

# Molecular Derivation of the Hydrodynamic Equations for a Binary Fluid

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In this paper, the hydrodynamic equations and the associated transport coefficients are derived for a simple binary fluid from molecular considerations. This is a generalization of the methods of Felderhof and Oppenheim and of Selwyn to multicomponent systems. A linear response formalism is used to describe the relaxation of the binary system from an initial nonequilibrium state. Explicit molecular expressions are given for the transport coefficients in terms of time correlation functions of generalized current densities. These densities have the useful property of not containing a conserved part. The correlation functions are then related to a set of phenomenological coefficients in the theory of nonequilibrium thermodynamics. This explicit identification enables one to relate the correlation functions to experimentally measured transport coefficients.

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**KEY WORDS:** Binary mixture; hydrodynamics; nonequilibrium statistical mechanics.

## 1. INTRODUCTION

In this paper, we will derive from molecular considerations the linearized hydrodynamic equations for a two-component simple fluid and obtain expressions for the transport coefficients in terms of time correlation functions. The derivation will be an extension to a binary system of the ideas set forth by Felderhof and Oppenheim<sup>(1)</sup> and Selwyn<sup>(2)</sup> for a one-component fluid. The macroscopic equations will be derived via Kubo's formalism<sup>(3)</sup> for calculating the linear response of the system to external forces. We will also relate the transport coefficients appearing in our equations to the phenomenological coefficients contained in expressions connecting the fluxes and forces in the theory of nonequilibrium thermodynamics.<sup>(4-6)</sup>

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The microscopic state of a classical system of  $N$  particles with no internal degrees of freedom is completely given by specifying the positions and momenta of all the particles at time  $t$ , i.e., by specifying the system phase point  $\mathbf{X}(t) = \{\mathbf{r}^N(t), \mathbf{p}^N(t)\}$ . On the other hand, the macroscopic description of the state of the system is given by a relatively small number of observables which are ensemble averages of a set of dynamical variables  $A_\alpha(\mathbf{X}(t); \mathbf{r}, t)$ , functions of the phase point and possibly depending explicitly on space and time. These observables, or macroscopic variables, have the property that their space variations are small and their time variations are slow compared to molecular quantities.

We shall define the correlation function  $\Psi_{\alpha\beta}$  of two dynamical variables  $A_\alpha$  and  $A_\beta$  for a canonical ensemble by

$$\Psi_{\alpha\beta}(\mathbf{r}, t; \mathbf{r}', t') = \left\langle [A_\alpha(\mathbf{X}(t); \mathbf{r}, t) - \langle A_\alpha(\mathbf{X}(t); \mathbf{r}, t) \rangle] \right. \\ \left. \times [A_\beta(\mathbf{X}(t'); \mathbf{r}', t') - \langle A_\beta(\mathbf{X}(t'); \mathbf{r}', t') \rangle] \right\rangle \quad (1)$$

The dynamical variables are assumed not to depend explicitly on time, so that their time dependence is given by

$$\dot{A} = -\{H_0, A\} \equiv iLA \quad (2)$$

where  $H_0$  is the time-independent Hamiltonian for the system,  $\{\}$  is the Poisson bracket, and the second equality defines the Liouville operator  $L$ . From (2), we may deduce that the correlation function depends only upon the time difference  $t - t'$ .

We will restrict our considerations to large fluidlike systems which have no external fields and in which we may neglect boundary terms. Consequently, the correlation functions will depend upon  $|\mathbf{r} - \mathbf{r}'|$  only. This will be rigorously true in the thermodynamic limit (number of particles  $N \rightarrow \infty$ , volume  $V \rightarrow \infty$ , density  $N/V = \text{const}$ ).

Since in a spatially homogeneous system the equilibrium averages of the dynamical variables must be independent of both  $\mathbf{r}$  and  $t$ ,

$$\Psi_{\alpha\beta}(\mathbf{r} - \mathbf{r}', t - t') = \left\langle [A_\alpha(\mathbf{X}(t); \mathbf{r}) - \langle A_\alpha(\mathbf{X}) \rangle] [A_\beta(\mathbf{X}(t'); \mathbf{r}') - \langle A_\beta(\mathbf{X}) \rangle] \right\rangle \quad (3)$$

The time and space transforms of (3) will be denoted by

$$\hat{\Psi}_{\alpha\beta}(\mathbf{k}, \omega) = \int_0^\infty dt e^{i\omega t} \int_V d\mathbf{r} [\exp(-i\mathbf{k} \cdot \mathbf{r})] \Psi_{\alpha\beta}(\mathbf{r}, t) \\ = (1/V) \langle A_{\alpha, \mathbf{k}\omega} A_{\beta, -\mathbf{k}} \rangle, \quad \mathbf{k} \neq 0 \quad (4)$$

from which we see that, for  $\mathbf{k} \neq 0$ ,

$$\langle A_{\alpha, \mathbf{k}\omega} A_{\beta, -\mathbf{k}} \rangle = \langle \delta A_{\alpha, \mathbf{k}\omega} \delta A_{\beta, -\mathbf{k}} \rangle, \quad \mathbf{k} \neq 0 \quad (5)$$

where the space and time Fourier transforms are defined by

$$A_{\alpha, \mathbf{k}\omega} = \int_0^\infty dt e^{i\omega t} \int_V d\mathbf{r} [\exp(i\mathbf{k} \cdot \mathbf{r})] A_\alpha(\mathbf{X}(t), \mathbf{r})$$

and

$$A_{\alpha, \mathbf{k}} = \int_V d\mathbf{r} [\exp(i\mathbf{k} \cdot \mathbf{r})] A_{\alpha}(\mathbf{X}(0), \mathbf{r})$$

The fluctuation in the dynamical variable is defined by

$$\delta A_{\alpha}(\mathbf{X}(t); \mathbf{r}) = A_{\alpha}(\mathbf{X}(t); \mathbf{r}) - \langle A_{\alpha}(\mathbf{X}(t); \mathbf{r}) \rangle \quad (6)$$

## 2. LINEAR RESPONSE THEORY AND THE HYDRODYNAMIC MATRIX

We shall now give a brief summary of the pertinent features of Kubo's formalism<sup>(3)</sup> for deriving hydrodynamic equations. We *assume* that there exists a set of macroscopic variables which completely describe the state of the fluid. Each macroscopic variable is associated with a dynamical variable  $A_{\alpha}(\mathbf{X}(t); \mathbf{r}, t)$ . Our purpose is to obtain the equations that describe the decay of the macroscopic variables from an initial nonequilibrium state. We postulate the existence of space- and time-dependent forces which couple to these dynamical variables to establish the initial nonequilibrium state.

If the forces are abruptly turned off, the system will decay to equilibrium. The forces will be eliminated during the derivation and do not appear in the final expressions. Thus, the forces serve as mathematical constructs and may or may not exist in reality. The fictitious forces are a useful device *provided* the correct macroscopic variables are known for the system.

The time-dependent Hamiltonian for the system is given by

$$H(t) = H_0 - \int_V A_{\alpha}(\mathbf{X}; \mathbf{r}) F_{\alpha}(\mathbf{r}, t) d\mathbf{r} \quad (7)$$

where each force  $F_{\alpha}$  couples to the dynamical variable  $A_{\alpha}$ . We will use Einstein's convention of summation over repeated indices. Here,  $H_0$  is the equilibrium Hamiltonian appearing in the canonical distribution function

$$f_0 = e^{-\beta H_0} / \int d\mathbf{X} e^{-\beta H_0} \quad (8)$$

The time-dependent distribution function for the system obeys the Liouville equation

$$\partial f(t) / \partial t = \{H(t), f(t)\} \quad (9)$$

In Kubo's theory,<sup>(3)</sup> one computes the linear response of the system to the forces. To terms linear in the forces, the formal solution is given by

$$\Delta f(t) \equiv f(t) - f_0 \quad (10)$$

$$\Delta f(t) = \int_V d\mathbf{r}' \int_{-\infty}^t dt' \{ \exp[-iL(t-t')] \} [f_0, A_{\alpha}(\mathbf{X}; \mathbf{r}')] F_{\alpha}(\mathbf{r}', t') \quad (11)$$

where the Liouville operator is defined by (2) and we have asserted that the system is in equilibrium at  $t = -\infty$ .

As noted, the macroscopic observables are given by ensemble averages of the dynamical variables. We will want to consider the deviations of the macroscopic variables from their equilibrium values; thus, the appropriate ensemble will be  $\mathcal{A}f(t)$  and we make the identification

$$\begin{aligned} a_\alpha(\mathbf{r}, t) &= \langle A_\alpha(\mathbf{X}; \mathbf{r}) \rangle_{\mathcal{A}f(t)} \\ &= \int d\mathbf{r}^N d\mathbf{p}^N \int_V d\mathbf{r}' \int_{-\infty}^t dt' A_\alpha(\mathbf{X}; \mathbf{r}) \{\exp[-iL(t-t')]\} \\ &\quad \times [f_0, A_\beta(\mathbf{X}; \mathbf{r}')] F_\beta(\mathbf{r}', t') \end{aligned} \quad (12)$$

With use of the properties (2) and (8), we have the more useful form

$$a_\alpha(\mathbf{r}, t) = (1/k_B T) \int_V d\mathbf{r}' \int_{-\infty}^t dt' \langle A_\alpha(\mathbf{X}(t-t'); \mathbf{r}) A_\beta(\mathbf{X}, \mathbf{r}') \rangle F_\beta(\mathbf{r}', t') \quad (13)$$

where the angular brackets denote an equilibrium canonical ensemble average and  $k_B$  is Boltzmann's constant. We may take the Fourier space transform

$$a_\alpha(\mathbf{k}, t) = \int_V d\mathbf{r} [\exp(-i\mathbf{k} \cdot \mathbf{r})] a_\alpha(\mathbf{r}, t)$$

which yields

$$a_\alpha(\mathbf{k}, t) = (1/k_B TV) \int_{-\infty}^t dt' \langle A_{\alpha, \mathbf{k}}(\mathbf{X}(t-t')) A_{\beta, -\mathbf{k}}(\mathbf{X}) \rangle F_\beta(\mathbf{k}, t'), \quad \mathbf{k} \neq 0 \quad (14)$$

Since we will be interested in describing the relaxation of the system for  $t > 0$  from a nonequilibrium state, we shall assume the following time dependence for the forces:

$$\begin{aligned} F_\alpha(\mathbf{k}, t) &= F_\alpha(\mathbf{k}) e^{\epsilon t} \quad (\epsilon \rightarrow 0_+), \quad t \leq 0 \\ &= 0, \quad t > 0 \end{aligned} \quad (15)$$

This time dependence implies that the forces are "turned on" adiabatically from  $t = -\infty$  and "turned off" abruptly at  $t = 0$ , with the net result that the system is in thermal equilibrium with respect to the external forces at  $t = 0_-$ .

With the explicit form of  $F_\alpha$  given by (15) and the assertion that the fluctuations become uncorrelated as  $t \rightarrow \infty$ , we may obtain from (14) the two equations

$$\hat{a}_\alpha(\mathbf{k}, \omega)_+ = (1/k_B TV) \langle A_{\alpha, \mathbf{k}\omega} A_{\beta, -\mathbf{k}} \rangle F_\beta(\mathbf{k}), \quad (\mathbf{k} \neq 0) \quad (16)$$

and

$$a_\alpha(\mathbf{k}, t = 0) = (1/k_B TV) \langle A_{\alpha, \mathbf{k}} A_{\beta, -\mathbf{k}} \rangle F_\beta(\mathbf{k}), \quad (\mathbf{k} \neq 0) \quad (17)$$

where in (16) we have taken the half-sided time transform

$$\hat{a}_\alpha(\mathbf{k}, \omega)_+ = \int_0^\infty dt e^{i\omega t} a_\alpha(\mathbf{k}, t) \quad (18)$$

By eliminating the force between (16) and (17), we have the result

$$\hat{a}_\alpha(\mathbf{k}, \omega)_+ = \langle A_{\alpha, \mathbf{k}\omega} A_{\beta, -\mathbf{k}} \rangle \langle A_{\beta, \mathbf{k}} A_{\gamma, -\mathbf{k}} \rangle^{-1} a_\gamma(\mathbf{k}, t = 0), \quad (\mathbf{k} \neq 0) \quad (19)$$

We remark in passing that when we solve for  $F_\alpha(\mathbf{k})$  in (17), we are in effect fulfilling our assertion that the forces determine the initial nonequilibrium state of the system, which is described by  $a_\alpha(\mathbf{k}, t = 0)$ . In (19),

$$\langle A_{\beta, \mathbf{k}} A_{\alpha, -\mathbf{k}} \rangle \equiv [\langle \mathbf{A}_\mathbf{k} \mathbf{A}_{-\mathbf{k}} \rangle^{-1}]_{\beta\alpha}$$

and we have a coupled set of equations for the time dependence of the macroscopic variables in terms of their initial values, derived under the assumption of linear response.

We know the hydrodynamic equations have the form

$$\partial a_\alpha(\mathbf{k}, t) / \partial t = -M_{\alpha\beta}(\mathbf{k}) a_\beta(\mathbf{k}, t) \quad (20)$$

or in transform language

$$\hat{a}_\alpha(\mathbf{k}, \omega)_+ = \{1/[-i\omega + M(\mathbf{k})]\}_{\alpha\beta} a_\beta(\mathbf{k}, t = 0) \quad (21)$$

Linear response theory predicts that (19) and (21) are identical. The time behavior of the average of the microscopic fluctuations in the macroscopic variables in the equilibrium ensemble, at least in the limit of small  $\mathbf{k}$  and  $\omega$ , correctly describes the time relaxation of the variables from an initial nonequilibrium state. This is equivalent to assuming Onsager's postulate.<sup>(7)</sup> Thus, we may define a new matrix  $M(\mathbf{k}, \omega)$  by the equation

$$\langle A_{\alpha, \mathbf{k}\omega} A_{\beta, -\mathbf{k}} \rangle \langle A_{\beta, \mathbf{k}} A_{\gamma, -\mathbf{k}} \rangle^{-1} = \{1/[-i\omega + M(\mathbf{k}, \omega)]\}_{\alpha\gamma}, \quad \mathbf{k} \neq 0 \quad (22)$$

We may then demonstrate that, up to some order in  $\mathbf{k}$ ,  $M(\mathbf{k}, \omega)$  will be independent of  $\omega$  and equal to  $M(\mathbf{k})$  in Eqs. (20) and (21).

At this point, we make a simplification in notation. The correlation functions  $\langle A_\alpha A_\beta \rangle$  are elements of matrices, as is the hydrodynamic matrix  $M_{\alpha\beta}(\mathbf{k})$ . We now drop the explicit notation of repeated indices and indicate matrix multiplication by the contraction symbol ( $\cdot$ ). Furthermore, in the following, the vector notation of  $\mathbf{k}$  will be suppressed when  $k$  appears as an argument of a function. Thus, (22) becomes

$$\langle A_{\mathbf{k}\omega} A_{-\mathbf{k}} \rangle \cdot \langle A_{\mathbf{k}} A_{-\mathbf{k}} \rangle^{-1} = \{1/[-i\omega + M(k, \omega)]\}, \quad \mathbf{k} \neq 0 \quad (23)$$

This equation is the starting point for deriving the hydrodynamic matrix  $M(k)$ .

### 3. DERIVATION OF THE HYDRODYNAMIC MATRIX IN TERMS OF CORRELATION FUNCTIONS

To derive the hydrodynamic matrix  $M(k)$  up to the Navier-Stokes approximation  $O(k^2)$ , we will use a  $k$ -ordering procedure first suggested by Van Leeuwen<sup>(8)</sup> and used by Selwyn in deriving the generalized matrix  $M(k, \omega)$ .<sup>(2)</sup>

In this method, one begins by rewriting (23) in the form

$$-i\omega\langle A_{k\omega}A_{-k}\rangle + M(k, \omega) \cdot \langle A_{k\omega}A_{-k}\rangle = \langle A_kA_{-k}\rangle, \quad \mathbf{k} \neq 0 \quad (24)$$

and makes use of the property

$$\langle \dot{A}_k(t)A_{-k}\rangle = -\langle A_k(t)\dot{A}_{-k}\rangle \quad (25)$$

to obtain

$$\langle \dot{A}_kA_{-k}\rangle - \langle \dot{A}_{k\omega}\dot{A}_{-k}\rangle + M(k, \omega) \cdot \langle A_kA_{-k}\rangle - M(k, \omega) \cdot \langle A_{k\omega}\dot{A}_{-k}\rangle = 0, \quad \mathbf{k} \neq 0 \quad (26)$$

It may be demonstrated for the dynamical variables under consideration that their time dependence may be expressed in the form

$$\dot{A}_{\alpha, \mathbf{k}} = -i\mathbf{k} \cdot \mathbf{j}_{\alpha, \mathbf{k}} \quad (27)$$

where  $\mathbf{j}_{\alpha, \mathbf{k}}$  is the current corresponding to  $A_\alpha$ . With this fact, (26) becomes

$$\begin{aligned} -i\mathbf{k} \cdot \langle \mathbf{j}_kA_{-k}\rangle + i\mathbf{k} \cdot \langle \mathbf{j}_{k\omega}\mathbf{j}_{-k}\rangle \cdot i\mathbf{k} - M(k, \omega) \cdot \langle A_{k\omega}\mathbf{j}_{-k}\rangle \cdot i\mathbf{k} \\ = -M(k, \omega) \cdot \langle A_kA_{-k}\rangle, \quad \mathbf{k} \neq 0 \end{aligned} \quad (28)$$

Attention will be restricted to the regime where  $k$  is small but finite. We assert that the correlation functions may be expanded in the series

$$\langle A_kA_{-k}\rangle = \langle A_kA_{-k}\rangle^{(0)} + \langle A_kA_{-k}\rangle^{(1)} + \dots \quad (29)$$

where the  $k$  dependence is denoted by the superscript, i.e., the term  $\langle A_kA_{-k}\rangle^{(n)} = \alpha k^n$ , where  $\alpha$  is independent of  $k$ . We assume a similar expansion for  $M(k, \omega)$  and the frequency-dependent correlation functions. When these expansions are inserted in (28) and powers in  $k$  collected, one finds immediately  $M^{(0)}(k, \omega) = 0$ ,

$$-i\mathbf{k} \cdot \langle \mathbf{j}_kA_{-k}\rangle^{(0)} = -M^{(1)}(k, \omega) \cdot \langle A_kA_{-k}\rangle^{(0)} \quad (30)$$

and

$$\begin{aligned} -i\mathbf{k} \cdot \langle \mathbf{j}_kA_{-k}\rangle^{(1)} + i\mathbf{k} \cdot \langle \mathbf{j}_{k\omega}\mathbf{j}_{-k}\rangle^{(0)} \cdot i\mathbf{k} - M^{(1)}(k, \omega) \cdot \langle A_{k\omega}\mathbf{j}_{-k}\rangle^{(0)} \cdot i\mathbf{k} \\ = -M^{(1)}(k, \omega) \cdot \langle A_kA_{-k}\rangle^{(1)} - M^{(2)}(k, \omega) \cdot \langle A_kA_{-k}\rangle^{(0)} \end{aligned} \quad (31)$$

It remains to solve for  $M^{(1)}(k, \omega)$ , the Euler matrix, and  $M^{(2)}(k, \omega)$  in (30) and (31). To do this, we must now give explicit information about the system and the dynamical variables we are considering.

#### 4. DYNAMICAL VARIABLES FOR A BINARY SYSTEM

We consider a binary fluid composed of  $N$  particles of type I and  $M$  particles of type II. The particles interact with each other through three potentials:  $\phi_{ij}^1$  denotes

interactions between two type I particles,  $\phi_{\alpha\beta}^{\text{II}}$  denotes interactions between two type II particles, and  $\phi_{i\alpha}^{\text{III}}$  denotes interactions between one particle of type I and one particle of type II.

The potential  $\phi_{ij}$  is a function of  $|\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$  only. The masses of type I and type II particles are denoted respectively by  $m_{\text{I}}$  and  $m_{\text{II}}$ .

The dynamical variables corresponding to the macroscopic variables are given as follows in their space Fourier representation.

(1) Total mass density:

$$\rho_k = \sum_{j=1}^N m_{\text{I}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha=1}^M m_{\text{II}} \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \quad (32)$$

(2) Total momentum density:

$$\begin{aligned} \mathbf{g}_k &= \sum_{j=1}^N \mathbf{P}_j \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha=1}^M \mathbf{P}_\alpha \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\ &= g_k^{\text{I}} + g_k^{\text{II}} \end{aligned} \quad (33)$$

(3) Total energy density:

$$\begin{aligned} e_k &= \sum_{j=1}^N (P_j^2/2m_{\text{I}}) \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha=1}^M (P_\alpha^2/2m_{\text{II}}) \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\ &+ \frac{1}{2} \sum_{j \neq s}^N \sum_{j \neq s}^N \phi_{js}^{\text{I}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \frac{1}{2} \sum_{\alpha \neq \beta}^M \sum_{\alpha \neq \beta}^M \phi_{\alpha\beta}^{\text{II}} \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\ &+ \frac{1}{2} \sum_j^N \sum_\alpha^M \phi_{j\alpha}^{\text{III}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \frac{1}{2} \sum_j^N \sum_\alpha^M \phi_{j\alpha}^{\text{III}} \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \end{aligned} \quad (34)$$

(4) Mass density of component I:

$$\rho_k^{\text{I}} = \sum_{j=1}^N m_{\text{I}} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \quad (35)$$

The time derivatives can be written in the form of (27). With the definitions

$$\begin{bmatrix} \dot{\rho}_k \\ \dot{\mathbf{g}}_k \\ \dot{e}_k \\ \dot{\rho}_k^{\text{I}} \end{bmatrix} = -i\mathbf{k} \cdot \begin{bmatrix} \mathbf{g}_k \\ \mathbf{T}_k \\ \mathbf{j}_k^e \\ \mathbf{g}_k^{\text{I}} \end{bmatrix} \quad (36)$$

the currents in their Fourier representation are as follows.

- (1) Mass current = momentum density,  $\mathbf{g}_k$  .  
 (2) Momentum current = stress tensor,  $\mathbf{T}_k$  :

$$\begin{aligned}
 \mathbf{T}_k = & \sum_{j=1}^N (\mathbf{P}_j \mathbf{P}_j / m_I) \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha=1}^M (\mathbf{P}_\alpha \mathbf{P}_\alpha / m_{II}) \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\
 & - \frac{1}{2} \sum_{j \neq s}^N \sum_{s=1}^N \mathbf{r}_{sj} \nabla_s \phi_{js}^I (\exp -i\mathbf{k} \cdot \mathbf{r}_j) (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{sj} + \dots) \\
 & - \frac{1}{2} \sum_{\alpha \neq \beta}^M \sum_{\beta=1}^M \mathbf{r}_{\beta\alpha} \nabla_\beta \phi_{\alpha\beta}^{II} (\exp -i\mathbf{k} \cdot \mathbf{r}_\alpha) (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{\beta\alpha} + \dots) \\
 & - \sum_j^N \sum_\alpha^M \mathbf{r}_{\alpha j} \nabla_\alpha \phi_{j\alpha}^{III} (\exp -i\mathbf{k} \cdot \mathbf{r}_j) (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{\alpha j} + \dots) \quad (37)
 \end{aligned}$$

- (3) Energy current  $\mathbf{j}_k^e$  :

$$\begin{aligned}
 \mathbf{j}_k^e = & \sum_{j=1}^N (\mathbf{P}_j P_j^2 / 2m_I^2) \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha=1}^M (\mathbf{P}_\alpha P_\alpha^2 / 2m_{II}^2) \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\
 & + \sum_{j \neq s}^N \sum_{s=1}^N (\mathbf{P}_j / 2m_I) \phi_{js}^I \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_{\alpha \neq \beta}^M \sum_{\beta=1}^M (\mathbf{P}_\alpha / 2m_{II}) \phi_{\alpha\beta}^{II} \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\
 & + \sum_j^N \sum_\alpha^M (\mathbf{P}_j / 2m_I) \phi_{j\alpha}^{III} \exp(-i\mathbf{k} \cdot \mathbf{r}_j) + \sum_j^N \sum_\alpha^M (\mathbf{P}_\alpha / 2m_{II}) \phi_{j\alpha}^{III} \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\
 & - \sum_{j \neq s}^N \sum_{s=1}^N \mathbf{r}_{sj} (\mathbf{P}_s / 2m_I) \cdot \nabla_s \phi_{js}^I (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{sj} + \dots) \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \\
 & - \sum_{\alpha \neq \beta}^M \sum_{\beta=1}^M \mathbf{r}_{\beta\alpha} (\mathbf{P}_\beta / 2m_{II}) \cdot \nabla_\beta \phi_{\alpha\beta}^{II} (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{\beta\alpha} + \dots) \exp(-i\mathbf{k} \cdot \mathbf{r}_\alpha) \\
 & + \sum_j^N \sum_\alpha^M \mathbf{r}_{\alpha j} [(\mathbf{P}_\alpha / 2m_{II}) \cdot \nabla_\alpha \phi_{j\alpha}^{III} - (\mathbf{P}_j / 2m_I) \cdot \nabla_j \phi_{j\alpha}^{III}] (1 - \frac{1}{2} i\mathbf{k} \cdot \mathbf{r}_{\alpha j} + \dots) \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \quad (38)
 \end{aligned}$$

- (4) Mass current of component I = momentum density of component I,  $\mathbf{g}_k^I$ :

$$\mathbf{g}_k^I = \sum_{j=1}^N \mathbf{P}_j \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \quad (39)$$

## 5. DERIVATION OF THE EULER MATRIX $M^{(1)}(k)$

The Euler matrix is obtained from (30). We see immediately that it is independent of  $\omega$  and may be written as

$$M^{(1)}(k) = i\mathbf{k} \cdot \langle \mathbf{j}_k A_{-k} \rangle^{(0)} \cdot \langle A_k A_{-k} \rangle^{(0)-1} \quad (40)$$



Consider each matrix on the r.h.s. of (40) separately. For our set of dynamical variables, we have

$$\langle A_k A_{-k} \rangle = \begin{bmatrix} \langle \rho_k \rho_{-k} \rangle & \mathbf{0} & \langle \rho_k e_{-k} \rangle & \langle \rho_k \rho_{-k}^I \rangle \\ \mathbf{0} & \langle \mathbf{g}_k \mathbf{g}_{-k} \rangle & \mathbf{0} & \mathbf{0} \\ \langle e_k \rho_{-k} \rangle & \mathbf{0} & \langle e_k e_{-k} \rangle & \langle e_k \rho_{-k}^I \rangle \\ \langle \rho_k^I \rho_{-k} \rangle & \mathbf{0} & \langle \rho_k^I e_{-k} \rangle & \langle \rho_k^I \rho_{-k}^I \rangle \end{bmatrix} \quad (41)$$

where because of symmetry  $\mathbf{g}_k$  is uncoupled from the other variables. This matrix may easily be shown to be symmetric.

In order to proceed, we must calculate

$$(1/V) \langle A_{\alpha,k} A_{\beta,-k} \rangle^{(0)} = \lim_{k \rightarrow 0} (1/V) \langle A_{\alpha,k} A_{\beta,-k} \rangle \quad (42)$$

The bracket average means a canonical average in the thermodynamic limit. Thus, (42) states that the thermodynamic limit is taken before  $k$  goes to zero. For small  $k$ ,  $k < \Omega^{-1/3}$ , where  $\Omega^{1/3}$  is a macroscopic length, the average will become independent of  $\mathbf{k}$  and equal to the average of the fluctuations of  $A_\alpha$  and  $A_\beta$  in a grand canonical ensemble in a volume  $\Omega$

$$\lim_{k \rightarrow 0} (1/V) \langle A_{\alpha,k} A_{\beta,-k} \rangle = (1/\Omega) \overline{\Delta A_\alpha \Delta A_\beta}^\Omega \quad (43)$$

The pertinent ensemble is the grand canonical ensemble as a consequence of the order of taking the limits. We compute the fluctuations of the macroscopic variables in the grand canonical ensemble in order to obtain their relationship to thermodynamic derivatives. The density fluctuations are

$$(1/k_B T V) \langle \rho_k \rho_{-k} \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta M \Delta M}^\Omega = \rho (\partial \rho / \partial p)_{T,\mu} \quad (44)$$

where  $M$  is the total mass in  $\Omega$  and we have defined

$$\rho = M/\Omega \quad \text{and} \quad \mu = [(\mu_I/m_I) - (\mu_{II}/m_{II})];$$

$$(1/k_B T V) \langle \rho_k \rho_{-k}^I \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta M \Delta c}^\Omega = \rho (\partial \rho^I / \partial p)_{T,\mu} \quad (45)$$

where  $\rho_I = c_I/\Omega$  and  $c$  is the total mass of component I in the volume  $\Omega$ ; and

$$(1/k_B T V) \langle \rho_k^I \rho_{-k}^I \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta c \Delta c}^\Omega = (\partial \rho^I / \partial \mu)_{T,\rho} + \rho^I (\partial \rho^I / \partial p)_{T,\mu} \quad (46)$$

The energy fluctuations are

$$(1/k_B T V) \langle \rho_k e_{-k} \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta M \Delta E}^\Omega = \rho (\partial e / \partial p)_{T,\mu} \quad (47)$$

where  $E$  is the total energy in the volume  $\Omega$  and  $e = E/\Omega$ ; and

$$(1/k_B TV) \langle \rho_k^1 e_{-k} \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta E \Delta c}^\Omega = (\partial e / \partial \mu)_{p,T} + \rho^1 (\partial e / \partial p)_{T,\mu} \quad (48)$$

The energy-energy fluctuation may easily be shown to be

$$(1/k_B TV) \langle e_k e_{-k} \rangle^{(0)} = (1/\Omega k_B T) \overline{\Delta E \Delta E}^\Omega = T(\partial e / \partial T)_{\mu,\mu^1} + \mu^1 \rho (\partial e / \partial p)_{T,\mu} \\ + \mu [(\partial e / \partial \mu)_{p,T} + (\partial e / \partial p)_{T,\mu} \rho^1] \quad (49)$$

where  $\mu^1 = [\mu_{II}/m_{II}]$ . Extensive use of thermodynamic identities shows

$$(1/\Omega k_B T) \overline{\Delta E \Delta E}^\Omega = (\partial e / \partial \rho^1)_{T,p} (\partial e / \partial \mu)_{T,p} + \rho (\partial e / \partial \rho)_{T,\mu} (\partial e / \partial p)_{T,\mu} + T(\partial e / \partial T)_{p,p^1} \quad (50)$$

Alternatively, these fluctuations may be evaluated by the method of thermodynamic fluctuation theory described by Landau and Lifshitz,<sup>(1)</sup> although care must be taken when using this procedure.<sup>3</sup>

Finally, we may compute the total momentum correlation function from (33),

$$(1/k_B TV) \langle \mathbf{g}_k \mathbf{g}_{-k} \rangle = \rho \mathbf{l} \quad (51)$$

which is independent of  $\mathbf{k}$  and where  $\mathbf{l}$  is the unit dyadic.

This completes the calculation of the  $\langle A_k A_{-k} \rangle^{(0)}$  matrix, which is summarized in matrix form as follows:

$$\frac{1}{k_B TV} \langle A_k A_{-k} \rangle^{(0)} = \begin{bmatrix} \rho \left( \frac{\partial \rho}{\partial p} \right)_{T,\mu} & \mathbf{0} & \rho \left( \frac{\partial e}{\partial p} \right)_{T,\mu} & \rho \left( \frac{\partial \rho^1}{\partial p} \right)_{T,\mu} \\ \mathbf{0} & \rho \mathbf{l} & \mathbf{0} & \mathbf{0} \\ \rho \left( \frac{\partial e}{\partial p} \right)_{T,\mu} & \mathbf{0} & \left[ \left( \frac{\partial e}{\partial \rho^1} \right)_{T,p} \left( \frac{\partial e}{\partial \mu} \right)_{T,p} + \left( \frac{\partial e}{\partial \rho} \right)_{T,\mu} \left( \frac{\partial e}{\partial p} \right)_{T,\mu} \right. \\ & & \left. + T \left( \frac{\partial e}{\partial T} \right)_{p,p^1} \right] & \left( \frac{\partial e}{\partial \mu} \right)_{T,p} + \rho^1 \left( \frac{\partial e}{\partial p} \right)_{T,\mu} \\ \left( \frac{\partial \rho^1}{\partial p} \right)_{T,\mu} & \mathbf{0} & \left( \frac{\partial e}{\partial \mu} \right)_{T,p} + \rho^1 \left( \frac{\partial e}{\partial p} \right)_{T,\mu} & \rho^1 \left( \frac{\partial \rho^1}{\partial p} \right)_{T,\mu} + \left( \frac{\partial \rho^1}{\partial \mu} \right)_{T,p} \end{bmatrix} \quad (52)$$

What we require in solving for  $M^{(1)}(k)$  in (40) is the inverse matrix  $[\langle A_k A_{-k} \rangle^{(0)}]^{-1}$ . This may be obtained from (52) in several standard ways, all of which require tedious calculations.

<sup>3</sup> When using thermodynamic fluctuation theory, a reference extensive variable must be held fixed. Fixed volume corresponds to the grand canonical ensemble, while fixed total mass or number corresponds to the isothermal-isobaric ensemble. Total energy fluctuations are not the same for these two cases (for one- or two-component systems). However, fluctuations in energy density (energy per unit volume) are the same in the two ensembles. These statements may easily be verified for a one-component system.

The final result is given by the following matrix:

$$\begin{aligned}
 & \left[ \frac{1}{k_B TV} \langle A_k A_{-k} \rangle^{(0)} \right]^{-1} \\
 = & \begin{bmatrix} -\frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e\rho^I} \left( \frac{\partial e}{\partial \rho} \right)_{\rho^I T} + \frac{1}{\rho} \left( \frac{\partial p}{\partial \rho} \right)_{T\mu} & 0 & \frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e\rho^I} & -\frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \left( \frac{\partial e}{\partial \rho} \right)_{\rho^I T} + \left( \frac{\partial \mu}{\partial \rho} \right)_{T\rho^I} \\ & - \left( \frac{\partial \rho^I}{\partial \rho} \right)_{T\mu} \left( \frac{\partial \mu}{\partial \rho} \right)_{T\rho^I} & & & \\ & 0 & \frac{1}{\rho} & 0 & 0 \\ & \frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e\rho^I} & 0 & \frac{1}{T} \left( \frac{\partial T}{\partial e} \right)_{\rho\rho^I} & \frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \\ -\frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \left( \frac{\partial e}{\partial \rho} \right)_{\rho^I T} + \left( \frac{\partial \mu}{\partial \rho} \right)_{T\rho^I} & 0 & \frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{e\rho} & -\frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \left( \frac{\partial e}{\partial \rho^I} \right)_{\rho T} + \left( \frac{\partial \mu}{\partial \rho^I} \right)_{T\rho} \end{bmatrix} \quad (53)
 \end{aligned}$$

We now wish to compute the matrix  $\langle j_k A_{-k} \rangle^{(0)}$  which appears in (40) to complete the task of solving for  $M^{(1)}(k)$ . For our set of dynamical variables, we may immediately write down

$$\begin{aligned}
 & (1/k_B TV) i\mathbf{k} \cdot \langle \mathbf{j}_k A_{-k} \rangle^{(0)} \\
 = & (1/k_B TV) i\mathbf{k} \cdot \begin{bmatrix} 0 & \langle \mathbf{g}_k \mathbf{g}_{-k} \rangle^{(0)} & 0 & 0 \\ \langle \tau_k \rho_{-k} \rangle^{(0)} & 0 & \langle \tau_k e_{-k} \rangle^{(0)} & \langle \tau_k \rho^I_{-k} \rangle^{(0)} \\ 0 & \langle \mathbf{j}_k^e \mathbf{g}_{-k} \rangle^{(0)} & 0 & 0 \\ 0 & \langle \mathbf{g}_k^I \mathbf{g}_{-k} \rangle^{(0)} & 0 & 0 \end{bmatrix} \quad (54)
 \end{aligned}$$

where the zeros are again due to symmetry in momentum in the correlation functions. It is easy to demonstrate that the matrix is symmetric. In order to do this, we make use of the properties (27) and (25) and also note that the elements of the matrix in (54) are even in  $k$ . Thus, we may write the successive equations for the  $\alpha\beta$  component of the matrix in (54):

$$\begin{aligned}
 i\mathbf{k} \cdot \langle \mathbf{j}_{k\alpha} A_{-k,\beta} \rangle^{(0)} &= -\langle \dot{A}_{k,\alpha} A_{-k,\beta} \rangle^{(0)} = \langle A_{k,\alpha} \dot{A}_{-k,\beta} \rangle^{(0)} \\
 &= \langle A_{k,\alpha} \mathbf{j}_{-k,\beta} \rangle^{(0)} \cdot i\mathbf{k} = \langle A_{-k,\alpha} \mathbf{j}_{k,\beta} \rangle^{(0)} \cdot i\mathbf{k} \\
 &= i\mathbf{k} \cdot \langle \mathbf{j}_{k,\beta} A_{-k,\alpha} \rangle^{(0)} \quad (55)
 \end{aligned}$$

which establishes the result. Therefore, we have

$$\begin{aligned}
 (1/k_B TV) i\mathbf{k} \cdot \langle \tau_k \rho_{-k} \rangle^{(0)} &= (1/k_B TV) i\mathbf{k} \cdot \langle \mathbf{g}_k \mathbf{g}_{-k} \rangle^{(0)} \\
 &= i\mathbf{k} \rho \quad (56)
 \end{aligned}$$

and

$$\begin{aligned}
 (1/k_B TV) i\mathbf{k} \cdot \langle \tau_k \rho^I_{-k} \rangle^{(0)} &= (1/k_B TV) i\mathbf{k} \cdot \langle \mathbf{g}_k^I \mathbf{g}_{-k} \rangle^{(0)} \\
 &= i\mathbf{k} \rho^I \quad (57)
 \end{aligned}$$

Now it is possible to show that<sup>(1)</sup>

$$\frac{1}{V} i\mathbf{k} \cdot \langle \tau_{\mathbf{k}} e_{-\mathbf{k}} \rangle^{(0)} \cdot i\mathbf{k} = i\mathbf{k} \cdot \left[ \lim_{k \rightarrow 0} \frac{-1}{V} \frac{\langle e_{\mathbf{k}} \mathbf{k} \cdot \tau_{-\mathbf{k}} \cdot \mathbf{k} \rangle}{k^2} \right] \cdot i\mathbf{k} \quad (58)$$

Since the pressure  $p$  is proportional to minus the diagonal elements of the stress tensor, the term in brackets is  $\overline{\Delta E \Delta p}^{\Omega}$ , so that we have the result

$$\begin{aligned} (1/k_B T V) i\mathbf{k} \cdot \langle \tau_{\mathbf{k}} e_{-\mathbf{k}} \rangle^{(0)} &= i\mathbf{k} (1/k_B T) \overline{\Delta E \Delta p}^{\Omega} \\ &= i\mathbf{k}(e + p) \end{aligned} \quad (59)$$

Thus, we have

$$\begin{aligned} (1/k_B T V) i\mathbf{k} \cdot \langle \tau_{\mathbf{k}} e_{-\mathbf{k}} \rangle^{(0)} &= (1/k_B T V) i\mathbf{k} \cdot \langle \mathbf{j}_{\mathbf{k}}^e \mathbf{g}_{-\mathbf{k}} \rangle^{(0)} \\ &= i\mathbf{k}(e + p) \end{aligned} \quad (60)$$

Therefore, we may write out the matrix (54) as

$$(1/k_B T V) i\mathbf{k} \cdot \langle \mathbf{j}_{\mathbf{k}} A_{-\mathbf{k}} \rangle^{(0)} = \begin{bmatrix} 0 & i\mathbf{k}\rho & 0 & 0 \\ i\mathbf{k}\rho & 0 & i\mathbf{k}(e + p) & i\mathbf{k}\rho^I \\ 0 & i\mathbf{k}(e + p) & 0 & 0 \\ 0 & i\mathbf{k}\rho^I & 0 & 0 \end{bmatrix} \quad (61)$$

We may now compute  $M^{(1)}(k)$  as given in (40) by using our expressions in (53) and (61). The final result is given by

$$M^{(1)}(k) = \begin{bmatrix} 0 & i\mathbf{k} & 0 & 0 \\ i\mathbf{k}(\partial p / \partial \rho)_{e, \rho^I} & 0 & i\mathbf{k}(\partial p / \partial e)_{\rho, \rho^I} & i\mathbf{k}(\partial p / \partial \rho^I)_{\rho e} \\ 0 & i\mathbf{k}(e + p)/\rho & 0 & 0 \\ 0 & i\mathbf{k}(\rho^I/\rho) & 0 & 0 \end{bmatrix} \quad (62)$$

The macroscopic equations as defined by (20) which correspond to the  $M^{(1)}(k)$  matrix in (62) are the Euler equations for an ideal fluid, i.e., no dissipative forces in the fluid. These equations may be written in space and time language as

$$\begin{aligned} \partial \bar{\rho} / \partial t &= -\nabla \cdot \bar{\mathbf{g}} \\ \partial \bar{\mathbf{g}} / \partial t &= -(\partial p / \partial \rho)_{e, \rho^I} \nabla \bar{\rho} - (\partial p / \partial e)_{\rho, \rho^I} \nabla \bar{e} - (\partial p / \partial \rho^I)_{\rho e} \nabla \bar{\rho}^I \\ \partial \bar{e} / \partial t &= -[(e + p)/\rho] \nabla \cdot \bar{\mathbf{g}} \\ \partial \bar{\rho}^I / \partial t &= -(\rho^I/\rho) \nabla \cdot \bar{\mathbf{g}} \end{aligned} \quad (63)$$

where the macroscopic variables  $a_{\alpha}(\mathbf{r}, t)$  are simply identified as  $\bar{a}$  and the space and time dependence has been suppressed. This concludes our derivation of the Euler matrix. We now want to derive a similar expression for  $M^{(2)}(k, \omega)$  from the expressions in (31).

## 6. DERIVATION OF THE NAVIER-STOKES MATRIX

The matrix  $M^{(2)}(k)$  will be obtained from (31). The first step is to note that for  $l$  a nonnegative integer,

$$\langle A_k A_{-k} \rangle^{(2l+1)} = \langle j_k A_{-k} \rangle^{(2l+1)} = 0 \quad (64)$$

The terms in (41) and (54) involve even-rank tensors only. Since the averages of even-rank tensors are even functions of  $k$ , the odd-order components of the average of an even-rank tensor are zero.

It is convenient to introduce<sup>(10)</sup> the “dissipative currents” defined by the relations

$$ik \cdot \mathbf{H}_k = ik \cdot \mathbf{j}_k - M^{(1)}(k) A_k \quad (65)$$

$$ik \cdot \mathbf{H}_{k\omega} = ik \cdot \mathbf{j}_{k\omega} - M^{(1)}(k) A_{k\omega} \quad (66)$$

By using our expressions (36) and (62), we have the following explicit form for  $\mathbf{H}_k$ :

$$\begin{bmatrix} \mathbf{H}_k^\rho \\ \mathbf{H}_k^g \\ \mathbf{j}_k^q \\ \mathbf{H}_k^{\rho I} \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \tau_k - [(\partial p / \partial \rho)_{e\rho I} \rho_k + (\partial p / \partial e)_{\rho\rho I} e_k + (\partial p / \partial \rho^I)_{\rho e} \rho_k^I] \\ \mathbf{j}_k^e - [(e + p) / \rho] \bar{\mathbf{g}}_k \\ \bar{\mathbf{g}}_k^I - (\rho^I / \rho) \bar{\mathbf{g}}_k \end{bmatrix} \quad (67)$$

where we have identified the “dissipative energy current” as the heat flux  $\mathbf{j}_k^q$ .

Note that we may rewrite (30) as

$$0 = ik \cdot \langle \mathbf{H}_k A_{-k} \rangle^{(0)} \quad (68)$$

By using (64) and (67), we may now rewrite (31) in the more compact form

$$M^{(2)}(k, \omega) \cdot \langle A_k A_{-k} \rangle^{(0)} = -ik \cdot \langle \mathbf{H}_{k\omega} \mathbf{j}_{-k} \rangle^{(0)} \cdot ik \quad (69)$$

It will prove convenient to express (69) in a more symmetric form.

Performing an integration by parts, using (68), (25), and (27), we may write the successive equations

$$\begin{aligned} -(i\omega) ik \cdot \langle \mathbf{H}_{k\omega} A_{-k} \rangle^{(0)} &= ik \cdot \langle \mathbf{H}_k A_{-k} \rangle^{(0)} + ik \cdot \langle \dot{\mathbf{H}}_{k\omega} A_{-k} \rangle^{(0)} \\ &= ik \cdot \langle \dot{\mathbf{H}}_{k\omega} A_{-k} \rangle^{(0)} \\ &= -ik \cdot \langle \mathbf{H}_{k\omega} \dot{A}_{-k} \rangle^{(0)} \\ &= -ik \cdot \langle \mathbf{H}_{k\omega} ik \cdot \mathbf{j}_{-k} \rangle^{(0)} = 0 \end{aligned}$$

or

$$ik \cdot \langle \mathbf{H}_{k\omega} A_{-k} \rangle^{(0)} = 0 \quad (70)$$

This implies that the “dissipative currents” contain no conserved parts, i.e., they are orthogonal to the conserved variables of the system. From the definition of the  $H_{k\omega}$ , we see that this orthogonality property is not possessed by the  $j_{k\omega}$ . We will shortly make use of this important distinction, first pointed out by Mori,<sup>(2,10)</sup> in our definitions of the transport coefficients.

From (65), we may write

$$\begin{aligned} i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega} \mathbf{H}_{-k} \rangle^{(0)} \cdot i\mathbf{k} &= i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega} \mathbf{j}_{-k} \rangle^{(0)} \cdot i\mathbf{k} - i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega} A_{-k} \rangle^{(0)} \cdot M^{(1)T}(k) \\ &= i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega} \mathbf{j}_{-k} \rangle^{(0)} \cdot i\mathbf{k} \end{aligned} \quad (71)$$

where we have noted in  $M^{(1)T}(k)$  the fact that we are really dealing with matrices of the correlation functions and need the transpose of  $M^{(1)}(k)$ . Thus, using (71), we may rewrite (69) in the desired form

$$M^{(2)}(k, \omega) \cdot \langle A_k A_{-k} \rangle^{(0)} = -i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega} \mathbf{H}_{-k} \rangle^{(0)} \cdot i\mathbf{k} \quad (72)$$

We note that

$$\mathbf{H}_{k\omega}^\rho = \mathbf{H}_k^\rho = \mathbf{0} \quad (73)$$

and, due to symmetry,

$$\begin{aligned} \langle \mathbf{H}_{k\omega}^g \mathbf{j}_{-k}^a \rangle^{(0)} &= \langle \mathbf{H}_{k\omega}^g \mathbf{H}_{-k}^{\rho I} \rangle^{(0)} = \langle \mathbf{j}_{k\omega}^a \mathbf{H}_{-k}^g \rangle^{(0)} \\ &= \langle \mathbf{H}_{k\omega}^{\rho I} \mathbf{H}_{-k}^g \rangle^{(0)} = 0 \end{aligned} \quad (74)$$

We may demonstrate that

$$i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega}^{\rho I} \mathbf{j}_{-k}^a \rangle^{(0)} \cdot i\mathbf{k} = i\mathbf{k} \cdot \langle \mathbf{j}_{k\omega}^a \mathbf{H}_{-k}^{\rho I} \rangle^{(0)} \cdot i\mathbf{k} \quad (75)$$

from space invariance and symmetry properties of the correlation functions in time, Eq. (25).

Standard thermodynamic manipulations may be used to show the following equalities:

$$T \left( \frac{\partial \mu / T}{\partial e} \right)_{\rho, \mathbf{I}} = \frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \quad (76)$$

$$T \left( \frac{\partial \mu / T}{\partial \rho} \right)_{\rho, \mathbf{I}} = -\frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \left( \frac{\partial e}{\partial \rho} \right)_{\rho^I T} + \left( \frac{\partial \mu}{\partial \rho} \right)_{\rho^I T} \quad (77)$$

$$T \left( \frac{\partial \mu / T}{\partial \rho^I} \right)_{\rho e} = -\frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} \left( \frac{\partial e}{\partial \rho^I} \right)_{\rho T} + \left( \frac{\partial \mu}{\partial \rho^I} \right)_{\rho T} \quad (78)$$

These equalities are used to transform the bottom row in the  $[\langle A_k A_{-k} \rangle^{(0)}]^{-1}$

matrix (53). Thus, we may now write down the result for  $M^{(2)}(k, \omega)$ , obtained by solving (72) with the information in (73)–(75), as follows:

$$\begin{aligned}
 & -(k_B T V) M^{(2)}(k, \omega) \\
 &= \left[ \begin{array}{cccc}
 0 & 0 & 0 & 0 \\
 0 & \frac{1}{\rho} i\mathbf{k} \cdot \mathfrak{B}_1 \cdot i\mathbf{k} & 0 & 0 \\
 \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_2 \cdot i\mathbf{k} \right. & 0 & \left[ \frac{1}{T} \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_2 \cdot i\mathbf{k} \right. & \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} i\mathbf{k} \cdot \mathfrak{B}_2 \cdot i\mathbf{k} \right. \\
 \left. + T \left( \frac{\partial \mu^I / T}{\partial \rho} \right)_{e, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right] & \left. + T \left( \frac{\partial \mu^I / T}{\partial e} \right)_{\rho, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right] & \left. + T \left( \frac{\partial \mu^I / T}{\partial \rho^I} \right)_{\rho e} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right] \\
 \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right. & 0 & \left[ \frac{1}{T} \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right. & \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho^I} \right)_{\rho e} i\mathbf{k} \cdot \mathfrak{B}_3 \cdot i\mathbf{k} \right. \\
 \left. + T \left( \frac{\partial \mu^I / T}{\partial \rho} \right)_{e, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_4 \cdot i\mathbf{k} \right] & \left. + T \left( \frac{\partial \mu^I / T}{\partial e} \right)_{\rho, \rho^I} i\mathbf{k} \cdot \mathfrak{B}_4 \cdot i\mathbf{k} \right] & \left. + T \left( \frac{\partial \mu^I / T}{\partial \rho^I} \right)_{\rho e} i\mathbf{k} \cdot \mathfrak{B}_4 \cdot i\mathbf{k} \right]
 \end{array} \right] \quad (79)
 \end{aligned}$$

where

$$\begin{aligned}
 \mathfrak{B}_1 &= \langle \mathbf{H}_{k\omega}^g \mathbf{H}_{-k}^g \rangle^{(0)}, & \mathfrak{B}_2 &= \langle \mathbf{j}_{k\omega}^a \mathbf{j}_{-k}^a \rangle^{(0)} \\
 \mathfrak{B}_3 &= \langle \mathbf{j}_{k\omega}^a \mathbf{H}_{-k}^{\rho^I} \rangle^{(0)}, & \mathfrak{B}_4 &= \langle \mathbf{H}_{k\omega}^{\rho^I} \mathbf{H}_{-k}^{\rho^I} \rangle^{(0)}
 \end{aligned}$$

We see from (79) or (72) that the frequency dependence of the  $M^{(2)}(k, \omega)$  matrix enters through the current-current correlation functions only. We assert that the time-dependent correlation functions  $\langle \mathbf{H}_k(t) \mathbf{H}_{-k} \rangle$  decay on a molecular time scale which is much more rapid than the hydrodynamic time scale of interest, i.e.,  $\tau_m \ll \tau_h$ . Since we will be interested in frequencies  $O(1/\tau_h)$ , the frequency dependence of the  $\langle H_{k\omega} H_{-k} \rangle$ , which enters on a scale  $\omega \tau_m \ll 1$ , is not of interest. This permits us to take the limit  $\omega \rightarrow 0$  in the  $\langle H_{k\omega} H_{-k} \rangle$  without any danger of losing information which is of interest in the hydrodynamic regime. Thus, the frequency dependence of  $M^{(2)}(k, \omega)$  may be ignored for our considerations and  $M^{(2)}(k, \omega)$  becomes simply the frequency-independent matrix  $M^{(2)}(k)$ . As we mentioned earlier, the  $H_{k\omega}$  have no conserved parts. Therefore, in the limit  $\omega \rightarrow 0$ , the  $\langle H_{k\omega} H_{-k} \rangle^{(0)}$  contain no divergent terms. This is not true for  $\langle j_{k\omega} j_{-k} \rangle^{(0)}$  since in the limit  $\omega \rightarrow 0$  the correlation functions contain an imaginary divergent part which goes as  $1/i\omega$ . This can be seen from (70) if we replace  $H$  by  $j$  in the equations. This divergent part would necessitate taking the real part of  $\langle j_{k\omega} j_{-k} \rangle^{(0)}$  to obtain a well-behaved limit. This problem is completely avoided by considering the “dissipative-current” correlation functions.

The correlation functions in (79) may be simplified to expressions involving only the components of the currents.

If one takes into account the isotropy of the fluid and chooses  $\mathbf{k}$  to lie along the  $\hat{\epsilon}_3$  direction, it is easy to show that

$$i\mathbf{k} \cdot \langle \mathbf{H}_{k,\omega}^g \mathbf{H}_{-k}^g \rangle^{(0)} \cdot i\mathbf{k} = -k^2 \{ \langle \tau_{k\omega,31} \tau_{-k,13} \rangle^{(0)} [\hat{\epsilon}_1 \hat{\epsilon}_1 + \hat{\epsilon}_2 \hat{\epsilon}_2] + \langle H_{k\omega,33}^g H_{-k,33}^g \rangle^{(0)} \hat{\epsilon}_3 \hat{\epsilon}_3 \}$$

$$i\mathbf{k} \cdot \langle \mathbf{j}_{k\omega}^g \mathbf{H}_{-k}^I \rangle^{(0)} \cdot i\mathbf{k} = -k^2 \langle j_{k\omega,3}^g H_{-k,3}^I \rangle^{(0)}$$

$$i\mathbf{k} \cdot \langle \mathbf{H}_{k\omega}^I \mathbf{H}_{-k}^I \rangle^{(0)} \cdot i\mathbf{k} = -k^2 \langle H_{k\omega,3}^I H_{-k,3}^I \rangle^{(0)}$$

and finally

$$i\mathbf{k} \cdot \langle \mathbf{j}_{k\omega}^g \mathbf{j}_{-k}^g \rangle^{(0)} \cdot i\mathbf{k} = -k^2 \langle j_{k\omega,3}^g j_{-k,3}^g \rangle^{(0)}$$

Here,  $(\hat{\epsilon}_1, \hat{\epsilon}_2, \hat{\epsilon}_3)$  are Cartesian unit vectors. Using these results, we will define the transport coefficients by the following expressions.

The coefficient of shear viscosity  $\eta$  is defined by

$$\eta = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/k_B TV) \langle \tau_{k\omega,31} \tau_{-k,13} \rangle \quad (80)$$

The coefficient of longitudinal viscosity  $\delta$ , which defines the coefficient of bulk viscosity  $\zeta$ , is defined by

$$\begin{aligned} \delta &= \left(\frac{4}{3}\eta + \zeta\right)/\rho \\ &= \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/\rho)(1/k_B TV) \langle H_{k\omega,33}^g H_{-k,33}^g \rangle \end{aligned} \quad (81)$$

The coefficient of thermal conductivity  $\kappa$  is defined by

$$\kappa = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/T)(1/k_B TV) \langle j_{k\omega,3}^g j_{-k,3}^g \rangle \quad (82)$$

The coefficient of thermal diffusion  $D_T$  is given by

$$D_T = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/k_B TV) \langle j_{k\omega,3}^g H_{-k,3}^I \rangle \quad (83)$$

The coefficient of diffusion  $D$  is given by

$$D = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/k_B TV) \langle H_{k\omega,3}^I H_{-k,3}^I \rangle \quad (84)$$

The explicit form of these transport coefficients may be obtained from the expressions for the dissipative currents in (67). As an example, the diffusion coefficient is given by

$$D = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} (1/k_B TV) \int_0^\infty dt e^{i\omega t} \langle \{ \mathbf{g}_{k,3}^I(t) - (\rho^I/\rho) \mathbf{g}_{k,3}(t) \} \{ \mathbf{g}_{-k,3}^I - (\rho^I/\rho) \mathbf{g}_{-k,3} \} \rangle$$

where  $\mathbf{g}_{k,3}^I$  and  $\mathbf{g}_{k,3}$  are defined by (33). Note that the limits in these time correlation function formulas must be taken in the order indicated. In the next section, we will relate the transport coefficients  $\kappa$ ,  $D_T$ , and  $D$  to the phenomenological equations of



nonequilibrium thermodynamics. It follows from these definitions that  $M^{(2)}(k)$  [Eq. (79)] takes the form of (85).

The total hydrodynamic matrix up to  $O(k^2)$ , the Navier–Stokes matrix, is given by adding  $M^{(1)}(k)$  and  $M^{(2)}(k)$ . Thus, the set of hydrodynamic equations implied by (62) and (85) is obtained by inverting (21). The result is

$$\begin{aligned}
 \partial \bar{\rho} / \partial t &= -\nabla \cdot \bar{\mathbf{g}} \\
 \partial \bar{\mathbf{g}} / \partial t &= -(\partial p / \partial \rho)_{e, \rho^1} \nabla \bar{\rho} - (\partial p / \partial e)_{\rho, \rho^1} \nabla \bar{e} - (\partial p / \partial \rho^1)_{e, e} \nabla \bar{\rho}^1 \\
 &\quad + (\eta / \rho) \nabla^2 \bar{\mathbf{g}} + [(\frac{1}{3}\eta + \zeta) / \rho] \nabla \nabla \cdot \bar{\mathbf{g}} \\
 M^{(2)}(k) &= \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & k^2 \left[ \frac{\eta}{\rho} (\hat{\epsilon}_1 \hat{\epsilon}_1 + \hat{\epsilon}_2 \hat{\epsilon}_2) + \delta \hat{\epsilon}_3 \hat{\epsilon}_3 \right] & 0 & 0 \\ k^2 \left[ \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^1} \kappa \right. & & k^2 \left[ \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^1} \kappa \right. & k^2 \left[ \left( \frac{\partial T}{\partial \rho^1} \right)_{e, e} \kappa \right. \\ + T \left( \frac{\partial \mu / T}{\partial \rho} \right)_{e, \rho^1} D_T & & + T \left( \frac{\partial \mu / T}{\partial e} \right)_{\rho, \rho^1} D_T & + T \left( \frac{\partial \mu / T}{\partial \rho^1} \right)_{e, e} D_T \\ k^2 \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^1} D_T \right. & & k^2 \left[ \frac{1}{T} \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^1} D_T \right. & k^2 \left[ \frac{1}{T} \left( \frac{\partial T}{\partial \rho^1} \right)_{e, e} D_T \right. \\ + T \left( \frac{\partial \mu / T}{\partial \rho} \right)_{e, \rho^1} D & & + T \left( \frac{\partial \mu / T}{\partial e} \right)_{\rho, \rho^1} D & + T \left( \frac{\partial \mu / T}{\partial \rho^1} \right)_{e, e} D \end{bmatrix} \\
 &\hspace{15em} (85)
 \end{aligned}$$

$$\begin{aligned}
 \frac{\partial \bar{e}}{\partial t} &= -\left( \frac{e+p}{\rho} \right) \nabla \cdot \bar{\mathbf{g}} + \kappa \left[ \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^1} \nabla^2 \bar{\rho} + \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^1} \nabla^2 \bar{e} + \left( \frac{\partial T}{\partial \rho^1} \right)_{e, e} \nabla^2 \bar{\rho}^1 \right] \\
 &\quad + D_T \left[ T \left( \frac{\partial \mu / T}{\partial \rho} \right)_{e, \rho^1} \nabla^2 \bar{\rho} + T \left( \frac{\partial \mu / T}{\partial e} \right)_{\rho, \rho^1} \nabla^2 \bar{e} + T \left( \frac{\partial \mu / T}{\partial \rho^1} \right)_{e, e} \nabla^2 \bar{\rho}^1 \right] \\
 \frac{\partial \bar{\rho}^1}{\partial t} &= -\frac{\rho^1}{\rho} \nabla \cdot \bar{\mathbf{g}} + \frac{D_T}{T} \left[ \left( \frac{\partial T}{\partial \rho} \right)_{e, \rho^1} \nabla^2 \bar{\rho} + \left( \frac{\partial T}{\partial e} \right)_{\rho, \rho^1} \nabla^2 \bar{e} + \left( \frac{\partial T}{\partial \rho^1} \right)_{e, e} \nabla^2 \bar{\rho}^1 \right] \\
 &\quad + D \left[ T \left( \frac{\partial \mu / T}{\partial \rho} \right)_{e, \rho^1} \nabla^2 \bar{\rho} + T \left( \frac{\partial \mu / T}{\partial e} \right)_{\rho, \rho^1} \nabla^2 \bar{e} + T \left( \frac{\partial \mu / T}{\partial \rho^1} \right)_{e, e} \nabla^2 \bar{\rho}^1 \right] \\
 &\hspace{15em} (86)
 \end{aligned}$$

These equations may be contracted and written in more conventional notation as

$$\begin{aligned}
 \partial \bar{\rho} / \partial t &= -\nabla \cdot \bar{\mathbf{g}} \\
 \partial \bar{\mathbf{g}} / \partial t &= -\nabla p + (\eta / \rho) \nabla^2 \bar{\mathbf{g}} + [(\frac{1}{3}\eta + \zeta) / \rho] \nabla \nabla \cdot \bar{\mathbf{g}} \\
 \partial \bar{e} / \partial t &= -[(e+p) / \rho] \nabla \cdot \bar{\mathbf{g}} + \kappa \nabla^2 T + D_T T \nabla^2 [\mu / T] \\
 \partial \bar{\rho}^1 / \partial t &= -(\rho^1 / \rho) \nabla \cdot \bar{\mathbf{g}} + (D_T / T) \nabla^2 T + T D \nabla^2 [\mu / T] \\
 &\hspace{15em} (86')
 \end{aligned}$$

This completes the derivation of the hydrodynamic equations up to the Navier-Stokes approximation and identification of the transport coefficients in terms of time correlation functions.

The remaining task is to show how these particular transport coefficients are related to phenomenological coefficients in the theory of nonequilibrium thermodynamics.

## 7. COMPARISON OF $\kappa$ , $D_T$ , AND $D$ WITH THE PHENOMENOLOGICAL COEFFICIENTS

In this section, we will discuss the various definitions for the transport coefficients as they appear in Refs. [4-6]. Then we will be able to relate our definitions for  $\kappa$ ,  $D_T$ , and  $D$  to a specific thermodynamic system.

In the following, we will make extensive use of certain thermodynamic fluxes which must be carefully defined:

(1) The diffusion current density  $\mathbf{j}_i$  of component  $i$  relative to the local center of mass is defined by

$$\mathbf{j}_i = \rho_i(\mathbf{V}_i - \mathbf{V}) \quad (87)$$

where  $\mathbf{V}$  is the velocity of the local center of mass;  $\mathbf{V}_i$  is the local mean velocity of component  $i$ , i.e., the average velocity, with respect to the external coordinate system, of the molecules of  $i$  in a microscopically large, macroscopically small region of the fluid; and  $\rho_i$  is the local mass density of component  $i$ .

(2) The energy current consists of two parts, the convection current, due to the bulk flow of the fluid, and the conduction current  $\mathbf{j}_E$ , which includes energy flow due to diffusion and to heat flow. There exists no unique way of dividing  $\mathbf{j}_E$  into a diffusive term and pure conduction or heat flow term. Consequently, we define two heat fluxes in the following way.

(3) The conduction current for pure heat flow  $\mathbf{q}'$  based on the first law of thermodynamics is defined by the relation

$$\mathbf{j}_E = \mathbf{q}' + \sum_i \bar{E}_i \mathbf{j}_i \quad (88)$$

where  $\bar{E}_i$  is the partial specific energy  $\bar{E}_i = (\partial E / \partial m_i)_{T, p, m_j}$ , and the sum is over all components of the system.

(4) The heat flux  $\mathbf{q}$  based on the second law is defined by the relation

$$\mathbf{j}_E = \mathbf{q} + \sum_i \bar{H}_i \mathbf{j}_i \quad (89)$$

where  $\bar{H}_i$  is the partial specific enthalpy. At this point, we should point out that  $\mathbf{j}_E$  in (88) corresponds to  $\mathbf{J}_q$ , the "heat flux," in deGroot and Mazur's<sup>(5)</sup> (DM) notation, and  $\mathbf{q}$  in (89) corresponds in DM notation to  $\mathbf{J}_{q'}$ , the "reduced heat flow." The heat flow usually measured experimentally<sup>(5)</sup> is  $\mathbf{j}_E$ . Comparing the notation above with

that of Landau and Lifshitz<sup>(6)</sup> (LL), we see that  $\mathbf{j}_E$  corresponds to  $\mathbf{q}$ (LL) and  $\mathbf{j}_I$  corresponds to  $\mathbf{i}$ (LL), where  $\mathbf{j}_I$  is the diffusion current density for component I. Due to this confusing multiplicity of notation, we will stick to the quantities introduced above.

We may write the phenomenological equations for the fluxes in a binary system in the form

$$-\mathbf{j}_E = L_{00}\nabla(\ln T) + L_{01}T\nabla(\mu/T) \quad (90)$$

$$-\mathbf{j}_I = L_{01}\nabla(\ln T) + L_{11}T\nabla(\mu/T) \quad (91)$$

where  $\mu$  is the chemical potential defined in Section 5. In the appendix, the hydrodynamic equations (86') are written in terms of  $\mathbf{j}_E$  and  $\mathbf{j}_I$ . A comparison of (A.7) and (A.8) with (90) and (91) leads to the following relations between our transport coefficients and the phenomenological coefficients:

$$\kappa = L_{00}/T \quad (92)$$

$$D_T = L_{01} \quad (93)$$

$$D = L_{11} \quad (94)$$

The barycentric diffusion coefficient  $D_B$  is determined at constant  $T$  and  $p$ . From (91), we see that  $D_B$  is

$$D_B = D(\partial\mu/\partial\rho^I)_{T,p}$$

The situation with regard to thermal conduction is more complicated since the heat flux may be measured in a variety of ways, e.g., relative to uniform  $\rho^I$  or relative to  $\mathbf{j}_I = 0$ . If the "thermal conductivity"  $\lambda_T$  is defined by

$$-\mathbf{j}_E = \lambda_T \nabla T, \quad \mathbf{j}_I = 0,$$

we find

$$\lambda_T = \kappa - (D_T^2/TD)$$

The different possible conventions are discussed in beautiful detail by deGroot and Mazur.<sup>(5)</sup>

## 8. DISCUSSION

In this paper, we have derived the hydrodynamic equations for a binary system from molecular considerations and found expressions for the associated transport coefficients. The method used here has been used previously to derive equations for a simple one-component fluid.<sup>(1,2)</sup> The present work has shown the generality of the method in that it may be extended to a multicomponent system.

Explicit expressions have been given for the transport coefficients in terms of time-dependent correlation functions of generalized current densities. We have related these correlation functions to a set of phenomenological coefficients in the

theory of nonequilibrium thermodynamics. This explicit identification enables one to relate the correlation functions to experimentally measured transport coefficients.

Our results may be compared most easily with those of Mori<sup>(10)</sup> and Kirkwood and Fitts.<sup>(11)</sup> Kirkwood and Fitts' results are derived for the set of phenomenological equations we considered in (90) and (91). Their expressions for the time-dependent correlation functions for  $\kappa$ ,  $D$ , and  $D_T$  agree in form with ours except that they have not gone to Fourier  $k$ -space. Our results also agree with an early quantum mechanical derivation by Mori.<sup>(12)</sup> In a later paper, Mori<sup>(10)</sup> carried out a projection operator derivation of the macroscopic equations starting from the equations of motion for the dynamical variables. His expressions for the transport coefficients are in terms of the dissipative current densities so that he has no divergent imaginary part. His dissipative currents and correlation function expressions are identical to those obtained in this work. There is an important difference between Mori's derivation<sup>(10)</sup> and the derivation presented here. Mori makes use of the device of constrained local nonequilibrium states to describe the relation. The derivation presented here avoids the local equilibrium assumption. In the low- $k$ -limit description of relaxation, the use of local equilibrium may presumably be justified and indeed we find our results in agreement with those of Mori. However, if one wishes to extend the hydrodynamic description to higher  $k$  to describe, for example, the results of light scattering experiments,<sup>(13)</sup> the assumption of local equilibrium may not be satisfactory. The methods we use here may be extended to higher  $k$ , as has been done by Selwyn<sup>(2)</sup> for a one-component system.

Thus, we see that a variety of techniques have been employed to arrive at the same or nearly the same results. The technique employed in this work seems to have certain advantages in that the method is general enough to obtain higher-order terms in the hydrodynamic matrix and the divergence problems which frequently occur in other methods are banished by the natural consequences of the dissipative current densities used in the correlation functions.

## APPENDIX: HYDRODYNAMIC EQUATIONS EXPRESSED IN TERMS OF THE THERMODYNAMIC FLUXES

We will now write the hydrodynamic equations in (86') in another form in which we introduce explicitly the diffusion current  $\mathbf{j}_I$  defined by (87) and the energy conduction current  $\mathbf{j}_E$  also defined in Section 7. Our notation will correspond to that used by Fitts.<sup>(4)</sup>

The energy transport equation and the equation of continuity for component I may be written in the well-known forms

$$\{\partial[\rho(U + \frac{1}{2}V^2)]/\partial t\} + \nabla \cdot [\rho(U + \frac{1}{2}V^2)\mathbf{V}] = \nabla \cdot (\mathbf{V} \cdot \boldsymbol{\sigma}) - \nabla \cdot \mathbf{j}_E \quad (\text{A.1})$$

$$(\partial\rho^I/\partial t) + \nabla \cdot (\rho^I\mathbf{V}_I) = 0 \quad (\text{A.2})$$

where  $U$  is the specific internal energy,  $\mathbf{V}$  is the velocity of the local center of mass,  $\mathbf{V}_I$  is the local mean velocity of component I, and  $\boldsymbol{\sigma}$  is the stress tensor, which may be

written in terms of the equilibrium hydrostatic pressure  $p$  and the viscosity tensor  $\sigma'$  in the form

$$\sigma = -p\mathbf{l} + \sigma' \quad (\text{A.3})$$

where  $\mathbf{l}$  is the unit dyadic.

The term in (A.1) involving  $\sigma$  may be expressed in the form

$$\nabla \cdot (\mathbf{V} \cdot \sigma) = -\nabla \cdot (p\mathbf{V}) + \nabla \cdot (\mathbf{V} \cdot \sigma') \quad (\text{A.4})$$

We are interested only in the linearized forms of (A.1) and (A.2). Thus, making use of the definition (87) for the diffusion current density  $\mathbf{j}_I$ , we have the set of linearized equations

$$\partial e / \partial t = -[(e + p)/\rho] \nabla \cdot \mathbf{g} - \nabla \cdot \mathbf{j}_E \quad (\text{A.5})$$

and

$$\partial \rho^I / \partial t = -(\rho^I / \rho) \nabla \cdot \mathbf{g} - \nabla \cdot \mathbf{j}_I \quad (\text{A.6})$$

where we have introduced the total energy density  $e$ , defined in (47), and the total momentum density  $\mathbf{g}$ .

If we compare (A.5) and (A.6) to the corresponding equations in (86'), we have the following identifications:

$$-\mathbf{j}_E = \kappa \nabla T + D_T T_0 \nabla(\mu/T) \quad (\text{A.7})$$

$$-\mathbf{j}_I = (D_T/T_0) \nabla T + DT_0 \nabla(\mu/T) \quad (\text{A.8})$$

where  $T_0$  denotes the equilibrium temperature.

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