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FINAL REPORT FOR
"TRANSPORT PROPERTIES OF
MULTI-COMPONENT FLUIDS
AND OF SUSPENSIONS"

Science Applications International Corporation
An Employee-Owned Company

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I. INTRODUCTION

This report summarizes work performed under Grant Number DE-FG03-88ER13911 for the period June 15, 1988 through October 31, 1990. The first year's work dealt with derivations of the fundamental equations describing suspensions of inelastic particles. This work was documented in last year's annual progress report (Report Number SAIC-89/1570:APPAT-115), and has since been published in *Physica A*. We include the published version as an Appendix to this report. During the past year our work has focused on derivations of the nonlinear hydrodynamic equations for multi-component systems. The remainder of this report summarizes the results of these latter studies.

The report is organized as follows. In Section II, we derive a general set of nonlinear hydrodynamic equations for a two-component, classical fluid system. We then show under what circumstances the exact equations can be approximated by the phenomenological, nonlinear Navier-Stokes equations. In Section III, we use the general results of Section II to obtain explicit, nonlinear equations for the evolution of the hydrodynamic variables of two-component fluid mixtures (total mass density, mass density of one of the two species, momentum density and energy density). In Section IV, we give the linearized, fundamental equations that follow from the results of Section III. In Section V, we discuss a particular thermodynamic quantity of interest in the hydrodynamic equations, which follows from the composition dependences of the chemical potentials. The dispersion relations which arise from the linearized hydrodynamic equations are derived in Section VI. Finally, in Section VII, we discuss certain effects of long time tail behavior, and Section VIII contains a summary.

II. DERIVATION OF THE NONLINEAR HYDRODYNAMIC EQUATIONS

In this section we derive the nonlinear hydrodynamic equations for two component systems. The extension of these results to multi-component systems is straightforward.

We consider a classical fluid system consisting of N_A particles of species A and N_B particles of species B in a volume V . The particles are spherical and have no internal degrees of freedom. The A particles have mass m_A and center of mass positions $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_{N_A} \equiv \mathbf{r}^{N_A}$ and momenta $\mathbf{p}_1, \dots, \mathbf{p}_{N_A} \equiv \mathbf{p}^{N_A}$. The B particles have mass m_B and center of mass positions $\mathbf{R}^{N_B}$ and momenta $\mathbf{P}^{N_B}$. At a later stage we will consider the situation in which $m_B \gg m_A$. The Hamiltonian for the system is

$$H = \frac{\mathbf{p}^{N_A} \cdot \mathbf{p}^{N_A}}{2m_A} + \frac{\mathbf{P}^{N_B} \cdot \mathbf{P}^{N_B}}{2m_B} + U(\mathbf{r}^{N_A}) + V(\mathbf{R}^{N_B}) + \Phi(\mathbf{r}^{N_A}, \mathbf{R}^{N_B}) \quad (2.1)$$

where

$$U(\mathbf{r}^{N_A}) = \sum_{i < j}^{N_A} u(|\mathbf{r}_i - \mathbf{r}_j|) \quad (2.2a)$$

$$V(\mathbf{R}^{N_B}) = \sum_{\alpha < \gamma}^{N_B} v(|\mathbf{R}_\alpha - \mathbf{R}_\gamma|) \quad (2.2b)$$

and

$$\Phi(\mathbf{r}^{N_A}, \mathbf{R}^{N_B}) = \sum_{i=1}^{N_A} \sum_{\alpha=1}^{N_B} \phi(|\mathbf{r}_i - \mathbf{R}_\alpha|) \quad (2.2c)$$

Thus, all the potentials of interaction are sums of two-body potentials which depend on the scalar distance between the centers of mass of the particles. The potentials u , v and ϕ are assumed to be short range, i.e.

$$\begin{aligned} u(r) &= 0 & r > \xi_A \\ v(R) &= 0 & R > \xi_B \\ \phi(|\mathbf{r} - \mathbf{R}|) &= 0 & |\mathbf{r} - \mathbf{R}| > \xi_{AB} \end{aligned} \quad (2.3)$$

and the ξ 's are small compared to hydrodynamic length scales.

The dynamical variables whose averages are the densities of the conserved quantities in this system are: the total mass density

$$M(X, \mathbf{r}) = m_A \sum_{j=1}^{N_A} \delta(\mathbf{r}_j - \mathbf{r}) + m_B \sum_{\alpha=1}^{N_B} \delta(\mathbf{R}_\alpha - \mathbf{r}) ; \quad (2.4)$$

the mass density of species B

$$M_B(X, \mathbf{r}) = m_B \sum_{\alpha=1}^{N_B} \delta(\mathbf{R}_\alpha - \mathbf{r}) ; \quad (2.5)$$

the total momentum density

$$\mathbf{P}(X, \mathbf{r}) = \sum_{j=1}^{N_A} \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}) + \sum_{\alpha=1}^{N_B} \mathbf{P}_\alpha \delta(\mathbf{R}_\alpha - \mathbf{r}) ; \quad (2.6)$$

and the total energy density

$$E(X, \mathbf{r}) = \sum_{j=1}^{N_A} e_j \delta(\mathbf{r}_j - \mathbf{r}) + \sum_{\alpha=1}^{N_B} E_\alpha \delta(\mathbf{R}_\alpha - \mathbf{r}) \quad (2.7)$$

where

$$e_j = \frac{p_j^2}{2m_A} + \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{N_A} u(|\mathbf{r}_i - \mathbf{r}_j|) + \frac{1}{2} \sum_{\alpha=1}^{N_B} \phi(|\mathbf{r}_i - \mathbf{R}_\alpha|) \quad (2.8a)$$

and

$$E_\alpha = \frac{p_\alpha^2}{2m_B} + \frac{1}{2} \sum_{\substack{\gamma=1 \\ \gamma \neq \alpha}}^{N_B} v(|\mathbf{R}_\alpha - \mathbf{R}_\gamma|) + \frac{1}{2} \sum_{j=1}^{N_A} \phi(|\mathbf{r}_j - \mathbf{R}_\alpha|) . \quad (2.8b)$$

Here X stands for the phase point of the system, i.e. $X \equiv \mathbf{r}^{N_A}, \mathbf{p}^{N_A}, \mathbf{R}^{N_B}, \mathbf{p}^{N_B} \equiv X_A, X_B$. The linear variables, $M, M_B, \mathbf{P}$ and E (or linear combinations of them) are unique in that the averages of their time derivatives vanish if there are no spatial gradients in the system.

We introduce the vector $\mathbf{A}(X, \mathbf{r})$ which has six components: $M, M_B, \mathbf{P}, E$ and will use the following notation

$$\begin{aligned} \mathbf{A}(\mathbf{r}) &\equiv \mathbf{A}(X, \mathbf{r}) \\ \mathbf{A}(\mathbf{r}, t) &\equiv \mathbf{A}(X(t), \mathbf{r}) \\ \mathbf{A}_T &\equiv \int_V \mathbf{A}(\mathbf{r}) d\mathbf{r} \end{aligned} \quad (2.9)$$

The time derivative of $\mathbf{A}(\mathbf{r})$ is given by

$$\dot{\mathbf{A}}(\mathbf{r}) = -L \mathbf{A}(\mathbf{r}) = -\nabla_{\mathbf{r}} \cdot \mathbf{J}(\mathbf{r}) \quad (2.10)$$

where L is the Liouville operator for the system:

$$L = -\frac{\mathbf{p}_A^{N_A}}{m_A} \cdot \nabla_{\mathbf{r}^{N_A}} + \nabla_{\mathbf{r}^{N_A}} H \cdot \nabla_{\mathbf{p}^{N_A}} - \frac{\mathbf{p}_B^{N_B}}{m_B} \cdot \nabla_{\mathbf{R}^{N_B}} + \nabla_{\mathbf{R}^{N_B}} H \cdot \nabla_{\mathbf{p}^{N_B}} ; \quad (2.11)$$

and the six component vector $\mathbf{J}(\mathbf{X}, \mathbf{r})$ denotes the currents of the components of $\mathbf{A}(\mathbf{r})$:

$$\mathbf{J}_M(\mathbf{r}) = \mathbf{P}(\mathbf{r}) \quad (2.12a)$$

$$\mathbf{J}_{M_B}(\mathbf{r}) = \mathbf{P}_B(\mathbf{r}) = \sum_{\alpha=1}^{N_B} \mathbf{P}_\alpha \delta(\mathbf{r} - \mathbf{R}_\alpha) \quad (2.12b)$$

$$\mathbf{J}_P(\mathbf{r}) = \underline{\underline{\tau}}(\mathbf{r}) \quad (2.12c)$$

$$\mathbf{J}_E(\mathbf{r}) . \quad (2.12d)$$

The explicit expressions for the stress tensor $\underline{\underline{\tau}}(\mathbf{r})$ and the energy current $\mathbf{J}_E(\mathbf{r})$ are:

$$\begin{aligned} \underline{\underline{\tau}}(\mathbf{r}) = & \sum_{j=1}^{N_A} \left(\frac{\mathbf{p}_j \mathbf{p}_j}{m_A} - \frac{1}{2} \sum_{\substack{i=1 \\ i \neq j}}^{N_A} \mathbf{r}_{ij} \nabla_j u_{ij} - \frac{1}{2} \sum_{\alpha=1}^{N_B} (\mathbf{R}_\alpha - \mathbf{r}_j) \nabla_\alpha \phi_{\alpha j} \right) \delta(\mathbf{r} - \mathbf{r}_j) \\ & + \sum_{\alpha=1}^{N_B} \left(\frac{\mathbf{P}_\alpha \mathbf{P}_\alpha}{m_B} - \frac{1}{2} \sum_{\substack{\gamma=1 \\ \gamma \neq \alpha}}^{N_B} \mathbf{R}_{\gamma\alpha} \nabla_\alpha v_{\alpha\gamma} - \frac{1}{2} \sum_{j=1}^{N_A} (\mathbf{r}_j - \mathbf{R}_\alpha) \nabla_j \phi_{\alpha j} \right) \delta(\mathbf{r} - \mathbf{R}_\alpha) \end{aligned} \quad (2.13)$$

and

$$\mathbf{J}_E(\mathbf{r}) = \sum_{j=1}^{N_A} \left(\frac{e_j \mathbf{p}_j}{m_A} - \frac{1}{2m_A} \sum_{\substack{i=1 \\ i \neq j}}^{N_A} \mathbf{r}_{ij} \mathbf{p}_j \cdot \nabla_j u_{ij} - \frac{1}{2m_A} \sum_{\alpha=1}^{N_B} (\mathbf{R}_\alpha - \mathbf{r}_j) \mathbf{p}_j \cdot \nabla_j \phi_{\alpha j} \right) \delta(\mathbf{r} - \mathbf{r}_j)$$

$$\begin{aligned}
& + \sum_{\alpha=1}^{N_B} \left(\frac{E_{\alpha} P_{\alpha}}{m_B} - \frac{1}{2m_B} \sum_{\substack{\gamma=1 \\ \gamma \neq \alpha}}^{N_B} \mathbf{R}_{\gamma\alpha} P_{\alpha} \cdot \nabla_{\alpha} v_{\alpha\gamma} \right. \\
& \quad \left. - \frac{1}{2m_B} \sum_{j=1}^N (\mathbf{r}_j - \mathbf{R}_{\alpha}) P_{\alpha} \cdot \nabla_{\alpha} \phi_{\alpha j} \right) \delta(\mathbf{r} - \mathbf{R}_{\alpha}) .
\end{aligned} \tag{2.14}$$

Eqs. (2.12a) and (2.12b) are exact; higher order spatial gradients have been neglected in Eqs. (2.12c) and (2.12d).

Before proceeding with the derivation of the nonlinear hydrodynamic equations, it is useful to define a local equilibrium distribution function, σ , by the equation:

$$\sigma(X, t) \equiv \sigma(t) = \frac{\rho_0 e^{\mathbf{A} * \phi(t)}}{\langle e^{\mathbf{A} * \phi(t)} \rangle_0} \tag{2.15}$$

where ρ_0 is the equilibrium distribution function; the notation $\mathbf{A} * \phi(t)$ implies an integration over space as well as a dot product, i.e.

$$\mathbf{A} * \phi(t) = \int_V d\mathbf{r}' \mathbf{A}(\mathbf{r}') \cdot \phi(\mathbf{r}', t) ; \tag{2.16}$$

the $\phi(\mathbf{r}', t)$ are time and space dependent conjugate forces of the components of $\mathbf{A}$ and do not depend on the phase point of the system; the notation $\langle B \rangle_0$ implies an average of the dynamical variable B over the equilibrium distribution function,

$$\langle B \rangle_0 = \text{Tr}(B\rho_0) \tag{2.17}$$

where the trace operation includes an integration over phase space and a sum over all possible numbers of particles of A and B .

The forms of the conjugate forces ϕ follow from thermodynamic considerations⁽¹⁾

$$\begin{aligned}
A * \phi(t) &= N_A * \left(\left[\beta \left(\mu_A - \frac{1}{2} m_A v^2 \right) \right] (t) - \beta_o \mu_{Ao} \right) \\
&+ N_B * \left(\left[\beta \left(\mu_B - \frac{1}{2} m_B v^2 \right) \right] (t) - \beta_o \mu_{Bo} \right) \\
&+ P * [\beta v] (t) - E * (\beta (t) - \beta_o) \\
&= M * \left(\left[\beta \left(\tilde{\mu}_A - \frac{1}{2} v^2 \right) \right] (t) - \beta_o \tilde{\mu}_{Ao} \right) \\
&+ M_B * [(\beta \tilde{\mu})(t) - \beta_o \tilde{\mu}_o] + P * [\beta v](t) \\
&- E * (\beta(t) - \beta_o)
\end{aligned} \tag{2.18}$$

where the second equality follows from the facts that

$$\begin{aligned}
M(x) &= N_A(x)m_A + N_B(x)m_B \\
M_B(x) &= N_B(x)m_B
\end{aligned} \tag{2.19}$$

and the definitions

$$\tilde{\mu}_i \equiv \frac{\mu_i}{m_i}$$

and

$$\tilde{\mu} \equiv \tilde{\mu}_B - \tilde{\mu}_A . \tag{2.20}$$

In Eq. (2.18), $\beta(x, t) = [k_B T(x, t)]^{-1}$ where $T(x, t)$ is a time and space dependent temperature, $\beta_o = (k_B T_o)^{-1}$ where T_o is the equilibrium temperature, $\mu_A(x, t)$ ($\mu_B(x, t)$) is the time and space dependent chemical potential per molecule of species A(B) and μ_{Ao} (μ_{Bo}) its corresponding equilibrium value, and $v(x, t)$ is the time and space dependent mean velocity in the fluid.

It follows from Eq. (2.18) that:

$$\phi_M(\mathbf{r}, t) = \left[\beta \left(\tilde{\mu}_A - \frac{1}{2} v^2 \right) \right] (\mathbf{r}, t) - \beta_0 \tilde{\mu}_{A0} \quad (2.21a)$$

$$\phi_B(\mathbf{r}, t) = (\beta \tilde{\mu}) (\mathbf{r}, t) - \beta_0 \tilde{\mu}_0 \quad (2.21b)$$

$$\phi_P(\mathbf{r}, t) = (\beta \tilde{v}) (\mathbf{r}, t) \quad (2.21c)$$

and

$$\phi_E(\mathbf{r}, t) = - \left(\beta (\mathbf{r}, t) - \beta_0 \right) . \quad (2.21d)$$

Averages over the local equilibrium distribution function are denoted by

$$\langle B \rangle_t \equiv \text{Tr} (B \sigma(t)) \quad (2.22)$$

and averages over the exact distribution function at time t are denoted by

$$b(t) = \bar{B}(t) \equiv \text{Tr} (B \rho(t)) . \quad (2.23)$$

The quantity $b(t)$ is the exact macroscopic quantity at time t .

It is clear that the $\phi(t)$ can be chosen in such a way that the average of $A(\mathbf{r})$ over $\sigma(t)$ is identical to the average of $A(\mathbf{r})$ over $\rho(t)$, i.e.

$$\begin{aligned} a(\mathbf{r}, t) &= \text{Tr} (A(\mathbf{r}) \rho(t)) = \text{Tr} (A(\mathbf{r}) \sigma(t)) \\ &= \overline{A(\mathbf{r})}(t) = \langle A(\mathbf{r}) \rangle_t \end{aligned} \quad (2.24)$$

This property is, of course, not true in general, i.e.

$$\bar{B}(t) \neq \langle B \rangle_t \quad (2.25)$$

for an arbitrary dynamical variable. The quantity $\mathbf{a}(\mathbf{r}, t)$ is the space and time dependent macroscopic density (mass density, mass of species B density, momentum density and energy density) in the non-equilibrium system. The hydrodynamic equations provide expressions for the time derivatives of these densities:

$$\dot{\mathbf{a}}(\mathbf{r}, t) = \left(\frac{\partial \mathbf{a}(\mathbf{r}, t)}{\partial t} \right)_{\mathbf{r}} \quad (2.26)$$

In the following, we shall obtain exact expressions for $\dot{\mathbf{a}}(\mathbf{r}, t)$ and will then study under what conditions these exact equations can be simplified to obtain the phenomenological nonlinear Navier-Stokes equations. We find it convenient to define the following time-dependent projection operators:²

$$P^+(t)B \equiv \text{Tr}(BC_t) * \underline{K}(t)^{-1} * C_t \sigma(t) \quad (2.27)$$

$$P(t)B = \langle BC_t \rangle_t * \underline{K}(t)^{-1} * C_t \quad (2.28)$$

$$Q^+(t) \equiv 1 - P^+(t), \quad Q(t) \equiv 1 - P(t) \quad (2.29)$$

where C_t is a seven dimensional vector with components:

$$C_t = \begin{pmatrix} 1 \\ \tilde{A}_t \equiv A - \langle A \rangle_t \end{pmatrix}, \quad (2.30)$$

and

$$\underline{K}(t) \equiv \langle C_t C_t \rangle_t ; \quad (2.31)$$

the spatial dependence of C and A in these equations is implicit. The projection operators have the following properties:

$$\begin{aligned} P^+(s) P^+(t) &= P^+(s) \\ Q^+(s) Q^+(t) &= Q^+(t) \\ P(s) P(t) &= P(t) \\ Q(s) Q(t) &= Q(s) . \end{aligned} \quad (2.32)$$

The most useful property of $P^+(t)$ is the following

$$P^+(t)\rho(t) = \sigma(t) \quad (2.33)$$

where we have used Eq. (2.24). Furthermore, since

$$\dot{\sigma}(t) = \tilde{A}_t * \dot{\phi}(t) \sigma(t) , \quad (2.34)$$

$$P^+(t) \dot{\rho}(t) = \dot{\sigma}(t) \quad (2.35)$$

where we have used the facts that

$$Tr(\dot{\rho}(t) C_t) = \dot{C}(t) = Tr(C \dot{\sigma}(t)) . \quad (2.36)$$

The exact equation of motion for $\rho(t)$ is

$$\dot{\rho}(t) = L\rho(t) \quad (2.37)$$

where

$$\begin{aligned} \rho(t) &= P^+(t)\rho(t) + Q^+(t)\rho(t) \\ &= \sigma(t) + \chi(t) \end{aligned} \quad (2.38)$$

and $\chi(t)$ is defined by

$$\chi(t) \equiv Q^+(t)\rho(t) \quad (2.39)$$

By applying $P^+(t)$ and $Q^+(t)$ to Eq. (2.37) we obtain

$$\dot{\sigma}(t) = P^+(t)L\sigma(t) + P^+(t)L\chi(t) \quad (2.40)$$

and

$$\dot{\chi}(t) = Q^+(t)L\chi(t) + Q^+(t)L\sigma(t) \quad (2.41)$$

where we have made use of Eqs. (2.33) and (2.35). Since

$$L\sigma(t) = -\dot{\mathbf{A}} * \underline{\phi}(t) \sigma(t) , \quad (2.42)$$

it follows that

$$\begin{aligned} Q^+(t)L\sigma(t) &= -\left[\dot{\mathbf{A}} - \langle \dot{\mathbf{A}} \mathbf{C}_t \rangle * \underline{\mathbf{K}}(t)^{-1} * \mathbf{C}_t\right] * \underline{\phi}(t) \sigma(t) \\ &= -\left[(1 - P(t))\dot{\mathbf{A}}\right] * \underline{\phi}(t) \sigma(t) . \end{aligned} \quad (2.43)$$

The formal solution to Eq. (2.41) is

$$\begin{aligned} \chi(t) &= T_+ \exp\left(\int_0^t Q^+(s) L ds\right) \chi(0) \\ &\quad - \int_0^t T_+ \exp\left(\int_0^t Q^+(s) L ds\right) \left[Q(\tau)\dot{\mathbf{A}}\right] \sigma(\tau) * \underline{\phi}(\tau) d\tau \end{aligned} \quad (2.44)$$

and the time-dependent average of an arbitrary dynamical variable B is:

$$\begin{aligned} b(\mathbf{r}, t) &= \langle B(\mathbf{r}) \rangle_t + \text{Tr} \left(B(\mathbf{r}) T_+ \exp\left(\int_0^t Q^+(s) L ds\right) \chi(0) \right) \\ &\quad - \int_0^t d\tau \text{Tr} \left(B(\mathbf{r}) T_+ \exp\left(\int_0^t Q^+(s) L ds\right) \left[Q(\tau)\dot{\mathbf{A}}\right] \sigma(\tau) \right) * \underline{\phi}(\tau) \\ &= \langle B(\mathbf{r}) \rangle_t + \text{Tr} \left(Q(0) \left[T_- \exp\left(-\int_0^t L Q(s) ds\right) B(\mathbf{r}) \right] \chi(0) \right) \\ &\quad - \int_0^t d\tau \left\langle \left[T_- \exp\left(-\int_0^t L Q(s) ds\right) B(\mathbf{r}) \right] \left[Q(\tau)\dot{\mathbf{A}}\right] \right\rangle_{\tau} * \underline{\phi}(\tau) \end{aligned} \quad (2.45)$$

where the second equality follows by integration by parts. Eq. (2.45) is exact. The symbols T_+ and T_- denote time ordering operators.

In the special case that $B = \dot{A}$, Eq. (2.45) becomes

$$\begin{aligned} \dot{a}(\mathbf{r}, t) &= -\nabla_{\mathbf{r}} \cdot \langle \mathbf{J}(\mathbf{r}) \rangle_{\tau} \\ &= -\nabla_{\mathbf{r}} \cdot Tr \left(Q(o) \left[T_- \exp \left(- \int_0^t L Q(s) ds \right) \mathbf{J}(\mathbf{r}) \right] \chi(o) \right) \\ &\quad + \nabla_{\mathbf{r}} \cdot \int_0^t d\tau \int_V d\mathbf{r}' \left\langle \left[T_- \exp \left(- \int_{\tau}^t L Q(s) ds \right) \mathbf{J}(\mathbf{r}) \right] [Q(\tau) \mathbf{J}(\mathbf{r}')] \right\rangle_{\tau} : \nabla_{\mathbf{r}'} \phi(\mathbf{r}', \tau) \\ &\equiv (1) + (2) + (3) \end{aligned} \quad (2.46)$$

Again Eq. (2.46) is exact.

We shall now study under what circumstances Eq. (2.46) can be approximated by the phenomenological nonlinear hydrodynamic equations. We cannot expect the hydrodynamic equations to be valid unless the macroscopic variables a and ϕ vary slowly in space and therefore in time. More precisely

$$\xi \nabla_{\mathbf{r}} \ln \phi \sim \xi \nabla_{\mathbf{r}} \ln a \ll 1 \quad (2.47)$$

where ξ is the range of the potentials or the correlation length in the system. Eq. (2.47) is equivalent to

$$\tau_m \frac{\partial \ln \phi}{\partial t} \sim \tau_m \frac{\partial \ln a}{\partial t} \ll 1 \quad (2.48)$$

where τ_m is a molecular time of order 10^{-13} sec. To simplify matters we shall assume

$$\nabla_{\mathbf{r}} \phi \sim \dot{\phi} \sim \nabla_{\mathbf{r}} a \sim \dot{a} \sim \lambda \quad (2.49)$$

where λ is a smallness parameter.

The first term on the RHS of Eq. (2.46) can be simplified using the following considerations:

$$\langle J(r) \rangle_t = \frac{\left\langle J(r) e^{A_T \cdot \phi(r, t)} \right\rangle_0}{\left\langle e^{A_T \cdot \phi(r, t)} \right\rangle_0} = \frac{\left\langle J(r) e^{A_T \cdot \phi(r, t)} \exp \left[\int_V d\mathbf{r}' A(\mathbf{r}') \cdot (\phi(\mathbf{r}', t) - \phi(\mathbf{r}, t)) \right] \right\rangle_0}{\left\langle e^{A_T \cdot \phi(r, t)} \exp \left[\int_V d\mathbf{r}' A(\mathbf{r}') \cdot (\phi(\mathbf{r}', t) - \phi(\mathbf{r}, t)) \right] \right\rangle_0}. \quad (2.50)$$

We denote the average

$$\frac{\left\langle J(r) e^{A_T \cdot \phi(r, t)} \right\rangle_0}{\left\langle e^{A_T \cdot \phi(r, t)} \right\rangle_0} \equiv \langle J(r) \rangle_H(r, t); \quad (2.51)$$

this average is taken over a homogeneous equilibrium system in which the conjugate forces are $\phi(r, t)$. Since the system is homogeneous

$$\langle J(r) \rangle_H(r, t) = \frac{\langle J_T \rangle_H(r, t)}{V} \quad (2.52)$$

and all of the space and time dependence resides in the $\phi(r, t)$.

Expansion of the exponential terms involving spatial integrations of the last term in Eq. (2.50) yields:

$$\begin{aligned} \langle J(r) \rangle_t &= \langle J(r) \rangle_H(r, t) + \int_V d\mathbf{r}' \left\langle J(r) [A(\mathbf{r}') - \langle A(\mathbf{r}') \rangle_H(r, t)] \right\rangle_H(r, t) \\ &\quad \cdot (\phi(\mathbf{r}', t) - \phi(\mathbf{r}, t)) \\ &\quad + \dots \end{aligned} \quad (2.53)$$

The correlation function on the RHS of Eq. (2.53) decays to zero when $|\mathbf{r} - \mathbf{r}'| > \xi$. Thus the second term on the RHS of Eq. (2.53) is at most of order $\xi \nabla_r \ln \phi \ll \phi$ compared to the first term. This property holds for the higher order terms in the expansion as well. Thus, we can write:

$$\langle J(r) \rangle_t \equiv \frac{\langle J_T \rangle_H(r, t)}{V} \quad (2.54)$$

The simplification of the second and third terms on the RHS of Eq. (2.46) relies on the arguments given above but more importantly on the time-dependent properties of the propagators in them. These propagators contain factors of LQ ; e.g.

$$LQ(t)B = L \left(B - \langle B C_t \rangle_t + \underline{K}(t)^{-1} * C_t \right) \quad (2.55)$$

and the quantity in () on the RHS of Eq. (2.56) contains no projection on C_t . If the linear modes were the only slow modes in the system, $Q(t)B$ would vary quickly with time and the second term on the RHS of Eq. (2.45) would become equal to zero for $t > \tau_m$. Thus, this term would make a negligible contribution. Furthermore, the only significant contribution to the third term on the RHS of Eq. (2.46) would come from $\tau \sim t$. Unfortunately, multi-linear modes which involve products of the linear modes M, M_B, P, E are also slowly varying. The most important of these are the bilinear modes. It is these slowly varying nonlinear modes which give rise to the long time tail behavior of the propagators and the correlation functions.

In this section we shall neglect the contribution of these nonlinear modes and proceed as if the propagators were short-lived. We shall return to the contributions of the nonlinear modes in Section VII.

Thus we neglect the second term on the RHS of Eq. (2.46) and rewrite the third term as:

$$(3) = \nabla_r \cdot \int_0^t dy \int_V d\mathbf{r}' \left\langle \left[T_- \exp \left(- \int_{t-y}^t LQ(s) ds \right) J(\mathbf{r}) \right] [Q(t-y)J(\mathbf{r}')] \right\rangle_{t-y} : \nabla_{r'} \phi(r', t-y) . \quad (2.56)$$

Since the integral is zero for $y > \tau_m$, and Q, σ and ϕ are slowly varying functions of time, Eq. (2.56) can be written

$$(3) = \nabla_r \cdot \left[\int_0^t dy \int_V d\mathbf{r}' \left\langle [e^{-LQ(t)y} Q(t)J(\mathbf{r})] [Q(t)J(\mathbf{r}')] \right\rangle_t : \nabla_{r'} \phi(r', t) (1 + o(\lambda)) \right] . \quad (2.57)$$

Further, since the integral becomes zero for $y > \tau_m$, we can use arguments identical to those for term (1) to write:

$$\int d\mathbf{r}' J(\mathbf{r}') \rangle_t : \nabla_{\mathbf{r}'} \phi(\mathbf{r}', t) = J_T \rangle_t : \nabla_{\mathbf{r}} \phi(\mathbf{r}, t) (1 + 0(\lambda)) ; \quad (2.58)$$

to replace the projection operators by homogeneous forms, i.e.

$$\begin{aligned} P(t) J(\mathbf{r}) &= \langle J(\mathbf{r}) C_t \rangle_t * \langle C_t C_t \rangle_t^{-1} * C_t \\ &\equiv \langle J_T C_{tT} \rangle_H(\mathbf{r}, t) \cdot \langle C_{tT} C_{tT} \rangle_H^{-1}(\mathbf{r}, t) \cdot C_t(\mathbf{r}) (1 + 0(\lambda)) \\ &= P_H(\mathbf{r}, t) J(\mathbf{r}) , \end{aligned} \quad (2.59)$$

where $P_H(\mathbf{r}, t)$ is defined by Eq. (2.59) to replace the local equilibrium average by a homogeneous average. Finally, the $Q(t)$ in the exponential can be replaced by 1 since $LP(t) \sim P(t) L \sim \lambda$.

Equation (2.57) can now be written

$$(3) = \nabla_{\mathbf{r}} \cdot \left[\underline{\chi}(\mathbf{r}, t) : \nabla_{\mathbf{r}} \phi(\mathbf{r}, t) \right] (1 + 0(\lambda)) \quad (2.60)$$

where

$$\underline{\chi}(\mathbf{r}, t) = \int_0^\infty dy \frac{\langle [e^{-Ly} Q_H(\mathbf{r}, t) J_T] [Q_H(\mathbf{r}, t) J_T] \rangle_H(\mathbf{r}, t)}{V} \quad (2.61)$$

$$Q_H(\mathbf{r}, t) = 1 - P_H(\mathbf{r}, t) \quad (2.62)$$

$$P_H(\mathbf{r}, t) J_T \equiv \langle J_T C_{HT} \rangle_H(\mathbf{r}, t) \cdot \langle C_{HT} C_{HT} \rangle_H^{-1}(\mathbf{r}, t) \cdot C_{HT} \quad (2.63)$$

and

$$C_{HT} = \left(1 - \langle A_T \rangle_H(\mathbf{r}, t) \right) \cdot \quad (2.64)$$

Again, $\underline{\chi}(\mathbf{r}, t)$ involves an average over a homogeneous equilibrium ensemble with $\underline{\phi} = \underline{\phi}(\mathbf{r}, t)$.

Eq. (2.46) now reads

$$\dot{\underline{a}}(\mathbf{r}, t) = -\nabla_r \cdot \frac{\langle \underline{J}_T \rangle_H(\mathbf{r}, t)}{V} + \nabla_r \cdot [\underline{\chi}(\mathbf{r}, t) : \nabla_r \underline{\phi}(\mathbf{r}, t)] \quad (2.65)$$

where $\underline{\chi}(\mathbf{r}, t)$ is given by Eq. (2.61) and we have neglected terms of order λ compared to those that have been retained.

The detailed forms of the hydrodynamic equations for the two component mixture are presented in the next section.

III. HYDRODYNAMIC EQUATIONS FOR TWO COMPONENT FLUID MIXTURES

In this section, we shall use the general results developed in Section II to obtain the nonlinear hydrodynamic equations for two component fluid mixtures.

The calculations of the averages contained in Eqs. (2.65) and (2.61) are facilitated by introducing momenta relative to the center of mass motion. The quantities $\mathbf{p}^+$, and $\mathbf{P}_\alpha^+$ are defined by:

$$\begin{aligned}\mathbf{p}_j &= \mathbf{p}_j^+ + m_A \mathbf{v}(\mathbf{r}_j, t) \\ \mathbf{P}_\alpha &= \mathbf{P}_\alpha^+ + m_B \mathbf{v}(\mathbf{R}_\alpha, t) .\end{aligned}\quad (3.1)$$

Here $\mathbf{v}(\mathbf{r}_j, t)$ ($\mathbf{v}(\mathbf{R}_\alpha, t)$) is the mean velocity at position $\mathbf{r}_j$ ($\mathbf{R}_\alpha$) at time t . Substitution of Eqs. (3.1) into Eqs. (2.6) and (2.7) yields

$$\mathbf{P}(\mathbf{r}) = \mathbf{P}^+(\mathbf{r}) + M(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) \quad (3.2)$$

$$E(\mathbf{r}) = E^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) \cdot \mathbf{P}^+(\mathbf{r}) + \frac{1}{2} M(\mathbf{r}) v^2(\mathbf{r}, t) \quad (3.3)$$

where $\mathbf{P}^+(\mathbf{r})$ ($E^+(\mathbf{r})$) is obtained from Eq. (2.6) (Eq. (2.7)) by replacing all momenta by their daggered counterparts. The quantity $E^+(\mathbf{r})$ is the dynamical variable corresponding to the internal energy density at $\mathbf{r}$. Substitution of Eqs. (3.2) and (3.3) into Eq. (2.18) yields

$$\mathbf{A} * \left[\phi(t) + \phi_{\sim 0} \right] = M * [\beta \tilde{\mu}_A](t) + M_B * [\beta \tilde{\mu}](t) - E^+ * \beta(t) . \quad (3.4)$$

Thus, we find

$$\langle M(\mathbf{r}) \rangle_t = \rho(\mathbf{r}, t) \quad (3.5)$$

$$\langle M_B(\mathbf{r}) \rangle_t = \rho_B(\mathbf{r}, t) \quad (3.6)$$

$$\langle \mathbf{P}(\mathbf{r}) \rangle_t = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \quad (3.7)$$

$$\langle E(\mathbf{r}) \rangle_t = e(\mathbf{r}, t) = e^+(\mathbf{r}, t) + \frac{1}{2} \rho(\mathbf{r}, t) v^2(\mathbf{r}, t) . \quad (3.8)$$

Here $\rho(\mathbf{r}, t)$ is the total mass density at position $\mathbf{r}$ at time t , $\rho_B(\mathbf{r}, t)$ is the mass density of species B , $e(\mathbf{r}, t)$ is the total energy density and $e^+(\mathbf{r}, t)$ is the internal energy density.

Substitution of Eqs. (3.2) and (3.3) into the expressions for the currents, Eqs. (2.12a) - (2.12d), yields:

$$J_M(\mathbf{r}) = P^+(\mathbf{r}) + M(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) \quad (3.9)$$

$$J_{M_B}(\mathbf{r}) = P_B^+(\mathbf{r}) + M_B(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) \quad (3.10)$$

$$\underline{J}_P(\mathbf{r}) = \underline{\tau}^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) P^+(\mathbf{r}) + P^+(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) + M(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \quad (3.11)$$

$$J_E(\mathbf{r}) = J_E^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) \cdot \underline{\tau}^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) E^+(\mathbf{r}) \\ + \frac{1}{2} v^2(\mathbf{r}, t) P^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \cdot P^+(\mathbf{r}) + \frac{1}{2} M(\mathbf{r}) \mathbf{v}(\mathbf{r}, t) v^2(\mathbf{r}, t) . \quad (3.12)$$

Eqs. (3.11) and (3.12) follow from Eqs. (2.13) and (2.14). Again, $\underline{\tau}^+(\mathbf{r}) \left(J_E^+(\mathbf{r}) \right)$ follows from Eq. (2.13) (Eq. (2.14)) when all of the momenta are replaced by their daggered counterparts.

The averages of these currents over the local equilibrium distribution function are:

$$\langle J_M(\mathbf{r}) \rangle_t = \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \quad (3.13)$$

$$\langle J_{M_B}(\mathbf{r}) \rangle_t = \rho_B(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \quad (3.14)$$

$$\langle \underline{J}_P(\mathbf{r}) \rangle_t = \langle \underline{\tau}^+(\mathbf{r}) \rangle_t + \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) \quad (3.15)$$

$$\begin{aligned} \langle J_E(\mathbf{r}) \rangle_t &= \mathbf{v}(\mathbf{r}, t) \cdot \langle \underline{\underline{T}}^+(\mathbf{r}) \rangle_t + \mathbf{v}(\mathbf{r}, t) e^+(\mathbf{r}, t) \\ &+ \frac{1}{2} \rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) v^2(\mathbf{r}, t) . \end{aligned} \quad (3.16)$$

The average of the stress tensor over the homogeneous ensemble is

$$\langle \underline{\underline{T}}^+(\mathbf{r}) \rangle_H(\mathbf{r}, t) = \frac{\langle \underline{\underline{T}}^+ \rangle}{V}(\mathbf{r}, t) = p_h(\mathbf{r}, t) \underline{\underline{I}} \quad (3.17)$$

where $p_h(\mathbf{r}, t)$ is the space and time dependent hydrostatic pressure. Because of the form of Eq. (3.4), $p_h(\mathbf{r}, t)$ has the same functional dependence on $\rho(\mathbf{r}, t)$, $\rho_B(\mathbf{r}, t)$ and $e^+(\mathbf{r}, t)$ as p_{ho} has on ρ_o , ρ_{Bo} and e_o . This result follows from the development presented here and is not a supplementary hypothesis as in previous developments.

The dissipative currents which enter into $\underline{\underline{X}}(\mathbf{r}, t)$, Eq. (2.61), are given by:

$$J_d(\mathbf{r}) \equiv Q_H(\mathbf{r}, t) J(\mathbf{r}) \quad (3.18)$$

which leads to:

$$J_{Md}(\mathbf{r}) = 0 \quad (3.19)$$

$$J_{M_B d}(\mathbf{r}) = Q_H(\mathbf{r}, t) P_B^+(\mathbf{r}) \quad (3.20)$$

$$J_{=Pd}(\mathbf{r}) = \underline{\underline{T}}_d^+(\mathbf{r}) = Q_H(\mathbf{r}, t) \underline{\underline{T}}^+(\mathbf{r}) \quad (3.21)$$

$$J_{Ed}(\mathbf{r}) = J_{Ed}^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}, t) \cdot \underline{\underline{T}}_d^+(\mathbf{r}) . \quad (3.22)$$

Because of the homogeneous averages in the definitions of the $\underline{\underline{X}}$'s, they have the same tensorial symmetries that they have in equilibrium.

We introduce the notation

$$\langle B, D \rangle \equiv \int_0^\infty dy \frac{\langle [e^{-Ly} Q_H(\mathbf{r}, t) B] [Q_H(\mathbf{r}, t) D] \rangle}{V} H(\mathbf{r}, t) \quad (3.23)$$

in order to summarize concisely the properties of the various elements of the $\underline{\chi}$ matrix. We use Eqs. [(3.19) - (3.22)] to arrive at the following results:

$$\chi_{M\alpha} = \chi_{\alpha M} = 0, \quad (3.24)$$

where α is any element of the **A** vector;

$$\underline{\chi}_{M_B M_B}(\mathbf{r}, t) = \{P_B^+, P_B^+\} \equiv \underline{\theta}(\mathbf{r}, t) = \theta(\mathbf{r}, t) \underline{I} \quad (3.25)$$

$$\underline{\chi}_{M_B E}(\mathbf{r}, t) = \underline{\chi}_{E M_B}(\mathbf{r}, t) = \{P_B^+, J_E^+\} \equiv \phi(\mathbf{r}, t) \underline{I} \quad (3.26)$$

$$\underline{\chi}_{M_B P} = \underline{\chi}_{P M_B} = 0 \quad (3.27)$$

$$\underline{\chi}_{PP}(\mathbf{r}, t) = \{\underline{\tau}^+, \underline{\tau}^+\} \equiv \underline{\chi}(\mathbf{r}, t) \quad (3.28)$$

$$\underline{\chi}_{PE}(\mathbf{r}, t) = \{\underline{\tau}^+, \underline{\tau}^+\} \cdot \mathbf{v} = \underline{\chi}(\mathbf{r}, t) \cdot \mathbf{v}(\mathbf{r}, t) \quad (3.29)$$

$$\underline{\chi}_{EP}(\mathbf{r}, t) = \mathbf{v} \cdot \{\underline{\tau}^+, \underline{\tau}^+\} = \mathbf{v}(\mathbf{r}, t) \cdot \underline{\chi}(\mathbf{r}, t) \quad (3.30)$$

$$\underline{\chi}_{EE}(\mathbf{r}, t) = \mathbf{v} \cdot \{\underline{\tau}^+, \underline{\tau}^+\} \cdot \mathbf{v} + \{J_E^+, J_E^+\} \quad (3.31)$$

$$\equiv [\mathbf{v} \cdot \underline{\chi} \cdot \mathbf{v}](\mathbf{r}, t) + \kappa(\mathbf{r}, t) \underline{I}. \quad (3.32)$$

Note the very important property that all of the transport coefficients ($\theta, \phi, \underline{\chi}, \kappa$) are the same functional forms of $\rho(\mathbf{r}, t)$, $\rho_B(\mathbf{r}, t)$ and $e^+(\mathbf{r}, t)$ as they are of ρ_0 , ρ_{B0} , and e_0 when the average in Eq. (3.23) is replaced by an equilibrium average. Again this follows naturally from the development here and is not a separate hypothesis.³

The hydrodynamic equations now follow from Eq. (2.65), the average currents computed in Eqs. [(3.13) - (3.16)], the χ 's computed in Eqs. [(3.24) - (3.32)], and the ϕ 's given in Eq. (2.21). The results are:

$$\dot{\rho}(\mathbf{r}, t) = -\nabla_r \cdot [\rho \mathbf{v}](\mathbf{r}, t) \quad (3.33)$$

$$\begin{aligned} \dot{\rho}_B(\mathbf{r}, t) = & -\nabla_r \cdot [\rho_B \mathbf{v}](\mathbf{r}, t) \\ & + \nabla_r \cdot \left(\theta(\mathbf{r}, t) \nabla_r [\beta \tilde{\mu}](\mathbf{r}, t) - \phi(\mathbf{r}, t) \nabla_r \beta(\mathbf{r}, t) \right) \end{aligned} \quad (3.34)$$

$$\begin{aligned} \dot{\mathbf{p}}(\mathbf{r}, t) = & -\nabla_r p_h(\mathbf{r}, t) - \nabla_r \cdot [\rho \mathbf{v} \mathbf{v}](\mathbf{r}, t) \\ & + \nabla_r \cdot \left(\underline{\underline{\chi}}(\mathbf{r}, t) : \nabla_r [\beta \mathbf{v}](\mathbf{r}, t) - \underline{\underline{\chi}}(\mathbf{r}, t) : \mathbf{v}(\mathbf{r}, t) \nabla_r \beta(\mathbf{r}, t) \right) \end{aligned} \quad (3.35)$$

$$\begin{aligned} \dot{e}(\mathbf{r}, t) = & -\nabla_r \cdot [h^+ \mathbf{v}](\mathbf{r}, t) - \nabla_r \cdot \left[\frac{1}{2} \rho \mathbf{v} \mathbf{v}^2 \right](\mathbf{r}, t) \\ & + \nabla_r \cdot \left(\kappa(\mathbf{r}, t) \cdot \nabla_r (-\beta(\mathbf{r}, t)) + \phi(\mathbf{r}, t) \cdot \nabla_r [\beta \tilde{\mu}](\mathbf{r}, t) + \left[\mathbf{v} \cdot \underline{\underline{\chi}} : \mathbf{v} \right](\mathbf{r}, t) \nabla_r (-\beta(\mathbf{r}, t)) \right. \\ & \left. + \left[\mathbf{v} \cdot \underline{\underline{\chi}} \right](\mathbf{r}, t) : \nabla_r [\beta \mathbf{v}](\mathbf{r}, t) \right) \end{aligned} \quad (3.36)$$

where

$$h^+(\mathbf{r}, t) = e^+(\mathbf{r}, t) + p_h(\mathbf{r}, t) \quad (3.37)$$

is the internal enthalpy density. Finally, the elements of the fourth rank tensor $\underline{\underline{\chi}}(\mathbf{r}, t)$ can be written:

$$\begin{aligned} [\beta \chi_{ijkl}](\mathbf{r}, t) = & a(\mathbf{r}, t) \delta_{ij} \delta_{kl} + b(\mathbf{r}, t) (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \\ = & \left[\zeta - \frac{2}{3} \eta \right](\mathbf{r}, t) \delta_{ij} \delta_{kl} + \eta(\mathbf{r}, t) (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \end{aligned} \quad (3.38)$$

since $\underline{\underline{\tau}}^+$ is a symmetric tensor. Here η is the shear viscosity and ζ , the bulk viscosity.

Equations (3.33) - (3.37) are a closed set of nonlinear equations for $\rho(\mathbf{r}, t)$, $\rho_B(\mathbf{r}, t)$, $e(\mathbf{r}, t)$ and $p(\mathbf{r}, t)$. They can be written in a variety of suggestive ways, some of which will be given below.

Equations [(3.33) - (3.36)] can be written more succinctly as:

$$\dot{\rho}(\mathbf{r}, t) = -\nabla_r \cdot [\rho \mathbf{v}](\mathbf{r}, t) \quad (3.39)$$

$$\dot{\rho}_B(\mathbf{r}, t) = -\nabla_r \cdot [\rho_B \mathbf{v} - \theta \nabla_r(\beta \tilde{\mu}) + \phi \nabla_r \beta](\mathbf{r}, t) \quad (3.40)$$

$$\dot{p}(\mathbf{r}, t) = -\nabla_r \cdot \left[\frac{1}{\rho} p_h + \rho \mathbf{v} \mathbf{v} - \underline{\underline{\chi}} : \beta : \nabla_r \mathbf{v} \right](\mathbf{r}, t) \quad (3.41)$$

$$\dot{e}(\mathbf{r}, t) = -\nabla_r \cdot \left[\mathbf{v} \left(h^+ + \frac{1}{2} \rho v^2 \right) + \kappa \nabla_r \beta - \phi \nabla_r(\beta \tilde{\mu}) - \mathbf{v} \cdot \underline{\underline{\chi}} \beta : \nabla_r(\mathbf{v}) \right](\mathbf{r}, t) \quad (3.42)$$

where the notation $[\](\mathbf{r}, t)$ implies that all of the quantities inside the brackets are evaluated at position $\mathbf{r}$ at time t .

Note that the form of Eqs. (3.39) - (3.42) is

$$\dot{\mathbf{a}}(\mathbf{r}, t) = -\nabla_r \cdot \mathbf{j}(\mathbf{r}, t) \quad (3.43)$$

where $\mathbf{j}$ is the macroscopic current corresponding to $\mathbf{a}$; these equations are of this form since $\mathbf{a}$ is the density of a conserved variable.

The quantities which have thermodynamic significance are ρ , ρ_B , e^+ , β , p_h , h^+ , $\tilde{\mu}_A^+ \equiv \tilde{\mu}_A - \frac{1}{2} v^2$ and $\tilde{\mu} = \tilde{\mu}^+$. The functional relationships among these quantities are identical to those in equilibrium. Thus, it is useful to have an equation of motion for $e^+(\mathbf{r}, t)$. We use the relation (Eq. (3.8))

$$e^+(\mathbf{r}, t) = e(\mathbf{r}, t) - \frac{1}{2} p^2(\mathbf{r}, t) / \rho(\mathbf{r}, t)$$

to write

$$\begin{aligned}
 \dot{e}^+ (\mathbf{r}, t) &= \dot{e} (\mathbf{r}, t) - \mathbf{v} (\mathbf{r}, t) \cdot \dot{\mathbf{p}} (\mathbf{r}, t) + \frac{1}{2} v^2 (\mathbf{r}, t) \dot{\rho} (\mathbf{r}, t) \\
 &= -\nabla_r \cdot [\mathbf{v} e^+] (\mathbf{r}, t) - p_h (\mathbf{r}, t) \nabla_r \cdot \mathbf{v} (\mathbf{r}, t) \\
 &\quad - \nabla_r \cdot \left[\kappa \nabla_r \beta - \phi \nabla_r (\beta \tilde{\mu}) \right] (\mathbf{r}, t) \\
 &\quad + \left[\nabla \mathbf{v} : \underline{\underline{\chi}} \beta : \nabla_r \mathbf{v} \right] (\mathbf{r}, t) .
 \end{aligned} \tag{3.44}$$

Note that e^+ is not the density of a conserved quantity.

In the phenomenological treatment of irreversible processes, the time dependence of the entropy density and the form of the entropy production are of great interest. Despite confusion in the literature, the only sensible choice for the definition of the entropy density in a non-equilibrium system is that it is the same functional of ρ, ρ_B and e^+ as it is of ρ_0, ρ_{B0} and e_0 in equilibrium. No other definition makes operational sense since the entropy cannot be measured directly.

The equilibrium form of the combined first and second laws is:

$$ds = \frac{1}{T} de - \tilde{\mu}_A d\rho - \tilde{\mu} d\rho_B \tag{3.45}$$

where $s = S/V$ is the enthalpy per unit volume. In light of the discussion above, the non-equilibrium form of Eq. (3.45) is

$$ds (\mathbf{r}, t) = \left[\frac{1}{T} \left(de^+ - \tilde{\mu}_A^+ d\rho - \tilde{\mu} d\rho_B \right) \right] (\mathbf{r}, t) . \tag{3.46}$$

It follows from Eq. (3.46) that

$$\dot{s} (\mathbf{r}, t) = \left[\frac{1}{T} \left(\dot{e}^+ - \tilde{\mu}_A^+ \dot{\rho} - \tilde{\mu} \dot{\rho}_B \right) \right] (\mathbf{r}, t) \tag{3.47}$$

and

$$\nabla_r s(\mathbf{r}, t) = \left[\frac{1}{T} \left(\nabla_r e^+ - \tilde{\mu}_A^+ \nabla_r \rho - \tilde{\mu} \nabla_r \rho_B \right) \right]. \quad (3.48)$$

Substitution of Eqs. (3.39), (3.40) and (3.44) into Eq. (3.47) yields

$$\begin{aligned} \dot{s}(\mathbf{r}, t) = & -\nabla_r \cdot \left[\mathbf{v} s + k_B \left(\beta \kappa \nabla_r \beta - \beta \phi \nabla_r (\beta \tilde{\mu}) - (\beta \tilde{\mu}) \phi \nabla_r \beta \right) \right](\mathbf{r}, t) \\ & + k_B \left[\left(\beta \nabla_r \mathbf{v} \right) : \underline{\underline{\chi}} : \left(\beta \nabla_r \mathbf{v} \right) + \kappa \left(\nabla_r \beta \cdot \nabla_r \beta \right) + \theta \left(\nabla_r (\beta \tilde{\mu}) \cdot \nabla_r (\beta \tilde{\mu}) \right) - 2\phi \left(\left(\nabla_r \beta \right) \cdot \left(\nabla_r \beta \tilde{\mu} \right) \right) \right] \\ & (\mathbf{r}, t) \end{aligned} \quad (3.49)$$

There are two types of terms on the RHS of Eq. (3.49); the first type is of the form $-\nabla_r \cdot \mathbf{j}_s$ and disappears when integrated over $\mathbf{r}$. The second type involves dissipative terms only and is associated with entropy production. We rewrite Eq. (3.49) as

$$\dot{s}(\mathbf{r}, t) = -\nabla_r \cdot \mathbf{j}_s(\mathbf{r}, t) + \sigma(\mathbf{r}, t) \quad (3.50)$$

where the entropy production density is given by

$$\begin{aligned} \sigma(\mathbf{r}, t) = & k_B \left[\left(\beta \nabla_r \mathbf{v} \right) : \underline{\underline{\chi}} : \left(\beta \nabla_r \mathbf{v} \right) + \kappa \left(\nabla_r \beta \cdot \nabla_r \beta \right) \right. \\ & \left. + \theta \left(\nabla_r (\beta \tilde{\mu}) \cdot \nabla_r (\beta \tilde{\mu}) \right) \right. \\ & \left. - 2\phi \left(\left(\nabla_r \beta \right) \cdot \nabla_r (\beta \tilde{\mu}) \right) \right](\mathbf{r}, t) \end{aligned} \quad (3.51)$$

The first term on the RHS of Eq. (3.51) is obviously positive semi-definite since $\underline{\underline{\chi}}$ is the time integral of an autocorrelation function. The last three terms can be written

$$\left\{ \left(J_{Ex}^+ \nabla_r \beta - P_{Bx}^+ \nabla_r (\beta \tilde{\mu}) \right) \cdot \left(J_{Ex}^+ \nabla_r \beta - P_{Bx}^+ \nabla_r (\beta \tilde{\mu}) \right) \right\} \quad (3.52)$$

where we have used the notation of Eq. (3.23) and the definitions of θ , ϕ and κ which appear in Eqs. (3.25), (3.26) and (3.32), respectively. Thus, $\sigma(\mathbf{r}, t)$ is positive unless there are no spatial gradients and the system is in equilibrium.

In order to further the analysis of the hydrodynamic equations, it is useful to introduce the composition variable

$$w(\mathbf{r}, t) \equiv \rho_B(\mathbf{r}, t) / \rho(\mathbf{r}, t) \quad (3.53)$$

which is the weight fraction density of component B in place of ρ_B . It is related to the mole fractions at $\mathbf{r}$ and t by

$$w(\mathbf{r}, t) = \left(\frac{m_B x_B}{m_A x_A + m_B x_B} \right)(\mathbf{r}, t) \quad (3.54)$$

We use Eqs. (3.53) and (3.39) and (3.40) to write:

$$\begin{aligned} \dot{w}(\mathbf{r}, t) &= \left[\frac{\dot{\rho}_B}{\rho} - \frac{\rho_B}{\rho^2} \dot{\rho} \right](\mathbf{r}, t) \\ &= -[\mathbf{v} \cdot \nabla_{\mathbf{r}} w](\mathbf{r}, t) + \left[\frac{1}{\rho} \nabla_{\mathbf{r}} \cdot (\theta \nabla_{\mathbf{r}} (\beta \tilde{\mu}) - \phi \nabla_{\mathbf{r}} \beta) \right](\mathbf{r}, t) \quad (3.55) \end{aligned}$$

It is frequently useful to express $\beta \tilde{\mu}$ in terms of more directly measurable quantities such as temperature, pressure and weight fraction. In equilibrium

$$d(\beta \tilde{\mu}) = \tilde{h} d\beta + \beta \tilde{v} dp_h + g dw \quad (3.56)$$

where

$$g \equiv \left(\frac{\partial \beta \tilde{\mu}}{\partial w} \right)_{\beta, p_h}, \quad (3.57)$$

$$\tilde{h} = \frac{\bar{H}_B}{m_B} - \frac{\bar{H}_A}{m_A} \quad (3.58)$$

and

$$\tilde{v} = \frac{\bar{V}_B}{m_B} - \frac{\bar{V}_A}{m_A} \quad (3.59)$$

where $\bar{H}_i$ ($\bar{V}_i$) is the partial molar enthalpy (volume) of species i . Thus

$$\nabla_r (\beta \tilde{\mu})(x, t) = \left[\tilde{h} \nabla_r \beta + \beta \tilde{v} \nabla_r p_h + g \nabla_r w \right](x, t) \quad (3.60)$$

The dissipative current in Eq. (3.40) can be written

$$\begin{aligned}
 j_{Bd}(\mathbf{r}, t) &= \left[(\phi - \theta \tilde{h}) \nabla_r \beta - \theta \tilde{\nu} \nabla_r p_h - \theta g \nabla_r w \right] (\mathbf{r}, t) \\
 &= \left[(-\theta g) \left(\nabla_r w + \frac{1}{g} \left(\tilde{h} - \frac{\phi}{\theta} \right) \nabla_r \beta + \frac{\beta \tilde{\nu}}{g} \nabla_r p_h \right) \right] (\mathbf{r}, t) .
 \end{aligned} \tag{3.61}$$

The dissipative energy current in Eq. (3.41) is:

$$\begin{aligned}
 j_{ed}(\mathbf{r}, t) &= - \left[\mathbf{v} \cdot \underline{\underline{\chi}} \beta : \nabla_r \mathbf{v} \right] (\mathbf{r}, t) \\
 &\quad + \left[\left(\kappa - \tilde{h} \phi \right) \nabla_r \beta - \phi \beta \tilde{\nu} \nabla_r p_h - g \phi \nabla_r w \right] (\mathbf{r}, t) .
 \end{aligned} \tag{3.62}$$

The second bracketed terms in Eq. (3.62) can be written:

$$\begin{aligned}
 &\left[(-\phi g) \left(\nabla_r w + \frac{\beta \tilde{\nu}}{g} \nabla_r p_h + \frac{1}{g} \left(\tilde{h} - \frac{\kappa}{\phi} \right) \nabla_r \beta \right) \right] (\mathbf{r}, t) \\
 &= \left[\left(\frac{\phi}{\theta} \right) (-\theta g) \left(\nabla_r w + \frac{\beta \tilde{\nu}}{g} \nabla_r p_h \right) + \frac{1}{g} \left(\tilde{h} - \frac{\kappa}{\phi} \right) \nabla_r \beta \right] (\mathbf{r}, t) \\
 &= \left[\frac{\phi}{\theta} j_{BD} \right] (\mathbf{r}, t) + \left[\left(\kappa - \frac{\phi^2}{\ell} \right) \nabla_r \beta \right] (\mathbf{r}, t)
 \end{aligned} \tag{3.63}$$

The dissipative energy current consists of three parts: a viscous term, a part proportional to the dissipative current of the mass density of species B , and a part proportional to $\nabla \cdot \beta$. This last term is associated with the heat current in the absence of particle flow.

In Section IV, the equations derived in this section are linearized and the dispersion relations are presented in Section VI.

IV. LINEAR HYDRODYNAMIC EQUATIONS FOR TWO COMPONENT FLUID MIXTURES

The results in Section III can be linearized in a straightforward manner. The fundamental equations, Eqs. (3.39) - (3.42) become

$$\dot{\rho}(\mathbf{r}, t) = -\rho \nabla_{\mathbf{r}} \cdot \mathbf{v}(\mathbf{r}, t) \quad (4.1)$$

$$\dot{\rho}_B(\mathbf{r}, t) = -\rho_B \nabla_{\mathbf{r}} \cdot \mathbf{v}(\mathbf{r}, t) + \theta \nabla_{\mathbf{r}}^2 (\beta \tilde{\mu})(\mathbf{r}, t) - \phi \nabla_{\mathbf{r}}^2 \beta(\mathbf{r}, t) \quad (4.2)$$

$$\dot{\mathbf{p}}(\mathbf{r}, t) = -\nabla_{\mathbf{r}} \cdot \mathbf{p}_h(\mathbf{r}, t) + \beta \underline{\underline{\chi}} : \nabla_{\mathbf{r}} \nabla_{\mathbf{r}} \mathbf{v}(\mathbf{r}, t) \quad (4.3)$$

$$\dot{e}(\mathbf{r}, t) = -h \nabla_{\mathbf{r}} \cdot \mathbf{v}(\mathbf{r}, t) - \kappa \nabla_{\mathbf{r}}^2 \beta(\mathbf{r}, t) + \phi \nabla_{\mathbf{r}}^2 (\beta \tilde{\mu})(\mathbf{r}, t) \quad (4.4)$$

In these equations, the $\mathbf{r}$ and t dependence of the quantities is denoted explicitly. The thermodynamic quantities ρ , ρ_B and h do not depend on $\mathbf{r}$ and t and have their equilibrium values. Further, the transport coefficients θ , ϕ , κ , and $\underline{\underline{\chi}}$ do not depend on $\mathbf{r}$ and t and are computed using an equilibrium average; i.e. Eq. (3.23) becomes

$$\langle B, D \rangle = \int_0^\infty dy \frac{\langle [e^{-Ly} QB] [QD] \rangle_0}{V} \quad (4.5)$$

where

$$QB = B - \langle B C \rangle_0 * \langle CC \rangle_0^{-1} * C. \quad (4.6)$$

Equations (4.1) - (4.4) are a closed set of equations for $[\rho, \rho_B, \mathbf{p}, e](\mathbf{r}, t)$ but that closure is implicit because of the occurrence of $[\rho_h, \mathbf{v}, \beta \tilde{\mu}, \beta](\mathbf{r}, t)$ on the right hand side. The closure can be made explicit by using the relations:

$$\mathbf{p}(\mathbf{r}, t) = \rho \mathbf{v}(\mathbf{r}, t) \quad (4.7)$$

which is the linearized version of Eq. (3.7),

$$\begin{aligned} \nabla_r^2 \beta(\mathbf{r}, t) = & \left(\frac{\partial \beta}{\partial \rho} \right)_{\rho_B, e} \nabla_r^2 \rho(\mathbf{r}, t) + \left(\frac{\partial \beta}{\partial \rho_B} \right)_{\rho, e} \nabla_r^2 \rho_B(\mathbf{r}, t) \\ & + \left(\frac{\partial \beta}{\partial e} \right)_{\rho, \rho_B} \nabla_r^2 e(\mathbf{r}, t) \end{aligned} \quad (4.8)$$

and a similar result for $\nabla_r^2 (\beta \tilde{\mu})(\mathbf{r}, t)$. The thermodynamic derivatives in Eq. (4.8) are equilibrium quantities.

It is convenient to take the spatial Fourier Transform of the hydrodynamic equations and to use the notation:

$$a_k(t) \equiv \int_V e^{i\mathbf{k} \cdot \mathbf{r}} a(\mathbf{r}, t) d\mathbf{r} \quad (4.9)$$

It is also convenient to consider the components of the vector $\mathbf{p}_k(t)$ along the wave vector $\mathbf{k}$ and perpendicular to it. We use the notation

$$p_k(t) = \hat{\mathbf{k}} \cdot \mathbf{p}_k(t) \quad (4.10)$$

$$\mathbf{p}_{kt}(t) = \hat{\mathbf{k}} \times \mathbf{p}_k(t) \quad (4.11)$$

where $\hat{\mathbf{k}}$ is a unit vector along $\mathbf{k}$.

The results of these various operations are:

$$\dot{\rho}_k(t) = ik p_k(t) \quad (4.12)$$

$$\dot{\rho}_{Bk}(t) = \frac{\rho_B}{\rho} ik p_k(t) - k^2 \left[\left(\theta \left(\frac{\partial \beta \tilde{\mu}}{\partial \rho} \right)_{\rho_B, e} - \phi \left(\frac{\partial \beta}{\partial \rho} \right)_{\rho_B, e} \right) \rho_k(t) \right]$$

$$\begin{aligned}
& + \left(\theta \left(\frac{\partial (\beta \tilde{\mu})}{\partial \rho_B} \right)_{\rho, \epsilon} - \phi \left(\frac{\partial \beta}{\partial \rho_B} \right)_{\rho, \epsilon} \right) \rho_{Bk}(t) \\
& + \left(\theta \left(\frac{\partial (\beta \tilde{\mu})}{\partial \epsilon} \right)_{\rho, \rho_B} - \phi \left(\frac{\partial \beta}{\partial \epsilon} \right)_{\rho, \epsilon} \right) e_k(t) \Big] \quad (4.13)
\end{aligned}$$

$$\begin{aligned}
\dot{p}_k(t) = & i k \left[\left(\frac{\partial p_h}{\partial \rho} \right)_{\rho_B, \epsilon} \rho_k(t) + \left(\frac{\partial p_h}{\partial \rho_B} \right)_{\rho, \epsilon} \rho_{Bk}(t) + \left(\frac{\partial p_h}{\partial \epsilon} \right)_{\rho, \rho_B} e_k(t) \right] \\
& - k^2 \frac{\left(\zeta + \frac{4}{3} \eta \right)}{\rho} p_k(t) \quad (4.14)
\end{aligned}$$

$$\begin{aligned}
\dot{e}_k(t) = & \frac{\hbar}{\rho} i k p_k(t) - k^2 \left[\left(\phi \left(\frac{\partial \beta \tilde{\mu}}{\partial \rho} \right)_{\rho_B, \epsilon} - \kappa \left(\frac{\partial \beta}{\partial \rho} \right)_{\rho_B, \epsilon} \right) \rho_k(t) \right. \\
& \left. + \left(\phi \left(\frac{\partial \beta \tilde{\mu}}{\partial \rho_B} \right)_{\rho, \epsilon} - \kappa \left(\frac{\partial \beta}{\partial \rho_B} \right)_{\rho, \epsilon} \right) \rho_{Bk}(t) + \left(\phi \left(\frac{\partial \beta \tilde{\mu}}{\partial \epsilon} \right)_{\rho, \rho_B} - \kappa \left(\frac{\partial \beta}{\partial \epsilon} \right)_{\rho, \rho_B} \right) e_k(t) \right] \quad (4.15)
\end{aligned}$$

and

$$\dot{p}_{kt}(t) = -k^2 \frac{\eta}{\rho} p_{kt}(t) \quad (4.16)$$

where we have introduced the shear viscosity, η , and the bulk viscosity, ζ [see Eq. (3.38)]. Note that the four variables $\rho_k(t)$, $\rho_{Bk}(t)$, $p_k(t)$ and $e_k(t)$ are coupled together while the two transverse components of the momentum are uncoupled to the above variables and to each other.

The transport equations, (4.12) - (4.16), are of the form

$$\dot{\mathbf{a}}_k(t) = \underline{\underline{M}}_k \cdot \mathbf{a}_k(t) \quad (4.17)$$

where the hydrodynamic matrix contains terms proportional to ik , Euler terms, and terms proportional to k^2 , Navier-Stokes terms. More explicitly:

$$\dot{\mathbf{b}}_k(t) = \underline{M}_k \cdot \mathbf{b}_k(t) \quad (4.18)$$

$$\dot{p}_{kt}(t) = -k^2 \frac{\eta}{\rho} p_{kt}(t) \quad (4.19)$$

where $\mathbf{b}_k(t)$ is a four component vector with components ρ_k, ρ_{Bk}, p_k and e_k and $\underline{M}_k$ is a 4×4 matrix.

Another informative way of summarizing the hydrodynamic equations is to write

$$\dot{\mathbf{a}}_k(t) = i\mathbf{k} \cdot \mathbf{j}_k(t)$$

where $\mathbf{j}_k(t)$ is the macroscopic current of $\mathbf{a}_k$. The currents $\mathbf{j}_k(t)$ consist of Euler and dissipative parts. The relationship between the dissipative parts of the energy current and the current for the mass density of component B is

$$\mathbf{j}_{edk}(t) = \frac{\phi}{\theta} \mathbf{j}_{Bdk}(t) + i\mathbf{k} \left(\kappa - \frac{\phi^2}{\theta} \right) \beta_k(t) \quad (4.20)$$

which follows from Eq. (3.63).

Finally, we note that the linearized equation for $\dot{\omega}_k(t)$ is given by

$$\dot{\omega}_k(t) = \frac{1}{\rho} i\mathbf{k} \cdot \mathbf{j}_{Bdk}(t) \quad (4.21)$$

In Section VI, the dispersion relations for the linearized hydrodynamic equations will be discussed.

V. THERMODYNAMIC INTERLUDE

An extremely large number of thermodynamic relationships are necessary to simplify the dispersion relations given in Section VI. All of these are standard and will not be derived here. In this section we shall focus our attention on the dependence of the chemical potentials as functions of a composition variable at constant T and p . In particular, we shall be interested in solutions dilute in species B where the size of a B particle is substantially larger than the size of an A particle. As a rough approximation, we shall assume that the ratio of the molar volumes of species A and B is the same as the ratio of their masses. Under these circumstances:

$$\phi_A = \frac{n_A \bar{V}_A}{n_A \bar{V}_A + n_B \bar{V}_B} \cong \frac{n_A m_A}{n_A m_A + n_B m_B} = \frac{\rho_A}{\rho} = 1 - \frac{\rho_B}{\rho}$$

$$\phi_B = \rho_B / \rho = w \quad (5.1)$$

where ϕ_A and ϕ_B are the volume fractions of species A and B , respectively.

For dilute solutions of B in A , we find for the chemical potentials:

$$\mu_A = \mu_A^o(T, p) + k_B T \left[\ln \phi_A + (1 - y^{-1}) \phi_B \right]$$

$$\mu_B = \mu_B^{(oo)}(T, p) + k_B T \left[\ln \phi_B + (1 - y) \phi_A \right] \quad (5.2)$$

where $y = \frac{m_B}{m_A} \gg 1$. These results are derived using considerations identical to those of Flory and Hildebrand for polymer solutions. Note that Eq. (5.2) assumes that species B is large compared to species A and is rigid.

The thermodynamic quantity of interest in the hydrodynamic equations is

$$g = \left(\frac{\partial (\beta \tilde{\mu})}{\partial w} \right)_{T, p} = \left(\frac{\partial \beta \tilde{\mu}}{\partial \phi_B} \right)_{T, p} \quad (5.3)$$

The result is

$$\begin{aligned}
\left(\frac{\partial(\beta \tilde{\mu})}{\partial w} \right)_{T, p} &= \beta \left[\left(\frac{\partial \mu_B}{\partial w} \right)_{T, p} \frac{1}{m_B} - \left(\frac{\partial \mu_A}{\partial w} \right)_{T, p} \frac{1}{m_A} \right] \\
&= \left[\frac{1}{m_B} \left(\frac{1}{\phi_B} + y - 1 \right) - \frac{1}{m_A} \left(-\frac{1}{\phi_A} + 1 - y^{-1} \right) \right] \\
&= \frac{1}{m_B} \left(\frac{1}{\phi_B} + \frac{y}{\phi_A} \right) = \frac{(x_A + x_B y^2)(x_A + x_B y)}{m_B x_A x_B y}.
\end{aligned} \tag{5.4}$$

In a very dilute solution, $x_B y^2 \ll 1$,

$$m_B g \cong \frac{1}{x_B y} = \frac{y}{x_B y^2} \gg 1. \tag{5.5}$$

In a moderately dilute solution, $x_B y < 1$,

$$m_B g \cong \frac{1 + x_B y^2}{x_B y} > 1. \tag{5.6}$$

VI. DISPERSION RELATIONS

The linear hydrodynamic equations [Eqs. (4.12) - (4.15)] may now be used to obtain the dispersion relations for two-component fluid mixtures. Laplace transforming the linear equations leads to the following equation for the dispersion relations:

$$\det (z \underline{I} - \underline{M}) = 0, \quad (6.1)$$

where the components of the matrix $\underline{M}$ are

$$M_{\rho\rho} = z, \quad M_{\rho\rho_B} = 0, \quad M_{\rho e} = 0, \quad M_{\rho p} = -ik$$

$$M_{\rho_B\rho} = k^2 \Gamma_{\rho_B\rho}, \quad M_{\rho_B\rho_B} = z + k^2 \Gamma_{\rho_B\rho_B}, \quad M_{\rho_B e} = k^2 \Gamma_{\rho_B e}, \quad M_{\rho_B p} = -ik\rho_B / \rho$$

$$M_{e\rho} = k^2 \Gamma_{e\rho}, \quad M_{e\rho_B} = k^2 \Gamma_{e\rho_B}, \quad M_{ee} = z + k^2 \Gamma_{ee}, \quad M_{ep} = -ikh / \rho$$

$$M_{p\rho} = -ik\gamma_{p\rho}, \quad M_{p\rho_B} = -ik\gamma_{p\rho_B}, \quad M_{pe} = -ik\gamma_{pe}, \quad M_{pp} = z + k^2 \Gamma_{pp}.$$

We have defined

$$\Gamma_{\rho_B\rho} = \theta \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_{\rho_B, e} - \phi \left(\frac{\partial \beta}{\partial \rho} \right)_{\rho_B, e}$$

$$\Gamma_{\rho_B\rho_B} = \theta \left(\frac{\partial \tilde{\mu}}{\partial \rho_B} \right)_{\rho, e} - \phi \left(\frac{\partial \beta}{\partial \rho_B} \right)_{\rho, e}$$

$$\Gamma_{\rho_B e} = \theta \left(\frac{\partial \tilde{\mu}}{\partial e} \right)_{\rho, \rho_B} - \phi \left(\frac{\partial \beta}{\partial e} \right)_{\rho, e}$$

$$\Gamma_{e\rho} = \phi \left(\frac{\partial \tilde{\mu}}{\partial \rho} \right)_{\rho_B, e} - \kappa \left(\frac{\partial \beta}{\partial \rho} \right)_{\rho_B, e}$$

$$\Gamma_{e\rho_B} = \phi \left(\frac{\partial \tilde{\mu}}{\partial \rho_B} \right)_{\rho, e} - \kappa \left(\frac{\partial \beta}{\partial \rho_B} \right)_{\rho, e}$$

$$\Gamma_{ee} = \phi \left(\frac{\partial \tilde{\beta}}{\partial e} \right)_{\rho, \rho_B} - \kappa \left(\frac{\partial \beta}{\partial e} \right)_{\rho, \rho_B}$$

$$\Gamma_{pp} = \left(\zeta + \frac{4\eta}{3} \right) / \rho$$

$$\gamma_{pp} = \left(\frac{\partial p_h}{\partial p} \right)_{\rho_B, e}, \gamma_{p\rho_B} = \left(\frac{\partial p_h}{\partial \rho_B} \right)_{\rho, e}, \gamma_{pe} = \left(\frac{\partial p_h}{\partial e} \right)_{\rho, \rho_B}.$$

Multiplying out the determinant in Eq. (6.1), we arrive at the following fourth order polynomial equation for z:

$$z^4 + A z^3 + B z^2 + C z + D + E z^2 + F = 0 \quad (6.2)$$

The coefficients of the various powers of z contain the following defined quantities:

$$A = \Gamma_{pp} + \Gamma_{ee} + \Gamma_{\rho_B \rho_B}$$

$$B = \gamma_{pe} h / \rho + \gamma_{p\rho_B} \rho_B / \rho + \gamma_{pp}$$

$$C = \Gamma_{pp} \Gamma_{ee} + \Gamma_{\rho_B \rho_B} (\Gamma_{ee} + \Gamma_{pp}) - \Gamma_{\rho_B e} \Gamma_{e\rho_B}$$

$$D = (\Gamma_{\rho_B \rho_B} \gamma_{pe} - \Gamma_{\rho_B e} \gamma_{p\rho_B}) h / \rho + (\Gamma_{ee} \gamma_{p\rho_B} - \Gamma_{e\rho_B} \gamma_{pe}) \rho_B / \rho$$

$$+ (\Gamma_{ee} + \Gamma_{\rho_B \rho_B}) \gamma_{pp} - \Gamma_{\rho_B \rho} \gamma_{p\rho_B} - \Gamma_{e\rho} \gamma_{pe}$$

$$E = \Gamma_{pp} (\Gamma_{\rho_B \rho_B} \Gamma_{ee} - \Gamma_{\rho_B e} \Gamma_{e\rho_B})$$

$$F = \gamma_{pe} (\Gamma_{\rho_B \rho} \Gamma_{e\rho_B} - \Gamma_{\rho_B \rho_B} \Gamma_{e\rho}) + \gamma_{p\rho_B} (\Gamma_{\rho_B e} \Gamma_{e\rho} - \Gamma_{\rho_B \rho} \Gamma_{ee})$$

$$+ \gamma_{pp} (\Gamma_{\rho_B \rho_B} \Gamma_{ee} - \Gamma_{\rho_B e} \Gamma_{e\rho_B}).$$

Writing

$$z = z^{(0)} + ikz^{(1)} - k^2 z^{(2)} + \dots,$$

substituting into Eq. (6.2), and equating coefficients of like powers of k to zero, we obtain the following four approximate solutions to the dispersion relation, Eq. (6.1):

$$z_{\pm} = \pm i k c_o - k^2 \frac{(A c_o^2 - D)}{2c_o^2}$$

$$z_{3,4} = \frac{-k^2}{2c_o^2} \left[D \pm \left(D^2 - 4F c_o^2 \right)^{\frac{1}{2}} \right].$$

In writing Eqs. (6.3) and (6.4), we have recognized that $B = c_o^2$, where c_o is the adiabatic sound speed in a two component mixture. Thus the roots $z_{\pm}$ in Eq. (6.3) correspond to propagating sound waves.

Equations (6.3) and (6.4) can be reduced to simpler forms with the help of Eq. (3.56) and a multitude of standard thermodynamic relationships. The amount of algebra involved is rather large and we simply state the results:

$$z_{\pm} = \pm i k c_o - \frac{k^2}{2} \left\{ \xi + \frac{4}{3} \eta + (\gamma - 1) \Lambda + (g k_B T) \frac{\bar{D}(\gamma - 1) c_p \rho}{\alpha^2 T} \left(\frac{k_p}{p_h} + \frac{\alpha k_T}{c_p} \right) \cdot \left[\left(\frac{k_p}{p_h} + \frac{\alpha k_T}{c_p} \right) - \frac{w}{c_o^2 \rho} \right] \right\} \quad (6.5)$$

$$z_{3,4} = -\frac{k^2}{2} \left\{ \Lambda + \bar{D} + \Delta + \Sigma \pm \left(\Lambda - \bar{D} - \Delta - \Sigma \right) \left[1 + \frac{4 \Lambda (\Delta + \Sigma)}{(\Lambda - \bar{D} - \Delta - \Sigma)^2} \right]^{1/2} \right\}. \quad (6.6)$$

In arriving at Eqs. (6.5) and (6.6), we have used the definition of $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant, and have defined a diffusion constant

$$\bar{D} = g \Gamma_{\rho_B \rho_B} / \rho. \quad (6.7)$$

Recall that g is given by Eq. (3.57). We have also used the symmetry property $\Gamma_{\rho_B e} = \Gamma_{e \rho_B}$ [see Eq. (3.26)], and have defined

$$\Lambda = \frac{1}{c_p k_B T^2} \left(\Gamma_{ee} - \Gamma_{e\rho_B}^2 / \Gamma_{\rho_B \rho_B} \right) \quad (6.8)$$

$$\Delta = \frac{g \rho k_B k_T^2}{c_p} \overline{D} \quad (6.9)$$

$$\Sigma = (g k_B T) \overline{D} \frac{(\gamma - 1) c_p \rho}{\alpha^2 T} \frac{w}{c_o^2 \rho} \left(\frac{k_p}{p_h} + \frac{\alpha k_T}{c_p} \right). \quad (6.10)$$

The quantities k_p and k_T are defined as follows:

$$\frac{k_p}{p_h} = \frac{\tilde{v}}{g k_B T} \quad (6.11)$$

$$k_T = - \frac{\Gamma_{\rho_B e} - \tilde{h} \Gamma_{\rho_B \rho_B}}{g k_B T \Gamma_{\rho_B \rho_B}}. \quad (6.12)$$

The thermodynamic quantities c_v and c_p are the specific heats at constant volume and pressure respectively in a closed system (constant mode numbers),

$$c_V = T \left(\frac{\partial s}{\partial T} \right)_{V, \square} = \left(\frac{\partial e}{\partial T} \right)_{V, \square} \quad (6.13)$$

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_{p, \square} \quad (6.14)$$

$$\gamma = \frac{c_p}{c_V}, \quad (6.15)$$

and α is the coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{p, \square}. \quad (6.16)$$

The symbol $\square$ implies a closed system; i.e. derivatives calculated at constant mode numbers. The specific heats are related by

$$c_p = c_v + \frac{\alpha^2 T}{\kappa_T}, \quad (6.17)$$

where κ_T is the isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T, \square}. \quad (6.18)$$

In summary, there are two propagating roots, $z_{\pm}$, which correspond to sound waves, and two non-propagating roots which are mixtures of thermal and diffusive contributions.

VII. LONG TIME TAIL CALCULATIONS

The reduction of the exact equations of motion for $\dot{\mathbf{a}}(\mathbf{r}, t)$, Eq. (2.46), to equations which are of the form of the phenomenological nonlinear hydrodynamic equations, Eqs. (2.65), involves several approximations with different degrees of validity. In this section, we describe the approximations in detail and point out potential weaknesses in some of the arguments. We use mode-coupling theory to refine these arguments and present corrections to Eqs. (2.65) which are similar to the long-time tail corrections which appear in the linear theory.³

We have restricted our attention to fluid systems in which the macroscopic variables, $\mathbf{a}(\mathbf{r}, t)$, and the conjugate forces, $\underline{\phi}(\mathbf{r}, t)$, vary slowly in space and, therefore, in time. More precisely, $\mathbf{a}$ and $\underline{\phi}$ have negligible variations over molecular distances (1-10 angstroms) and molecular times (10^{-13} sec). Under these circumstances and because of the properties of equal time averages over the local equilibrium distribution function, namely

$$\langle \mathbf{A}(\mathbf{r}) \mathbf{B}(\mathbf{r}') \rangle_t \xrightarrow{|\mathbf{r} - \mathbf{r}'| > \xi} \langle \mathbf{A}(\mathbf{r}) \rangle_t \langle \mathbf{B}(\mathbf{r}') \rangle_t \quad (7.1)$$

where the correlation length ξ is of the order of a few Angstroms, the reduction of the local equilibrium average in the first term on the right hand side of Eq. (2.45) to a homogeneous average is justified.

The neglect of the initial value term in Eq. (2.46) depends on the following arguments:
a) the exact distribution function is of the local equilibrium form at $t = 0$ and, therefore, $\mathbf{x}(0) = 0$; or
b) the projected propagator has no slow time dependence and therefore the term is zero for $t > \tau_m$.
It is assumed that all the slow time dependence has been eliminated because of the projection operator Q which projects out the slow motions associated with the linear variables $\mathbf{A}(\mathbf{r})$. However, if $\mathbf{A}(\mathbf{r})$ is slowly varying, i.e.

$$\dot{\mathbf{A}}(\mathbf{r}) = -\nabla_{\mathbf{r}} \cdot \mathbf{J}(\mathbf{r}) \quad , \quad (7.2)$$

then the bilinear variable $\mathbf{A}(\mathbf{r}) \mathbf{A}(\mathbf{r}')$ is also slowly varying. Therefore the projected propagator has some slow components and argument b) cannot be used. We shall assume that argument a) applies and the term can be neglected.

The simplification of the last term on the RHS of Eq. (2.46) depends crucially on the assumption that the projected propagator has no slow components. As above, this is not true because the slow motions associated with the bilinear $(\mathbf{A}\mathbf{A})$, trilinear $(\mathbf{A}\mathbf{A}\mathbf{A})$, etc. modes have not been projected out.

We consider term (3) in Eq. (2.46) in which all the projection operators $Q(s)$ are replaced by

$$\hat{Q}(s) \equiv 1 - \hat{P}(s) \quad (7.3)$$

where

$$\hat{P}(s) B \equiv \sum_{l=0}^{\infty} \left\langle B \mathbf{C}_s^{(l)} \right\rangle_s * K^{(l)}(s)^{-1} * \mathbf{C}_s^{(l)} \equiv \sum_{l=0}^{\infty} P^{(l)}(s) B \quad (7.4)$$

where the superscript (l) denotes the order of the mode,

$$C^{(0)} = 1$$

$$C_s^{(1)} = \tilde{A}_s$$

$$C_s^{(2)} = \tilde{A}_s \tilde{A}_s - \langle \tilde{A}_s \tilde{A}_s \rangle_s - \langle \tilde{A}_s \tilde{A}_s \tilde{A}_s \rangle_s^* K_{\equiv}^{(1)}(s)^{-1} * \tilde{A}_s$$

.

(7.5)

where $C^{(1)}$ denotes the linear modes, $C^{(2)}$ the bilinear modes, etc. Note that the modes are constructed in such a way that the modes of different order, l , are orthogonal to each other; i.e.

$$\langle C_s^{(l)} C_s^{(l')} \rangle_s = \Delta_{ll'} \langle C_s^{(l)} C_s^{(l)} \rangle_s \quad (7.6)$$

where $\Delta_{ll'}$ is the Kronecker delta. The quantity $K_{\equiv}^{(l)}(s)$ is given by

$$K_{\equiv}^{(l)}(s) = \langle C_s^{(l)} C_s^{(l)} \rangle_s \quad (7.7)$$

and $\hat{Q}(s)B$ is orthogonal to all of the slow quantities in the system. Now we can assert that the projected propagator which involves $\hat{L}\hat{Q}(s)$ has no slow components and, using the arguments presented in Section II, we can write

$$\begin{aligned}
& \nabla_{\mathbf{r}} \cdot \int_0^t d\tau \int_V d\mathbf{r}' \left\langle \left[T_- \exp \left(- \int_{\tau}^t L \hat{Q}(s) ds \right) \mathbf{J}(\mathbf{r}) \right] \left[\hat{Q}(\tau) \mathbf{J}(\mathbf{r}') \right] \right\rangle_{\tau} : \nabla_{\mathbf{r}'} \underline{\phi}(\mathbf{r}', t) \\
& = \nabla_{\mathbf{r}} \cdot \int_0^{\infty} dy \int_V d\mathbf{r}' \left\langle \left[e^{-\hat{Q}(t)Ly} \hat{Q}(t) \mathbf{J}(\mathbf{r}) \right] \left[\hat{Q}(t) \mathbf{J}(\mathbf{r}') \right] \right\rangle_t : \nabla_{\mathbf{r}'} \underline{\phi}(\mathbf{r}', t) \quad (7.8)
\end{aligned}$$

which is similar to Eq. (2.57) for $t > \tau_m$. Furthermore, it is legitimate to replace the averages over the local equilibrium distribution functions by homogeneous averages at $\mathbf{r}$ and t . Eq. (7.8) becomes:

$$\nabla_{\mathbf{r}} \cdot \int_0^{\infty} dy \left\langle \left[e^{-\hat{Q}_H(\mathbf{r}, t)Ly} \hat{Q}_H(\mathbf{r}, t) \mathbf{J}(\mathbf{r}) \right] \left[\hat{Q}_H(\mathbf{r}, t) \mathbf{J}_T \right] \right\rangle_H(\mathbf{r}, t) : \nabla_{\mathbf{r}} \underline{\phi}(\mathbf{r}, t) \quad (7.9)$$

where

$$P_H^{(0)}(\mathbf{r}, t) \mathbf{J}(\mathbf{r}) = \langle \mathbf{J}(\mathbf{r}) \rangle_H(\mathbf{r}, t) = \langle \mathbf{J}_T \rangle_H(\mathbf{r}, t) / V, \quad (7.10)$$

$$P_H^{(1)}(\mathbf{r}, t) \mathbf{J}(\mathbf{r}) = \left\langle \mathbf{J}_T \mathbf{C}_{HT}^{(1)} \right\rangle_H(\mathbf{r}, t) \cdot \left[\left\langle \mathbf{C}_{HT}^{(1)} \mathbf{C}_{HT}^{(1)} \right\rangle_H(\mathbf{r}, t) \right]^{-1} \cdot \mathbf{C}_t^{(1)}(\mathbf{r}) \quad (7.11)$$

where $\mathbf{C}_{HT}^{(1)}$ is given by Eq. (2.63), and

$$\begin{aligned}
P_H^{(2)}(\mathbf{r}, t) J(\mathbf{r}) = & \int \left\langle J(\mathbf{r}) C_i^{(2)}(\mathbf{r}', \mathbf{r}'') \right\rangle_H (\mathbf{r}, t) \\
& \cdot \left[\left\langle C_i^{(2)} C_i^{(2)} \right\rangle_H (\mathbf{r}, t) \right]^{-1} (\mathbf{r}', \mathbf{r}''; \mathbf{R}', \mathbf{R}'') \\
& \cdot C_i^{(2)}(\mathbf{R}', \mathbf{R}'') d\mathbf{r}' d\mathbf{r}'' d\mathbf{R}' d\mathbf{R}'' .
\end{aligned} \tag{7.12}$$

The spatial properties of the correlation functions in Eq. (7.12) are of great importance. The first correlation function decays to zero if $|\mathbf{r} - \mathbf{r}'|$ and/or $|\mathbf{r} - \mathbf{r}''| > \xi$; the second correlation function is zero if $|\mathbf{r} - \mathbf{R}'|$ or $|\mathbf{r}'' - \mathbf{R}''| > \xi$. We shall use these properties below.

The exact term (3) in Eq. (2.46) will be denoted by $I(\mathbf{r}, t)$. A term of the same form but with all projection operators Q replaced by $\hat{Q}$ will be denoted $\hat{I}(\mathbf{r}, t)$. All of the arguments presented in Section II for simplifying the form of $I(\mathbf{r}, t)$ to that in Eqs. (2.60) and (2.65) are valid for $\hat{I}(\mathbf{r}, t)$ because the projected propagator has no slow time dependence. We can write:

$$I(\mathbf{r}, t) \equiv \hat{I}(\mathbf{r}, t) + \Delta(\mathbf{r}, t) \tag{7.13}$$

where $\Delta(\mathbf{r}, t)$ is defined by Eq. (7.13). The most important difference between I and $\hat{I}$ is due to the projection on to the bilinear modes. The contributions due to the higher order modes are usually negligible.

We can now replace $\hat{I}(\mathbf{r}, t)$ by $\nabla_{\mathbf{r}} \cdot \left[\hat{\underline{\chi}}(\mathbf{r}, t) : \nabla_{\mathbf{r}} \underline{\phi}(\mathbf{r}, t) \right]$ where $\hat{\underline{\chi}}(\mathbf{r}, t)$ is given by Eq. (2.61) with Q_H replaced by $\hat{Q}_H$. The quantities $\hat{\underline{\chi}}(\mathbf{r}, t)$ are the space and time dependent bare transport coefficients. The long-time tail contributions to the bare transport coefficients are approximately of the form:

$$\Delta \underline{\chi}(\mathbf{r}, t) \equiv - \int_0^{\infty} dy \left\langle \left[e^{-Ly} P^{(2)}(\mathbf{r}, t) \mathbf{J}(\mathbf{r}) \right] \left[P^{(2)}(\mathbf{r}, t) \mathbf{J}_T \right] \right\rangle_H (\mathbf{r}, t) \quad (7.14)$$

where

$$\underline{\chi}(\mathbf{r}, t) = \hat{\underline{\chi}}(\mathbf{r}, t) + \Delta \underline{\chi}(\mathbf{r}, t) . \quad (7.15)$$

In most cases, $\Delta \underline{\chi}$ makes a small, but not negligible, contribution to $\underline{\chi}$. However, in some cases, these contributions are dominant. In particular, in two component systems in which the molecular size of one component (B) is much larger than the other, (A), $\Delta \underline{\chi}$ changes the form of the diffusion coefficient from a Chapman-Enskog form to a Navier-Stokes form. More work has to be done before a detailed discussion of long-time tail effects can be presented.

VIII. SUMMARY

We have developed techniques for obtaining exact nonlinear transport equations for macroscopic variables. For slowly varying quantities these equations can be considerably simplified and yield the phenomenological nonlinear hydrodynamic equations for two component fluid systems. Expressions for the effects of long-time tails on the values of the transport coefficients have been derived but detailed calculations have been deferred for the future.

The nonlinear transport equations have been linearized and dispersion relations have been obtained. In the two component system, there are two uncoupled transverse momentum modes which are non-propagating. In addition there are four modes, two of which are propagating (sound modes) and two of which are non-propagating (thermal and diffusive).

New expressions for the chemical potentials in two component dilute systems have been obtained for situations in which the solute species molecules (particles) are much larger than the solvent molecules. In these systems, mode-coupling effects dominate the values of the diffusion constant for the solute.

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