann equation is

$$\frac{\partial f}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla f = J[f,f] \tag{A.1}$$

where $J[f,f]$ is the nonlinear Boltzmann operator. The solution to (A.1) may be expressed in terms of the deviation from local equilibrium

$$f = f_L(1+h) \tag{A.2}$$

where f_L is the one-particle local equilibrium distribution

$$f_L = \exp[-q(t) - \psi_\alpha(\mathbf{p})y_\alpha(\mathbf{q},t)] \tag{A.3}$$

Here, the y_α are the same thermodynamic variables as in Eq. (2.10), and the $\psi_\alpha(\mathbf{p})$ are the single-particle functions of $\mathbf{p}$ corresponding to the N-particle densities of Eq. (2.2) [see Eqs. (3.10) and (3.12)],

$$\psi_\alpha(\mathbf{p}) \leftrightarrow (m, p^2/2m, p_i) \tag{A.4}$$

Substitution of (A.3) into (A.1) gives

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\boldsymbol{\nabla} + I\right)h = \frac{1}{2}J_s[h, h] + (1 + h)\left(\psi_\alpha \frac{\partial y_\alpha}{\partial t} + \gamma_{\alpha i}\frac{\partial y_\alpha}{\partial q_i}\right) \tag{A.5}$$

Here I and J_s are defined by Eq. (3.9), and $\gamma_{\alpha i}(\mathbf{p})$ is the single-particle current associated with $\psi_\alpha(\mathbf{p})$,

$$\boldsymbol{\gamma}_\alpha \equiv (\mathbf{p}/m)\psi_\alpha(\mathbf{p}) \tag{A.6}$$

The macroscopic conservation laws, analogous to Eq. (2.13), follow from the fact that the ψ_α are summational invariants,

$$\frac{\partial y_\alpha}{\partial t} + c^i_{\alpha\beta}\frac{\partial y_\beta}{\partial q_i} = \bar{g}_{\alpha\beta}^{-1}\frac{\partial \gamma^*_{\beta i}}{\partial q_i} \tag{A.7}$$

where $\bar{g}_{\alpha\beta} \equiv \int d\mathbf{r}'\, g_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and otherwise the notation is the same as that of the text. Use of (A.7) to eliminate the time derivative in (A.5) gives

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\boldsymbol{\nabla} + I\right)h = \frac{1}{2}J_s[h, h] + (1 + h)\left(\phi_{\alpha i}\frac{\partial y_\alpha}{\partial q_i} + \xi_\alpha\frac{\partial \gamma^*_{\alpha i}}{\partial q_i}\right) \tag{A.8}$$

with

$$\phi_{\alpha i}(\mathbf{p}) \equiv \gamma_{\alpha i}(\mathbf{p}) - \psi_\beta(\mathbf{p})c^i_{\beta\alpha}, \qquad \xi_\alpha(\mathbf{p}) \equiv \psi_\beta(\mathbf{p})\bar{g}_{\beta\alpha}^{-1} \tag{A.9}$$

The irreversible fluxes $\gamma^*_{\alpha i}$ defined by Eq. (2.12) are

$$\gamma^*_{\alpha i} \equiv \int d\mathbf{p}\, \gamma_{\alpha i}(\mathbf{p})(f - f_L) = \int d\mathbf{p}\, f_L\gamma_{\alpha i}h \tag{A.10}$$

The definition (2.7) of the thermodynamic parameters in f_L implies that h must be orthogonal to the ψ_α

$$\int d\mathbf{p}\, f_L\psi_\alpha h = 0 \tag{A.11}$$

so Eq. (A.10) may be expressed in the more convenient form, using (A.9)

$$\gamma^*_{\alpha i} = \int d\mathbf{p}\, f_L\phi_{\alpha i}h \tag{A.12}$$

The Chapman–Enskog solution to (A.8) may be described as follows. A solution (the normal solution) is sought such that h depends on $\mathbf{q}$, t only through $y_\alpha(\mathbf{q}, t)$ and their derivatives. Furthermore, since the time derivatives may be eliminated using (A.7), the solution may be characterized by

$y_\alpha(\mathbf{q}, t)$ and their space derivatives. The Chapman–Enskog solution is an expansion of the normal solution in the space derivatives, assuming convergence for smoothly varying $y_\alpha(\mathbf{q}, t)$. To set up the expansion, (A.8) may be rewritten

$$Ih = (1 + h)\left(\phi_{\alpha i}\frac{\partial y_\alpha}{\partial q_i} + \xi_\alpha \frac{\partial \gamma_{\alpha i}^*}{\partial q_i}\right) + \frac{1}{2}J_s[h, h] - D_t h \qquad \text{(A.13)}$$

Here $D_t h \equiv [\partial/\partial t + (\mathbf{p}/m)\cdot\nabla]h$ is the material derivative of h treating y and the space derivatives of y as independent variables, i.e.,

$$D_t h = \frac{\partial h}{\partial y_\alpha}\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right) y_\alpha + \frac{\partial h}{\partial(\partial y_\alpha/\partial q_i)}\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\nabla\right)\frac{\partial y_\alpha}{\partial q_i} + \cdots \qquad \text{(A.14)}$$

The time derivatives in (A.14) may then be eliminated by (A.7), yielding an expression in terms of the space derivatives only. Equation (A.13) may therefore be solved perturbatively, treating gradients of y_α as small. Formally this is accomplished by introducing a uniformity parameter, say ϵ, as a factor of each gradient operator $\partial/\partial q_i$. Then h is assumed to have the form

$$h = \epsilon h^{(1)} + \epsilon^2 h^{(2)} + \cdots \qquad \text{(A.15)}$$

The irreversible flux $\gamma_{\alpha i}^*$ has a similar expansion generated by (A.10),

$$\gamma_{\alpha i}^* = \sum_{n=1}^{\infty} \epsilon^n [\gamma_{\alpha i}^*]^{(n)}, \qquad [\gamma_{\alpha i}^*]^{(n)} = (\phi_{\alpha i}, h^{(n)}) \qquad \text{(A.16)}$$

The lower order contributions to h and hence $\gamma_{\alpha i}^*$ are easily identified from Eq. (A.13):

Navier–Stokes order: To first order in $\partial y_\alpha/\partial q$, Eq. (A.13) gives

$$Ih^{(1)} = \phi_{\alpha i}\, \partial y_\alpha/\partial q_i$$

Using the requirement that $h^{(1)}$ be orthogonal to the ψ_α, a unique solution is obtained,

$$h^{(1)} = (\partial y_\alpha/\partial q_i) I^{-1}\phi_{\alpha i} \qquad \text{(A.17)}$$

The Navier–Stokes-order irreversible flux is then

$$[\gamma_{\alpha i}^*]^{(1)} \equiv \int d\mathbf{p}\, f_0(\mathbf{p})\phi_{\alpha i} h^{(1)} = \gamma_{\alpha i,\beta j}^{(1)}\, \partial y_\beta/\partial q_j \qquad \text{(A.18)}$$

where the transport coefficients $\gamma_{\alpha i,\beta j}^{(1)}$ are identified as

$$\gamma_{\alpha i,\beta j}^{(1)} = (\phi_{\alpha i}, I^{-1}\phi_{\beta j}) \qquad \text{(A.19)}$$

Burnett order: The second-order contributions to Eq. (A.13) are

$$
\begin{aligned}
Ih^{(2)} &= h^{(1)}\phi_{\alpha i}\frac{\partial y_\alpha}{\partial q_i} + \xi_\alpha \frac{\partial[\gamma^*_{\alpha i}]^{(1)}}{\partial q_i} + \frac{1}{2}J_s[h^{(1)}, h^{(1)}] \\
&\quad + (I^{-1}\phi_{\alpha i})\frac{\partial}{\partial q_i}\left[\left(c^j_{\beta\mu} - \frac{p_j}{m}\delta_{\alpha\beta}\right)\frac{\partial y_\beta}{\partial q_j}\right] \\
&\quad + \left[\frac{\partial}{\partial y_\beta}(I^{-1}\phi_{\alpha i})\right]\frac{\partial y_\alpha}{\partial q_i}\left(c^j_{\beta\mu} - \frac{p_j}{m}\delta_{\beta\mu}\right)\frac{\partial y_\mu}{\partial q_j} \\
h^{(2)} &= I^{-1}\biggl((I^{-1}\phi_{\alpha i})\left(c^j_{\alpha\beta} - \frac{p_j}{m}\delta_{\alpha\beta}\right)\frac{\partial^2 y_\beta}{\partial q_i\,\partial q_j} \\
&\quad + \biggl\{(I^{-1}\phi_{\beta j})\phi_{\alpha i} + \frac{1}{2}J_s[(I^{-1}\phi_{\alpha i}), (I^{-1}\phi_{\beta j})] \\
&\quad + (I^{-1}\phi_{\mu i})\frac{c^j_{\mu\beta}}{\partial y_\alpha} + \left[\frac{\partial}{\partial y_\mu}(I^{-1}\phi_{\alpha i})\right]\left(c^j_{\mu\beta} - \frac{p_j}{m}\delta_{\beta\mu}\right)\biggr)\biggr\} \\
&\quad \times \frac{\partial y_\alpha}{\partial q_i}\frac{\partial y_\beta}{\partial q_j} + \xi_\alpha\frac{\partial[\gamma^*_{\alpha i}]^{(1)}}{\partial q_i}\biggr)
\end{aligned}
\tag{A.20}
$$

The Burnett contribution to the irreversible fluxes is

$$
\begin{aligned}
[\gamma^*_{\alpha i}]^{(2)} &= \left(\phi_{\alpha i}, I^{-2}\phi_{\beta j}\left[c^k_{\beta\mu} - \frac{p_k}{m}\delta_{\beta\mu}\right]\right)\frac{\partial^2 y_\mu}{\partial q_j\,\partial q_k} \\
&\quad + \left((\phi_{\alpha i}, I^{-1}\left[\phi_{\mu k}(I^{-1}\phi_{\beta j}) + \left(c^k_{\nu\mu} - \frac{p_k}{m}\delta_{\mu\nu}\right)\frac{\partial}{\partial y_\nu}(I^{-1}\phi_{\beta j})\right]\right)\frac{\partial y_\beta}{\partial q_j}\frac{\partial y_\mu}{\partial q_k} \\
&\quad + (\phi_{\alpha i}, I^{-2}\phi_{\mu j})\frac{\partial c^k_{\mu\nu}}{\partial y_\beta}\frac{\partial y_\nu}{\partial q_k}\frac{\partial y_\beta}{\partial q_j} \\
&\quad + (\phi_{\alpha i}, I^{-1}\frac{1}{2}J_s[(I^{-1}\phi_{\beta j}), (I^{-1}\phi_{\mu k})])\frac{\partial y_\beta}{\partial q_j}\frac{\partial y_\mu}{\partial q_k} \\
&\quad + (\phi_{\alpha i}, I^{-1}\xi_\beta)\frac{\partial[\gamma^*_{\beta i}]^{(1)}}{\partial q_i}
\end{aligned}
\tag{A.21}
$$

The last term in (A.21) vanishes as a consequence of (A.11) and the fact that I is self-adjoint,

$$(\phi_{\alpha i}, I^{-1}\xi_\beta) = ((I^{-1}\phi_{\alpha i}), \xi_\beta) = 0$$

Also, the second term in (A.21) may be rewritten as

$$\left(I^{-1}\phi_{\alpha i}, \left(c^k_{\mu\nu} - \frac{p_k}{m}\delta_{\mu\nu}\right)f_0^{-1}\frac{\partial}{\partial y_\mu}(f_0 I^{-1}\phi_{\beta j})\right)\frac{\partial y_\beta}{\partial q_j}\frac{\partial y_\nu}{\partial q_k}$$

so that the Burnett-order contribution is

$$[\gamma^{*}_{\alpha i}]^{(2)} = \gamma^{(2,1)}_{\alpha i,\beta jk}\frac{\partial^2 y_\beta}{\partial q_j\,\partial q_k} + \gamma^{(2,2)}_{\alpha i,\beta j,\mu k}\frac{\partial y_\beta}{\partial q_j}\frac{\partial y_\mu}{\partial q_k} \tag{A.22}$$

where the linear and nonlinear transport coefficients are identified as, respectively,

$$\gamma^{(2,1)}_{\alpha i,\beta jk} = \left(I^{-1}\phi_{\alpha i}, (I^{-1}\phi_{\mu j})\left(c^k_{\mu\beta} - \frac{p_k}{m}\,\delta_{\mu\beta}\right)\right) \tag{A.23}$$

$$\begin{aligned}\gamma^{(2,2)}_{\alpha i,\beta j,\mu k} &= (I^{-1}\phi_{\alpha i}, I^{-1}\phi_{\nu j})\,\frac{\partial c^k_{\nu\mu}}{\partial y_\beta}\\ &\quad + \left(I^{-1}\phi_{\alpha i}, \frac{1}{2}\,J_s[(I^{-1}\phi_{\beta j}), (I^{-1}\phi_{\mu k})]\right)\\ &\quad + \left(I^{-1}\phi_{\alpha i}, \left(c^k_{\nu\mu} - \frac{p_k}{m}\,\delta_{\mu\nu}\right) f_0^{-1}\,\frac{\partial}{\partial y_\nu}\,(f_0 I^{-1}\phi_{\beta j})\right)\end{aligned} \tag{A.24}$$

The results (A.19), (A.23), and (A.24) agree with the corresponding results, (3.13), (3.15), and (3.21), obtained from the correlation function expressions.

APPENDIX B. KINETIC EQUATION FOR LOCAL EQUILIBRIUM CORRELATION FUNCTIONS

The low-density kinetic equations for the local equilibrium time correlation functions, Eqs. (3.33) and (3.39), follow from the corresponding equation for the generating functional $f^{(s)}_\lambda$ given by Eq. (3.30)

$$f^{(s)}_\lambda(1,\ldots, s; t, \tau) \equiv \sum_{N>s}\frac{1}{h^{3N}(N-s)!}\int dx_{s+1}\cdots dx_N\, e^{-L(t-\tau)}F_L(\tau|\lambda) \tag{B.1}$$

with $F_L(\tau|\lambda)$ defined by

$$F_L(\tau|\lambda) \equiv \exp\left\{-Q(\tau|\lambda) - \int d\mathbf{r}\,[y_\alpha(\mathbf{r}, \tau)\psi_\alpha(\mathbf{r}) - \lambda_{\alpha i}(\mathbf{r}, \tau)\phi_{\alpha i}(\mathbf{r})]\right\} \tag{B.2}$$

It is readily verified that $f^{(s)}_\lambda$ satisfies the BBGKY hierarchy, the first equation of which is

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\nabla\right) f^{(1)}_\lambda(1; t, \tau) = \int dx_2\,\theta_{12} f^{(2)}_\lambda(1, 2; t, \tau) \tag{B.3}$$

A kinetic equation follows from (B.3) by expressing $f^{(2)}_\lambda$ as a functional of $f^{(1)}_\lambda$. Expansion of this functional to lowest order in the density gives the desired equation. The density expansion may be accomplished by means of a cluster expansion which has been studied and discussed in detail elsewhere.(15,16) Consequently only an outline of the derivation will be given here.

Define the N-particle function $F(1,\dots, N)$ by

$$F(1,\dots, N) \equiv e^{-L(t-\tau)} \exp\left\{-\int d\mathbf{r}\,[y_\alpha(\mathbf{r}, \tau)\psi_\alpha(\mathbf{r}) - \lambda_{\alpha i}(\mathbf{r}, \tau)\phi_{\alpha i}(\mathbf{r})]\right\} \tag{B.4}$$

and the associated modified cluster functions $U(1,\dots, s|s + 1,\dots, l)$ by

$$F(1,\dots, N) = \sum_{l=s}^{N} \mathscr{S}\, U(1,\dots, s|s + 1,\dots, l)F_{N-l}(l + 1,\dots, N) \tag{B.5}$$

Here $\mathscr{S}$ denotes a sum over all $(l - s)$-tuples in the set $(s + 1,\dots, N)$. Specifically, for $s = 1, 2$ these expansions are

$$F(1,\dots, N) = U(1)F_{N-1}(2,\dots, N) + \sum_{i\neq 1} U(1|i)F_{N-2}(2,\underset{\neq i}{\dots}, N) + \cdots \tag{B.6}$$

and

$$F(1,\dots, N) = U(1, 2)F_{N-2}(3,\dots, N) + \sum_{i\neq 1,2} U(1, 2|i)F_{N-3}(3,\underset{\neq i}{\dots}, N) + \cdots \tag{B.7}$$

The corresponding expansions for $f_\lambda^{(1)}$ and $f_\lambda^{(2)}$ are obtained by substituting (B.6) and (B.7) in (B.1):

$$f_\lambda^{(1)}(1; t, \tau) = \left[U(1) + \int dx_2\, U(1|2) + \cdots\right] e^{-Q(\tau|\lambda)} \tag{B.8}$$

$$f_\lambda^{(2)}(1, 2; t, \tau) = \left[U(1, 2) + \int dx_3\, U(1, 2|3) + \cdots\right] e^{-Q(\tau|\lambda)} \tag{B.9}$$

The cluster functions may be identified from (B.6) and (B.7) by setting $N = 1, 2,\dots$ successively. The low-order functions are

$$\begin{aligned} U(1) = F(1) &= \exp[-L(1)(t - \tau)] \exp\left\{-\int d\mathbf{r}\,[y_\alpha(\mathbf{r}, \tau)\psi_\alpha^{(1)}(\mathbf{r}) \right.\\ &\qquad \left. - \lambda_{\alpha i}(\mathbf{r}, \tau)\phi_{\alpha i}^{(1)}(\mathbf{r})]\right\} \\ U(1, 2) = F(1, 2) &= \exp[-L(1, 2)(t - \tau)] \\ &\qquad \times \exp\left\{-\int d\mathbf{r}\,[y_\alpha(\mathbf{r}, \tau)(\psi_\alpha^{(1)} + \psi_\alpha^{(2)}) \right.\\ &\qquad \left. - \lambda_{\alpha i}(\mathbf{r}, \tau)(\phi_{\alpha i}^{(1)}(\mathbf{r}) + \phi_{\alpha i}^{(2)}(\mathbf{r}))]\right\} \\ U(1|2) &= F(12) - F(1)F(2) \\ U(1, 2|3) &= F(123) - F(1, 2)F(3) \end{aligned}$$

Here $\psi_\alpha^{(1)}$, $\psi_\alpha^{(2)}$ and $\phi_{\alpha i}^{(1)}$, $\phi_{\alpha i}^{(2)}$ are the single-particle and pair functions associated with ψ_α and $\phi_{\alpha i}$, respectively [see Eq. (3.10)]. The expansions (B.8) and (B.9) may be identified as expansions in the activity, so that to lowest order in the density only the leading terms need to be retained. Using the form of $U(1)$, Eq. (B.8) may be inverted to give

$$\begin{aligned}\exp\left\{-\int d\mathbf{r}\,[y_\alpha(\mathbf{r},\tau)\psi_\alpha^{(1)}(\mathbf{r}) - \psi_{\alpha i}(\mathbf{r},\tau)\phi_{\alpha i}^{(1)}(\mathbf{r})]\right\}\\ = \{\exp[L(1)(t-\tau)]\}[f_\lambda^{(1)}(1;t,\tau) + \text{order } n^2]\exp[Q(\tau|\lambda)]\end{aligned}$$

Substitution of this result into $U(1,2)$ of Eq. (B.9) then gives the desired low-density functional

$$f_\lambda^{(2)}(1,2;t,\tau) = e^{-L(1,2)(t-\tau)}g(1,2)e^{[L(1)+L(2)](t-\tau)}f_\lambda^{(1)}(1;t,\tau)f_\lambda^{(1)}(2;t,\tau) \tag{B.10}$$

where $g(1,2)$ is defined by

$$g(1,2) \equiv \exp\left\{-\int d\mathbf{r}\,[y_\alpha(\mathbf{r},\tau)\psi_\alpha^{(2)}(\mathbf{r}) - \lambda_{\alpha i}(\mathbf{r},\tau)\phi_{\alpha i}^{(2)}(\mathbf{r})]\right\}$$

Equation (B.10) may be simplified by rewriting it as

$$f_\lambda^{(2)}(1,2;t,\tau) = \bar{g}(1,2;t,\tau)\mathscr{S}_{t-\tau}(1,2)f_\lambda^{(1)}(1;t,\tau)f_\lambda^{(1)}(2;t,\tau)$$

with

$$\mathscr{S}_t(1,2) \equiv e^{-L(1,2)t}e^{[L(1)+L(2)]t}$$

and

$$\begin{aligned}\bar{g}(1,2;t,\tau) = \exp\biggl(-\int d\mathbf{r}\,[y_\alpha(\mathbf{r},\tau)\{\exp[-L(t-\tau)]\}\psi_\alpha^{(2)}(\mathbf{r})\\ - \lambda_{\alpha i}(\mathbf{r},\tau)\{\exp[-L(t-\tau)]\}\phi_{\alpha i}^{(2)}(\mathbf{r})]\biggr)\end{aligned}$$

For initial configurations, $|\mathbf{q}_1 - \mathbf{q}_2| \leqslant$ force range, and for repulsive interactions, the phase functions $e^{-L(t-\tau)}\psi_\alpha^{(2)}$ and $e^{-L(t-\tau)}\phi_{\alpha i}^{(2)}$ vanish after times $t-\tau$ large compared to a typical collision time τ_0. Therefore $\lim_{t-\tau\gg\tau_0}\bar{g} \to 1$, for $|\mathbf{q}_1 - \mathbf{q}_2| \leqslant$ force range, and

$$\lim_{t-\tau\gg\tau_0} \theta_{12}f_\lambda^{(2)}(1,2;t,\tau) \to \theta_{12}\mathscr{S}_\infty f_\lambda^{(1)}(1;t,\tau)f_\lambda^{(1)}(2;t,\tau) \tag{B.11}$$

and

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\cdot\boldsymbol{\nabla}\right)f_\lambda^{(1)}(1,2;t,\tau) = \int dx_2\,\theta_{12}\mathscr{S}_\infty f_\lambda^{(1)}(1;t,\tau)f^{(1)}(2;t,\tau) \tag{B.12}$$

Further reduction of the right side of Eq. (B.12) to the standard Boltzmann form of the text is straightforward and involves the further limitation to variations of $f^{(1)}$ on a spatial scale large compared to the force range.

APPENDIX C. DETERMINATION OF G_{ijkl} AND H_{ij} FOR MAXWELL MOLECULES

In this appendix Eqs. (4.21) are obtained. Consider first G_{ijkl}, defined by Eq. (4.17),

$$G_{ijkl}(t, \tau) = m \int dx_1\, \delta(\mathbf{r} - \mathbf{q}_1) v'_{1i} v'_{1j} \tilde{\Phi}_{kl}^{(1)}(t, \tau | v_1{}') \tag{C.1}$$

where Φ_{kl} satisfies the equation

$$(\partial/\partial t + \mathbf{v}\cdot\boldsymbol{\nabla})\tilde{\Phi}_{kl}^{(1)} = \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] \tag{C.2}$$

and f satisfies the nonlinear Boltzmann equation. From (C.2), an equation for G_{ijkl} follows,

$$\frac{\partial}{\partial t} G_{ijkl} + \frac{\partial U_i}{\partial x_m} G_{mjkl} + \frac{\partial U_j}{\partial x_m} G_{imkl} = m \int d\mathbf{v}_1\, v'_{1i} v'_{1j} \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] \tag{C.3}$$

Use has been made of the fact that moments of $\tilde{\Phi}_{kl}^{(1)}$ equal to or higher than second order are space independent, as a consequence of the conditions of Section 5. Generally Eq. (C.3) is not a closed equation for G_{ijkl} because of the term on the right side. However, for Maxwell molecules, with interatomic potential

$$V(r) = \epsilon_0(\sigma/r)^4$$

the right side is simply proportional to G_{ijkl},

$$m \int d\mathbf{v}_1\, v'_{1i} v'_{1j} \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] = -\nu G_{ijkl} \tag{C.4}$$

where $\nu \equiv 1.23n(3\pi/2)\sigma^2(\epsilon_0/m)^{1/2}$. The proof of (C.4) is as follows:

$$\begin{aligned} m \int d\mathbf{v}_1\, & v'_{1i} v'_{1j} \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] \\ &= m \int d\mathbf{v}_1\, d\mathbf{v}_2\, [\tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_1) f(\mathbf{v}_2) \\ &\qquad + \tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_2) f(\mathbf{v}_1)] \int_0^\infty db\, b|\mathbf{v}_1 - \mathbf{v}_2| \int_0^{2\pi} d\epsilon\, [\tilde{v}_{1i}\tilde{v}_{1j} - v_{1i}v_{1j}] \end{aligned} \tag{C.5}$$

where $\tilde{v}$ denotes the velocity after collision, and use has been made of the invariance of the cross section under the transformation $\tilde{v} \to v$. Define the center-of-mass and relative velocities by

$$G_i = \tfrac{1}{2}(v_{1i} + v_{2i}), \qquad g_i = v_{1i} - v_{2i}$$

Then Eq. (C.5) becomes

$$\begin{aligned} m \int d\mathbf{v}_1\, v_{1i}' v_{1j}' \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] &= -m \int d\mathbf{v}_1\, d\mathbf{v}_2\, [\tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_1) f(\mathbf{v}_2) + \tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_2) f(\mathbf{v}_1)] \int_0^\infty db\, bg \\ &\quad \times \int_0^{2\pi} d\epsilon\, [\tfrac{1}{2}(G_i g_j + G_j g_i) + \tfrac{1}{4} g_i g_j - \tfrac{1}{2}(G_i \tilde{g}_j + G_j \tilde{g}_i) - \tfrac{1}{4} \tilde{g}_i \tilde{g}_j] \end{aligned} \tag{C.6}$$

Now let $\tilde{g}_i = g_i \cos\theta - a_i g \sin\theta$, where $\mathbf{a}$ is a unit vector orthogonal to g. Then

$$\begin{aligned} m \int d\mathbf{v}_1\, v_{1i}' v_{1j}' \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] &= -m \int d\mathbf{v}_1\, d\mathbf{v}_2\, [\tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_1) f(\mathbf{v}_2) + \tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_2) f(\mathbf{v}_1)] \\ &\quad \times \int_0^\infty db\, bg \int_0^{2\pi} d\epsilon\, [\tfrac{1}{2}(G_i g_j + G_j g_i)(1 - \cos\theta) \\ &\quad + \tfrac{1}{2}(g \sin\theta)(G_i a_j + G_j a_i) + \tfrac{1}{4} g_i g_j (1 - \cos^2\theta) \\ &\quad - \tfrac{1}{4} g^2 a_i a_j \sin^2\theta + \tfrac{1}{4}(g_i a_j + g_j a_i) g \sin\theta \cos\theta] \end{aligned}$$

But $\int_0^{2\pi} d\epsilon\, a_i = 0 \int_0^{2\pi} d\epsilon\, a_i a_j = \pi(\delta_{ij} - g_i g_j / g^2)$, so

$$\begin{aligned} m \int d\mathbf{v}_1\, v_{1i}' v_{1j}' \bar{J}[\tilde{\Phi}_{kl}^{(1)}, f] &= -m \int d\mathbf{v}_1\, d\mathbf{v}_2 [\tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_1) f(\mathbf{v}_2) + \tilde{\Phi}_{kl}^{(1)}(\mathbf{v}_2) f(\mathbf{v}_1)] \\ &\quad \times \left[\tfrac{1}{2}(G_i g_j + G_j g_i) \int_0^\infty db\, bg 2\pi (1 - \cos\theta) \right. \\ &\quad \left. + \tfrac{3}{8}(g_i g_j - \tfrac{1}{3}\delta_{ij} g^2) \int_0^\infty db\, bg \sin^2\theta \right] \end{aligned}$$

For Maxwell molecules $\int_0^\infty db\, bgh(\theta)$ is independent of the velocities and hence a constant. The term with $(G_i g_j + G_j g_i) = (v_{1i} v_{1j} + v_{1i} v_{2j}) -$

$(v_{2i}v_{2j} + v_{2i}v_{2j})$ vanishes on change of variables $v_2 \to v_1$ in the second term. Thus,

$$
\begin{aligned}
m \int d\mathbf{v}_1\, v'_{1i}v'_{1j}\bar{J}[\tilde{\Phi}^{(1)}_{kl}, f] \\
&= -\nu \frac{m}{2n} \int d\mathbf{v}_1\, d\mathbf{v}_2\, [\tilde{\Phi}^{(1)}_{kl}(\mathbf{v}_1) f(\mathbf{v}_2) + \tilde{\Phi}^{(1)}_{kl}(\mathbf{v}_2) f(v_1)] \\
&\quad \times [v_{1i}v_{1j} + v_{2i}v_{2j} - v_{1i}v_{2j} - v_{1j}v_{2i} - \tfrac{1}{3}\delta_{ij}(v_1{}^2 + v_2{}^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2)] \\
&= -\nu \frac{m}{n} \int d\mathbf{v}_1\, d\mathbf{v}_2\, \tilde{\Phi}^{(1)}_{kl}(\mathbf{v}_1) f(\mathbf{v}_2) \\
&\quad \times [v_{1i}v_{1j} + v_{1i}v_{1j} - v_{1i}v_{2j} - v_{1j}v_{2i} - \tfrac{1}{3}\delta_{ij}(v_1{}^2 + v_2{}^2 - 2\mathbf{v}_1 \cdot \mathbf{v}_2)]
\end{aligned}
\tag{C.7}
$$

where

$$\nu \equiv (3\pi/2)n \int_0^\infty db\, bg \sin^2\theta$$

or

$$\nu = (3\pi/2)n\sigma^2(\epsilon_0/m)^{1/2}1.23 \tag{C.8}$$

Equation (C.7) simplifies considerably when it is noted that $\tilde{\Phi}^{(1)}_{kl}(\mathbf{v}_1)$ is orthogonal to 1, $\mathbf{v}$, and v^2 [see Eq. (2.19)]. Integrating over v_2 in Eq. (C.7) then gives

$$m \int d\mathbf{v}_1\, v'_{1i}v'_{1j}\bar{J}[\tilde{\Phi}^{(1)}_{kl}, f] = -\nu G_{ijkl}$$

which verifies Eq. (C.4).

Substitution of Eq. (C.4) into (C.3) gives the desired equation for G_{ijkl}

$$\left(\frac{\partial}{\partial t} + \nu\right) G_{ijkl} + \frac{\partial U_i}{\partial x_m} G_{mjkl} + \frac{\partial U_j}{\partial x_m} G_{imkl} = 0$$

This is the first of equations (4.21). The second equation, for H_{ij}, follows in an entirely analogous calculation.

APPENDIX D. ONE-COMPONENT FLUID RESULTS AND TRANSFORMATION TO REST FRAME

The formal results of Section 2 for the thermodynamic variables y_α and fluxes $\gamma^*_{\alpha i}$ are given more explicitly in this appendix and the correlation functions are transformed to the local rest frame where calculations are often simpler. To do so a pseudo-Galilean transformation

$$\mathbf{p}_\alpha' = \mathbf{p}_\alpha - m\mathbf{U}(\mathbf{q}_\alpha, t) \tag{D.1}$$

is performed on the ψ_α and $\gamma_{\alpha i}$ of Eqs. (2.2) and (2.3) to give

$$\begin{aligned}
&\psi_\alpha' \leftrightarrow (\rho, \epsilon - \mathbf{g}\cdot\mathbf{U} + \tfrac{1}{2}\rho U^2, g_i - \rho U_i) \\
&\gamma_{\alpha i}' \leftrightarrow (g_i - \rho U_i, s_i - (\epsilon + \tfrac{1}{2}\rho U^2 - \mathbf{g}\cdot\mathbf{U})U_i + \tfrac{1}{2} g_i U^2 - t_{ij}U_j, \\
&\qquad\qquad t_{ij} - g_i U_j - g_j U_i + \rho U_i U_j)
\end{aligned} \tag{D.2}$$

These transformations may also be effected by the matrix operation

$$\psi' = A(\mathbf{U})\psi, \qquad \gamma_i' = A(\mathbf{U})(\gamma_i - U_i\psi) \tag{D.3}$$

where the matrix A is given by

$$A = \begin{pmatrix} 1 & 0 & 0 \\ \tfrac{1}{2}U^2 & 1 & -U_j \\ -U_i & 0 & \delta_{ij} \end{pmatrix}, \qquad A^{-1}(\mathbf{U}) = A(-\mathbf{U}) \tag{D.4}$$

The thermodynamic parameters y_α transform as

$$y = A^+ y^0 \tag{D.5}$$

$$y^0 = y|_{\mathbf{U}=0} \leftrightarrow (-\zeta, \beta, 0) \tag{D.6}$$

Here A^+ is the transpose of A. Similarly, the correlation functions may be expressed in terms of local equilibrium averages in the rest frame. For example, the transformation (D.1) on $g_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$, Eq. (2.13), gives

$$\begin{aligned}
g(\mathbf{r}, \mathbf{r}') &= A^{-1}(\mathbf{U}(\mathbf{r}, t))g^0(\mathbf{r}, \mathbf{r}')A^{+\,-1}(\mathbf{U}(\mathbf{r}', t)) \\
g^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}') &\equiv \langle \tilde{\psi}_\alpha(\mathbf{r}, t)\tilde{\psi}_\beta(\mathbf{r}', t); t\rangle_{L_0}
\end{aligned} \tag{D.7}$$

Here $\langle\cdots; t\rangle_{L_0}$ denotes an average over the local equilibrium ensemble with $\mathbf{U} = 0$. The $g^0_{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ are readily found to be

$$g^0(\mathbf{r}, \mathbf{r}') = \begin{pmatrix} \left.\dfrac{\delta\bar{\rho}(\mathbf{r})}{\delta\zeta(\mathbf{r}')}\right|_\beta & -\left.\dfrac{\delta\bar{\rho}(\mathbf{r})}{\delta\beta(\mathbf{r}')}\right|_\zeta & 0 \\ \left.\dfrac{\delta\bar{u}(\mathbf{r})}{\delta\zeta(\mathbf{r}')}\right|_\beta & -\left.\dfrac{\delta\bar{u}(\mathbf{r})}{\delta\beta(\mathbf{r}')}\right|_\zeta & 0 \\ 0 & 0 & \dfrac{\bar{\rho}(\mathbf{r})}{\beta(\mathbf{r}')}\,\delta_{ij}\,\delta(\mathbf{r} - \mathbf{r}') \end{pmatrix} \tag{D.8}$$

Similarly, the matrix $K^i_{\alpha\beta}$ of Eq. (2.14) transforms as

$$K^i(\mathbf{r}, \mathbf{r}') = A^+ K^{0i} A^{+\,-1} + U_i I$$

$$K^{0i}_{\alpha\beta}(\mathbf{r}, \mathbf{r}') = \int d\mathbf{r}''\, g^{0\,-1}_{\alpha\lambda}(\mathbf{r}, \mathbf{r}'')\langle\tilde{\psi}_\lambda(\mathbf{r}'')\tilde{\gamma}_{\beta i}(\mathbf{r}'); t\rangle_{L_0} \tag{D.9}$$

Evaluation of K^{0i} leads to

$$K^{0i} = \begin{pmatrix} 0 & 0 & \delta_{ij} \left.\dfrac{\delta P(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})}\right|_{\bar{u}} \\ 0 & 0 & \delta_{ij} \left.\dfrac{\delta P(\mathbf{r}')}{\delta \bar{u}(\mathbf{r})}\right|_{\bar{\rho}} \\ \delta_{ij}\, \delta(\mathbf{r} - \mathbf{r}') & \dfrac{\beta(\mathbf{r})}{\bar{\rho}(\mathbf{r})} \langle g_i(\mathbf{r}) s_j(\mathbf{r}') \rangle_{L_0} & \end{pmatrix} \tag{D.10}$$

With these results, Eq. (2.13) becomes the following set of exact equations for $\beta(\mathbf{r}, t)$, $\zeta(\mathbf{r}, t)$, and $\mathbf{U}(\mathbf{r}, t)$:

$$\left(\frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla\right) U_i + \frac{1}{\bar{\rho}} \frac{\partial P}{\partial r_i} = -\frac{1}{\bar{\rho}} \frac{\partial t_{ij}^*}{\partial r_j}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla\right)\beta - \int d\mathbf{r}'\, \beta(\mathbf{r}') \left.\frac{\delta P(\mathbf{r}')}{\delta \bar{u}(\mathbf{r})}\right|_{\bar{\rho}} \nabla'\cdot\mathbf{U}(\mathbf{r}')$$

$$= -\int d\mathbf{r}' \left.\frac{\delta \beta(\mathbf{r}')}{\delta \bar{u}(\mathbf{r})}\right|_{\bar{\rho}} \left[\nabla'\cdot\mathbf{q}^*(\mathbf{r}') + t_{ij}^*(\mathbf{r}') \frac{\partial U_i(\mathbf{r}')}{\partial r_j'}\right]$$

$$\left(\frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla\right)\zeta + \int d\mathbf{r}'\, \beta(\mathbf{r}') \left.\frac{\delta P(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})}\right|_{\bar{u}} \nabla'\cdot\mathbf{U}(\mathbf{r}')$$

$$= +\int d\mathbf{r}' \left.\frac{\delta \beta(\mathbf{r}')}{\delta \bar{\rho}(\mathbf{r})}\right|_{\bar{u}} \left[\nabla'\cdot\mathbf{q}^*(\mathbf{r}') + t_{ij}^*(\mathbf{r}') \frac{\partial U_i(\mathbf{r}')}{\partial r_j'}\right] \tag{D.11}$$

Here $\mathbf{q}^*(\mathbf{r}, t)$ and $t_{ij}^*(\mathbf{r}, t)$ are, respectively, the irreversible heat flux and momentum flux,

$$\gamma^{0*} \equiv A(\mathbf{U})\gamma^* = (0, q_i^*, t_{ij}^*) \tag{D.12}$$

Equations (D.11) are spatially nonlocal in two regards, first because q_i^* and t_{ij}^* are nonlocal functionals of the thermodynamic parameters, and second due to the explicit nonlocality of the forms (D.11). The latter is due to the definition of the y_α and may be eliminated by choosing instead as thermodynamic parameters $\bar{\rho}$, $\bar{u}$, and $\mathbf{U}$. Then Eqs. (D.11) take the more familiar form

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla\cdot\bar{\rho}\mathbf{U} = 0$$

$$\left(\frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla\right)\bar{u} + h\nabla\cdot\mathbf{U} = -\nabla\cdot\mathbf{q}^* - t_{ij}^* \frac{\partial U_i}{\partial r_j}$$

$$\left(\frac{\partial}{\partial t} + \mathbf{U}\cdot\nabla\right) U_i + \frac{1}{\bar{\rho}} \frac{\partial P}{\partial r_i} = -\frac{1}{\bar{\rho}} \frac{\partial t_{ij}^*}{\partial r_j} \tag{D.13}$$

The irreversible fluxes $\gamma_{\alpha i}^{0*}$ may be obtained in a similar way using Eqs. (D.12) and (2.20) with the result

$$\begin{aligned}
q_i{}^*(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}' \Big\{ &\langle [e^{L(t-\tau)} q_i{}'(\mathbf{r}, t)] q_j{}'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial \beta(\mathbf{r}', \tau)}{\partial r_j{}'} \\
&- \langle [e^{L(t-\tau)} q_i{}'(\mathbf{r}, t)] \sigma'_{jk}(\mathbf{r}', \tau); \tau \rangle_L \beta(\mathbf{r}', \tau) \frac{\partial U_j(\mathbf{r}', \tau)}{\partial r_k{}'} \\
&- \langle [e^{L(t-\tau)} q_i{}'(\mathbf{r}, t)] \xi'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial q_j{}^*}{\partial r_j{}'} (\mathbf{r}', \tau) \\
&+ \langle [e^{L(t-\tau)} q_i{}'(\mathbf{r}, t)] g_j{}'(\mathbf{r}', \tau); \tau \rangle_L \frac{\beta(\mathbf{r}', \tau)}{\bar{\rho}(\mathbf{r}', \tau)} \frac{\partial t_{jk}^*(\mathbf{r}', \tau)}{\partial r_k{}'} \Big\}
\end{aligned} \tag{D.14}$$

$$\begin{aligned}
t_{ij}^*(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}' \Big\{ &\langle [e^{L(t-\tau)} \sigma'_{ij}(\mathbf{r}, t)] q_k{}'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial \beta(\mathbf{r}', \tau)}{\partial r_k{}'} \\
&- \langle [e^{L(t-\tau)} \sigma'_{ij}(\mathbf{r}, t)] \sigma'_{kl}(\mathbf{r}', \tau); \tau \rangle_L \beta(\mathbf{r}', \tau) \frac{\partial U_l(\mathbf{r}', \tau)}{\partial r_k{}'} \\
&- \langle [e^{L(t-\tau)} \sigma'_{ij}(\mathbf{r}, t)] \xi'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial q_k{}^*(\mathbf{r}', \tau)}{\partial r_k{}'} \\
&+ \langle [e^{L(t-\tau)} \sigma'_{ij}(\mathbf{r}, t)] g_l{}'(\mathbf{r}', \tau); \tau \rangle_L \frac{\beta(\mathbf{r}', \tau)}{\bar{\rho}(\mathbf{r}', \tau)} \frac{\partial t_{lk}^*(\mathbf{r}', \tau)}{\partial r_k{}'} \Big\}
\end{aligned} \tag{D.15}$$

The phase functions q_i, σ_{ij}, and ξ are defined as

$$q_i(\mathbf{r}, t) = s_i(\mathbf{r}) - \int d\mathbf{r}' \frac{\beta(r)}{\bar{\rho}(r)} \langle g_i(\mathbf{r}) s_j(\mathbf{r}') \rangle_{L_0} g_j(\mathbf{r}')$$

$$\begin{aligned}
\sigma_{ij}(\mathbf{r}, t) = t_{ij}(\mathbf{r}) - \delta_{ij} \Big[P(\mathbf{r}) &+ \int d\mathbf{r}' \Big\{ \tilde{\rho}(\mathbf{r}') \frac{\delta P(\mathbf{r})}{\delta \bar{\rho}(\mathbf{r}')} \\
&+ \tilde{\epsilon}(\mathbf{r}') \frac{\delta P(\mathbf{r})}{\delta \bar{u}(\mathbf{r}')} \Big\} \Big] + t_{ij}^*(r) \frac{1}{\beta(\mathbf{r})} \xi(\mathbf{r})
\end{aligned}$$

$$\xi(\mathbf{r}, t) = \int d\mathbf{r}' \left[\frac{\delta \beta(\mathbf{r}, t)}{\delta \bar{\rho}(\mathbf{r}', t)} \bigg|_{\bar{u}} \tilde{\rho}(\mathbf{r}', t) + \frac{\delta \beta(\mathbf{r}, t)}{\delta \bar{u}(\mathbf{r}', t)} \bigg|_{\bar{\rho}} \tilde{\epsilon}(\mathbf{r}', t) \right] \tag{D.16}$$

The results (D.11) or (D.13), and (D.14) and (D.15) represent the exact macroscopic conservation laws with constitutive equations for the dynamics of β, ζ, and $\mathbf{U}$ (or any other set of thermodynamic variables). With the pseudo-Galilean transformation (D.1), Eqs. (D.14) and (D.15) may be shown to be independent of the flow velocity. The results are clearly quite formal, but serve as a suitable basis for the investigation of linear and nonlinear hydrodynamic equations, and associated transport coefficients. It may be noted that for practical purposes, the functional derivatives occurring in these equations are short-ranged functions of $\mathbf{r}$ and $\mathbf{r}'$ (of the order of the force range), so they are well approximated by a delta function times the associated usual thermodynamic derivative. Such an approximation fails, however, for systems with Coulomb forces or near a critical point.

The irreversible fluxes in the projection operator formalism, Eq. (2.31), may be analyzed in a similar way to give the equivalent results,

$$\begin{aligned} q_i^*(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}' \biggl\{ &\langle [U(t, \tau) q_i'(\mathbf{r}, t)] q_j'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial \beta(\mathbf{r}', \tau)}{\partial r_j'} \\ &- \langle [U(t, \tau) q_i'(\mathbf{r}, t)] \hat{\sigma}_{jk}'(\mathbf{r}', \tau); \tau \rangle_L \beta(\mathbf{r}', \tau) \frac{\partial U_j(\mathbf{r}', \tau)}{\partial r_k'} \biggr\} \end{aligned} \tag{D.17}$$

$$\begin{aligned} t_{ij}^*(\mathbf{r}, t) = \int_0^t d\tau \int d\mathbf{r}' \biggl\{ &\langle [U(t, \tau) \hat{\sigma}_{ij}'(\mathbf{r}, t)] q_k'(\mathbf{r}', \tau); \tau \rangle_L \frac{\partial \beta(\mathbf{r}', \tau)}{\partial r_k'} \\ &- \langle [U(t, \tau) \hat{\sigma}_{ij}'(\mathbf{r}, t)] \hat{\sigma}_{kl}'(\mathbf{r}', \tau); \tau \rangle_L \beta(\mathbf{r}', \tau) \frac{\partial U_k(\mathbf{r}', \tau)}{\partial r_l'} \biggr\} \end{aligned} \tag{D.18}$$

Here $\hat{\sigma}_{ij}$ is equal to σ_{ij}, defined in Eq. (D.16), with $t_{ij}^* = 0$. These equations are formally simpler than Eqs. (D.14) and (D.15), since no explicit reference is made to the irreversible fluxes on the right sides of (D.17) and (D.18).

For the special case of steady shear flow considered in Section 4, these results simplify considerably. In particular, Eq. (D.15) becomes

$$t_{ij}^*(\mathbf{r}, t) = -\int_0^t d\tau \int d\mathbf{r}' \, \langle [e^{L(t-\tau)} \sigma_{ij}'(\mathbf{r}, t)] \sigma_{kl}'(\mathbf{r}', \tau); \tau \rangle_L \beta(\mathbf{r}', \tau) \, \partial U_k(\mathbf{r}', \tau) / \partial r_l' \tag{D.19}$$

Also, since $\partial U_k / \partial r_l = a_{kl}$ is nondiagonal, σ_{kl}' may be replaced with

$$\sigma_{kl}' \rightarrow t_{kl}' + \left.\frac{\partial \beta}{\partial \bar{u}}\right|_{\bar{\rho}} \left(\tilde{\epsilon}' - \left.\frac{\partial \zeta}{\partial \beta}\right|_{\bar{\rho}} \tilde{\rho}' \right) t_{kl}^* \tag{D.20}$$

to give

$$
\begin{aligned}
t^*_{ij}(\mathbf{r}, t) = {} & -a_{kl} \int_0^t d\tau \, \langle [e^{L(t-\tau)} t'_{ij}] \beta(\tau) T'_{kl};\, \tau \rangle_L \\
& - a_{kl} \int_0^t d\tau \, \langle [e^{L(t-\tau)} t'_{ij}] \left. \frac{\partial \beta(\tau)}{\partial \bar{u}(\tau)} \right|_{\bar{\rho}} [(H' - \langle H';\, \tau \rangle_L) \\
& - \left. \frac{\partial \zeta(\tau)}{\partial \beta(\tau)} \right|_{\bar{\rho}} m(N' - \langle N;\, \tau \rangle_L)];\, \tau \rangle_L t^*_{kl}(\tau) \\
\equiv {} & -a_{kl} \int_0^t d\tau \, [G_{ijkl}(t, \tau) + H_{ij}(t, \tau) t^*_{kl}(\tau)] \qquad \text{(D.21)}
\end{aligned}
$$

which is the result, Eqs. (4.11) and (4.12), used in Section 4.

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