Journal of Statistical Physics, Vol. 57, Nos. 3/4, 1989

Long-Time Tails of the Green–Kubo Integrands for a Binary Mixture

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Received February 24, 1989

The long-time tails for the mutual diffusion coefficient, the thermal diffusivity, the thermal conductivity, and the shear and longitudinal viscosities (from which the tail of the bulk viscosity can be calculated) of a nonreactive binary mixture are calculated from mode-coupling theory, and compared with a prior calculation by Pomeau. Three different choices of the thermal forces and currents are considered, with the results found to take their simplest form in the case of the de Groot "double-primed set." The decompositions into the kinetic, potential, and cross terms are given.

KEY WORDS: Long-time tails; mode coupling; Green–Kubo integrands; hydrodynamic modes; binary mixture.

1. INTRODUCTION

During a visit at the Los Alamos National Laboratory in the summer of 1984, J. J. Erpenbeck asked me to consider extending the mode-coupling calculations by Ernst *et al.*(1) of the long-time tails of the transport correlation functions for a pure fluid to the case of a binary mixture, for which he was beginning to undertake some molecular dynamics calculations. I soon became aware of the paper by Pomeau(2) reporting similar calculations within the framework of the Landau–Placzek theory. Unfortunately, however, it also soon became clear that that paper, although correct in the large, contained so many apparently typographical errors in the relevant formulas as to necessitate careful recalculation before the results could safely be used. The results of such a recalculation, based on the mode-coupling formalism, are presented here. In addition to the corrected results

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being of some interest in their own right, the results for the hydrodynamic modes of the mixture may be useful in other connections. The decomposition of the asymptotic time correlation functions into their kinetic, potential, and cross terms (omitted in ref. 2) is also given, since that is sometimes of interest in comparing with the results from molecular dynamics studies. Finally, careful attention is given to three alternative choices of the thermal forces and currents. For one of these, the "double-primed set" given by de Groot,$^{(3)}$ the results take on reasonably simple form. Some of the present results have been used in a recent paper by Erpenbeck.$^{(4)}$

The organization of the paper is as follows. The hydrodynamic equations and the several choices of the thermal forces and currents are given in Section 2 for a general multicomponent, nonreactive mixture. In Section 3 the microscopic currents appearing in the Green–Kubo formulas are discussed for each of the force-current choices, and the mode-coupling formalism of Ernst *et al.* is introduced. The equations are specialized to the case of a binary mixture in Section 4, and the hydrodynamic modes required for use in the mode-coupling formulas are calculated. The long-time tails are calculated in Section 5 for the mutual diffusion coefficient, in Section 6 for the thermal diffusivity, in Section 7 for the thermal conductivity, Section 8 for the shear viscosity, and in Section 9 for the longitudinal viscosity. Some calculational details are relegated to two appendices.

2. HYDRODYNAMIC EQUATIONS

The system initially considered here is a d-dimensional fluid consisting of n_s chemically nonreactive species of particles in the absence of external forces. The hydrodynamic equations used here are mostly those of de Groot (ref. 3, §§42–44).

The equation of continuity for species a is

$$\frac{\partial \rho_a}{\partial t} = -\nabla \cdot \rho_a \mathbf{v}_a$$

with t denoting the time, ρ_a and $\mathbf{v}_a$ the mass density and flow velocity, respectively, of species a, and ∇ the d-dimensional gradient operator. Summing over all n_s species leads to the overall equation of continuity

$$\frac{d\rho}{dt} = -\rho \nabla \cdot \mathbf{v} \tag{1}$$

in which $\rho = \sum \rho_a$ is the overall mass density,

$$\mathbf{v} = \frac{1}{\rho} \sum_a \rho_a \mathbf{v}_a \tag{2}$$

is the barycentric average flow velocity, and

$$\frac{d}{dt}=\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla$$

is the substantive time derivative. With the introduction of the mass fractions

$$w_a=\rho_a/\rho$$

then Eqs. (1) and (2) lead to

$$\rho\frac{dw_a}{dt}=-\nabla\cdot\mathbf{J}_a \tag{3}$$

with

$$\mathbf{J}_a=\rho_a(\mathbf{v}_a-\mathbf{v}) \tag{4}$$

denoting the barycentric diffusion current of species a.

The equation of motion is

$$\rho\frac{d\mathbf{v}}{dt}=-\nabla\cdot\mathsf{P} \tag{5}$$

in which P is the pressure tensor.

The entropy transport equation is

$$\rho\frac{ds}{dt}=-\nabla\cdot\mathbf{J}_s+\sigma_s \tag{6}$$

in which s is the specific entropy, $\mathbf{J}_s$ the entropy current, and σ_s the rate of irreversible entropy production. It is convenient to write the latter as the sum $\sigma_s=\sigma_T+\sigma_\eta$ of a contribution σ_T from thermal transport processes and another σ_η from viscous processes.

Under the assumption of local equilibrium, ρ, s, and any n_s-1 of the mass fractions, say $\{w_a, a=1, 2,..., n_s-1\}$, may be regarded as a set of independent intensive thermodynamic variables specifying all other intensive thermodynamic field variables. Together with the flow velocity $\mathbf{v}$ they determine the hydrodynamic state. Equations (1), (3), (5), and (6) form a complete set of n_s+d+1 nonlinear partial differential equations for those hydrodynamic field variables, provided that the diffusion currents $\mathbf{J}_a$, the entropy current $\mathbf{J}_s$, the pressure tensor P, and the entropy productions σ_T and σ_η can be expressed in terms of the field variables.

2.1. Linear Phenomenological Relations

In the thermodynamics of irreversible processes it is postulated that the needed additional relations take the form of a linear dependence of the currents and the pressure tensor on the gradients of the field variables. For the pressure tensor the standard Newtonian form is

$$\mathsf{P} = p\mathbf{1} - \eta[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\dagger}] + \left(\frac{2}{d}\eta - \zeta\right)(\nabla\cdot\mathbf{v})\,\mathbf{1}$$

in which p denotes the scalar pressure, $\mathbf{1}$ the d-dimensional unit tensor, η and ζ the coefficients of shear and bulk viscosity, respectively, and $(\nabla\mathbf{v})^{\dagger}$ the transpose of the dyadic tensor $\nabla\mathbf{v}$. The corresponding entropy production is

$$\sigma_{\eta} = \frac{1}{T}\left\{\eta[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\dagger}] - \left(\frac{2}{d}\eta - \zeta\right)(\nabla\cdot\mathbf{v})\,1\right\}: \nabla\mathbf{v}$$

in which T denotes the thermodynamic temperature.

For better or worse, there are a number (ref. 3, §§44, 45, 52, and 53) of ways of expressing $\mathbf{J}_a$, $\mathbf{J}_s$, and σ_T in terms of the field variables. Three are of interest here. Following de Groot's notation, we will refer to them as the unprimed, primed, and double-primed sets. They all use the same diffusion currents and thermal "force," but they differ in their "heat current" and diffusion "forces." As a result, there are corresponding differences in the "thermal conductivities" and "thermal diffusivities." Thus, there is no little confusion in the literature regarding the meaning of the latter terms.

2.1.1. Unprimed Currents and Forces.

In the unprimed system of currents and forces, the entropy current is written as

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}_q - \sum_a \mu_a \mathbf{J}_a\right) \tag{7}$$

in which μ_a is the specific chemical potential of species a, and $\mathbf{J}_q$ is the "heat current." The "forces" are

$$\mathbf{X}_u = -(1/T)\,\nabla T = -\nabla \ln T$$

$$\mathbf{X}_a = -T\nabla(\mu_a/T)$$

and the linear relations are

$$\mathbf{J}_q = L_{uu}\mathbf{X}_u + \sum_a L_{ua}\mathbf{X}_a$$

$$\mathbf{J}_a = L_{au}\mathbf{X}_u + \sum_b L_{ab}\mathbf{X}_b$$

The coefficients are not all independent, being constrained (ref. 3, §§45, 46) by the Onsager relations

$$L_{au} = L_{ua}, \qquad L_{ab} = L_{ba} \tag{8}$$

as well as the summation conditions

$$\sum_a L_{au} = 0, \qquad \sum_a L_{ab} = 0 \tag{9}$$

The thermal entropy production is

$$\sigma_T = \frac{1}{T}\left(\mathbf{J}_q \cdot \mathbf{X}_u + \sum_a \mathbf{J}_a \cdot \mathbf{X}_a\right) \tag{10}$$

The requirement that this be positive definite for any values of the forces leads (ref. 3, §46) to additional constraints on the phenomenological coefficients, namely

$$\begin{aligned} L_{aa} &\geqslant 0 \\ L_{uu} &\geqslant 0 \\ L_{uu}L_{aa} - L_{ua}^2 &\geqslant 0 \\ L_{aa}L_{bb} - L_{ab}^2 &\geqslant 0 \end{aligned} \tag{11}$$

As noted by Erpenbeck,$^{(4)}$ this set of forces and currents is particularly convenient for molecular dynamics calculations of the Green–Kubo time correlation functions.

2.1.2. Single-Primed Currents and Forces. In this system (ref. 3, §52.I), the entropy current is written as

$$\mathbf{J}_s = \frac{1}{T}\mathbf{J}'_q \tag{12}$$

while the diffusion currents are the same as in the unprimed set,

$$\mathbf{J}'_a = \mathbf{J}_a$$

Comparing Eqs. (7) and (12), we see that

$$\mathbf{J}'_q = \mathbf{J}_q - \sum_a \mu_a \mathbf{J}_a$$

The requirement that the entropy production have the same form as in

Eq. (10), except with single-primed currents and forces replacing the unprimed ones, then leads to the single-primed forces

$$\mathbf{X}'_u = \mathbf{X}_u = -\frac{1}{T}\nabla T$$

$$\mathbf{X}'_a = \mathbf{X}_a + \mu_a \mathbf{X}_u = -\nabla \mu_a$$

Note that the single-primed diffusion force is just the negative gradient of the chemical potential. The single-primed linear phenomenological relations are

$$\begin{aligned} \mathbf{J}'_q &= L'_{uu}\mathbf{X}'_u + \sum_a L'_{ua}\mathbf{X}'_a \\ \mathbf{J}'_a &= L'_{au}\mathbf{X}'_u + \sum_b L'_{ab}\mathbf{X}'_b \end{aligned} \tag{13}$$

The connections between the single-primed and the unprimed coefficients are easily found to be

$$\begin{aligned} L'_{uu} &= L_{uu} - 2\sum_a L_{ua}\mu_a + \sum_a \sum_b L_{ab}\mu_a\mu_b \\ L'_{ua} &= L_{ua} - \sum_b L_{ab}\mu_b \\ L'_{ab} &= L_{ab} \end{aligned} \tag{14}$$

with constraints analogous to Eqs. (8), (9), and (11). This single-primed system is the one used by Pomeau.$^{(2)}$ We use it here in order to be able to compare with his results, and also because it appears to be the most convenient one for the calculation of the hydrodynamic modes.

2.1.3. Double-Primed Currents and Forces. In this system (ref. 3, §52.II), the entropy current is written as

$$\mathbf{J}_s = \frac{1}{T}\left(\mathbf{J}''_q + \sum_a Ts_a\, \mathbf{J}''_a\right) \tag{15}$$

with s_a denoting the partial specific entropy of species a. The diffusion currents are again the same as before,

$$\mathbf{J}''_a = \mathbf{J}'_a = \mathbf{J}_a$$

Comparing Eqs. (15) and (7), it is seen that

$$\mathbf{J}''_q = \mathbf{J}_q - \sum_a h_a \mathbf{J}_a$$

with h_a denoting the partial specific enthalpy of species a. The entropy production is again of the same form as Eq. (10), but with the double-primed currents and forces replacing the unprimed ones. The forces are

$$\mathbf{X}_u'' = \mathbf{X}_u' = \mathbf{X}_u = -\frac{1}{T}\nabla T$$

$$\mathbf{X}_a'' = \mathbf{X}_a + h_a \mathbf{X}_u = -(\nabla \mu_a + s_a \nabla T)$$

Since

$$s_a = -\left(\frac{\partial \mu_a}{\partial T}\right)_{p, \{w_b\}}$$

the double-primed diffusion force is often written as

$$\mathbf{X}_a'' = -\left[\nabla \mu_a - \left(\frac{\partial \mu_a}{\partial T}\right)_{p, \{w_b\}} \nabla T\right] = -\nabla_T \mu_a$$

The quantity on the right side is sometimes called the "isothermal gradient" of μ_a, since it is the part of the gradient not due to the temperature gradient. The linear phenomenological relations are

$$\mathbf{J}_q'' = L_{uu}'' \mathbf{X}_u'' + \sum_a L_{ua}'' \mathbf{X}_a''$$

$$\mathbf{J}_a'' = L_{au}'' \mathbf{X}_u'' + \sum_b L_{ab}'' \mathbf{X}_b''$$

The connections of the coefficients to the unprimed ones are

$$\begin{aligned} L_{uu}'' &= L_{uu} - 2 \sum_a L_{ua} h_a + \sum_a \sum_b L_{ab} h_a h_b \\ L_{ua}'' &= L_{ua} - \sum_b L_{ab} h_b \\ L_{ab}'' &= L_{ab} \end{aligned} \tag{16}$$

The Onsager relations, summation conditions, and positivity conditions are identical in form to those for the unprimed set, Eqs. (8), (9), and (11). This system is of interest here in that in it the mode-coupling results for the long-time tails of the time correlation functions in the Green–Kubo formulas for the linear phenomenological coefficients take their simplest form.

3. GREEN–KUBO AND MODE-COUPLING FORMULAS

The Green–Kubo formula, expressing a transport coefficient $L_{\alpha_1\alpha_2}$ in terms of an integral over the corresponding time correlation function $\rho_{\alpha_1\alpha_2}(t)$, has the general form

$$L_{\alpha_1\alpha_2}=\beta\int_0^\infty \rho_{\alpha_1\alpha_2}(t)\,dt \tag{17}$$

with $\beta=1/k_{\mathrm{B}}T$, k_{B} denoting the Boltzmann constant, and with the time correlation function being an equilibrium ensemble average of a product of two microscopic currents,

$$\rho_{\alpha_1\alpha_2}=\text{t-lim}\,\frac{1}{V}\,\langle\mathscr{J}_{\alpha_1}(0)\,\mathscr{J}_{\alpha_2}(t)\rangle \tag{18}$$

Here α_1 and α_2 are u, a, or b in the case of the thermal transport coefficients L_{uu}, L_{ua}, and L_{ab}, and can both be taken equal to η if we adopt the notation $\eta=L_{\eta\eta}$. The currents are functions of the mechanical phase variables of the particles. The notation $\mathscr{J}_{\alpha_1}(0)$ means that the current is evaluated for a given "initial" phase, while $\mathscr{J}_{\alpha_2}(t)$ indicates that the current is evaluated for the phase corresponding to the dynamical evolution of the system for a time t starting from the "initial" phase. The $\langle\cdots\rangle$ denotes a grand canonical average (i.e., for fixed values of the volume V of the system, the chemical potentials, and the temperature) over the "initial" phase, as specified by the numbers N_a of particles of each species, the positions $\mathbf{r}_i$, and the momenta $\mathbf{p}_i$ of the particles, $i=1, 2,..., \sum_a N_a$. Indices $i, j,...$ designate particles, while indices $a, b,...$ designate species. In Eq. (18), t-lim signals the necessity of taking the thermodynamic limit ($V\to\infty$ at constant T and $\{\mu_a\}$) prior to doing the infinite-time integral in Eq. (17). The t-lim notation will be omitted in the sequel.

For some purposes it is desirable to separate the microscopic currents $\mathscr{J}_\alpha$ into kinetic contributions $\mathscr{J}_\alpha^{(K)}$ and potential contributions $\mathscr{J}_\alpha^{(\phi)}$, e.g.,

$$\mathscr{J}_{\alpha_1}=\mathscr{J}_{\alpha_1}^{(K)}+\mathscr{J}_{\alpha_1}^{(\phi)}$$

Equations (17) and (18) can then be similarly decomposed into

$$L_{\alpha_1\alpha_2}=L_{\alpha_1\alpha_2}^{(KK)}+L_{\alpha_1\alpha_2}^{(K\phi)}+L_{\alpha_1\alpha_2}^{(\phi K)}+L_{\alpha_1\alpha_2}^{(\phi\phi)}$$

$$L_{\alpha_1\alpha_2}^{(AB)}=\beta\int_0^\infty \rho_{\alpha_1\alpha_2}^{(AB)}(t)\,dt$$

$$\rho_{\alpha_1\alpha_2}^{(AB)}(t)=\frac{1}{V}\,\langle\mathscr{J}_{\alpha_1}^{(A)}(0)\,\mathscr{J}_{\alpha_2}^{(B)}(t)\rangle$$

$$\rho_{\alpha_1\alpha_2}(t)=\rho_{\alpha_1\alpha_2}^{(KK)}(t)+\rho_{\alpha_1\alpha_2}^{(K\phi)}(t)+\rho_{\alpha_1\alpha_2}^{(\phi K)}(t)+\rho_{\alpha_1\alpha_2}^{(\phi\phi)}(t)$$

in which A and B are K or ϕ. Finally, in the case of the thermal transport processes and depending on which set of forces and currents is under consideration, the time correlation functions and microscopic currents may appear in their unprimed versions, as above, or in their single-primed (e.g., $\rho'_{\alpha_1\alpha_2}$, $\rho'^{(AB)}_{\alpha_1\alpha_2}$, $\mathscr{J}'^{(A)}_{\alpha_1}$) or double-primed versions.

It seems to be an unfortunate fact that no single reference in the literature is a completely reliable source for the formulas for the currents $\mathscr{J}_\alpha$ for a mixture. In addition to outright errors and misprints, confusion can arise due to the various possible choices of forces and currents. The following subsection gives what I believe to be the correct formulas for the primed choice. In Section 3.2 those formulas are transcribed into the unprimed set for subsequent use.

The microscopic currents for the viscosity coefficients are of course unaffected by the choice of the diffusion and thermal forces and currents. The expressions given by Steele$^{(5)}$ and by Zubarev$^{(6)}$ for the shear viscosity can be shown to be equivalent to

$$\mathscr{J}_\eta = T_{xy} \tag{19}$$

in which T_{xy} is the xy component of the dyadic tensor

$$\mathbf{T} = \sum_i m_i \mathbf{v}_i \mathbf{v}_i - \frac{1}{2} \sum_i \sum_j{}' \mathbf{r}_{ij} \nabla_i \phi_{ij} \tag{20}$$

The mass of particle i is denoted by m_i, and depends on its species. A sum such as $\sum_i^{(a)}$ denotes a sum over particles of species a only, while $\sum_i$ indicates a sum over all particles of all species. The relative position $\mathbf{r}_i - \mathbf{r}_j$ is abbreviated as $\mathbf{r}_{ij}$. The potential energy of the system is assumed to be pairwise additive, with ϕ_{ij} denoting the interparticle potential energy of particles i and j; it of course depends on their respective species identities. The gradient with respect to $\mathbf{r}_i$ is denoted by ∇_i. The prime on the sum over j indicates the usual omission of the self-interaction term $j = i$. It should be noted that these expressions are identical to those for a pure fluid in ref. 1, the only difference being that here the mass of particle i depends upon its species identity. The Green–Kubo formula for η in Eq. (4.3d) of ref. 2 appears to be equivalent to that used here, providing that the factor d^{-1} in the former is replaced by $(d-1)^{-1}$.

Following ref. 1, it will be convenient to write the Green–Kubo formulas for the longitudinal viscosity $D_l = [2(d-1)\,\eta/d + \zeta]/\rho$ in the form

$$D_l = \frac{\beta}{\rho} \int_0^\infty \rho_l(t)\, dt$$

$$\rho_l(t) = \frac{1}{V} \langle \mathscr{J}_l(0)\, \mathscr{J}_l(t) \rangle$$

so that the correlation functions for the three viscosities are related by

$$\rho_l(t) = \frac{2(d-1)}{d}\,\rho_\eta(t) + \rho_\zeta(t) \tag{21}$$

In the sequel, the long-time approximations for $\rho_l(t)$ and $\rho_\eta(t)$ will be obtained, with the last equation then permitting the calculation of $\rho_\zeta(t)$. There is substantial agreement among Pomeau,$^{(2)}$ Zubarev,$^{(6)}$ and McLennan$^{(7)}$ that the appropriate Green–Kubo current in ρ_l is

$$\mathscr{J}_l = T_{xx} - pV - \left(\frac{\partial p}{\partial e}\right)_{\rho_1,\rho_2\ldots} (\mathscr{H} - \langle \mathscr{H} \rangle) - \sum_a \left(\frac{\partial p}{\partial \rho_a}\right)_{e,\rho_a'} (M_a - \langle M_a \rangle) \tag{22}$$

in which $\mathscr{H} = \sum_i e_i$ is the Hamiltonian function, with $e = \langle \mathscr{H} \rangle / V$ denoting the equilibrium internal energy density, and

$$e_i = \frac{1}{2} m_i v_i^2 + \frac{1}{2} \sum_j{}' \phi_{ij} \tag{23}$$

is the energy of particle i. The quantity $M_a = m_a N_a = \sum_i^{(a)} m_i$ is the mass of species a, and $\rho_a = \langle M_a \rangle / V$. Finally, in Eq. (22), p is the equilibrium pressure, regarded as a function of e and ρ_a, $a = 1, 2, \ldots, n_s$.

3.1. Single-Primed Microscopic Currents

Green$^{(8)}$ has given formulas for the single-primed Green–Kubo currents. The form of his equations is quite different from that used here; but, with use of the conservation of momentum along any given dynamical trajectory, his results for the thermal transport coefficients can be put into the form of Eqs. (17) and (18) with currents

$$\begin{aligned} \mathscr{J}'_a &= \hat{J}_{ax} \\ \mathscr{J}'_u &= \hat{J}'_{ux} \end{aligned} \tag{24}$$

Here $\hat{J}_{ax}$ and $\hat{J}'_{ux}$ denote the x components of the vectors $\hat{\mathbf{J}}_a$ and $\hat{\mathbf{J}}'_u$ given by

$$\begin{aligned} \hat{\mathbf{J}}_a &= \sum_i^{(a)} m_i \mathbf{v}_i - w_a \sum_i m_i \mathbf{v}_i \\ \hat{\mathbf{J}}'_u &= \hat{\mathbf{J}}_u - \sum_a \mu_a \hat{\mathbf{J}}_a \\ \hat{\mathbf{J}}_u &= \sum_i \left(e_i \mathbf{v}_i - \frac{1}{2} \sum_j{}' \mathbf{r}_{ij} \nabla_i \phi_{ij} \cdot \mathbf{v}_i \right) - h \sum_i m_i \mathbf{v}_i \end{aligned} \tag{25}$$

and h is the macroscopic specific enthalpy of the system. Comparing these currents with those in Eqs. (4.4) of ref. 2, it appears that the diffusion currents are equivalent; but Pomeau's heat current apparently contains several misprints, and it is not clear if it is intended to be the same as that used here.

3.2. Unprimed Microscopic Currents

If Eqs. (14) are solved to express the unprimed coefficients $L_{a_1\alpha_2}$ in terms of the single-primed coefficients $L'_{\alpha_1\alpha_2}$, and if the latter are then expressed in terms of the primed currents $\mathscr{J}'_\alpha$ by means of Eqs. (17) and (18), one can identify the unprimed microscopic currents as

$$\begin{aligned} \mathscr{J}_a &= \mathscr{J}'_a = \hat{J}_{ax} \\ \mathscr{J}_u &= \mathscr{J}'_u + \sum_a \mu_a \mathscr{J}'_a = \hat{J}_{ux} \end{aligned} \tag{26}$$

with use also of Eqs. (24) and (25). These relations can be shown to be equivalent to those given by Zubarev,$^{(6)}$ taking into account that he uses ∇T^{-1} for the thermal force instead of $-\nabla \ln T$.

3.3. Mode-Coupling Formula

Ernst *et al.*$^{(1)}$ have derived the mode-coupling formula

$$\begin{aligned} \rho_{\alpha_1\alpha_2}(t) \asymp \frac{1}{2}\int \frac{d\mathbf{k}}{(2\pi)^d} \sum_{\mu,\nu} [\mathscr{J}_{\alpha_1}, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})][a_\nu(-\mathbf{k})\, a_\mu(\mathbf{k}), \mathscr{J}_{\alpha_2}] \\ \times \exp\{[z_\mu(k)+z_\nu(k)]\, t\} \end{aligned} \tag{27}$$

in the limit of an infinite system. The quantities $a_\mu(\mathbf{k})$ are the microscopic hydrodynamic eigenmodes, to be calculated in Section 4. They depend on the microscopic phase variables $\{\mathbf{r}_i\}$ and $\{\mathbf{p}_i\}$ and on the d-dimensional Fourier wave vector $\mathbf{k}$, and are enumerated by the index μ. The double sum is over all ordered pairs of these modes. The $z_\mu(k)$ are the corresponding eigenvalues. The integral is over the infinite d-dimensional Fourier space. The $[f(\mathbf{k}), g(\mathbf{k}')]$ inner product is defined by

$$[f(\mathbf{k}), g(\mathbf{k}')] = \frac{1}{V}\langle f(\mathbf{k})^*\, g(\mathbf{k}')\rangle \tag{28}$$

for a finite system, with the asterisk denoting the complex conjugate. Translational invariance leads to the property

$$[f(\mathbf{k}), g(\mathbf{k}')] = [f(\mathbf{k}), g(\mathbf{k})]\, \delta_{\mathbf{k}\mathbf{k}'}$$

for microscopic functions f and g of the type considered here, with $\delta_{\mathbf{kk}'}$ denoting the d-dimensional Kronecker delta function.

The validity of Eq. (27) requires that the following conditions be satisfied by the hydrodynamic modes and the microscopic currents:

1. The modes must be orthonormal in the sense of the inner product of Eq. (28), i.e.

$$[a_\mu(\mathbf{k}), a_\nu(\mathbf{k})] = \delta_{\mu\nu} \tag{29}$$

with $\delta_{\mu\nu}$ being the usual one-dimensional Kronecker delta function.

2. The currents must be orthogonal to the modes,

$$[\mathscr{J}_\alpha, a_\mu(\mathbf{k})] = 0 \tag{30}$$

3. The currents must have vanishing equilibrium values,

$$[\mathscr{J}_\alpha, 1] = 0 \tag{31}$$

4. HYDRODYNAMIC MODES

4.1. Specialization to a Binary Mixture, Linearization, and Fourier Transformation

The discussion to this point has considered a general n_s-component mixture. For the binary ($n_s = 2$) case, the linear relations of Eqs. (13) reduce, with the aid of the primed versions of the reciprocal and summation relations (8) and (9), as well as the relation $\mathbf{J}_1 + \mathbf{J}_2 = 0$ [as follows from Eqs. (2) and (4)], to

$$\mathbf{J}_1 = \mathbf{J}'_1 = -L'_{11}\nabla\hat{\mu} - \frac{1}{T}L'_{1u}\nabla T$$

$$\mathbf{J}'_q = -L'_{1u}\nabla\hat{\mu} - \frac{1}{T}L'_{uu}\nabla T$$

using the notation $\hat{\mu} = \mu_1 - \mu_2$. Equations (14) and (16) become

$$\begin{aligned} L'_{uu} &= L_{uu} - 2L_{1u}\hat{\mu} + L_{11}\hat{\mu}^2 \\ L'_{1u} &= L_{1u} - L_{11}\hat{\mu} \\ L'_{11} &= L_{11} \end{aligned} \tag{32}$$

and

$$\begin{aligned} L''_{uu} &= L_{uu} - 2L_{1u}\hat{h} + L_{11}\hat{h}^2 \\ L''_{1u} &= L_{1u} - L_{11}\hat{h} \\ L''_{11} &= L_{11} \end{aligned} \tag{33}$$

with $\hat{h} = h_1 - h_2 = \hat{\mu} - T\hat{\mu}_T$.

With use of Eq. (12) and the abbreviation $w = w_1$, the hydrodynamic field equations now become

$$\begin{aligned} \frac{d\rho}{dt} &= -\rho\nabla\cdot\mathbf{v} \\ \rho\frac{dw}{dt} &= -\nabla\cdot\mathbf{J}'_1 \\ \rho T\frac{ds}{dt} &= -\nabla\cdot\mathbf{J}'_q + \frac{1}{T}\mathbf{J}'_q\cdot\nabla T + T\sigma \\ \rho\frac{d\mathbf{v}}{dt} &= -\nabla\cdot\mathsf{P} \end{aligned} \tag{34}$$

At this point it is appropriate to compare these equations with those of Pomeau [ref. 2, Eqs. (2.5)]. There appears to be substantial agreement if we make the identifications $L'_{11} = D$, $L'_{1u} = D_1$, and $L'_{uu} = \kappa$, except for several apparent misprints, and except for his omission of the last two terms in the equation for ds/dt. The latter has no consequences in the subsequent analysis, as those terms disappear when the equations are linearized.

The next step is the "acoustic" linearization of the equations, in which the nonequilibrium state of the fluid is considered to be a small perturbation on a spatially uniform, time-independent equilibrium state in which the fluid is at rest. The local flow velocity $\mathbf{v}$, the deviations $\delta\rho = \rho - \rho_0$, $\delta w = w - w_0$, $\delta s = s - s_0$, etc., of the thermodynamic functions from their unperturbed values (the latter denoted temporarily by the subscript zero), and all spatial and temporal gradients of the field quantities are treated as small ("first-order") quantities; products of two or more of them are neglected. As a result, the substantive derivative d/dt reduces to the partial derivative $\partial/\partial t$, and the transport coefficients appearing to the right of the gradient operators in Eqs. (34) can be taken to the left. With the subscript zeros now dropped, so that from this point all field quantities except $\mathbf{v}$ appearing in the equations refer to the unperturbed state, the hydrodynamic equations become

$$\frac{\partial \delta\rho}{\partial t} = -\rho\nabla\cdot\mathbf{v}$$

$$\rho\frac{\partial \delta w}{\partial t} = L'_{11}\nabla^2\,\delta\hat{\mu} + \frac{L'_{1u}}{T}\nabla^2\,\delta T$$

$$\rho T\frac{\partial \delta s}{\partial t} = L'_{1u}\nabla^2\,\delta\hat{\mu} + \frac{L'_{uu}}{T}\nabla^2\,\delta T$$

$$\rho\frac{\partial \mathbf{v}}{\partial t} = -\nabla\,\delta p + \eta\nabla^2\mathbf{v} + \left(\frac{d-2}{d}\eta + \zeta\right)\nabla\nabla\cdot\mathbf{v}$$

Now a d-dimensional Fourier transformation (under the usual assumption of a finite periodic system, or an infinite system in which the perturbations vanish sufficiently rapidly at infinity) gives, with

$$\rho_{\mathbf{k}}(t) = \int d\mathbf{r}\;\delta\rho(\mathbf{r}, t)\exp(-i\mathbf{k}\cdot\mathbf{r}) \tag{35}$$

etc., the system of $d+3$ ordinary differential equations

$$\frac{d\rho_{\mathbf{k}}}{dt} = -\rho i\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}}$$

$$\frac{dw_{\mathbf{k}}}{dt} = -\frac{L'_{11}}{\rho}k^2\hat{\mu}_{\mathbf{k}} - \frac{L'_{1u}}{\rho T}k^2 T_{\mathbf{k}}$$

$$\frac{ds_{\mathbf{k}}}{dt} = -\frac{L'_{1u}}{\rho T}k^2\hat{\mu}_{\mathbf{k}} - \frac{L'_{uu}}{\rho T^2}k^2 T_{\mathbf{k}}$$

$$\frac{d\mathbf{v}_{\mathbf{k}}}{dt} = -\frac{i}{\rho}\mathbf{k}p_{\mathbf{k}} - \frac{\eta}{\rho}k^2 v_{\mathbf{k}} - \frac{1}{\rho}\left(\frac{d-2}{d}\eta + \zeta\right)\mathbf{k}\mathbf{k}\cdot\mathbf{v}_{\mathbf{k}}$$

for the time dependence of the Fourier components of the d velocity components and the three thermodynamic variables ρ, w, and s. Actually, the Fourier components of six thermodynamic quantities ($\hat{\mu}$, T, and p, in addition to the first three) appear, any three of which can be taken to be independent in the thermodynamic sense.

With the choice of w, p, and s for this purpose, standard thermodynamic calculations lead to the following expressions for the other Fourier components:

$$\rho_{\mathbf{k}} = \frac{1}{c^2}p_{\mathbf{k}} + \frac{\rho\chi}{c_p}s_{\mathbf{k}} + \frac{\rho\chi}{c_p}\left(\hat{\mu}_T - \frac{\rho c_p}{\chi}\hat{\mu}_p\right)w_{\mathbf{k}}$$

$$\hat{\mu}_{\mathbf{k}} = \left(\hat{\mu}_p - \frac{\chi\hat{\mu}_T}{\rho c_p}\right)p_{\mathbf{k}} + \frac{T\hat{\mu}_T}{c_p}s_{\mathbf{k}} + \left(\hat{\mu}_w + \frac{T\hat{\mu}_T^2}{c_p}\right)\mathbf{w}_k$$

$$T_{\mathbf{k}} = -\frac{\chi}{\rho c_p}p_{\mathbf{k}} + \frac{T}{c_p}s_{\mathbf{k}} + \frac{T\hat{\mu}_T}{c_p}w_{\mathbf{k}}$$

In these equations the notation is mostly that of ref. 2; c denotes the adiabatic sound speed, $c^2 = (\partial p/\partial \rho)_{w,s}$; c_p is the constant-pressure specific heat capacity; $\chi = -\alpha T = (T/\rho)(\partial \rho/\partial T)_{p,w}$, with α denoting the usual thermal expansion coefficient. The subscripts p, T, and w on $\hat{\mu}$ denote the corresponding partial derivatives with the other two variables held constant.

The system of differential equations with constant coefficients (all evaluated in the unperturbed state) now becomes

$$\begin{aligned}
\frac{dp_{\mathbf{k}}}{dt} &= k^2(\Delta_3 p_{\mathbf{k}} + \Delta_4 s_{\mathbf{k}} + \Delta_5 w_{\mathbf{k}}) - \rho c^2 i\mathbf{k} \cdot \mathbf{v}_k \\
\frac{ds_{\mathbf{k}}}{dt} &= -\frac{k^2}{\rho}(\Delta_1 p_{\mathbf{k}} + \Delta_s s_{\mathbf{k}} + \Delta'_w w_{\mathbf{k}}) \\
\frac{dw_{\mathbf{k}}}{dt} &= -\frac{k^2}{\rho}(\Delta_2 p_{\mathbf{k}} + \Delta'_s s_{\mathbf{k}} + \Delta_w w_{\mathbf{k}}) \\
\frac{d\mathbf{v}_{\mathbf{k}}}{dt} &= -\frac{1}{\rho}\left[i\mathbf{k}p_{\mathbf{k}} + \eta k^2 \mathbf{v}_{\mathbf{k}} + \left(\frac{d-2}{d}\eta + \zeta\right)\mathbf{k}\mathbf{k} \cdot \mathbf{v}_{\mathbf{k}} \right]
\end{aligned} \tag{36}$$

Here the abbreviations

$$\begin{aligned}
\Delta_s &= \frac{1}{c_p}\left(L'_{1u}\hat{\mu}_T + \frac{L'_{uu}}{T}\right) \\
\Delta'_s &= \frac{1}{c_p}(L'_{11}T\hat{\mu}_T + L'_{1u}) \\
\Delta_w &= \hat{\mu}_T \Delta'_s + L'_{11}\hat{\mu}_w \\
\Delta'_w &= \hat{\mu}_T \Delta_s + \frac{L'_{1u}}{T}\hat{\mu}_w
\end{aligned} \tag{37}$$

follow the notation in ref. 2, and in addition we use

$$\begin{aligned}
\Delta_1 &= \frac{1}{T}\left(L'_{1u}\hat{\mu}_p - \frac{\chi}{\rho}\Delta_s\right) \\
\Delta_2 &= -\frac{\chi}{\rho T}\Delta'_s + L'_{11}\hat{\mu}_p \\
\tilde{\mu} &= \hat{\mu}_T - \frac{\rho c_p}{\chi}\hat{\mu}_p \\
\Delta_3 &= \frac{\chi c^2}{c_p}(\Delta_1 + \tilde{\mu}\Delta_2)
\end{aligned}$$

$$\Delta_4 = \frac{\chi c^2}{c_p} (\Delta'_w + \tilde{\mu} \Delta_w)$$

$$\Delta_5 = \frac{\chi c^2}{c_p} (\Delta_s + \tilde{\mu} \Delta'_s)$$

The normal modes of this system of ordinary differential equations with constant coefficients constitute the macroscopic hydrodynamic modes of the physical system.

4.2. Macroscopic Hydrodynamic Modes

In matrix form the system (36) becomes

$$\frac{d\mathbf{B}(t)}{dt} = \mathbf{M}\mathbf{B}(t) \tag{38}$$

in terms of the $(d+3)$-dimensional column vector

$$\mathbf{B}(t) = [p_{\mathbf{k}}(t), s_{\mathbf{k}}(t), w_{\mathbf{k}}(t), \mathbf{v}_{\mathbf{k}}(t) \cdot \hat{\mathbf{k}}, \mathbf{v}_{\mathbf{k}}(t) \cdot \hat{\mathbf{k}}_{\perp 1}, ..., \mathbf{v}_{\mathbf{k}}(t) \cdot \hat{\mathbf{k}}_{\perp, d-1}]^{\dagger}$$

and the matrix (written out here for the $d = 3$ case)

$$\mathbf{M} = \begin{pmatrix} \Delta_3 k^2 & \Delta_4 k^2 & \Delta_5 k^2 & -ik\rho c^2 & 0 & 0 \\ -\Delta_1 k^2/\rho & -\Delta_s k^2/\rho & -\Delta'_w k^2/\rho & 0 & 0 & 0 \\ -\Delta_2 k^2/\rho & -\Delta'_s k^2/\rho & -\Delta_w k^2/\rho & 0 & 0 & 0 \\ -ik/\rho & 0 & 0 & -D_l k^2 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\nu k^2 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\nu k^2 \end{pmatrix} \tag{39}$$

in which $\hat{\mathbf{k}}$ is the unit vector in the direction of $\mathbf{k}$, and $\hat{\mathbf{k}}_{\perp i}$, $i = 1, 2, ..., d-1$, is a set of mutually perpendicular unit vectors transverse to $\hat{\mathbf{k}}$. The kinematic viscosity is $\nu = \eta/\rho$.

Let ψ_i and ϕ_i, $i = 1, 2, ..., d+3$, be, respectively, a set of left (row) and right (column) eigenvectors of $\mathbf{M}$ with corresponding eigenvalues z_i, so that

$$\psi_i \mathbf{M} = z_i \psi_i \qquad \text{and} \qquad \mathbf{M}\phi_i = z_i \phi_i \tag{40}$$

It will be later verified that these eigenvectors can be chosen to form a normalized biorthogonal system such that

$$\psi_i \phi_j = \delta_{ij} \qquad \text{and} \qquad \sum_i \phi_i \psi_i = \mathbf{1} \tag{41}$$

in which $\mathbf{1}$ is the $(d+3)$-dimensional unit matrix. The solution of Eq. (38) for given initial data $\mathbf{B}(0)$ is then

$$\mathbf{B}(t) = \sum_i \boldsymbol{\phi}_i \boldsymbol{\psi}_i \mathbf{B}(0) \exp(z_i t)$$

In terms of the macroscopic normal modes, defined by

$$\mathbf{A}_i = \boldsymbol{\phi}_i \boldsymbol{\psi}_i \mathbf{B} \tag{42}$$

the solution can be written simply as

$$\mathbf{B}(t) = \sum_i \mathbf{A}_i(t)$$

with

$$\mathbf{A}_i(t) = \mathbf{A}_i(0) \exp(z_i t)$$

It should be mentioned that the field vector $\mathbf{B}$, the matrix M, the eigenvectors $\boldsymbol{\psi}_i$ and $\boldsymbol{\phi}_i$, and the normal modes $\mathbf{A}_i$ all depend on $\mathbf{k}$, even though the dependence is not explicitly denoted. Evidently the next step in the calculation of the normal modes is the determination of the eigenvectors and eigenvalues of M. Inspection of Eq. (39) reveals that M is block diagonal in the $d-1$ transverse directions, corresponding to the shear modes denoted (for $i = 1, 2,..., d-1$) by

$$z_{\perp i} = -\nu k^2$$
$$\boldsymbol{\psi}_{\perp i} = \boldsymbol{\phi}^{\dagger}_{\perp i} = \mathbf{u}_i$$
$$\mathbf{A}_{\perp i} = \mathbf{v}_{\mathbf{k}} \cdot \hat{\mathbf{k}}_{\perp i} \boldsymbol{\phi}_{\perp i}$$

with $\mathbf{u}_i$ denoting a $(d+3)$-component row unit vector whose components are all zero, except the $(i+4)$th. As would be expected, these modes are the same as those for a pure fluid,$^{(1)}$ and are valid for all values of $\mathbf{k}$.

With the decoupling of the shear modes, the characteristic equation for the remaining eigenvalues becomes a quartic in z_i whose coefficients are polynomials in k of up to degree eight. However, as shown in ref. 1, it is sufficient for the determination of the dominant time behavior of the time correlation functions to find the eigenvalues through $O(k^2)$ and the eigenvectors $\boldsymbol{\psi}_i$ and $\boldsymbol{\phi}_i$ to $O(1)$. Accordingly, one can write

$$\mathsf{M} = k(\mathsf{M}^{(0)} + \mathsf{M}^{(1)} k)$$

in which $\mathbf{M}^{(0)}$ and $\mathbf{M}^{(1)}$ are independent of $\mathbf{k}$, and expand the eigenvalues and eigenvectors as

$$z_i = k[z_i^{(0)} + z_i^{(1)}k + O(k^2)]$$
$$\boldsymbol{\phi}_i = \boldsymbol{\phi}_i^{(0)} + \boldsymbol{\phi}_i^{(1)}k + O(k^2)$$
$$\boldsymbol{\psi}_i = \boldsymbol{\psi}_i^{(0)} + \boldsymbol{\psi}_i^{(1)}k + O(k^2)$$

In this way one finds the following results for the macroscopic hydrodynamic modes.

Shear modes, $i = 1, 2, \ldots, d-1$:

$$\begin{aligned} z_{\perp i} &= -\nu k^2 \\ \boldsymbol{\psi}_{\perp i} &= \boldsymbol{\phi}^{\dagger}_{\perp i} = \mathbf{u}_i \\ \mathbf{A}_{\perp i} &= \mathbf{v}_{\mathbf{k}} \cdot \hat{\mathbf{k}}_{\perp i} \boldsymbol{\phi}_{\perp i} \end{aligned} \tag{43}$$

Sound modes, $\sigma = \pm 1$ (with the 1 omitted in subscripts):

$$\begin{aligned} z_{S\sigma} &= -(\sigma i k c + \tfrac{1}{2}\Gamma_s k^2) \\ \boldsymbol{\psi}_{S\sigma}^{(0)} &= \tfrac{1}{2}(1, 0, 0, \sigma\rho c, 0, 0, \ldots) \\ \boldsymbol{\phi}_{S\sigma}^{(0)} &= (1, 0, 0, \sigma/\rho c, 0, 0, \ldots)^{\dagger} \\ \mathbf{A}_{S\sigma} &= a_{S\sigma}\boldsymbol{\phi}_{S\sigma}^{(0)} \\ a_{S\sigma} &= \tfrac{1}{2}(p_{\mathbf{k}} + \sigma\rho c \hat{\mathbf{k}} \cdot \mathbf{v}_k) \end{aligned} \tag{44}$$

Diffusion modes, $\sigma = \pm 1$ (with the 1 omitted in subscripts):

$$\begin{aligned} z_{D\sigma} &= -\eta_\sigma k^2/\rho \\ \boldsymbol{\psi}_{D\sigma}^{(0)} &= \frac{\sigma(\eta_\sigma - \Delta_w)}{\eta_+ - \eta_-}\left(0, 1, \frac{\eta_\sigma - \Delta_s}{\Delta'_s}, 0, 0, 0, \ldots\right) \\ \boldsymbol{\phi}_{D\sigma}^{(0)} &= \left(0, 1, \frac{\eta_\sigma - \Delta_s}{\Delta'_w}, 0, 0, 0, \ldots\right)^{\dagger} \\ \mathbf{A}_{D\sigma} &= a_{D\sigma}\boldsymbol{\phi}_{D\sigma}^{(0)} \\ a_{D\sigma} &= \frac{\sigma}{\eta_+ - \eta_-}\,[(\eta_\sigma - \Delta_w)\, s_{\mathbf{k}} + \Delta'_w w_{\mathbf{k}}] \end{aligned} \tag{45}$$

In these equations

$$\begin{aligned} \Gamma_s &= D_l + \frac{\gamma - 1}{\rho c_p T}(L'_{uu} + 2L'_{1u}T\tilde{\mu} + L'_{11}T^2\tilde{\mu}^2) \\ &= D_l + \frac{\gamma - 1}{\rho c_p T}\left[L''_{uu} - 2\,\frac{\rho\hat{\mu}_p c_p T}{\chi}\,L''_{1u} + \left(\frac{\rho\hat{\mu}_p c_p T}{\chi}\right)^2 L''_{11}\right] \end{aligned}$$

is the acoustic damping coefficient, with $\gamma = c_p/c_v$, and use having been made of the thermodynamic relation $\gamma - 1 = \chi^2 c^2/c_p T$. The quantities η_σ, $\sigma = \pm$, are the roots

$$\eta_\pm = \tfrac{1}{2}(\varDelta_s + \varDelta_w \pm \mathscr{D}^{1/2})$$

of the quadratic equation

$$(\eta_\pm - \varDelta_s)(\eta_\pm - \varDelta_w) - \varDelta'_s \varDelta'_w \equiv \eta_\pm^2 - (\varDelta_s + \varDelta_w)\,\eta_\pm + \varDelta_s \varDelta_w - \varDelta'_s \varDelta'_w = 0 \tag{46}$$

with the discriminant

$$\mathscr{D} = (\varDelta_s + \varDelta_w)^2 - 4(\varDelta_s \varDelta_w - \varDelta'_s \varDelta'_w)$$

It is not difficult to show from Eqs. (32), (33), and (37) that

$$\begin{aligned} \varDelta_s + \varDelta_w &= \frac{1}{c_p T}(L'_{uu} + 2L'_{1u} T \hat{\mu}_T + L'_{11} T^2 \hat{\mu}_T^2) + \hat{\mu}_w L'_{11} \\ &= \frac{L''_{uu}}{c_p T} + \hat{\mu}_w L''_{11} \end{aligned}$$

and

$$\varDelta_s \varDelta_w - \varDelta'_s \varDelta'_w = \frac{\hat{\mu}_w}{c_p T}(L'_{uu} L'_{11} - L'^2_{1u}) = \frac{\hat{\mu}_w}{c_p T}(L''_{uu} L''_{11} - L''^2_{1u})$$

It then follows that

$$\mathscr{D} = \left(\frac{L''_{uu}}{c_p T} - \hat{\mu}_w L''_{11}\right)^2 + 4\frac{\hat{\mu}_w}{c_p T} L''^2_{1u}$$

Now, stability of the mixture against phase separation requires $\hat{\mu}_w > 0$. This, together with the positive entropy production conditions (11), then shows that $\mathscr{D}$, $\varDelta_s + \varDelta_w$, and $\varDelta_s \varDelta_w - \varDelta'_s \varDelta'_w$ are all positive quantities, with $\mathscr{D}^{1/2} < \varDelta_s + \varDelta_w$. Hence the roots $\eta_\pm$ are both positive, as must be the case if the mode-coupling formula is to make sense. The following relations, obtained in similar fashion, will also be useful in the sequel:

$$\begin{gathered} \varDelta_s + \hat{\mu}_T \varDelta'_s = L''_{uu}/c_p T \\ \varDelta'_s = L''_{1u}/c_p \\ \varDelta_w = \hat{\mu}_w L''_{11} + \hat{\mu}_T L''_{1u}/c_p \\ \eta_\sigma - \varDelta_w + \hat{\mu} \varDelta'_s/T = \eta_\sigma - \hat{\mu}_w L''_{11} + \hat{h} L''_{1u}/c_p T \\ (\eta_\sigma - L''_{uu}/c_p T)(\eta_\sigma - \hat{\mu}_w L''_{11}) = \hat{\mu}_w L''^2_{1u}/c_p T \\ \eta_+ + \eta_- = \varDelta_s + \varDelta_w \\ \eta_+ \eta_- = \varDelta_s \varDelta_w - \varDelta'_s \varDelta'_w \\ (\eta_+ - \varDelta_w)(\eta_- - \varDelta_w) = (\eta_+ - \varDelta_s)(\eta_- - \varDelta_s) = -\varDelta'_s \varDelta'_w \end{gathered} \tag{47}$$

In the terminology of ref. 1, which we follow in the sequel, the scalar quantities $a_{\perp i}, a_{S\sigma}$, and $a_{D\sigma}$ are the hydrodynamic modes a_μ and a_ν appearing in the mode-coupling formula, except that: (1) they are presently macroscopic quantities, and so have to be translated into microscopic phase functions, and (2) when that has been done, they must then be normalized in the sense of Eq. (29).

4.3. Microscopic Hydrodynamic Modes

In obtaining the expressions for the microscopic hydrodynamic modes for a binary mixture, I follow rather closely the methods used in ref. 1 for a pure fluid. The essential step is to obtain microscopic expressions for the various Fourier components appearing in the macroscopic modes.

4.3.1. Composition and Density Components. The usual expression for the instantaneous fluctuation of the density of species a from its uniform equilibrium value ρ_a is

$$\delta\rho_a(\mathbf{r}, t) = \rho_a(\mathbf{r}, t) - \rho_a = \sum_i^{(a)} m_i \delta[\mathbf{r}_i(t) - \mathbf{r}] - \rho_a$$

Recall that ρ_a (as with other variables, such as ρ, p, w, s, etc.), without any explicit indication of dependence on $\mathbf{r}$ and t, denotes the unperturbed value.

Fourier transformation as in Eq. (35) then yields

$$\rho_{a\mathbf{k}} = \sum_i^{(a)} m_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) - \rho_a V \delta_{\mathbf{k}0}$$

in which V is the constant volume of the system. Here and in the other Fourier components to follow, the explicit notation of their time dependence arising from the time dependence of the molecular positions $\mathbf{r}_i = \mathbf{r}_i(t)$ has been suppressed for the sake of brevity. The sum, as already mentioned, is over the N_a particles of species a, with N_a of course being one of the fluctuating variables in the grand canonical ensemble averages which will follow. Summing over both species of particles ($a = 1, 2$) gives the Fourier component of the overall mass density as

$$\rho_{\mathbf{k}} = \sum_i m_i \exp(-i\mathbf{k}\cdot r_i) - \rho V \delta_{\mathbf{k}0} \tag{48}$$

The composition variable w is the mass fraction of species 1, $w(\mathbf{r}, t) = \rho_1(\mathbf{r}, t)/\rho(\mathbf{r}, t)$, so

$$\begin{aligned} \delta w(\mathbf{r}, t) &= \frac{1}{\rho}(\delta\rho_1 - w\,\delta\rho) \\ w_{\mathbf{k}} &= \frac{1}{\rho}\left[\sum_i^{(1)} m_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) - w \sum_i m_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i)\right] \end{aligned} \tag{49}$$

4.3.2. Momentum, Velocity, and Energy Components. In the sequel it will be convenient to express the macroscopic velocity components $\mathbf{v}_\mathbf{k}$ in terms of the components $\mathbf{g}_\mathbf{k}$ of the macroscopic momentum density $\mathbf{g}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\, \mathbf{v}(\mathbf{r}, t)$. The corresponding fluctuation relation is simply $\delta\mathbf{g}(\mathbf{r}, t) = \rho\, \delta\mathbf{v}(\mathbf{r}, t)$, since, by assumption, $\mathbf{v} = \mathbf{g} = 0$ in the equilibrium state. Thus,

$$\mathbf{v}_\mathbf{k} = \frac{1}{\rho}\, \mathbf{g}_\mathbf{k} \tag{50}$$

and in microscopic form

$$\begin{aligned} \mathbf{g}(\mathbf{r}, t) &= \sum_i m_i \mathbf{v}_i(t)\, \delta[\mathbf{r}_i(t) - \mathbf{r}] \\ \mathbf{g}_\mathbf{k} &= \sum_i m_i \mathbf{v}_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) \end{aligned} \tag{51}$$

The local energy density is

$$e(\mathbf{r}, t) = \sum_i e_i \delta[\mathbf{r}_i(t) - \mathbf{r}]$$

in which e_i is the energy of particle i already defined in Eq. (23). The ensemble average of $e(\mathbf{r}, t)$, assuming translational invariance, is just the equilibrium internal energy density $e = U/V = \langle \mathscr{H} \rangle / V$, with U denoting the equilibrium internal energy of the system. The fluctuation in the local energy density is accordingly just $\delta e(\mathbf{r}, t) = e(\mathbf{r}, t) - e$, and its Fourier component is

$$e_\mathbf{k} = \sum_i e_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) - eV\delta_{\mathbf{k}0} \tag{52}$$

4.3.3. Pressure and Entropy Components. The standard thermodynamic relation

$$de = \rho T\, ds + h\, d\rho + \rho\hat{\mu}\, dw$$

in which $h = (e + p)/\rho$ is again the specific enthalpy, becomes the fluctuation relation

$$\delta e = \rho T\, \delta s + h\, \delta\rho + \rho\hat{\mu}\, \delta w$$

which allows us to express the Fourier component of the entropy fluctuation as

$$s_\mathbf{k} = \frac{1}{\rho T}\, e_\mathbf{k} - \frac{h}{\rho T}\, \rho_\mathbf{k} - \frac{\hat{\mu}}{T}\, w_\mathbf{k} \tag{53}$$

In similar fashion, the chain rule gives

$$p_{\mathbf{k}} = p_e e_{\mathbf{k}} + p_\rho \rho_{\mathbf{k}} + p_w w_{\mathbf{k}} \tag{54}$$

in which p is regarded as a function $p(e, \rho, w)$, with the subscripts indicating the usual partial derivatives.

4.3.4. Summary. In summary, Eqs. (48), (49), (51), and (52) express $\rho_{\mathbf{k}}$, $w_{\mathbf{k}}$, $e_{\mathbf{k}}$, and $\mathbf{g}_{\mathbf{k}}$ directly as microscopic phase functions, with Eqs. (50), (53), and (54) then giving $\mathbf{v}_{\mathbf{k}}$, $\mathbf{s}_{\mathbf{k}}$, and $p_{\mathbf{k}}$ in the same terms. With use of those expressions, Eqs. (43)–(45) then give the (as yet unnormalized) hydrodynamic modes $a_{\perp i}$, $a_{S\sigma}$, and $a_{D\sigma}$ in the desired microscopic form.

4.4. Orthonormality of the Hydrodynamic Modes

The next step is the verification that the unnormalized modes a_μ obtained to this point are in fact mutually orthogonal in the sense of Eq. (29), and then to normalize them. In the following subsections the various pairs of modes are considered seriatim.

4.4.1. Shear Modes. Using the symmetry and equipartition ($\langle m_i v_i^2 \rangle = 1/\beta = k_B T$) properties of the equilibrium velocity distribution, one can obtain the relations

$$\begin{aligned}
[\mathbf{g}_{\mathbf{k}}, \mathbf{g}_{\mathbf{k}}] &= \frac{\rho}{\beta}\mathbf{1} \\
[\mathbf{g}_{\mathbf{k}}, p_{\mathbf{k}}] &= 0 \\
[\mathbf{g}_{\mathbf{k}}, s_{\mathbf{k}}] &= 0 \\
[\mathbf{g}_{\mathbf{k}}, w_{\mathbf{k}}] &= 0
\end{aligned} \tag{55}$$

from which there follow

$$\begin{aligned}
[a_{\perp i}, a_{\perp j}] &= \frac{1}{\rho\beta}\delta_{ij} \\
[a_{\perp i}, a_{S\sigma}] &= [a_{\perp i}, a_{D\sigma}] = 0
\end{aligned} \tag{56}$$

showing the orthogonality of these pairs of modes.

4.4.2. Sound Modes. For a pair of sound modes, Eqs. (44) and (55) give, with use also of the vanishing of $[p_{\mathbf{k}}, \mathbf{g}_{\mathbf{k}}]$,

$$[a_{S\sigma}, a_{S\sigma'}] = \frac{1}{4}\left([p_{\mathbf{k}}, p_{\mathbf{k}}] + \sigma\sigma'\frac{\rho c^2}{\beta}\right) \tag{57}$$

At this point it becomes evident that this inner product can not be exactly zero for $\sigma \neq \sigma'$, since it can be anticipated that $[p_{\mathbf{k}}, p_{\mathbf{k}}]$ will depend on k. In fact, it will be shown that the right side of Eq. (57) does vanish to $O(k^2)$, as will also be the case for the approximate orthogonality of the remaining pairs of modes, Similarly, the eventual normalization of the sound and diffusion modes will be correct only to $O(k^2)$. That, however, will be sufficient for use in the calculation of the dominant time behavior of the time correlation functions according to the mode-coupling formula.

To explore this question in more detail, consider the contribution

$$\begin{aligned}[e_{\mathbf{k}}, e_{\mathbf{k}}] &= \frac{1}{V}\left(\left\langle \sum_{i,j} e_i e_j \exp(i\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle - e^2 V^2 \delta_{\mathbf{k}0}\right) \\ &= \frac{1}{V}\left(\left\langle \sum_{i,j} e_i e_j \cos(\mathbf{k} \cdot \mathbf{r}_{ij}) \right\rangle - e^2 V^2 \delta_{\mathbf{k}0}\right)\end{aligned}$$

to $[p_{\mathbf{k}}, p_{\mathbf{k}}]$ which results when Eqs. (52) and (54) are used. It is evident that the $i \neq j$ terms do not vanish, and that

$$[e_{\mathbf{k}}, e_{\mathbf{k}}] = [e_0, e_0] + O(k^2)$$

It appears that it is unlikely that the various $O(k^2)$ terms arising in $[p_{\mathbf{k}}, p_{\mathbf{k}}]$ in this fashion will cancel, and thus we presume that likewise

$$[p_{\mathbf{k}}, p_{\mathbf{k}}] = [p_0, p_0] + O(k^2)$$

and similarly for other inner products among $p_{\mathbf{k}}$, $s_{\mathbf{k}}$, $w_{\mathbf{k}}$, etc. In the sequel, for the sake of brevity, the explicit notation of the $O(k^2)$ terms will be omitted.

Appendix A gives, following closely the corresponding discussion in ref. 1 for a pure fluid, the derivations of the binary inner products of the general form $[a_0, b_0]$ needed here and in the sequel. With $[p_0, p_0]$ as given in Eq. (A19), Eq. (57) becomes

$$[a_{S\sigma}, a_{S\sigma'}] = \frac{\rho c^2}{4\beta}(1 + \sigma\sigma') = \frac{\rho c^2}{2\beta}\delta_{\sigma\sigma'} \tag{58}$$

which verifies the approximate mutual orthogonality of the sound modes.

With use of Eqs. (44) and (45) and the vanishing of $[\mathbf{g}_{\mathbf{k}}, s_{\mathbf{k}}]$ and $[\mathbf{g}_{\mathbf{k}}, w_{\mathbf{k}}]$, the inner product of a sound mode and a diffusion mode is found to be

$$[a_{S\sigma}, a_{D\sigma'}] = \frac{\sigma'}{2(\eta_+ - \eta_-)}\{(\eta_\sigma - \Delta_w)[p_0, s_0] + \Delta'_w[p_0, w_0]\}$$

The inner products on the right side vanish, according to Eqs. (A20), and thus the sound and diffusion modes are mutually orthogonal.

4.4.3. Diffusion Modes. It remains to verify the orthogonality of the diffusion modes of different index and to calculate the approximate normalizing factor. Use of Eqs. (45), (A16), (A21), and (A22) gives

$$[a_{D\sigma}, a_{D\sigma'}] = \frac{\sigma\sigma'}{\beta\rho\hat{\mu}_w(\eta_+ - \eta_-)^2}\left[(\eta_\sigma - \Delta_w)(\eta_{\sigma'} - \Delta_w)\left(\frac{c_p\hat{\mu}_w}{T} + \hat{\mu}_T^2\right)\right.$$
$$\left. - \hat{\mu}_T\Delta'_w(\eta_\sigma + \eta_{\sigma'} - 2\Delta_w) + \Delta'^2_w\right]$$

With the aid of Eqs. (37), (46), and (47) it can be shown that this vanishes for $\sigma \neq \sigma'$, and for $\sigma = \sigma'$ reduces to

$$[a_{D\sigma}, a_{D\sigma}] = \frac{-\sigma\Delta'_w[\hat{\mu}_T(\eta_\sigma - \Delta_w) - \Delta'_w]}{\beta\rho\hat{\mu}_w(\eta_+ - \eta_-)(\eta_\sigma - \Delta_s)} \tag{59}$$

4.4.4. Normalized Microscopic Modes. With the aid of the normalizing factors in Eqs. (56), (58), and (59), the microscopic hydrodynamic modes can now be written in their final, normalized form, in the small-wavenumber limit, as

$$\begin{aligned} a_{\perp i}(\mathbf{k}) &= \left(\frac{\beta}{\rho}\right)^{1/2} \hat{\mathbf{k}}_{\perp i}\cdot\mathbf{g}_0 \\ a_{S\sigma}(\mathbf{k}) &= \left(\frac{\beta}{2\rho c^2}\right)^{1/2} (p_0 + \sigma c\hat{\mathbf{k}}\cdot\mathbf{g}_0) \\ a_{D\sigma}(\mathbf{k}) &= \frac{\sigma}{A_\sigma(\eta_+ - \eta_-)}[(\eta_\sigma - \Delta_w)\, s_0 + \Delta'_w w_0] \end{aligned} \tag{60}$$

in which $A_\sigma = [a_{D\sigma}, a_{D\sigma}]^{1/2}$ as given in Eq. (59). In the sequel, the symbols $a_{\perp i}$, $a_{S\sigma}$, and $a_{D\sigma}$ will always refer to these normalized modes.

4.5. Orthogonality of the Modes and Currents

It is also necessary to assure that the various currents (including their kinetic and potential parts) appearing in the Green–Kubo formulas are orthogonal to the hydrodynamic modes, and that they have vanishing equilibrium averages, as indicated in Eqs. (30) and (31). In the following subsections these conditions will be verified for the unprimed currents. That will be sufficient, since the time correlation functions for the other choices can be expressed in terms of those for the unprimed case.

4.5.1. Diffusion Current. Since $\mathscr{J}_1 + \mathscr{J}_2 = 0$, it suffices to consider only the diffusion current for species 1, which is, according to Eqs. (25), (26), and (51), $\mathscr{J}_1 = \hat{J}_{1x}$ with

$$\hat{\mathbf{J}}_1 = \mathbf{g}_0^{(1)} - w\mathbf{g}_0 \tag{61}$$

and with the additional notation

$$\mathbf{g}_0^{(1)} = \sum_i^{(1)} m_i \mathbf{v}_i \tag{62}$$

From the symmetry properties of the velocity distribution and of the hydrodynamic modes, it is apparent that the diffusion current has a vanishing average and is orthogonal to the diffusion modes. Orthogonality with respect to the shear and sound modes follows from Eq. (55) and the similar relation

$$[\mathbf{g}_0^{(1)}, \mathbf{g}_0] = \frac{\rho w}{\beta} \mathbf{1} \tag{63}$$

which lead to

$$[\hat{\mathbf{J}}_1, \mathbf{g}_0] = 0 \tag{64}$$

4.5.2. Heat Current. The unprimed heat current, as given by Eqs. (25) and (26), is seen to be odd in the particle velocities, so that the condition $[\mathscr{J}_u, 1] = 0$ is trivially satisfied, and also the orthogonality to the diffusion modes. It will be convenient to write it in the form

$$\begin{aligned} \hat{\mathbf{J}}_u &= \hat{\mathbf{J}}_e - h\mathbf{g}_0 \\ \hat{\mathbf{J}}_e &= \sum_i \left(e_i \mathbf{v}_i - \frac{1}{2} \sum_j{}' \mathbf{r}_{ij} \nabla_i \phi_{ij} \cdot \mathbf{v}_i \right) \end{aligned} \tag{65}$$

From the virial theorem and the properties of the velocity distribution it can be shown that

$$\begin{aligned} \frac{1}{2}\left[\mathbf{g}_0, \sum_j m_j v_j^2 \mathbf{v}_j\right] &= \frac{(d+2)\langle N\rangle}{2\beta^2 V} \\ \frac{1}{2}\left[\mathbf{g}_0, \sum_{i,j}{}' \phi_{ij}\mathbf{v}_i\right] &= \frac{1}{\beta V}\langle \Phi\rangle \\ \left[\mathbf{g}_0, \sum_i e_i \mathbf{v}_i\right] &= \frac{1}{\beta V}(U + \langle N\rangle k_B T) \\ -\frac{1}{2}\left[\mathbf{g}_0, \sum_{i,j}{}' \mathbf{r}_{ij} \nabla_i \phi_{ij} \cdot \mathbf{v}_i\right] &= \frac{1}{\beta V}(pV - \langle N\rangle k_B T) \end{aligned} \tag{66}$$

In these equations, $\Phi = \frac{1}{2}\sum_{i,j}' \phi_{ij}$ is the total interparticle potential energy of the system, $\langle N \rangle$ is the average number of particles in the system, and the internal energy is $U = \frac{1}{2}d\langle N \rangle k_{\mathrm{B}}T + \langle \Phi \rangle$. It then follows that

$$[\hat{\mathbf{J}}_e, \mathbf{g}_0] = \frac{\rho h}{\beta}\mathbf{1} \tag{67}$$

This, together with Eq. (55), shows that

$$[\hat{\mathbf{J}}_u, \mathbf{g}_0] = 0 \tag{68}$$

and, as a result, that the heat current is orthogonal to the shear and sound modes.

The kinetic part of the heat current is defined in the same way as in ref. 1, namely $\mathscr{J}_u^{(K)} = \hat{J}_{ux}^{(K)}$, with

$$\hat{\mathbf{J}}_u^{(K)} = \sum_i \left(\frac{1}{2}m_i v_i^2 - \frac{d+2}{2\beta}\right)\mathbf{v}_i \tag{69}$$

in order to satisfy the orthogonality conditions. The usual parity considerations then show that $[\hat{\mathbf{J}}_u^{(K)}, 1] = 0$. As before, one can show that

$$\left[\mathbf{g}_0, \sum_i \mathbf{v}_i\right] = \frac{\langle N \rangle}{\beta V} \tag{70}$$

from which, with use also of Eqs. (66), there follows $[\hat{\mathbf{J}}_u^{(K)}, \mathbf{g}_0] = 0$, and hence the orthogonality of the kinetic part of the heat current with respect to the shear modes. The last result and the usual parity considerations then show that it is also orthogonal to the sound and diffusion modes. Finally, since $\mathscr{J}_u$ and $\mathscr{J}_u^{(K)}$ have been seen to satisfy the necessary orthogonality conditions, it follows that the same is true of the potential part $\mathscr{J}_u^{(\phi)}$.

4.5.3. Shear Viscosity Current. The shear viscosity current, as given in Eqs. (19) and (20), has an obvious separation into kinetic and potential parts in the form

$$\begin{aligned}
\mathscr{J}_\eta &= \mathscr{J}_\eta^{(K)} + \mathscr{J}_\eta^{(\phi)} \\
\mathscr{J}_\eta^{(K)} &= T_{xy}^{(K)} = \sum_i m_i v_{ix} v_{iy} \\
\mathscr{J}_\eta^{(\phi)} &= T_{xy}^{(\phi)} = -\frac{1}{2}\sum_{i,j}' x_{ij}\frac{\partial \phi_{ij}}{\partial y_{ij}}
\end{aligned} \tag{71}$$

Note that $T_{xy}^{(K)}$, while even with respect to reversal of all the velocities, is odd with respect to the reversal of (say) the x components only. Thus, it is clear that

$$[T_{xy}^{(K)}, 1] = \frac{1}{V} \langle T_{xy}^{(K)} \rangle = 0 \tag{72}$$

Similarly, $T_{xy}^{(\phi)}$ is even with respect to a change of sign of all the coordinates, but odd with respect to such a change in (say) the x coordinates only. Thus, translational invariance leads to the desired condition

$$[T_{xy}^{(\phi)}, 1] = \frac{1}{V} \langle T_{xy}^{(\phi)} \rangle = 0 \tag{73}$$

With respect to the shear modes, which are overall odd functions of the velocities, the overall even character of both parts of the shear viscosity current shows that the corresponding orthogonality conditions are satisfied.

Turning to the sound modes, one has with use of Eqs. (60), for $A = K$ or ϕ,

$$[T_{xy}^{(A)}, a_{S\sigma}] = \left(\frac{\beta}{2\rho c^2}\right)^{1/2} \{[p_0, T_{xy}^{(A)}] + \sigma c \hat{\mathbf{k}} \cdot [\mathbf{g}_0, T_{xy}^{(A)}]\}$$

The preceding discussion of the shear modes shows that $[\mathbf{g}_0, T_{xy}^{(A)}] = 0$, while $[p_0, T_{xy}^{(A)}] = 0$ follows from Eq. (A17), since $\langle T_{xy}^{(A)} \rangle$ vanishes according to Eqs. (72) and (73). Similarly, with use also of Eqs. (A12) and (A18), one sees that $[w_0, T_{xy}^{(A)}]$ and $[s_0, T_{xy}^{(A)}]$ are both zero. Thus, $T_{xy}^{(A)}$, and therefore the total viscosity current, are orthogonal to the diffusion modes, as given in Eqs. (60).

4.6. Longitudinal Viscosity Current

When specialized to a binary mixture, Eq. (22) becomes

$$\begin{aligned} \mathcal{J}_l &= t_{0xx} - \left(\frac{\partial p}{\partial e}\right)_{\rho_1, \rho_2} e_0 - \left(\frac{\partial p}{\partial \rho_1}\right)_{e, \rho_2} \rho_{10} - \left(\frac{\partial p}{\partial \rho_2}\right)_{e, \rho_1} \rho_{20} \\ &= t_{0xx} - \left(\frac{\partial p}{\partial e}\right)_{\rho, w} e_0 - \left(\frac{\partial p}{\partial \rho}\right)_{e, w} \rho_0 - \left(\frac{\partial p}{\partial w}\right)_{e, \rho} w_0 \end{aligned} \tag{74}$$

in which $t_{0xx} = T_{xx} - pV$. By the virial theorem $\langle T_{xx} \rangle = pV$, so $[\mathcal{J}_l, 1] = 0$ is satisfied. Moreover, t_{0xx} is a microscopic function in the sense of the appendices, and so for any intensive thermodynamic function a,

$$
\begin{aligned}
[\mathscr{J}_l, a_0] &= [p_0, a_0] - \left(\frac{\partial p}{\partial e}\right)_{\rho_1, \rho_2} [e_0, a_0] - \left(\frac{\partial p}{\partial \rho_1}\right)_{e, \rho_2} [\rho_{10}, a_0] \\
&\quad - \left(\frac{\partial p}{\partial \rho_2}\right)_{e, \rho_1} [\rho_{20}, a_0] \\
&= [p_0, a_0] - \left(\frac{\partial p}{\partial e}\right)_{\rho, w} [e_0, a_0] - \left(\frac{\partial p}{\partial \rho}\right)_{e, w} [\rho_0, a_0] - \left(\frac{\partial p}{\partial w}\right)_{e, \rho} [w_0, a_0]
\end{aligned}
\tag{75}
$$

Now suppose that a_0 is such that, for $b_0 = p_0, e_0, \rho_{10}, \rho_{20}, \rho_0$, or w_0, the inner product $[a_0, b_0]$ can be written as $c(\partial b/\partial \xi)_{\alpha,\beta}$ for some suitable choice of c, α, β, and ξ, the same for all the mentioned choices of b_0. Then $[\mathscr{J}_l, a_0]$ as given by either of Eqs. (75) vanishes by the chain rule. In Appendix A it is shown that the supposition is correct for $a_0 = e_0, \rho_0, \rho_{10}, \rho_{20}, w_0, p_0$, and s_0. In addition, $[\mathscr{J}_l, \mathbf{g}_0] = 0$ by parity. Thus, $\mathscr{J}_l$ is seen to be orthogonal to all of the hydrodynamic modes.

4.7. Contributing Mode Pairs

As discussed in detail by Ernst *et al.*,(1) the dominant[2] contributions to the long-time behavior of the time correlation functions, as given by the mode-coupling formula (27), arise from mode pairs (μ, ν) for which the coefficient $z_\mu(k) + z_\nu(k)$ in the exponential is proportional to k^2. From Eqs. (43)–(45), it is evident that the pairs of modes shown in Table I, and having the indicated parities with respect to the particle velocities, satisfy that criterion. For any given time correlation function, symmetry considerations may still result in one or more of these pairs having vanishing contributions.

Table I. Contributing Pairs of Modes

$(\perp i, \perp j)$	Even	$i, j = 1, 2,..., d-1$
$(S\sigma, S-\sigma)$	Even and odd	$\sigma = \pm$
$(\perp i, D\sigma)$	Odd	$i = 1, 2,..., d-1; \sigma = \pm$
$(D\sigma, D\sigma')$	Even	$\sigma, \sigma' = \pm$

Since the hydrodynamic modes have been calculated only to $O(1)$ in k, the inner products in the mode-coupling formula (27) depend only on

---

[2] It should perhaps be mentioned, however, that Erpenbeck and Wood(9) found that retention of some of the $O(k)$ contributions improved the agreement between the mode-coupling predictions and the molecular dynamics calculations of the velocity autocorrelation function at intermediate times for small, hard-sphere systems.

the direction $\hat{\mathbf{k}}$ of $\mathbf{k}$, and not on its magnitude. The integration over $\mathbf{k}$ can accordingly be separated into a time-independent angular part $B_{\mu\nu}^{\alpha_1\alpha_2}$ and a time-dependent radial part $R_{\mu\nu}(t)$:

$$\begin{aligned} \rho_{\alpha_1\alpha_2}(t) &\asymp \frac{1}{2}\sum_{\mu,\nu} B_{\mu\nu}^{\alpha_1\alpha_2} R_{\mu\nu}(t) \\ B_{\mu\nu}^{\alpha_1\alpha_2} &= \frac{1}{(2\pi)^d}\int d\hat{\mathbf{k}}[\mathscr{J}_{\alpha_1}, a_\mu a_\nu][\mathscr{J}_{\alpha_2}, a_\mu a_\nu] \\ R_{\mu\nu}(t) &= \int_0^\infty dk\, k^{d-1}\exp\{[z_\mu(k)+z_\nu(k)]\,t\} \\ &= \frac{1}{2}\Gamma\left(\frac{d}{2}\right)(\omega_{\mu\nu}t)^{-d/2} \end{aligned} \tag{76}$$

with $z_\mu(k)+z_\nu(k) = -\omega_{\mu\nu}k^2$, and with use having been made of the fact that the currents $\mathscr{J}_\alpha$ and modes a_μ are real.

5. MUTUAL DIFFUSION

From the odd parity of the diffusion current $\mathscr{J}_1 = \hat{J}_{1x}$ and the parities given in Table I, one sees that the mode pairs which may contribute to the long-time tail of the mutual diffusion coefficient are the odd parts of the $(S\sigma, S-\sigma)$ pairs, and the $(\perp i, D\sigma)$ pairs.

5.1. $(S\sigma, S-\sigma)$ Contributions

The odd part of the product of two sound modes of opposite index is, from Eqs. (60),

$$(a_{S\sigma}(\mathbf{k})\,a_{S-\sigma}(-\mathbf{k}))_{\text{odd}} = \frac{\sigma\beta}{\rho c}\hat{\mathbf{k}}\cdot\mathbf{g}_0\,p_0 \tag{77}$$

The corresponding inner products appearing in the mode-coupling formula (76) are then, with use of Eq. (61),

$$[\hat{J}_{1x}, (a_{S\sigma}a_{S-\sigma})_{\text{odd}}] = \frac{\sigma\beta}{\rho c}\mathbf{i}\cdot\{[\mathbf{g}_0^{(1)}, \mathbf{g}_0\,p_0] - w[\mathbf{g}_0, \mathbf{g}_0\,p_0]\}\cdot\hat{\mathbf{k}}$$

From Eqs. (55), (63), and (B9) one finds

$$\begin{aligned} [\mathbf{g}_0^{(1)}, \mathbf{g}_0\,p_0] &= \frac{\rho}{\beta}\left(\frac{\partial p w/\beta}{\partial \rho}\right)_{s,w}\mathbf{1} \\ [\mathbf{g}_0, \mathbf{g}_0\,p_0] &= \frac{\rho}{\beta}\left(\frac{\partial p/\beta}{\partial \rho}\right)_{s,w}\mathbf{1} \end{aligned} \tag{78}$$

Thus

$$[\hat{J}_{1x}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}] = 0 \tag{79}$$

and the sound mode pairs make no contribution to the long-time tail of the mutual diffusion coefficient.

5.2. ($\perp i$, $D\sigma$) Contributions

With use of Eqs. (60), one finds

$$\begin{aligned}
[\hat{\mathbf{J}}_1, a_{\perp i} a_{D\sigma}] &= \frac{\sigma}{A_\sigma(\eta_+ - \eta_-)} \left(\frac{\beta}{\rho}\right)^{1/2} \\
&\quad \times \{(\eta_\sigma - \Delta_w)[\hat{\mathbf{J}}_1, \mathbf{g}_0 s_0] + \Delta'_w [\hat{\mathbf{J}}_1, \mathbf{g}_0 w_0]\} \cdot \hat{\mathbf{k}}_{\perp i} \\
[\hat{\mathbf{J}}_1, \mathbf{g}_0 s_0] &= [\mathbf{g}_0^{(1)}, \mathbf{g}_0 s_0] - w[\mathbf{g}_0, \mathbf{g}_0 s_0] \\
[\hat{\mathbf{J}}_1, \mathbf{g}_0 w_0] &= [\mathbf{g}_0^{(1)}, \mathbf{g}_0 w_0] - w[\mathbf{g}_0, \mathbf{g}_0 w_0]
\end{aligned} \tag{80}$$

Then, use of Eqs. (55), (63), (B7), and (B8) gives[3]

$$\begin{aligned}
[\mathbf{g}_0^{(1)}, \mathbf{g}_0 s_0] &= -\left[\frac{w}{\rho T}\left(\frac{\partial \rho/\beta}{\partial \beta}\right)_{p,w} + \frac{\hat{\mu}_T}{\rho \beta^2 \hat{\mu}_w}\left(\frac{\partial \rho w}{\partial w}\right)_{\beta,p}\right]\mathbf{1} \\
[\mathbf{g}_0, \mathbf{g}_0 s_0] &= -\left[\frac{1}{\rho T}\left(\frac{\partial \rho/\beta}{\partial \beta}\right)_{p,w} + \frac{\hat{\mu}_T}{\rho \beta^2 \hat{\mu}_w}\left(\frac{\partial \rho}{\partial w}\right)_{\beta,p}\right]\mathbf{1} \\
[\mathbf{g}_0^{(1)}, \mathbf{g}_0 w_0] &= \frac{1}{\rho \beta^2 \hat{\mu}_w}\left(\frac{\partial \rho w}{\partial w}\right)_{\beta,p}\mathbf{1} \\
[\mathbf{g}_0, \mathbf{g}_0 w_0] &= \frac{1}{\rho \beta^2 \hat{\mu}_w}\left(\frac{\partial \rho}{\partial w}\right)_{\beta,p}\mathbf{1}
\end{aligned} \tag{81}$$

---

[3] Note that it would be an error to use Eq. (B7) to write, with use also of Eq. (64),

$$[\hat{\mathbf{J}}_1, \mathbf{g}_0 w_0] = \frac{1}{\beta \rho \hat{\mu}_w}\left(\frac{\partial [\hat{\mathbf{J}}_1, \mathbf{g}_0]}{\partial w}\right)_{\beta,p} = 0$$

The difficulty is due to the presence of the ensemble-average quantity w in $\hat{\mathbf{J}}_1$ as given in Eq. (61), with $\hat{\mathbf{J}}_1$ consequently not having the purely microscopic character assumed for the quantity a_0 in Appendix B. A similar remark applies to other ternary inner products involving the currents.

Thus, Eqs. (80) become

$$\begin{aligned}
[\hat{\mathbf{J}}_1, \mathbf{g}_0 s_0] &= -\frac{\hat{\mu}_T}{\beta^2 \hat{\mu}_w}\mathbf{1} \\
[\hat{\mathbf{J}}_1, \mathbf{g}_0 w_0] &= \frac{1}{\beta^2 \hat{\mu}_w}\mathbf{1} \\
[\hat{\mathbf{J}}_1, a_{\perp i} a_{D\sigma}] &= -\frac{\sigma}{\beta^2 \hat{\mu}_w A_\sigma(\eta_+ - \eta_-)}\left(\frac{\beta}{\rho}\right)^{1/2} \hat{\mathbf{k}}_{\perp i}[\hat{\mu}_T(\eta_\sigma - \Delta_w) - \Delta'_w]
\end{aligned} \tag{82}$$

When the last result and the eigenvalues from Eqs. (43) and (45) are used in the mode-coupling formulas (76), there results

$$\begin{aligned}
B^{11}_{\perp i, D\sigma} = B^{11}_{D\sigma, \perp i} &= \frac{2[\hat{\mu}_T(\eta_\sigma - \Delta_w) - \Delta'_w]^2}{(4\pi)^{d/2}\, d\Gamma(d/2)\, \rho\beta^3\hat{\mu}_w^2(\eta_+ - \eta_-)^2 A_\sigma^2} \\
R_{\perp i, D\sigma} &= \frac{1}{2}\Gamma\left(\frac{d}{2}\right)\left(\frac{\rho}{(\eta + \eta_\sigma)\, t}\right)^{d/2} \\
\rho_{11, \perp D}(t) &\asymp \frac{d-1}{d\rho\beta^3\hat{\mu}_w^2(\eta_+ - \eta_-)^2}\sum_\sigma \frac{[\hat{\mu}_T(\eta_\sigma - \Delta_w) - \Delta'_w]^2}{A_\sigma^2[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}}
\end{aligned} \tag{83}$$

with the sum over the $(d-1)$ shear modes and the permutation of the $\perp i$ and $D\sigma$ indices having been carried out in the last equation.

5.3. $\rho_{11}(t)$

Since the $\perp D$ terms are the only contributions to $\rho_{11}(t)$, and with use of Eqs. (32), (33), (46), (47), and (59), the last result can be written as

$$\begin{aligned}
\rho_{11}(t) &\asymp \frac{d-1}{d\beta^2\hat{\mu}_w(\eta_+ - \eta_-)} \\
&\quad \times \sum_\sigma \frac{\sigma[\eta_\sigma - (L'_{uu} + 2\hat{\mu}_T T L'_{1u} + \hat{\mu}_T^2 T^2 L'_{11})/c_p T]}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}} \\
&\asymp \frac{d-1}{d\beta^2\hat{\mu}_w(\eta_+ - \eta_-)}\sum_\sigma \frac{\sigma(\eta_\sigma - L''_{uu}/c_p T)}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}}
\end{aligned} \tag{84}$$

Note that $L_{11} = L'_{11} = L''_{11}$, so that $\rho_{11} = \rho'_{11} = \rho''_{11}$. The first of Eqs. (84) bears a general resemblance to the corresponding Eq. (4.14) in ref. 2, but two discrepancies remain after allowing for the differences in notation: Pomeau has a factor d in place of the factor $(d-1)/d$, and the opposite sign for the overall result.

5.3.1. Dilute Limit Reduction. It is to be expected that in the limit $w \to 0$, in which the binary mixture becomes a pure fluid of particles of species 2, the present results for the asymptotic behavior of the time correlation functions for the mixture should reduce to those of Ernst *et al.*$^{(1)}$ for the pure fluid. In order to verify that this is the case, it is sufficient to assume, first, that the mixture exhibits a Henry's law behavior such that in this limit

$$\hat{\mu} \asymp \frac{1}{\beta m^{(1)}} \ln w$$

$$\hat{\mu}_T \asymp \frac{k_B}{m^{(1)}} \ln w$$

$$\hat{\mu}_w \asymp \frac{1}{\beta m^{(1)} w}$$

with $m^{(a)}$ denoting the mass of a particle of species a, and, second, that

$$L_{11} = O(w)$$

$$L_{1u} = O(w)$$

Then consider the quantity

$$\hat{D} = \lim_{w \to 0} \frac{\hat{\mu}_w L_{11}}{\rho} = \int_0^\infty \hat{\rho}(t)\, dt$$

and its corresponding time correlation function

$$\hat{\rho}(t) = \lim_{w \to 0} \frac{\beta \hat{\mu}_w \rho_{11}(t)}{\rho}$$

Under the above assumptions, one can show that in this dilute limit

$$\Delta_s \to L'_{uu}/c_p T \to L''_{uu}/c_p T$$

$$\Delta_w \to \rho \hat{D}$$

and also that the two roots η_σ of Eq. (46) approach the values $L''_{uu}/c_p T$ and $\rho\hat{D}$. Then Eq. (84) reduces to

$$\hat{\rho}(t) \asymp \frac{d-1}{d\beta\rho} \left[4\pi(v + \hat{D})\, t\right]^{-d/2}$$

which is the familiar expression$^{(9)}$ for the long-time tail of the velocity autocorrelation function of a pure fluid having kinematic viscosity ν and self-diffusion coefficient $\hat{D}$.

6. THERMAL DIFFUSIVITY

The unprimed thermal diffusivity is given by the mode-coupling formula (76) as

$$\begin{aligned} \rho_{1u}(t) &\asymp \frac{1}{2}\sum_{\mu,\nu} B^{1u}_{\mu\nu} R_{\mu\nu}(t) \\ B^{1u}_{\mu\nu} &= \frac{1}{(2\pi)^d}\int d\hat{\mathbf{k}}[\hat{J}_{1x}, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})][\hat{J}_{ux}, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})] \end{aligned} \tag{85}$$

with the diffusion current given in Eq. (61) and the heat current in Eq. (65). Both currents are odd functions of the particle velocities, so the potentially contributing mode pairs are again $(S\sigma, S-\sigma)_{\text{odd}}$ and $(\perp i, D\sigma)$. But according to Eq. (79), the inner product of the diffusion current with $(a_{S\sigma}a_{S-\sigma})_{\text{odd}}$ vanishes, and thus the sound modes make no contribution to the tail of $\rho_{1u}(t)$. Then Eqs. (85) reduce to

$$\begin{aligned} \rho_{1u}(t) &= \rho_{1u,\perp D}(t) = \sum_{i=1}^{d-1}\sum_{\sigma} B^{1u}_{\perp i, D\sigma} R_{\perp i, D\sigma}(t) \\ B^{1u}_{\perp i, D\sigma} &= \frac{1}{(2\pi)^d}\int d\hat{\mathbf{k}}[\hat{J}_{1x}, a_{\perp i}a_{D\sigma}][\hat{J}_{ux}, a_{\perp i}a_{D\sigma}] \end{aligned} \tag{86}$$

including a factor of 2 arising from the interchange of the $\perp i$ and $D\sigma$ subscripts, and with $[\hat{\mathbf{J}}_1, a_{\perp i}a_{D\sigma}]$ given in Eq. (82). With the aid of Eqs. (55), (60), (65)–(67), (81), (B7) and (B8) there results

$$\begin{aligned} [\hat{\mathbf{J}}_u, a_{\perp i}a_{D\sigma}] &= \frac{\sigma(\beta/\rho)^{1/2}}{(\eta_+ - \eta_-)\,A_\sigma}\{(\eta_\sigma - \Delta_w)[\hat{\mathbf{J}}_u, \mathbf{g}_0 s_0] + \Delta'_w[\hat{\mathbf{J}}_u, \mathbf{g}_0 w_0]\}\cdot\hat{\mathbf{k}}_{\perp i} \\ [\hat{\mathbf{J}}_u, \mathbf{g}_0 s_0] &= [\hat{\mathbf{J}}_e, \mathbf{g}_0 s_0] - h[\mathbf{g}_0, \mathbf{g}_0 s_0] \\ [\hat{\mathbf{J}}_u, \mathbf{g}_0 w_0] &= [\hat{\mathbf{J}}_e, \mathbf{g}_0 w_0] - h[\mathbf{g}_0, \mathbf{g}_0 w_0] \\ [\hat{\mathbf{J}}_e, \mathbf{g}_0 s_0] &= -\left[\frac{1}{\rho T}\left(\frac{\partial(\rho h/\beta)}{\partial\beta}\right)_{p,w} + \frac{\hat{\mu}_T}{\rho\beta\hat{\mu}_w}\left(\frac{\partial(\rho h/\beta)}{\partial w}\right)_{\beta,p}\right]\mathbf{1} \\ [\hat{\mathbf{J}}_u, \mathbf{g}_0 s_0] &= \frac{1}{\beta^2}\left[c_p - \frac{\hat{\mu}_T}{\hat{\mu}_w}(\hat{\mu} - T\hat{\mu}_T)\right]\mathbf{1} \\ [\hat{\mathbf{J}}_e, \mathbf{g}_0 w_0] &= \frac{1}{\rho\beta\hat{\mu}_w}\left(\frac{\partial(\rho h/\beta)}{\partial w}\right)_{\beta,p}\mathbf{1} \\ [\hat{\mathbf{J}}_u, \mathbf{g}_0 w_0] &= \frac{1}{\beta^2\hat{\mu}_w}(\hat{\mu} - T\hat{\mu}_T)\,\mathbf{1} \end{aligned} \tag{87}$$

using also $(\partial h/\partial\beta)_{p,w} = -Tc_p/\beta$ and $(\partial h/\partial w)_{\beta,p} = \hat{h} = \hat{\mu} - T\hat{\mu}_T$. Thus,

$$[\hat{\mathbf{J}}_u, a_{\perp i}a_{D\sigma}] = \frac{\sigma(\beta/\rho)^{1/2}\,\hat{\mathbf{k}}_{\perp i}}{\beta^2(\eta_+ - \eta_-)\,A_\sigma}\left\{(\eta_\sigma - \Delta_w)\left[c_p - \frac{\hat{\mu}_T(\hat{\mu} - T\hat{\mu}_T)}{\hat{\mu}_w}\right] + \frac{\Delta'_w(\hat{\mu} - T\hat{\mu}_T)}{\hat{\mu}_w}\right\}$$

With the aid of Eqs. (37) and (46) this can be reduced to

$$[\hat{\mathbf{J}}_u, a_{\perp i}a_{D\sigma}] = \frac{\sigma(\beta/\rho)^{1/2}\,T\Delta'_w\hat{\mathbf{k}}_{\perp i}}{\beta^2\hat{\mu}_w(\eta_+ - \eta_-)(\eta_\sigma - \Delta_s)\,A_\sigma\Delta'_s} \times (\eta_\sigma - \Delta_s - \hat{\mu}_T\Delta'_s)\left(\eta_\sigma - \Delta_w + \frac{\hat{\mu}\Delta'_s}{T}\right) \tag{88}$$

With use of this result, together with Eqs. (47), (59), (82), and (83), in Eqs. (86) there results

$$\rho_{1u}(t) \asymp \frac{d-1}{d\beta^2\hat{\mu}_w(\eta_+ - \eta_-)}\,\frac{c_pT}{L''_{1u}} \times \sum_\sigma \frac{\sigma(\eta_\sigma - L''_{uu}/c_pT)(\eta_\sigma - \hat{\mu}_w L''_{11} + \hat{h}L''_{1u}/c_pT)}{[4\pi(\eta + \eta_\sigma)\,t/\rho]^{d/2}} \tag{89}$$

With regard to the dilute limit behavior of $\rho_{1u}(t)$, one expects it to vanish, since L_{1u} vanishes in that limit. As given in Eq. (89), it is indeterminate, but can be shown to vanish by treating $\hat{\mu}_w L''^2_{1u}$ as a small quantity and expanding η_σ to first order.

6.1 $\rho^{(KK)}_{1u}$, $\rho^{(K\Phi)}_{1u}$, and $\rho^{(\Phi\Phi)}_{1u}$

Recalling that $\hat{\mathbf{J}}_1$ has no potential part, one sees that

$$\rho_{1u}(t) = \rho^{(KK)}_{1u}(t) + \rho^{(K\phi)}_{1u}(t)$$

with $\rho^{(\phi\phi)}_{1u}(t) = \rho^{(\phi K)}_{1u}(t) = 0$. The kinetic part is

$$\begin{aligned} \rho^{(KK)}_{1u}(t) &\asymp \sum_{i=1}^{d-1}\sum_\sigma B^{1u,KK}_{\perp i,D\sigma}R_{\perp i,D\sigma}(t) \\ B^{1u,KK}_{\perp i,D\sigma} &= \frac{1}{(2\pi)^d}\int d\hat{\mathbf{k}}[\hat{J}_{1x}, a_{\perp i}a_{D\sigma}][\hat{J}^{(K)}_{ux}, a_{\perp i}a_{D\sigma}] \end{aligned} \tag{90}$$

With use of Eqs. (66), (70), (B7), and (B8) one obtains

$$\begin{aligned}
[\hat{\mathbf{J}}_u^{(K)}, a_{\perp i} a_{D\sigma}] &= \frac{\sigma(\beta/\rho)^{1/2}}{(\eta_+ - \eta_-)\, A_\sigma} \{(\eta_\sigma - \varDelta_w)[\hat{\mathbf{J}}_u^{(K)}, \mathbf{g}_0 s_0] \\
&\quad + \varDelta'_w[\hat{\mathbf{J}}_u^{(K)}, \mathbf{g}_0 w_0]\} \cdot \hat{\mathbf{k}}_{\perp i} \\
[\hat{\mathbf{J}}_u^{(K)}, \mathbf{g}_0 s_0] &= \frac{c_p^0}{\beta^2} \mathbf{1} \qquad (91) \\
[\hat{\mathbf{J}}_u^{(K)}, \mathbf{g}_0 w_0] &= 0 \\
[\hat{\mathbf{J}}_u^{(K)}, a_{\perp i} a_{D\sigma}] &= \frac{\sigma(\beta/\rho)^{1/2}\, (\eta_\sigma - \varDelta_w)\, c_p^0 \hat{\mathbf{k}}_{\perp i}}{\beta^2(\eta_+ - \eta_-)\, A_\sigma}
\end{aligned}$$

in which the ideal-gas constant-pressure specific heat has been introduced as in ref. 1,

$$c_p^0 = \frac{(d+2)\, k_{\mathrm{B}} \langle N \rangle}{2\rho V}$$

Then Eq. (90) can be reduced to

$$\rho_{1u}^{(KK)}(t) \asymp \frac{(d-1)\, c_p^0}{d\beta^2(\eta_+ - \eta_-)} \frac{L''_{1u}}{c_p} \sum_\sigma \frac{\sigma}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}}$$

The cross term can be calculated from the preceding results as

$$\rho_{1u}^{(K\phi)}(t) = \rho_{1u}(t) - \rho_{1u}^{(KK)}(t)$$

6.2. Single-Primed Thermal Diffusivity

It follows from Eq. (32) that

$$\rho'_{1u}(t) = \rho_{1u}(t) - \hat{\mu} \rho_{11}(t)$$

which permits the asymptotic form of the correlation function to be calculated from Eqs. (84) and (89) as

$$\begin{aligned}
\rho'_{1u}(t) &\asymp \frac{d-1}{d\beta^2 \hat{\mu}_w(\eta_+ - \eta_-)} \frac{c_p T}{L''_{1u}} \\
&\quad \times \sum_\sigma \frac{\sigma(\eta_\sigma - L''_{uu}/c_p T)(\eta_\sigma - \hat{\mu}_w L''_{11} - T\hat{\mu}_T L''_{1u}/c_p T)}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}}
\end{aligned}$$

In order to compare this result with that of Pomeau, one can use Eqs. (37), (46), and (47) to write it as

$$\rho'_{1u}(t) \asymp \frac{d-1}{d\beta^2 \hat{\mu}_w(\eta_+ - \eta_-)} \sum_\sigma \frac{\sigma}{[4\pi(\eta+\eta_\sigma)\, t/\rho]^{d/2}}$$
$$\times \left[\frac{\hat{\mu}_T}{c_p} (L'_{uu} + T\hat{\mu}_T L'_{1u}) + \left(\hat{\mu}_w + \frac{T\hat{\mu}_T^2}{c_p} \right) \right.$$
$$\left. \times (L'_{1u} + T\hat{\mu}_T L'_{11}) - T\hat{\mu}_T \eta_\sigma \right]$$

This agrees with Eq. (4.16b) in ref. 2, except for the overall sign.

6.3. Double-Primed Thermal Diffusivity

It follows from Eq. (33) that

$$\rho''_{1u}(t) = \rho_{1u}(t) - \hat{h}\rho_{11}(t)$$

With use of Eqs. (47), (84), and (89), this leads to

$$\rho''_{1u}(t) \asymp \frac{(d-1)\, L''_{1u}}{d\beta^2(\eta_+ - \eta_-)} \sum_\sigma \frac{\sigma}{[4\pi(\eta+\eta_\sigma)\, t/\rho]^{d/2}}$$

Incidentally, this result shows that $\rho''_{1u}(t)$ has, at long times, a sign opposite to that of L''_{1u}.

7. THERMAL CONDUCTIVITY

The potentially contributing mode pairs are again the odd parts of the $(S\sigma, S-\sigma)$ pairs, and the $(\perp i, D\sigma)$ pairs. Both types of pairs will be found to give nonvanishing contributions to the long-time behavior of $\rho_{uu}(t)$, and so it is convenient to write

$$\rho_{uu}(t) = \rho_{uu,SS}(t) + \rho_{uu,\perp D}(t)$$

7.1. $\rho_{uu,SS}(t)$

For this case the mode-coupling formulas (76) become

$$\rho_{uu,SS}(t) \asymp \frac{1}{2} \sum_\sigma B^{uu}_{S\sigma,S-\sigma} R_{SS}(t)$$
$$B^{uu}_{S\sigma,S-\sigma} = \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}_{ux}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}]^2 \qquad (92)$$
$$R_{SS}(t) = \frac{1}{2} \Gamma\left(\frac{d}{2}\right) (\Gamma_s t)^{-d/2}$$

With the aid of Eqs. (65), (67), (77), (78), and (B9), one has

$$\begin{aligned}
[\hat{J}_{ux}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}] &= \frac{\sigma\beta}{\rho c} [\hat{\mathbf{J}}_u, g_0 p_0] \cdot \hat{\mathbf{k}} \\
[\hat{\mathbf{J}}_u, g_0 p_0] &= [\hat{\mathbf{J}}_e, g_0 p_0] - h[g_0, g_0 p_0] \\
[\hat{\mathbf{J}}_e, g_0 p_0] &= \frac{\rho}{\beta} \left(\frac{\partial \rho h/\beta}{\partial \rho} \right)_{s,w} \mathbf{1} \\
[\hat{\mathbf{J}}_u, g_0 p_0] &= \frac{\rho^2}{\beta^2} \left(\frac{\partial h}{\partial \rho} \right)_{s,w} \mathbf{1} = \frac{\rho c^2}{\beta^2} \mathbf{1}
\end{aligned} \tag{93}$$

Finally, use of this last result in Eq. (92) gives

$$\rho_{uu,SS}(t) \asymp \frac{c^2}{d\beta^2 (4\pi \Gamma_s t)^{d/2}} \tag{94}$$

7.1.1. $\boldsymbol{\rho^{(KK)}_{uu,SS}}$, $\boldsymbol{\rho^{(K\Phi)}_{uu,SS}}$, and $\boldsymbol{\rho^{(\Phi\Phi)}_{uu,SS}}$. The kinetic part of $\rho_{uu,SS}$ is

$$\begin{aligned}
\rho^{(KK)}_{uu,SS}(t) &= \frac{1}{2} \sum_{\sigma} B^{uu,KK}_{S\sigma,S-\sigma} R_{SS}(t) \\
B^{uu,KK}_{S\sigma,S-\sigma} &= \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}^{(K)}_{ux}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}]^2
\end{aligned} \tag{95}$$

From Eqs. (69) and (77) one finds

$$\begin{aligned}
[\hat{\mathbf{J}}^{(K)}_u, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}] = \frac{\sigma\beta}{\rho c} \Bigg\{ &\left[\sum_i \frac{1}{2} m_i v_i^2 \mathbf{v}_i, g_0 p_0 \right] \\
&- \frac{d+2}{2\beta} \left[\sum_i \mathbf{v}_i, g_0 p_0 \right] \Bigg\} \cdot \mathbf{k}
\end{aligned}$$

With use of Eqs. (66), (70), and (B9), and the thermodynamic relation $(\partial T/\partial \rho)_{s,w} = \alpha T c^2/\rho c_p$, this reduces to

$$[\hat{\mathbf{J}}^{(K)}_u, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}] = \frac{\sigma c}{\beta} \frac{\alpha T c_p^0}{c_p} \hat{\mathbf{k}}$$

Then Eq. (95) becomes

$$\rho^{(KK)}_{uu,SS}(t) \asymp \left(\frac{\alpha T c_p^0}{c_p} \right)^2 \rho_{uu,SS}(t) \tag{96}$$

The cross term in $\rho_{uu,SS}$ is

$$\rho^{(K\phi)}_{uu,SS}(t) \asymp \frac{1}{2} \sum_{\sigma} B^{uu,K\phi}_{S\sigma,S-\sigma} R_{SS}(t)$$

$$B^{uu,K\phi}_{S\sigma,S-\sigma} = \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}^{(K)}_{ux}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}][\hat{J}^{(\phi)}_{ux}, (a_{S\sigma} a_{S-\sigma})_{\text{odd}}]$$

Since $\hat{\mathbf{J}}^{(\phi)}_u = \hat{\mathbf{J}}_u - \hat{\mathbf{J}}^{(K)}_u$, these quantities can be calculated in terms of the previous results, to give

$$\rho^{K\phi}_{uu,SS}(t) \asymp \frac{\alpha T c^0_p}{c_p} \left(1 - \frac{\alpha T c^0_p}{c_p}\right) \rho_{uu,SS}(t) \tag{97}$$

In similar fashion, the potential term is

$$\rho^{(\phi\phi)}_{uu,SS}(t) \asymp \left(1 - \frac{\alpha T c^0_p}{c_p}\right)^2 \rho_{uu,SS}(t) \tag{98}$$

7.2. $\rho_{uu,\perp D}(t)$

The shear and diffusion mode pairs give a contribution to $\rho_{uu}(t)$ given by

$$\begin{aligned} \rho_{uu,\perp D}(t) &\asymp \sum_{i=1}^{d-1} \sum_{\sigma} B^{uu}_{\perp i,D\sigma} R_{\perp i,D\sigma}(t) \\ B^{uu}_{\perp i,D\sigma} &= \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}_{ux}, a_{\perp i} a_{D\sigma}]^2 \end{aligned} \tag{99}$$

including a factor of 2 arising from the permutation of the $\perp i$ and $D\sigma$ subscripts. With use of Eqs. (47), (59), and (88) in Eq. (99), one then finds

$$\begin{aligned} \rho_{uu,\perp D}(t) \asymp{}& \frac{d-1}{d\beta^2 \hat{\mu}_w(\eta_+ - \eta_-)} \left(\frac{c_p T}{L''_{1u}}\right)^2 \\ &\times \sum_{\sigma} \frac{\sigma(\eta_\sigma - L''_{uu}/c_p T)(\eta_\sigma - \hat{\mu}_w L''_{11} + \hat{h} L''_{1u}/c_p T)^2}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}} \end{aligned} \tag{100}$$

7.2.1. $\rho^{(KK)}_{uu,\perp D}$, $\rho^{(K\Phi)}_{uu,\perp D}$, and $\rho^{(\Phi\Phi)}_{uu,\perp D}$. The kinetic part of $\rho_{uu,\perp D}$ is given by

$$\rho^{(KK)}_{uu,\perp D}(t) \asymp \sum_{i=1}^{d-1} \sum_{\sigma} B^{uu,KK}_{\perp i,D\sigma} R_{\perp i,D\sigma}(t)$$

$$B^{uu,KK}_{\perp i,D\sigma} = \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}^{(K)}_{ux}, a_{\perp i} a_{D\sigma}]^2$$

In similar fashion to the calculation of $\rho_{uu,\perp D}$, one finds with the use of Eq. (91)

$$\rho^{(KK)}_{uu,\perp D}(t) \asymp \frac{(d-1)\,\hat{\mu}_w (c^0_p)^2}{d\beta^2(\eta_+ - \eta_-)} \left(\frac{L''_{1u}}{c_p}\right)^2 \times \sum_\sigma \frac{\sigma}{(\eta_\sigma - L''_{uu}/c_p T)[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}} \tag{101}$$

The cross term $\rho^{(K\phi)}_{uu,\perp D}$ and potential term $\rho^{(\phi\phi)}_{uu,\perp D}$ are most easily calculated in indirect fashion, by noting that, since $\hat{\mathbf{J}}^{(\phi)}_u = \hat{\mathbf{J}}_u - \hat{\mathbf{J}}^{(K)}_u$, one can write

$$\begin{aligned} \rho^{(K\phi)}_{uu,\perp D}(t) &= \rho^{(KT)}_{uu,\perp D}(t) - \rho^{(KK)}_{uu,\perp D}(t) \\ \rho^{(\phi\phi)}_{uu,\perp D}(t) &= \rho_{uu,\perp D}(t) - 2\rho^{(KT)}_{uu,\perp D}(t) + \rho^{(KK)}_{uu,\perp D}(t) \end{aligned} \tag{102}$$

in which

$$\rho^{(KT)}_{uu,\perp D}(t) \asymp \sum_i^{d-1} \sum_\sigma B^{uu,KT}_{\perp i,D\sigma} R_{\perp i,D\sigma}(t)$$

$$B^{uu,KT}_{\perp i,D\sigma} = \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\hat{J}^{(K)}_{ux}, a_{\perp i} a_{D\sigma}][\hat{J}_{ux}, a_{\perp i} a_{D\sigma}]$$

One then finds

$$\rho^{(KT)}_{uu,\perp D}(t) \asymp \frac{(d-1)\, c^0_p T}{d\beta^2(\eta_+ - \eta_-)} \sum_\sigma \frac{\sigma(\eta_\sigma - \hat{\mu}_w L''_{11} + \hat{h} L''_{1u}/c_p T)}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}} \tag{103}$$

7.3. Dilute Limit Reduction

In verifying that the present results reduce to those of Ernst *et al.*[1] in the $w \to 0$ limit, it is necessary to consider some differences in notation. Their λ is the present L'_{uu}/T, and they write

$$\lambda = \frac{\beta}{T} \int_0^\infty c_\lambda(t)\, dt$$

whereas here

$$L'_{uu} = \beta \int_0^\infty \rho'_{uu}(t)\, dt$$

Thus, the two correlation functions should in fact be identical: $\rho'_{uu}(t) = c_\lambda(t)$. Furthermore, under the assumptions regarding the dilute limit detailed in Section 5, it can be shown that the three thermal conductivities L_{uu}, L'_{uu}, and L''_{uu} become equal, and thus equal to $T\lambda$ for the pure fluid. So it is to be expected that the present result for the long-time behavior of $\rho_{uu}(t)$ should reduce to that given in ref. 1 for $c_\lambda(t)$. In addition, it should be noted that the three thermal diffusivities L_{1u}, L'_{1u}, and L''_{1u} all approach zero, although not to the same order.[4]

With respect to the sound mode contributions, Eqs. (94), (96), and (98) agree exactly with the corresponding terms in Eqs. (32a), (33a), (34a), and (34c) of ref. 1. The cross term in Eq. (97) agrees with their Eq. (34b), except for sign.[5]

Turning to the contributions of the shear and diffusion mode pairs, it can be seen that $\rho_{uu,\perp D}(t)$ as given in Eq. (100) is indeterminate in the dilute limit, since $L''_{1u} \to 0$ and $\eta_\sigma \to L''_{uu}/c_p T$ or $\hat{\mu}_w L''_{11}$. By treating $\hat{\mu}_w L''^2_{1u}$ as a small quantity and considering the terms of that order in the approach of the η_σ to their limiting values, one can verify that Eq. (100) reduces to

$$\rho_{uu,\perp D}(t) \asymp \frac{(d-1)\, c_p T}{d\beta^2 [4\pi(\eta + L''_{uu}/c_p T)\, t/\rho]^{d/2}}$$

This agrees with the corresponding term in Eq. (32a) in ref. 1, note being taken that their C_p is per particle, rather than per unit mass. The kinetic and potential contributions, and also the cross term except for a similar sign error, can be likewise shown to reduce to the corresponding terms for the pure fluid in their Eqs. (34).

7.4. Single-Primed Thermal Conductivity

According to Eq. (32),

$$\rho'_{uu}(t) = \rho_{uu}(t) - 2\hat{\mu}\rho_{1u}(t) + \hat{\mu}^2 \rho_{11}(t)$$

can be calculated from the previous results for the unprimed correlation functions. With respect to the sound mode contributions, it has been seen that those contributions to the asymptotic time dependence of $\rho_{1u}(t)$ and $\rho_{11}(t)$ vanish. Thus, $\rho'_{uu,SS}(t) = \rho_{uu,SS}(t)$ as given in Eq. (94).

The shear-diffusion contribution is found from Eqs. (84), (89), and (100) to be

$$\rho'_{uu,\perp D}(t) = \frac{d-1}{d\beta^2 \hat{\mu}_w(\eta_+ - \eta_-)} \left(\frac{c_p T}{L''_{1u}}\right)^2 \times \sum_\sigma \frac{\sigma(\eta_\sigma - L''_{uu}/c_p T)(\eta_\sigma - \hat{\mu}_w L''_{11} - T\hat{\mu}_T L''_{1u}/c_p T)^2}{[4\pi(\eta + \eta_\sigma)\, t/\rho]^{d/2}}$$

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[4] It can be shown that if $L'_{1u} = O(w)$, then $L_{1u} = O(w \ln w)$.

[5] It can easily be seen that the sign in ref. 1 must be changed in order to satisfy the relation $K_{+-} = K^{KK}_{+-} + 2K^{K\phi}_{+-} + K^{\phi\phi}_{+-}$.

Upon comparing these results with those in Eq. (4.17b) of ref. 2, the following differences are noted:

1. The first term in Pomeau's equation should be the sound mode contribution, as given in the present Eq. (94). Instead, it contains a factor $1/\gamma$, where $\gamma = c_p/c_v$.

2. The shear-diffusion term again differs in overall sign, and in addition the minus sign in the factor $(c_p - T\hat{\mu}_T^2/\hat{\mu}_\gamma)$ should be changed to plus.

7.5. Double-Primed Thermal Conductivity

The correlation function $\rho''_{uu}(t)$ can be calculated from the unprimed functions, according to Eq. (33), as

$$\rho''_{uu}(t) = \rho_{uu}(t) - 2\hat{h}\rho_{1u}(t) + \hat{h}^2\rho_{11}(t)$$

Once again, $\rho''_{uu,SS}(t) = \rho_{uu,SS}(t)$ as given in Eq. (94), while from Eqs. (84), (89), (100) one obtains

$$\rho''_{uu,\perp D}(t) = \frac{(d-1)\,c_p T}{d\beta^2(\eta_+ - \eta_-)} \sum_\sigma \frac{\sigma(\eta_\sigma - \hat{\mu}_w L''_{11})}{[4\pi(\eta + \eta_\sigma)\,t/\rho]^{d/2}}$$

with use again of the last of Eqs. (47).

8. SHEAR VISCOSITY

The mode-coupling formula (76) for the shear viscosity correlation function becomes, with the use of Eqs. (71),

$$\begin{aligned} \rho_\eta^{(AB)}(t) &\asymp \frac{1}{2} \sum_{\mu\nu} B_{\mu\nu}^{\eta,AB} R_{\mu\nu}(t) \\ B_{\mu\nu}^{\eta,AB} &= \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}}\, [T_{xy}^{(A)}, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})][T_{xy}^{(B)}, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})] \end{aligned} \tag{104}$$

in which A and $B = K$ or ϕ. Since the shear viscosity current, as given in Eqs. (71), is even in the particle velocities, it follows from Table I that the possibly contributing pairs of modes are $(D\sigma, D\sigma')$, $(S\sigma, S-\sigma)_{\text{even}}$, and $(\perp i, \perp j)$.

From Eqs. (60) it can be seen that $[T_{xy}^{(A)}, a_{D\sigma}a_{D\sigma'}]$ is a linear function of the three inner products $[T_{xy}^{(A)}, s_0 s_0]$, $[T_{xy}^{(A)}, s_0 w_0]$, and $[T_{xy}^{(A)}, w_0 w_0]$. According to Eqs. (B11)–(B13), all of those products vanish (because $\langle T_{xy}^{(A)} \rangle = 0$), and therefore the $(D\sigma, D\sigma')$ pairs make no contribution to the long-time behavior of $\rho_\eta(t)$. Then, symbolically,

$$\rho_\eta^{(AB)}(t) = \rho_{\eta,\perp\perp}^{(AB)}(t) + \rho_{\eta,SS}^{(AB)}(t)$$

8.1. Shear Mode Contributions

With use of Eqs. (60), one finds[6]

$$[T_{xy}^{(A)}, a_{\perp i}(\mathbf{k})\, a_{\perp j}(-\mathbf{k})] = -\frac{\beta}{\rho} \sum_{\alpha} \sum_{\beta} \hat{k}_{\perp i\alpha} \hat{k}_{\perp j\beta} [T_{xy}^{(A)}, g_{0\alpha}\, g_{0\beta}] \tag{105}$$

From the symmetry of the velocity distribution and translational invariance, it can be seen that $[T_{xy}^{(\phi)}, g_{0\alpha}\, g_{0\beta}] = 0$, so that

$$\rho_{\eta, \perp\perp}^{(K\phi)}(t) \asymp \rho_{\eta, \perp\perp}^{(\phi\phi)}(t) \asymp 0$$

For $A = K$ one has

$$[T_{xy}^{(K)}, g_{0\alpha}\, g_{0\beta}] = \frac{1}{V} \left\langle \sum_{i} \sum_{j} \sum_{l} m_i m_j m_l \overline{v_{i\alpha} v_{j\beta} v_{lx} v_{ly}} \right\rangle$$

with the overbar denoting the average over the equilibrium velocity distribution for a fixed number of particles. As in ref. 1, one can show that

$$\begin{aligned} \overline{v_{i\alpha} v_{j\beta} v_{lx} v_{ly}} &= \frac{1}{\beta^2 m_l^2} \delta_{il} \delta_{jl} (\delta_{\alpha x} \delta_{\beta y} + \delta_{\alpha y} \delta_{\beta x}) \\ [T_{xy}^{(K)}, g_{0\alpha}\, g_{0\beta}] &= \frac{\rho}{\beta^2} (\delta_{\alpha x} \delta_{\beta y} + \delta_{\alpha y} \delta_{\beta x}) \end{aligned} \tag{106}$$

and thereby reduce Eq. (105) to

$$[T_{xy}^{(K)}, a_{\perp i}(\mathbf{k})\, a_{\perp j}(-\mathbf{k})] = -\frac{1}{\beta} (\hat{k}_{\perp ix} \hat{k}_{\perp jy} + \hat{k}_{\perp iy} \hat{k}_{\perp jx})$$

which is the same result as for a pure fluid.$^{(1)}$ The angular integrations in Eq. (104) are carried out as in ref. 1, and thus the result is the same as in Eq. (33b) in ref. 1 for a pure fluid,

$$\rho_{\eta, \perp\perp}(t) = \rho_{\eta, \perp\perp}^{(KK)}(t) = \frac{d^2 - 2}{d(d+2)\, \beta^2 (8\pi\eta t/\rho)^{d/2}}$$

This also agrees with the corresponding term in Eq. (4.18) of ref. 2.

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[6] The minus sign in Eq. (105) arises from taking $\hat{\mathbf{k}}_{\perp j}(-\mathbf{k}) = -\hat{\mathbf{k}}_{\perp j}(\mathbf{k})$. It has no effect upon the final results.

8.2. Sound Mode Contributions

With use again of Eqs. (60), one finds

$$[T_{xy}^{(A)}, (a_{S\sigma}(\mathbf{k})\, a_{S-\sigma}(-\mathbf{k}))_{\text{even}}] = \frac{\beta}{2\rho c^2}\left([T_{xy}^{(A)}, p_0 p_0] + c^2 \sum_\alpha \sum_\beta [T_{xy}^{(A)}, g_{0\alpha} g_{0\beta}]\, \hat{k}_\alpha \hat{k}_\beta\right)$$

According to Eq. (B10), $[T_{xy}^{(A)}, p_0 p_0] = 0$ for both $A = K$ and $A = \phi$, and it has already been noted that $[T_{xy}^{(\phi)}, g_{0\alpha} g_{0\beta}] = 0$. Thus again the cross and potential terms vanish,

$$\rho_{\eta, SS}^{(K\phi)}(t) \asymp \rho_{\eta, SS}^{(\phi\phi)} \asymp 0$$

and it is left to consider, using again Eq. (106),

$$[T_{xy}^{(K)}, (a_{S\sigma}(\mathbf{k})\, a_{S-\sigma}(-\mathbf{k}))_{\text{even}}] = \frac{1}{\beta} \hat{k}_x \hat{k}_y$$

This then leads to

$$\rho_{\eta, SS}(t) \asymp \rho_{\eta, SS}^{(KK)}(t) \asymp \frac{1}{d(d+2)\, \beta^2 (4\pi \Gamma_s t)^{d/2}}$$

which agrees with the corresponding pure fluid result of Eq. (33b) in ref. 1 and also with the corresponding term in Eq. (4.18) of ref. 2.

8.3. Summary

As might be expected, the asymptotic time dependence of the shear viscosity correlation function $\rho_\eta(t)$ is the same as for a pure fluid, with only the kinetic terms being nonzero.

9. LONGITUDINAL AND BULK VISCOSITIES

The mode-coupling formula (76) for the longitudinal viscosity is

$$\rho_l(t) \asymp \frac{1}{2} \sum_{\mu\nu} B_{\mu\nu}^l R_{\mu\nu}(t)$$

$$B_{\mu\nu}^l = \frac{1}{(2\pi)^d} \int d\hat{\mathbf{k}} [\mathscr{I}_l, a_\mu(\mathbf{k})\, a_\nu(-\mathbf{k})]^2$$

with the contributing mode pairs again being $(D\sigma, D\sigma')$, $(S\sigma, S-\sigma)_{\text{even}}$, and $(\perp i, \perp j)$.

9.1. Shear Mode Contributions

The calculation of $[\mathscr{J}_l, a_{\perp i}(\mathbf{k})\, a_{\perp j}(-\mathbf{k})]$ is carried out in the same manner as in ref. 1, and with the same result

$$\begin{aligned}[\mathscr{J}_l, a_{\perp i}(\mathbf{k})\, a_{\perp j}(-\mathbf{k})] &= -\frac{1}{\beta}\left[2\hat{k}_{\perp ix}\hat{k}_{\perp jx} - \delta_{ij}\left(\frac{\partial p}{\partial e}\right)_{\rho, w}\right] \\ &= -\frac{2}{\beta}\left[\hat{k}_{\perp ix}\hat{k}_{\perp jx} - \frac{\gamma-1}{2\alpha T}\delta_{ij}\right]\end{aligned}$$

The resulting long-time tail is therefore the same as in ref. 1 for the pure fluid,

$$\rho_{l,\perp\perp}(t) \asymp \frac{2(d-1)}{d\beta^2}\left[\frac{d+1}{d+2} - \frac{\gamma-1}{\alpha T} + d\left(\frac{\gamma-1}{2\alpha T}\right)^2\right](8\pi\nu t)^{-d/2}$$

9.2. Sound Mode Contributions

The required inner product is

$$\begin{aligned}&[\mathscr{J}_l, (a_{S\sigma}(\mathbf{k})\, a_{S-\sigma}(-\mathbf{k}))_{\text{even}}] \\ &\quad = \frac{\beta}{2\rho c^2}\left([\mathscr{J}_l, p_0 p_0] + c^2 \sum_{\alpha}\sum_{\beta} \hat{k}_\alpha \hat{k}_\beta [\mathscr{J}_l, g_{0\alpha}\, g_{0\beta}]\right)\end{aligned}$$

with the pure fluid result for the last term

$$[\mathscr{J}_l, g_{0\alpha}\, g_{0\beta}] = \delta_{\alpha\beta}\frac{\rho}{\beta^2}\left[2\delta_{\alpha x} - \left(\frac{\partial p}{\partial e}\right)_{\rho, w}\right]$$

having been found in the course of the calculation of the shear-mode contribution.

In calculating inner products such as $[\mathscr{J}_l, p_0\, p_0]$, two points should be kept in mind, both relating to $\mathscr{J}_l$ not being a purely microscopic quantity, so that one must first use either of Eqs. (74).

1. As noted in both refs. 1 and 2, considerable labor can be avoided by noting that, because of (a) the form of the first of Eqs. (74), (b) the fact that $\langle T_{xx}\rangle = pV$, and (c) the chain rule, terms involving first-order derivatives of a in Eqs. (B10)–(B13) will cancel. Thus, only the leading second-order derivative terms need to be considered.

2. Caution is needed if the second of Eqs. (74) is used, because Eqs. (B11)–(B13) are not valid for $a_0 = w_0$. [Somewhat by accident, Eq. (B10) happens to give the correct result in that case.] One must in

general first use Eq. (123) to evaluate $[w_0, w_0 w_0]$, $[w_0, s_0 w_0]$, etc.; but there are then first-order derivatives in the latter quantities which *do not* cancel with corresponding terms in $[e_0, w_0 w_0]$, $[\rho_0, w_0 w_0]$, etc. In practice, it seemed to me easier to use the first of Eqs. (74), since e_0, ρ_{10}, and ρ_{20} are all properly microscopic quantities.

For $[\mathscr{J}_l, p_0 p_0]$ one finds the same result as for a pure fluid,

$$[\mathscr{J}_l, p_0 p_0] = \frac{\rho c^2}{\beta^2}\left[\frac{2\rho}{c}\left(\frac{\partial c}{\partial \rho}\right)_{s,w} - \frac{\gamma-1}{\alpha T}\right]$$

Thus, the sound-mode contribution is the same as found in ref. 1,

$$\rho_{l,SS}(t) \asymp \frac{1}{\beta^2}\left\{\left[\frac{\rho}{c}\left(\frac{\partial c}{\partial \rho}\right)_{s,w} - \frac{\gamma-1}{\alpha T} + \frac{1}{d}\right]^2 + \frac{2(d-1)}{d^2(d+2)}\right\}(4\pi\Gamma_s t)^{-d/2}$$

9.3. Diffusion Mode Contributions

With the aid of Eqs. (60), one finds

$$\begin{aligned}[\mathscr{J}_l, a_{D\sigma} a_{D\sigma'}] = {} & \frac{\sigma\sigma'}{A_\sigma A_{\sigma'}(\eta_+ - \eta_-)^2}\{(\eta_\sigma - \Delta_w)(\eta_{\sigma'} - \Delta_w)[\mathscr{J}_l, s_0 s_0] \\ & + \Delta'_w(\eta_\sigma + \eta_{\sigma'} - 2\Delta_w)[\mathscr{J}_l, s_0 w_0] + \Delta'^2_w[\mathscr{J}_l, w_0 w_0]\}\end{aligned} \tag{107}$$

Since this is independent of $\hat{\mathbf{k}}$, Eqs. (76) reduce to

$$\rho_{l,DD}(t) \asymp \frac{1}{2}\sum_{\sigma\sigma'}\,[4\pi(\eta_\sigma + \eta_{\sigma'})\,t/\rho]^{-d/2}\,[\mathscr{J}_l, a_{D\sigma} a_{D\sigma'}]^2 \tag{108}$$

The inner products appearing in Eq. (107) can be computed as outlined in the preceding subsection, with the following results:

$$\begin{aligned}[\mathscr{J}_l, w_0 w_0] = {} & \frac{-1}{\rho^2\beta^2}\left[\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left(\frac{\partial^2 e}{\partial \hat{\mu}^2}\right)_{T,p} + \left(\frac{\partial p}{\partial \rho_1}\right)_{e,\rho_2}\left(\frac{\partial^2 \rho_1}{\partial \hat{\mu}^2}\right)_{T,p}\right. \\ & \left. + \left(\frac{\partial p}{\partial \rho_2}\right)_{e,\rho_1}\left(\frac{\partial^2 \rho_2}{\partial \hat{\mu}^2}\right)_{T,p}\right]\end{aligned} \tag{109}$$

$$\begin{aligned}= {} & \frac{-1}{\rho^2\beta^2\hat{\mu}_w^2}\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left[\left(\frac{\partial^2 e}{\partial w^2}\right)_{T,p} - \left(\frac{\partial e}{\partial \rho}\right)_{p,w}\left(\frac{\partial^2 \rho}{\partial w^2}\right)_{T,p}\right. \\ & \left. - \frac{2}{\rho}\left(\frac{\partial e}{\partial w}\right)_{p,\rho}\left(\frac{\partial \rho}{\partial w}\right)_{T,p}\right]\end{aligned} \tag{110}$$

$$
\begin{aligned}
[\mathscr{J}_l, s_0 w_0] = {} & \frac{-1}{\rho^2\beta^2}\left[\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left(\frac{\partial^2 e}{\partial T\,\partial\hat{\mu}}\right)_p + \left(\frac{\partial p}{\partial\rho_1}\right)_{e,\rho_2}\left(\frac{\partial^2\rho_1}{\partial T\,\partial\hat{\mu}}\right)_p\right. \\
& \left. + \left(\frac{\partial p}{\partial\rho_2}\right)_{e,\rho_1}\left(\frac{\partial^2\rho_2}{\partial T\,\partial\hat{\mu}}\right)_p\right] \qquad (111) \\
= {} & \frac{-1}{\rho^2\beta^2\hat{\mu}_w}\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left\{\left[\left(\frac{\partial^2 e}{\partial T\,\partial w}\right)_p - \frac{\hat{\mu}_T}{\hat{\mu}_w}\left(\frac{\partial^2 e}{\partial w^2}\right)_{T,p}\right]\right. \\
& - \left(\frac{\partial e}{\partial\rho}\right)_{p,w}\left[\left(\frac{\partial^2\rho}{\partial T\,\partial w}\right)_p - \frac{\hat{\mu}_T}{\hat{\mu}_w}\left(\frac{\partial^2\rho}{\partial w^2}\right)_{T,p}\right] \\
& \left. - \frac{1}{\rho}\left(\frac{\partial e}{\partial w}\right)_{p,\rho}\left[\left(\frac{\partial\rho}{\partial T}\right)_{p,w} - 2\frac{\hat{\mu}_T}{\hat{\mu}_w}\left(\frac{\partial\rho}{\partial w}\right)_{T,p}\right]\right\} \qquad (112)
\end{aligned}
$$

$$
\begin{aligned}
[\mathscr{J}_l, s_0 s_0] = {} & \frac{-1}{\rho^2\beta^2}\left[\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left(\frac{\partial^2 e}{\partial T^2}\right)_{p,\hat{\mu}} + \left(\frac{\partial p}{\partial\rho_1}\right)_{e,\rho_2}\left(\frac{\partial^2\rho_1}{\partial T^2}\right)_{p,\hat{\mu}}\right. \\
& \left. + \left(\frac{\partial p}{\partial\rho_2}\right)_{e,\rho_1}\left(\frac{\partial^2\rho_2}{\partial T^2}\right)_{p,\hat{\mu}}\right] \qquad (113) \\
= {} & \frac{-1}{\rho^2\beta^2}\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left\{\left(\frac{\partial^2 e}{\partial T^2}\right)_{p,\hat{\mu}} - \left(\frac{\partial e}{\partial\rho}\right)_{p,w}\left(\frac{\partial^2\rho}{\partial T^2}\right)_{p,\hat{\mu}}\right. \\
& \left. - \left(\frac{\partial e}{\partial w}\right)_{p,\rho}\left[\left(\frac{\partial^2 w}{\partial T^2}\right)_{p,\hat{\mu}} + 2\left(\frac{\partial\rho}{\partial T}\right)_{p,\hat{\mu}}\left(\frac{\partial w}{\partial T}\right)_{p,\hat{\mu}}\right]\right\} \qquad (114) \\
= {} & \frac{-1}{\rho^2 T^2}\left(\frac{\partial p}{\partial e}\right)_{\rho,w}\left\{\left[\left(\frac{\partial^2 e}{\partial\beta^2}\right)_{p,w} + 2w_\beta\left(\frac{\partial^2 e}{\partial\beta\,\partial w}\right)_p\right.\right. \\
& \left. + w_\beta^2\left(\frac{\partial^2 e}{\partial w^2}\right)_{\beta,p}\right] - \left(\frac{\partial e}{\partial\rho}\right)_{p,w}\left[\left(\frac{\partial^2\rho}{\partial\beta^2}\right)_{p,w}\right. \\
& \left. + 2w_\beta\left(\frac{\partial^2\rho}{\partial\beta\,\partial w}\right)_p + w_\beta^2\left(\frac{\partial^2\rho}{\partial w^2}\right)_{\beta,p}\right] \\
& \left. - 2w_\beta\left(\frac{\partial e}{\partial w}\right)_{p,\rho}\left[\left(\frac{\partial\rho}{\partial\beta}\right)_{p,w} + w_\beta\left(\frac{\partial\rho}{\partial w}\right)_{\beta,p}\right]\right\} \qquad (115)
\end{aligned}
$$

In these equations $w_\beta = -\hat{\mu}_\beta/\hat{\mu}_w$. For each of the three inner products, the first form agrees with the expressions in ref. 2, Eqs. (C2)–(C4), but the second form contains terms which are missing in ref. 2, Eqs. (C6a)–(C6c). The last form in each case is useful in isolating the divergent $\hat{\mu}_w$ factors when examining the behavior in the dilute limit; there is no corresponding result in ref. 2 for $[\mathscr{J}_l, s_0 s_0]$.

I was not able to verify the reduction of Eq. (108) to the form given in ref. 2, Eqs. (4.19), (4.20c), (4.21a)–(4.21c). No great simplification seems to occur over simply leaving the result in the form of Eqs. (107) and (108).

With regard to the dilute limit reduction, it has already been noted that the shear and sound mode contributions have the same form as for the pure fluid. Thus, only the diffusion mode contributions need further discussion. One can show, under the same assumptions as earlier, that when $[\mathcal{J}_l, a_{D\sigma}a_{D\sigma'}]$ as given in Eq. (107) is squared and inserted in Eq. (108), all the terms approach zero as $w \to 0$ except for the particular term containing $[\mathcal{J}_l, s_0 s_0]^2$, for which $\sigma = \sigma'$ such that $\eta_\sigma \to L''_{uu}/c_p T$. That term reduces to the result

$$\rho_{l,DD}(t) \asymp \frac{(\gamma-1)^2}{2\beta^2(8\pi D_T t)^{d/2}}\left[1+\frac{1}{\alpha^2}\left(\frac{\partial\alpha}{\partial T}\right)_{p,w}-\frac{1}{\alpha c_p}\left(\frac{\partial c_p}{\partial T}\right)_{p,w}\right]^2$$

given for the pure fluid in ref. 1, with $D_T = L''_{uu}/\rho c_p T$.

9.4. Bulk Viscosity and Kinetic, Potential, and Cross Terms

As already noted, the long-time behavior of the time-correlation function $\rho_\zeta(t)$ for the bulk viscosity can be calculated from the previously given results for $\rho_\eta(t)$ and $\rho_l(t)$, with use of Eq. (21).

With respect to the breakdown of $\rho_l(t)$ into its kinetic, potential, and cross-term contributions, it has been noted in ref. 1 that the appropriate definition of the kinetic part of the Green–Kubo current for the bulk viscosity is $\mathcal{J}_\zeta^K = 0$, with the consequences that $\rho_\zeta^{\phi\phi} = \rho_\zeta$ and $\rho_\zeta^{KK} = \rho_\zeta^{K\phi} = 0$. It then follows from Eq. (21) that ρ_l^{KK}, $\rho_l^{\phi\phi}$, and $\rho_l^{K\phi}$ can be calculated from the expressions already given for ρ_l, ρ_η^{KK}, $\rho_\eta^{\phi\phi}$, and $\rho_\eta^{K\phi}$.

APPENDIX A. BINARY INNER PRODUCTS $[a_0, b_0]$

This Appendix follows ref. 1 closely in generalizing to the case of a binary mixture their expressions for inner products having the form $[a_0, b_0]$, under the following assumptions. Let A be an extensive phase function of the form $A = A(\mathbf{r}^N, \mathbf{p}^N) = \sum_i a_i$, with the proviso that a_i is a phase function, such as e_i, which depends upon microscopic variables only. *That is, the function a_i must not contain ensemble parameters such as β, μ_a, or V, or ensemble averages such as ρ, e, w, etc.* For the sake of brevity, let such a quantity a_0, and its associated quantities A and a_i, be called "microscopic." Let $\langle A \rangle$ be the corresponding average extensive quantity, and $a = \langle A \rangle / V$ the corresponding average intensive density. The local microscopic fluctuation in a is then

$$\delta a(\mathbf{r}, t) = \sum_i a_i \delta[\mathbf{r}_i(t) - \mathbf{r}] - a \tag{A1}$$

with the Fourier component

$$a_{\mathbf{k}} = \sum_i a_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i) - aV\delta_{\mathbf{k}0} \tag{A2}$$

Then the zero-wavenumber Fourier component is

$$a_0 = A - \langle A \rangle \tag{A3}$$

which is just the fluctuation of the extensive function A from its equilibrium average. Finally, let B, b_i, and b correspond to another function of the same microscopic type. Note that the Fourier components $\rho_{a\mathbf{k}}$, $\rho_{\mathbf{k}}$, $e_{\mathbf{k}}$, and $\mathbf{g}_{\mathbf{k}}$ are all of this kind. [In the case of $\rho_{a\mathbf{k}}$, one would include in the sum in Eq. (A2) a factor equal to one if particle i is of type a, and equal to zero otherwise.]

The grand canonical average is

$$\langle A \rangle = \frac{1}{\Xi} \sum_{N_1=0}^{\infty} \sum_{N_2=0}^{\infty} \left(\prod_{a=1}^{2} \frac{\exp(N_a m_a \nu_a)}{N_a!\, \hbar^{dN_a}} \right) \int d\mathbf{r}^N \int d\mathbf{p}^N \exp(-\beta \mathscr{H})\, A(\mathbf{r}^N, \mathbf{p}^N)$$

in which $\nu_a = \beta \mu_a$ and Ξ is the grand partition function, equal to the same double sum with the factor $A(\mathbf{r}^N, \mathbf{p}^N)$ omitted. A standard calculation then yields the well-known fluctuation relation

$$\left(\frac{\partial a}{\partial \beta} \right)_{\nu_1, \nu_2} = -\frac{1}{V} \langle (\mathscr{H} - \langle \mathscr{H} \rangle)(A - \langle A \rangle) \rangle \tag{A4}$$

Now, since $\mathscr{H} = \sum e_i$, it is seen from Eq. (A3) that $e_0 = \mathscr{H} - \langle \mathscr{H} \rangle$ and $a_0 = A - \langle A \rangle$. Furthermore, all the $\mathbf{k} = 0$ Fourier components are real, and thus Eq. (119) reduces to

$$[a_0, e_0] = [e_0, a_0] = -\left(\frac{\partial a}{\partial \beta} \right)_{\nu_1, \nu_2} \tag{A5}$$

giving the inner product in terms of a thermodynamic quantity.

In analogous fashion one finds

$$[\rho_{a0}, a_0] = \left(\frac{\partial a}{\partial \nu_a} \right)_{\beta, \nu_a'} \tag{A6}$$

in which the subscript v_a' indicates the constancy of v_2 if $a=1$, etc. (Perhaps it should be mentioned that the subscript a refers to species a, while the function $a=\langle A\rangle/V$.) Summing over the two species gives

$$[\rho_0, a_0]=\left(\frac{\partial a}{\partial v_1}\right)_{\beta, v_2}+\left(\frac{\partial a}{\partial v_2}\right)_{\beta, v_1}$$
$$=\frac{\rho}{\beta}\left(\frac{\partial a}{\partial p}\right)_{\beta, \hat{\mu}} \tag{A7}$$

In order to obtain an expression for an inner product like $[w_0, a_0]$, in which

$$w_0=(\rho_{10}-w\rho_0)/\rho \tag{A8}$$

contains the average quantities w and ρ, and so does not satisfy the prescribed conditions for our general functions a and b, one simply writes

$$[w_0, a_0]=\frac{1}{\rho}[\rho_{10}, a_0]-\frac{w}{\rho}[\rho_0, a_0] \tag{A9}$$

Then Eqs. (A6) and (A7) give

$$[w_0, a_0]=\frac{1}{\rho}\left[(1-w)\left(\frac{\partial a}{\partial v_1}\right)_{\beta, v_2}-w\left(\frac{\partial a}{\partial v_2}\right)_{\beta, v_1}\right] \tag{A10}$$

By standard thermodynamic manipulations, one can show that

$$(1-w)\left(\frac{\partial a}{\partial v_1}\right)_{\beta, v_2}-w\left(\frac{\partial a}{\partial v_2}\right)_{\beta, v_1}=\frac{1}{\beta\hat{\mu}_w}\left(\frac{\partial a}{\partial w}\right)_{\beta, p} \tag{A11}$$

where, as earlier, $\hat{\mu}_w=(\partial\hat{\mu}/\partial w)_{T,p}$. Thus,

$$[w_0, a_0]=\frac{1}{\beta\rho\hat{\mu}_w}\left(\frac{\partial a}{\partial w}\right)_{\beta, p} \tag{A12}$$

Next, consider the problem of calculating inner products such as $[e_0, a_0']$, $[\rho_{a0}, a_0']$, $[\rho_0, a_0']$, and $[w_0, a_0']$ for a Fourier component a_0' which is not microscopic, but which can be expressed in terms of the Fourier components ρ_{10}, ρ_{20}, and e_0. Note that p_0 and s_0, as given in Eqs. (53) and (54) [see also (A8)], are of this type. The intensive variables ρ_1, ρ_2, and e can be taken as independent variables specifying the value of any other intensive thermodynamic variable. Thus, the fluctuation $\delta a'$ can be written as

$$\delta a'=\left(\frac{\partial a'}{\partial \rho_1}\right)_{\rho_2, e}\delta\rho_1+\left(\frac{\partial a'}{\partial \rho_2}\right)_{\rho_1, e}\delta\rho_2+\left(\frac{\partial a'}{\partial e}\right)_{\rho_1, \rho_2}\delta e \tag{A13}$$

and its Fourier component as

$$a_0' = \left(\frac{\partial a'}{\partial \rho_1}\right)_{\rho_2, e} \rho_{10} + \left(\frac{\partial a'}{\partial \rho_2}\right)_{\rho_1, e} \rho_{20} + \left(\frac{\partial a'}{\partial e}\right)_{\rho_1, \rho_2} e_0 \tag{A14}$$

Then, with use of Eqs. (A5) and (A6), one has, for example,

$$\begin{aligned}
[a_0', e_0] &= \left(\frac{\partial a'}{\partial \rho_1}\right)_{\rho_2, e} [\rho_{10}, e_0)] + \left(\frac{\partial a'}{\partial \rho_2}\right)_{\rho_1, e} [\rho_{20}, e_0] \\
&\quad + \left(\frac{\partial a'}{\partial e}\right)_{\rho_1, \rho_2} [e_0, e_0] \\
&= -\left(\frac{\partial a'}{\partial \rho_1}\right)_{\rho_2, e} \left(\frac{\partial \rho_1}{\partial \beta}\right)_{\nu_1, \nu_2} - \left(\frac{\partial a'}{\partial \rho_2}\right)_{\rho_1, e} \left(\frac{\partial \rho_2}{\partial \beta}\right)_{\nu_1, \nu_2} \\
&\quad - \left(\frac{\partial a'}{\partial e}\right)_{\rho_1, \rho_2} \left(\frac{\partial e}{\partial \beta}\right)_{\nu_1, \nu_2} \\
&= -\left(\frac{\partial a'}{\partial \beta}\right)_{\nu_1, \nu_2}
\end{aligned} \tag{A15}$$

in which the last step follows from the chain rule. But this is just the result obtained by ignoring the fact that a_0' did not satisfy our original microscopic assumption, and applying Eq. (A5) directly. Similar results are found for $[a_0', \rho_{a0}]$, $[a_0', \rho_0]$, and $[a_0', w_0]$. Thus, Eqs. (A5)–(A7) and (A12) can be used for any intensive thermodynamic variable a and the corresponding a_0. In particular, Eq. (A12) gives directly the relation

$$[w_0, w_0] = \frac{1}{\beta \rho \hat{\mu}_w} \tag{A16}$$

With use of the preceding results and standard thermodynamic manipulations, one can then obtain the following formulas, valid for any intensive thermodynamic function a:

$$[p_0, a_0] = \frac{\rho}{\beta} \left(\frac{\partial a}{\partial \rho}\right)_{s, w} \tag{A17}$$

$$\begin{aligned}
[s_0, a_0] &= -\frac{1}{\rho T} \left(\frac{\partial a}{\partial \beta}\right)_{p, w} - \frac{\hat{\mu}_T}{\beta \rho \hat{\mu}_w} \left(\frac{\partial a}{\partial w}\right)_{\beta, p} \\
&= \frac{-1}{\rho T} \left(\frac{\partial a}{\partial \beta}\right)_{p, \hat{\mu}}
\end{aligned} \tag{A18}$$

with the special cases

$$[p_0, p_0] = \rho c^2/\beta \tag{A19}$$

$$[p_0, s_0] = [p_0, w_0] = 0 \tag{A20}$$

$$[s_0, s_0] = \frac{k_B c_p}{\rho} + \frac{\hat{\mu}_T^2}{\beta\rho\hat{\mu}_w} \tag{A21}$$

$$[s_0, w_0] = -\frac{\hat{\mu}_T}{\beta\rho\hat{\mu}_w} \tag{A22}$$

APPENDIX B. TERNARY INNER PRODUCTS $[a_0, b_0c_0]$

Inner products containing three zero-wavenumber factors of the microscopic form given in Eq. (A3) can be written as

$$\begin{aligned}[a_0, b_0c_0] = [a_0b_0, c_0] &= \frac{1}{V}\langle\delta_A\delta_B\delta_C\rangle \\ &= \frac{1}{V}[\langle\delta_{AB}\delta_C\rangle - \langle\delta_A\delta_C\rangle\langle B\rangle - \langle\delta_B\delta_C\rangle\langle A\rangle]\end{aligned} \tag{B1}$$

where $\delta_A = A - \langle A\rangle$, etc., and the order of the factors in the inner product is immaterial since the zero-wavenumber Fourier components are real. Each of the three terms on the right side contains a binary fluctuation factor of the form $\langle\delta_D\delta_C\rangle$ with $D = AB$, A, and B, respectively. Let us suppose that the function C has the property that

$$\langle\delta_D\delta_C\rangle = \frac{\partial\langle D\rangle}{\partial\xi_C} \tag{B2}$$

where ξ_C is one of the ensemble parameters. In Appendix A it has already been seen that this is so for the cases

$$C = \mathscr{H}, \qquad \xi_C = -\beta$$

$$C = M_a, \qquad \xi_C = v_a$$

Then Eq. (B1) becomes

$$\begin{aligned}[a_0, b_0c_0] &= \frac{1}{V}\left(\frac{\partial\langle AB\rangle}{\partial\xi_C} - \langle B\rangle\frac{\partial\langle A\rangle}{\partial\xi_C} - \langle A\rangle\frac{\partial\langle B\rangle}{\partial\xi_C}\right) \\ &= \frac{1}{V}\frac{\partial}{\partial\xi_C}(\langle AB\rangle - \langle A\rangle\langle B\rangle) \\ &= \frac{1}{V}\frac{\partial}{\partial\xi_c}\langle(A - \langle A\rangle)(B - \langle B\rangle)\rangle = \frac{\partial[a_0, b_0]}{\partial\xi_C}\end{aligned} \tag{B3}$$

In this way an inner product of three microscopic factors, at least one of which is of the type just assumed for c_0, can be expressed in terms of a derivative of the inner product of the other two factors. Thus, one obtains the following relations:

$$[a_0, b_0 e_0] = -\left(\frac{\partial[a_0, b_0]}{\partial\beta}\right)_{v_1, v_2} \tag{B4}$$

$$[a_0, b_0 \rho_{a0}] = \left(\frac{\partial[a_0, b_0]}{\partial v_a}\right)_{\beta, v'_a} \tag{B5}$$

$$\begin{aligned} [a_0, b_0 \rho_0] &= \left(\frac{\partial[a_0, b_0]}{\partial v_1}\right)_{\beta, v_2} + \left(\frac{\partial[a_0, b_0]}{\partial v_2}\right)_{\beta, v_1} \\ &= \frac{\rho}{\beta}\left(\frac{\partial[a_0, b_0]}{\partial p}\right)_{\beta, \hat{\mu}} \end{aligned} \tag{B6}$$

One can use these results, together with Eqs. (53), (54), and (A8), to obtain in addition

$$[a_0, b_0 w_0] = \frac{1}{\beta\rho\hat{\mu}_w}\left(\frac{\partial[a_0, b_0]}{\partial w}\right)_{\beta, p} \tag{B7}$$

$$\begin{aligned} [a_0, b_0 s_0] &= -\frac{1}{\rho T}\left(\frac{\partial[a_0, b_0]}{\partial\beta}\right)_{p, w} - \frac{\hat{\mu}_T}{\beta\rho\hat{\mu}_w}\left(\frac{\partial[a_0, b_0]}{\partial w}\right)_{\beta, p} \\ &= \frac{-1}{\rho T}\left(\frac{\partial[a_0, b_0]}{\partial\beta}\right)_{p, \hat{\mu}} \end{aligned} \tag{B8}$$

$$[a_0, b_0 p_0] = \frac{\rho}{\beta}\left(\frac{\partial[a_0, b_0]}{\partial\rho}\right)_{s, w} \tag{B9}$$

Note the formal similarity of Eqs. (B4)–(B9) to the corresponding Eqs. (A5)–(A7), (A12), (A17), and (A18). However, it must be emphasized that Eqs. (B4)–(B9) are in general valid only for quantities a_0 and b_0 which are microscopic.

One can in addition obtain the following relations, valid for microscopic a_0:

$$\begin{aligned} [a_0, p_0 p_0] = \frac{\rho^2}{\beta^2}\Bigg[&\left(\frac{\partial^2 a}{\partial\rho^2}\right)_{s, w} - \left(\frac{\partial^2\beta}{\partial\rho^2}\right)_{s, w}\left(\frac{\partial a}{\partial\beta}\right)_{v_1, v_2} \\ &- \left(\frac{\partial^2 v_1}{\partial\rho^2}\right)_{s, w}\left(\frac{\partial a}{\partial v_1}\right)_{\beta, v_2} - \left(\frac{\partial^2 v_2}{\partial\rho^2}\right)_{s, w}\left(\frac{\partial a}{\partial v_2}\right)_{\beta, v_1}\Bigg] \end{aligned} \tag{B10}$$

$$[a_0, w_0 w_0] = \frac{1}{\rho^2 \beta^2} \left[\left(\frac{\partial^2 a}{\partial \hat{\mu}^2} \right)_{\beta, p} + \frac{\rho}{\hat{\mu}_w} \left(\frac{\partial a}{\partial p} \right)_{\beta, \hat{\mu}} \right] \tag{B11}$$

$$[a_0, s_0 w_0] = \frac{-k_B}{\rho^2} \left[\left(\frac{\partial^2 a}{\partial \beta\, \partial \hat{\mu}} \right)_p - \frac{1}{\beta} \left(\frac{\partial a}{\partial \hat{\mu}} \right)_{\beta, p} + \frac{\rho T \hat{\mu}_T}{\beta \hat{\mu}_w} \left(\frac{\partial a}{\partial p} \right)_{\hat{\mu}, \beta} \right] \tag{B12}$$

$$\begin{aligned}[a_0, s_0 s_0] = \frac{1}{\rho^2 T^2} \Bigg[& \left(\frac{\partial^2 a}{\partial \beta^2} \right)_{p, \hat{\mu}} - \frac{\rho}{\beta} \left(\frac{\partial h}{\partial \beta} \right)_{p, \hat{\mu}} \left(\frac{\partial a}{\partial p} \right)_{\beta, \hat{\mu}} \\ & - \frac{\hat{\mu}}{\rho \beta \hat{\mu}_w} \left(\frac{\partial \rho}{\partial \beta} \right)_{p, \hat{\mu}} \left(\frac{\partial a}{\partial \omega} \right)_{\beta, p} \Bigg] \end{aligned} \tag{B13}$$

ACKNOWLEDGMENTS

It is a pleasure to thank J. J. Erpenbeck for his suggestion that the results of Ernst *et al.*$^{(1)}$ should be extended to the case of the binary mixture, as well as for numerous useful discussions. A set of lecture notes by J. R. Dorfman on the mode-coupling theory and a discussion with E. G. D. Cohen were very useful. Much of the work was done during various visits at the Los Alamos National Laboratory, with partial support by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy.

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