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Macroscopic Phenomenological Relations for Nonlinear Processes in Kinetic Theory

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Nonlinear irreversible processes between states which are not local equilibrium states are investigated by methods of the kinetic theory. The phenomenological equations for the second-order fluxes in a multicomponent mixture are derived, and relations between some of the second-order phenomenological coefficients are established. It is shown that new independent forces appear in the second-order equation, namely the gradients of the chemical potentials. Expressions for the entropy, entropy flux, and entropy source are evaluated. These expressions are related to the phenomenological equations and coefficients, e.g., all the second-order contributions of the forces in the equations for the fluxes can be obtained by differentiation of the expression for the second-order entropy source with respect to the coupled forces.

KEY WORDS: Kinetic theory; irreversible thermodynamics; nonlinear processes; phenomenological relations; transport coefficients; multicomponent systems.

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1. INTRODUCTION

No general theory is available as yet for nonlinear irreversible processes. The existing theory of irreversible thermodynamic treats linear processes between states of local equilibrium.(4) Several attempts were made to extend the theory to nonlinear processes for states not far from equilibrium, i.e., with the assumption of local equilibrium.(6,7) Phenomenological relations can also be obtained by methods of the kinetic theory. The results obtained by these methods for processes between local equilibrium states are equivalent to those of the macroscopic theory of irreversible thermodynamics.(4) DeGroot and Mazur(4) implied that the description of second-order effects by the kinetic theory does not agree with any extension of the existing macroscopic theory. The reason for this discrepancy is that the kinetic theory is not restricted to local equilibrium states.

Chapman and Cowling(2) describe the mathematical analysis of the kinetic theory and the solution of the Boltzmann equation by Enskog's method of expanding the distribution function in series around the equilibrium state. The method is applicable only to "normal" states. Chapman and Cowling(2) fully describe the first-order solution for the distribution function and the first-order phenomenological equations. Burnett(1) evaluated the rather complicated second-order solution for the distribution function. Chapman and Cowling(2) developed a method for deriving the second-order phenomenological equations for a one-component gas where it is not necessary to use the cumbersome solution for the second-order distribution but only the equation for it. In a later work(3) they extended the method to calculate the diffusion flux in a two-component mixture.

The purpose of the present work is to investigate, using kinetic theory considerations, nonlinear processes between states which are not necessarily in local equilibrium. The discussion is restricted, however, to the class of processes between so-called normal states, namely states which are governed by the Boltzmann equation. In the present work, the results of Chapman and Cowling(3) are modified and extended. The phenomenological equations for a multicomponent mixture of simple gases are derived. (The term simple gas is used for a gas where all modes of energy other than the translational energy may be neglected.) The second-order entropy, entropy source, and entropy flux are evaluated for such a mixture and their relation to the thermodynamic fluxes and forces is established. It is shown that all the terms appearing in the phenomenological equations for the fluxes can be obtained by differentiating the entropy production rate with respect to the coupled forces.

The term "phenomenological" equations is used here for the equations relating the macroscopic average values of the thermodynamic fluxes to the thermodynamic forces. This term thus has a similar meaning to "transport" or "constitutive" equations.

2. DEFINITIONS AND CONSERVATION LAWS

A brief summary of the definitions and the conservation laws that are used in the present work is given in this section.

The microscopic state of a chemically nonreacting multicomponent mixture is specified by the number of molecules of each molecular species i which lie in the phase space volume element $\mathbf{dr}\,\mathbf{du}_i$ at time t, namely the distribution function $f_i(\mathbf{r}, \mathbf{u}; t)\,\mathbf{dr}\,\mathbf{du}_i$. The change of the distribution function which describes the behavior of the system is given by the Boltzmann equation

$$\frac{\partial f_i}{\partial t} = -\mathbf{u}_i \cdot \frac{\partial f_i}{\partial \mathbf{r}} - \mathbf{F}_i \cdot \frac{\partial f_i}{\partial u_i} + \sum_j C(f_i, f_j), \qquad i = 1, \ldots, N \tag{1}$$

where $\mathbf{F}_i$ is an extenal force (per unit mass) exerted on the component i and $C(f_i, f_j)$ are the collision integrals given by

$$C(f_i, f_j) = \iint [f_i(\mathbf{r}, \mathbf{u}_i'; t) f_j(\mathbf{r}, \mathbf{u}_j'; t) - f_i(\mathbf{r}, \mathbf{u}_i; t) f_j(\mathbf{r}, \mathbf{u}_j; t)] \cdot |\mathbf{u}_{ij}|\, W(\mathbf{k}_{ij}|\mathbf{k}_{ij}'; |\mathbf{u}_{ij}|)\, \mathbf{dk}_{ij}'\, \mathbf{du}_j \tag{2}$$

where the prime denotes values after the collision, $|\mathbf{u}_{ij}| = |\mathbf{u}_i - \mathbf{u}_j|$ is the absolute value of the relative molecular velocity, $\mathbf{k}_{ij}$ is a unit vector directed along the relative velocity, and $|\mathbf{u}_{ij}|\, W(\mathbf{k}_{ij}|\mathbf{k}_{ij}'; |\mathbf{u}_{ij}|)\, \mathbf{dk}_{ij}'$ is the conditional probability per unit time that the unit vector will be in the interval between $\mathbf{k}_{ij}'$ and $\mathbf{k}_{ij}' + \mathbf{dk}_{ij}'$ after the collision if before the collision it was in the direction $\mathbf{k}_{ij}$.

The number density n_i and the mass density ρ_i of a component i are defined by

$$n_i = \int f_i\, \mathbf{du}_i; \qquad \rho_i = m_i n_i = m_i \int f_i\, \mathbf{du}_i \tag{3}$$

where m_i is the molecular mass of component i.

The translational kinetic energy of the thermal motion per unit volume $\rho_i e_i$ is given by

$$\rho_i e_i = \tfrac{1}{2} m_i \int (\mathbf{u}_i - \mathbf{v})^2 f_i\, \mathbf{du}_i = \tfrac{1}{2} m_i \int \mathbf{U}_i^2 f_i\, \mathbf{du}_i \tag{4}$$

where $\mathbf{v}$ is the barycentric velocity (or the velocity of the local center of mass) and is given by

$$\mathbf{v} = \left(\sum_i \rho_i\right)^{-1} \sum_i m_i \int f_i \mathbf{u}_i\, \mathbf{du}_i \tag{5}$$

and $\mathbf{U}_i = \mathbf{u}_i - \mathbf{v}$ is the peculiar velocity.

The properties of the whole system are obtained by summing over all the components. Thus the number, mass, and energy densities are given by

$$n = \sum_i n_i \tag{6a}$$

$$\rho = \sum_i \rho_i = \sum_i m_i n_i \tag{6b}$$

$$e = \sum_i \rho_i e_i = \tfrac{1}{2} \sum_i m_i \int (\mathbf{u}_i - \mathbf{v})^2 f_i \, d\mathbf{u}_i \tag{6c}$$

The fluxes are defined as the sums of the molecular fluxes; thus the diffusion flux $\mathbf{J}_i$ is

$$\mathbf{J}_i = m_i \int f_i (\mathbf{u}_i - \mathbf{v}) \, d\mathbf{u}_i \tag{7}$$

The thermal energy flux (which for a simple gas is equivalent to the heat flux) is

$$\mathbf{J}_q = \tfrac{1}{2} \sum_i m_i \int f_i (\mathbf{u}_i - \mathbf{v})^2 (\mathbf{u}_i - \mathbf{v}) \, d\mathbf{u}_i \tag{8}$$

And the pressure tensor P is given by the momentum flux

$$\mathsf{P} = \sum_i m_i \int f_i (\mathbf{u}_i - \mathbf{v})(\mathbf{u}_i - \mathbf{v}) \, d\mathbf{u}_i \tag{9}$$

where $(\mathbf{u}_i - \mathbf{v})(\mathbf{u}_i - \mathbf{v})$ denotes a dyadic product.

The conservation laws can be written in the following way. The continuity equation:

$$dn_i/dt = -n_i \operatorname{div} \mathbf{v} - \operatorname{div}(n_i \bar{\mathbf{U}}_i), \qquad d\rho/dt = -\operatorname{div} \mathbf{v} \tag{10}$$

where $\bar{\mathbf{U}}_i \equiv \int \mathbf{U}_i f_i \, d\mathbf{u}_i$ is the average of the vector $\mathbf{U}_i$. The momentum equation:

$$\rho \, d\mathbf{v}/dt = -\operatorname{Div} \mathsf{P} + \sum_i \rho_i \mathbf{F}_i \tag{11}$$

The energy equation:

$$\rho \, de/dt = -\operatorname{div} \mathbf{J}_q - \mathsf{P} : \operatorname{Grad} \mathbf{v} + \sum_i \mathbf{J}_i \cdot \mathbf{F}_i \tag{12}$$

The temperature T is defined by

$$\tfrac{3}{2} nKT = \rho e \tag{13}$$

where K is the Boltzmann constant. The molecular and the average enthalpies are given by

$$h_i = \tfrac{5}{2} KT/m_i; \qquad \rho h = \sum_i \rho_i h_i = \tfrac{5}{2} nKT \tag{14}$$

The entropy and the entropy flux are defined by

$$\rho s = -K \sum_i \int f_i(\ln f_i - 1)\, \mathbf{du}_i \tag{15}$$

$$\mathbf{J}_s = -K \sum_i \int (\mathbf{u}_i - \mathbf{v}) f_i(\ln f_i - 1)\, \mathbf{du}_i \tag{16}$$

The balance equation for the entropy is

$$(\partial/\partial t)(\rho s) = -\mathrm{div}(\rho s \mathbf{v} + \mathbf{J}_s) + \sigma \tag{17}$$

By introducing the time derivative from the Boltzmann equation (1), the rate of entropy production (or entropy source) σ is found to be

$$\sigma = -K \sum_i \sum_j \int C(f_i, f_j) \ln f_i\, \mathbf{du}_i \geqslant 0 \tag{18}$$

3. THE SOLUTION OF BOLTZMANN'S EQUATION BY ENSKOG'S METHOD

Enskog's method for the solution of Boltzmann's equation is used to extend the results of Chapman and Cowling(2,3) and deGroot and Mazur(4) to the description of second-order effects in multicomponent systems.

The distribution function is expanded in series

$$f_i = f_i^{(0)} + f_i^{(1)} + f_i^{(2)} + \cdots = f_i^{(0)}(1 + \phi_i^{(1)} + \phi_i^{(2)} + \cdots) \tag{19}$$

where the orders of magnitudes are determined according to the effect of the thermodynamic forces.

The zeroth order $f_i^{(0)}$ is related to the states where no forces exist locally, and, therefore, to local equilibrium states.

By using Eq. (19), we can put the fluxes, pressure tensor, and rate of entropy production into the following forms:

$$\mathbf{J} = \mathbf{J}^{(0)} + \mathbf{J}^{(1)} + \mathbf{J}^{(2)} + \cdots = \mathbf{J}^{(1)} + \mathbf{J}^{(2)} + \cdots \tag{20}$$

$$\mathsf{P} = \mathsf{P}^{(0)} + \mathsf{P}^{(1)} + \mathsf{P}^{(2)} + \cdots = p\mathsf{U} + \Pi^{(1)} + \Pi^{(2)} + \cdots \tag{21}$$

$$\sigma = \sigma^{(0)} + \sigma^{(1)} + \sigma^{(2)} + \cdots = \sigma^{(1)} + \sigma^{(2)} + \cdots \tag{22}$$

where the zeroth-order terms of the fluxes and the entropy source vanish and the equilibrium pressure is hydrostatic.

The solution for $f_i^{(0)}$ is given by the Maxwell distribution:

$$f_i^{(0)} = n_i(m_i/2\pi KT)^{3/2} \exp(-m_i U_i^2/2KT) \tag{23}$$

The solution for the first-order distribution function is given by[(4)]

$$\phi_i^{(1)} = -A_i \mathbf{U}_i \cdot \frac{\operatorname{grad} T}{T} - \sum_{k=1}^{N-1} D_{ik} \mathbf{U}_i \cdot \mathbf{R}_k - B_i \mathbf{U}_i{}^{\circ}\mathbf{U}_i : \mathsf{E}, \qquad i = 1, 2, \ldots, N \tag{24}$$

where E is the velocity-gradient tensor:

$$\mathsf{E} \equiv \operatorname{Grad} \mathbf{v} \tag{25}$$

$\mathbf{U}_i{}^{\circ}\mathbf{U}_i$ denotes the traceless tensor produced by the appropriate dyadic product; $\mathbf{R}_k$ denotes the diffusion forces:

$$\mathbf{R}_k \equiv \{\operatorname{grad}(\mu_k - \mu_N)\}_T - (\mathbf{F}_k - \mathbf{F}_N) \tag{26}$$

where μ_k is the chemical potential of component k and the index T denotes that the temperature is kept constant while carrying out the differentiation. The functions A_i, D_{ik}, and B_i depend on the absolute values U_i of the velocities and on the local properties: temperature and composition. The solutions for these functions can be expanded in series of the Sonine polynomials $S_m^{(2)}$.[(2)] The coefficients of these expansions depend on the molecular character of the system and the intermolecular forces.

It is sometimes useful to write the first-order solution (24) in the following form:

$$f_i^{(1)} = f_i^{(0)}\phi_i^{(1)} = \hat{A}_i \mathbf{U}_i \cdot \operatorname{grad} T + \sum_{k=1}^{N-1} \hat{D}_{ik} \mathbf{U}_i \cdot \mathbf{R}_k + \hat{B}_i \mathbf{U}_i{}^{\circ}\mathbf{U}_i : \mathsf{E} \tag{27}$$

where

$$\hat{A}_i = -(1/T) f_i^{(0)} A_i, \qquad \hat{D}_{ik} = -f_i^{(0)} D_{ik}, \qquad \hat{B}_i = -f_i^{(0)} B_i \tag{28}$$

The equation for $\phi^{(2)}$ is obtained by grouping the second-order terms in the Boltzmann equation:

$$Y_i = \frac{\partial_1 f_i^{(0)}}{\partial t} + \frac{\partial_0 f_i^{(1)}}{\partial t} + \mathbf{u}_i \cdot \frac{\partial f_i^{(1)}}{\partial \mathbf{r}} + \mathbf{F}_i \cdot \frac{\partial f_i^{(1)}}{\partial \mathbf{u}_i} + \sum_j C(f_i^{(1)}, f_j^{(1)}) \tag{29}$$

where Y_i is defined as follows

$$Y_i \equiv \sum_j \{-C(f_i^{(0)}, f_j^{(2)}) - C(f_i^{(2)}, f_j^{(0)})\} \tag{30}$$

and where $\partial_l f_i^{(k)}/\partial t$ contains all the terms of the order l which appear after the introduction of the conservation equations into the expression of $\partial f_i^{(k)}/\partial t$. For example, the first term in Eq. (29) is calculated by

$$\frac{\partial_1 f_i^{(0)}}{\partial t} = f_i^{(0)} \frac{\partial_1 \ln f_i^{(0)}}{\partial t} = f_i^{(0)} \frac{\partial_1}{\partial t}\left(\ln n_i - \frac{3}{2}\ln T - \frac{m_i U_i^2}{2KT}\right)$$

$$= f_i^{(0)} \left[\frac{1}{n_i}\frac{\partial_1 n_i}{\partial t} - \left(\frac{3}{2}\frac{1}{T} - \frac{m_i U_i^2}{2KT^2}\right)\frac{\partial_1 T}{\partial t} + \frac{m_i}{KT}\mathbf{U}_i \cdot \frac{\partial_1 \mathbf{U}_i}{\partial t}\right] \tag{31}$$

The time derivatives in the last equations are evaluated by taking the first-order terms in the conservation equations (10)–(12) with the definition (13) of the temperature. Thus Eq. (31) is replaced by

$$\begin{aligned}\frac{\partial_1 f_i^{(0)}}{\partial t} = f_i^{(0)}\Bigg\{ & -\frac{1}{n_i}\operatorname{div}(n_i\bar{\mathbf{U}}_i^{(1)}) \\ & + \left(\frac{m_i U_i^2}{2KT} - \frac{3}{2}\right)\frac{1}{nT}\Bigg[T\operatorname{div}\Big(\sum_j n_j\bar{\mathbf{U}}_j^{(1)}\Big) \\ & + \frac{2}{3K}\sum_j \rho_j\bar{\mathbf{U}}_j^{(1)}\cdot\mathbf{F}_j - \frac{2}{3K}\operatorname{div}\mathbf{J}_q^{(1)} - \frac{2}{3K}\Pi^{(1)} : \mathsf{E}\Bigg] \\ & - \frac{m_i}{KT}\mathbf{U}_i\cdot\frac{1}{\rho}\operatorname{Div}\Pi^{(1)}\Bigg\}\end{aligned} \tag{32}$$

The next three terms in Eq. (29) can be written in the following way, by substituting $\mathbf{u}_i = \mathbf{v} + \mathbf{U}_i$:

$$\begin{aligned}\frac{\partial_0 f_i^{(1)}}{\partial t} + \mathbf{u}_i\cdot\frac{\partial f_i}{\partial \mathbf{r}} + \mathbf{F}_i\cdot\frac{\partial f_i^{(1)}}{\partial \mathbf{u}_i} = {} & \frac{d_0 f_i^{(1)}}{dt} + \mathbf{U}_i\cdot\frac{\partial f_i^{(1)}}{\partial \mathbf{r}} \\ & + \mathbf{G}_i\cdot\frac{\partial f_i^{(1)}}{\partial \mathbf{U}_i} - \frac{\partial f_i^{(1)}}{\partial \mathbf{U}_i}\mathbf{U}_i : \mathsf{E}\end{aligned} \tag{33}$$

where $\mathbf{G}_i \equiv \mathbf{F}_i - d_0\mathbf{v}/dt$ can be expressed in terms of the diffusion forces

$$G_i = \sum_{j=1}^{N-1}[\delta_{ij} - (\rho_j/\rho)]\mathbf{R}_j - (\operatorname{grad}\mu_i)_T \tag{34}$$

The derivatives of $f_i^{(1)}$ are obtained by differentiating Eq. (27). Use is made again of the conservation laws (10)–(12), the definition of temperature (13), and the relation

$$\operatorname{grad} n_j = (\rho_j/KT)(\operatorname{grad}\mu_j)_T$$

The resulting derivatives of $f_i^{(1)}$ are

$$\begin{aligned}\frac{d_0 f_i^{(1)}}{dt} = {} & -\Bigg(\frac{\partial \hat{A}_i}{\partial T}\mathbf{U}_i\cdot\operatorname{grad}T + \sum_{k=1}^{N-1}\frac{\partial \hat{D}_{ik}}{\partial T}\mathbf{U}_i\cdot\mathbf{R}_k \\ & + \frac{\partial \hat{B}_i}{\partial T}\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}\Bigg)\frac{2T}{3}\operatorname{div}\mathbf{v} \\ & - \sum_j n_j\Bigg(\frac{\partial \hat{A}_i}{\partial n_j}\mathbf{U}_i\cdot\operatorname{grad}T + \sum_{k=1}^{N-1}\frac{\partial \hat{D}_{ik}}{\partial n_j}\mathbf{U}_i\cdot\mathbf{R}_k \\ & + \frac{\partial \hat{B}_i}{\partial n_j}\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}\Bigg)\operatorname{div}\mathbf{v} + \hat{A}_i\mathbf{U}_i\cdot\frac{d_0}{dt}(\operatorname{grad}T) \\ & + \sum_{k=1}^{N-1}\hat{D}_{ik}\mathbf{U}_i\cdot\frac{d_0}{dt}\mathbf{R}_k + \hat{B}_i\mathbf{U}_i{}^\circ\mathbf{U}_i : \frac{d}{dt}\mathsf{E}\end{aligned} \tag{35}$$

$$
\begin{aligned}
\frac{\partial f_i}{\partial \mathbf{r}} = {} & \left(\frac{\partial \hat{A}_i}{\partial T}\, \mathbf{U}_i\cdot \operatorname{grad} T + \sum_{k=1}^{N-1} \frac{\partial \hat{D}_{ik}}{\partial T}\, \mathbf{U}_i\cdot \mathbf{R}_k \right.\\
& \left. + \frac{\partial \hat{B}_i}{\partial T}\, \mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E}\right) \operatorname{grad} T\\
& + \sum_j \left(\frac{\partial \hat{A}_i}{\partial n_j}\, \mathbf{U}_i\cdot \operatorname{grad} T + \sum_{k=1}^{N-1} \frac{\partial \hat{D}_{ik}}{\partial n_j}\, \mathbf{U}_i\cdot \mathbf{R}_k \right.\\
& \left. + \frac{\partial \hat{B}_i}{\partial n_j}\, \mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E}\right) \frac{\rho_j}{KT} (\operatorname{grad} \mu_j)_T + \hat{A}_i \mathbf{U}_i\cdot \operatorname{Div} \operatorname{grad} T\\
& + \sum_{k=1}^{N-1} \hat{D}_{ik} \mathbf{U}_i\cdot \operatorname{grad} \mathbf{R}_k + \hat{B}_i \operatorname{Grad}(\mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E}) \qquad (36)
\end{aligned}
$$

$$
\begin{aligned}
\frac{\partial f_i^{(1)}}{\partial \mathbf{U}_i} = {} & 2\left(\frac{\partial \hat{A}_i}{\partial U_i{}^2}\, \mathbf{U}_i\cdot \operatorname{grad} T + \sum_{k=1}^{N-1} \frac{\partial \hat{D}_{ik}}{\partial U_i{}^2}\, \mathbf{U}_i\cdot \mathbf{R}_k \right.\\
& \left. + \frac{\partial \hat{B}_i}{\partial U_i{}^2}\, \mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E}\right) \mathbf{U}_i + \hat{A}_i \operatorname{grad} T + \sum_{k=1}^{N-1} \hat{D}_{ik} \mathbf{R}_k + 2\hat{B}_i \mathbf{U}_i\cdot \overset{\circ}{\overline{\overline{\mathsf{E}}}} \qquad (37)
\end{aligned}
$$

by using Eqs. (11) and (26) and the Gibbs–Duhem equation: $\sum_k \rho_k (\operatorname{grad} \mu_k)_T = \operatorname{grad} p$. $\overline{\overline{\mathsf{E}}}$ is the symmetric part of the tensor E.

Finally, the solution (27) for the distribution function is introduced into the collision integrals to yield

$$
\begin{aligned}
C(f_i^{(1)}, f_j^{(1)}) = {} & C[\hat{A}_i(\mathbf{U}_i\cdot \operatorname{grad} T)\hat{A}_j(\mathbf{U}_j\cdot \operatorname{grad} T)]\\
& + C[\hat{A}_i(\mathbf{U}_i\cdot \operatorname{grad} T) \sum_{k=1}^{N-1} \hat{D}_{jk}(\mathbf{U}_j\cdot \mathbf{R}_k)]\\
& + C[\hat{A}_i(\mathbf{U}_i\cdot \operatorname{grad} T)\hat{B}_j(\mathbf{U}_j{}^\circ \mathbf{U}_j : \mathsf{E})]\\
& + C\left[\sum_{k=1}^{N-1} \hat{D}_{ik}(\mathbf{U}_i\cdot \mathbf{R}_k)\hat{A}_j(\mathbf{U}_j\cdot \operatorname{grad} T)\right]\\
& + C\left[\sum_{k=1}^{N-1} \hat{D}_{ik}(\mathbf{U}_i\cdot \mathbf{R}_k) \sum_{l=1}^{N-1} \hat{D}_{jl}(\mathbf{U}_j\cdot \mathbf{R}_l)\right]\\
& + C\left[\sum_{k=1}^{N-1} \hat{D}_{ik}(\mathbf{U}_i\cdot \mathbf{R}_k)\hat{B}_j(\mathbf{U}_i{}^\circ \mathbf{U}_j : \mathsf{E})\right]\\
& + C[\hat{B}_i(\mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E})\hat{A}_j(\mathbf{U}_j\cdot \operatorname{grad} T)]\\
& + C\left[\hat{B}_i(\mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E}) \sum_{k=1}^{N-1} \hat{D}_{jk}(\mathbf{U}_j\cdot \mathbf{R}_k)\right]\\
& + C[\hat{B}_i(\mathbf{U}_i{}^\circ \mathbf{U}_i : \mathsf{E})\hat{B}_j(\mathbf{U}_j{}^\circ \mathbf{U}_j : \mathsf{E})] \qquad (38)
\end{aligned}
$$

Equations (32)–(38) can be substituted into the right-hand side of Eq. (29) to yield an expression for Y_i in terms of the peculiar velocity and the other parameters. This expression will be used in Section 4 for the derivation of the phenomenological equations, where it will be convenient to divide Y_i into groups of terms according to their dependence on the peculiar velocity:

$$Y_i = Y_{i_0} + Y_{i_{\mathrm{odd}}} + Y_{i_{\mathrm{even}}} \tag{39}$$

$$\begin{aligned} Y_{i_0} = f_i^{(0)} \bigg\{ & -\frac{1}{n_i} \operatorname{div}(n_i \bar{\mathbf{U}}_i^{(1)}) + \left(\frac{m_i U_i^2}{3KT} - 1 \right) \bigg\} \\ & \times \frac{1}{nKT} \left[T \operatorname{div}\left(\sum_j n_j \bar{\mathbf{U}}_j^{(1)} \right) \right. \\ & \left. + \sum_j \rho_j \bar{\mathbf{U}}_j^{(1)} \cdot \mathbf{F}_j - \operatorname{div} \mathbf{J}_q^{(1)} - \Pi^{(1)} : \mathsf{E} \right] \\ & + \hat{A}_i \mathbf{G}_i \cdot \operatorname{grad} T + \mathbf{G}_i \cdot \sum_{k=1}^{N-1} \hat{D}_{ik} \mathbf{R}_k \end{aligned} \tag{40}$$

$$\begin{aligned} Y_{i_{\mathrm{odd}}} = & -\frac{f_i^{(0)} m_i}{\rho KT} \mathbf{U}_i \cdot \operatorname{Div} \Pi^{(1)} \\ & - \frac{2}{3} (\operatorname{div} \mathbf{v}) \left(T \frac{\partial \hat{A}_i}{\partial T} + \frac{3}{2} \sum_j n_j \frac{\partial \hat{A}_j}{\partial n_j} + \mathbf{U}_i^2 \frac{\partial \hat{A}_i}{\partial U_i^2} \right) (\mathbf{U}_i \cdot \operatorname{grad} T) \\ & - \frac{2}{3} (\operatorname{div} \mathbf{v}) \sum_{k=1}^{N-1} T \left\{ \left[\frac{\partial \hat{D}_{ik}}{\partial T} + \frac{3}{2} \sum_j n_j \frac{\partial \hat{D}_{ik}}{\partial n_j} + \mathbf{U}_i^2 \frac{\partial \hat{D}_{ik}}{\partial U_i^2} \right] (\mathbf{U}_i \cdot \mathbf{R}_k) \right\} \\ & + \hat{A}_i \mathbf{U}_i \cdot \left(\frac{d_0}{dt} \operatorname{grad} T - \mathsf{E} \cdot \operatorname{grad} T \right) \\ & + \sum_{k=1}^{N-1} \hat{D}_{ik} \mathbf{U}_i \cdot \left(\frac{d_0}{dt} \mathbf{R}_k - \mathsf{E} \cdot \mathbf{R}_k \right) \\ & + (\mathbf{U}_i \cdot \operatorname{grad} T)(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \left(\frac{\partial \hat{B}_i}{\partial T} - 2 \frac{\partial \hat{A}_i}{\partial U_i^2} \right) \\ & + \sum_j \left\{ [\mathbf{U}_i \cdot (\operatorname{grad} \mu_j)_T] \frac{\rho_j}{KT} \frac{\partial \hat{B}_i}{\partial n_j} \right\} (\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \\ & - \sum_{k=1}^{N-1} 2 \frac{\partial \hat{D}_{ik}}{\partial U_i^2} (\mathbf{U}_i \cdot \mathbf{R}_k)(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \\ & + 2(\mathbf{U}_i \cdot \mathbf{G}_i)(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \frac{\partial \hat{B}_i}{\partial U_i^2} + 2\hat{B}_i \mathbf{U}_i \cdot (\mathbf{G}_i \cdot \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \\ & + \hat{B}_i \mathbf{U}_i \cdot \operatorname{grad}(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \\ & - \sum_j \left\{ C \left[\hat{A}_i (\mathbf{U}_i \cdot \operatorname{grad} T) + \sum_{k=1}^{N-1} \hat{D}_{ik} (\mathbf{U}_i \cdot \mathbf{R}_k),\ \hat{B}_j (\mathbf{U}_j \mathbf{U}_j : \overset{\circ}{\bar{\bar{\mathsf{E}}}}) \right] \right. \\ & \left. + C \left[\hat{B}_i (\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\bar{\bar{\mathsf{E}}}}),\ \hat{A}_j (\mathbf{U}_j \cdot \operatorname{grad} T) + \sum_{k=1}^{N-1} \hat{D}_{jk} (\mathbf{U}_j \cdot \mathbf{R}_k) \right] \right\} \end{aligned} \tag{41}$$

$$\begin{aligned}
Y_{i_{\text{even}}} = & -\frac{2}{3}(\operatorname{div}\mathbf{v})\left(T\frac{\partial \hat{B}_i}{\partial T} + \frac{3}{2}\sum_j n_j \frac{\partial \hat{B}_i}{\partial n_j} + U_i^2 \frac{\partial \hat{B}_i}{\partial U_i^2}\right)(\mathbf{U}_i{}^{\circ}\mathbf{U}_i : \mathsf{E}) \\
& + \hat{B}_i \mathbf{U}_i\mathbf{U}_i : \left(\frac{d_0}{dt}\mathring{\bar{\bar{\mathsf{E}}}} - 2\mathring{\bar{\bar{\mathsf{E}}}}\cdot\mathsf{E}\right) \\
& + \frac{\partial \hat{A}_i}{\partial T}\mathbf{U}_i\mathbf{U}_i : \operatorname{grad} T \operatorname{grad} T + \sum_{k=1}^{N-1}\frac{\partial \hat{D}_{ik}}{\partial T}\mathbf{U}_i\mathbf{U}_i : \mathbf{R}_k \operatorname{grad} T \\
& + \sum_j \frac{\partial \hat{A}_i}{\partial n_j}\frac{\rho_j}{KT}\mathbf{U}_i\mathbf{U}_i : \operatorname{grad} T(\operatorname{grad}\mu_j)_T \\
& + \sum_j \sum_{k=1}^{N-1}\frac{\partial \hat{D}_{ik}}{\partial n_j}\frac{\rho_j}{KT}\mathbf{U}_i\mathbf{U}_i : \mathbf{R}_k(\operatorname{grad}\mu_j)_T \\
& - 2\frac{\partial \hat{B}_i}{\partial U_i^2}(\mathbf{U}_i\mathbf{U}_i : \mathring{\bar{\bar{\mathsf{E}}}})(\mathbf{U}_i\mathbf{U}_i : \mathring{\bar{\bar{\mathsf{E}}}}) + \hat{A}_i\mathbf{U}_i\mathbf{U}_i : \operatorname{Grad}\operatorname{grad} T \\
& + \sum_{k=1}^{N-1}\hat{D}_{ik}\mathbf{U}_i\mathbf{U}_i : \operatorname{Grad}\mathbf{R}_k + 2\frac{\partial \hat{A}_i}{\partial U_i^2}\mathbf{U}_i\mathbf{U}_i : (\operatorname{grad} T)\mathbf{G}_i \\
& + 2\sum_{k=1}^{N-1}\frac{\partial \hat{D}_{ik}}{\partial U_i^2}\mathbf{U}_i\mathbf{U}_i : \mathbf{R}_k\mathbf{G}_i \\
& - \sum_j \left\{ C\left[\hat{A}_i(\mathbf{U}_i\cdot\operatorname{grad} T), \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T) + \sum_{k=1}^{N-1}\hat{D}_{jk}(\mathbf{U}_j\cdot\mathbf{R}_k)\right]\right. \\
& + C\left[\sum_{k=1}^{N-1}\hat{D}_{ik}(\mathbf{U}_i\cdot\mathbf{R}_k), \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T) + \sum_{l=1}^{N-1}\hat{D}_{jl}(\mathbf{U}_j\cdot\mathbf{R}_l)\right] \\
& \left. + C[\hat{B}_i(\mathbf{U}_i\mathbf{U}_i : \mathring{\bar{\bar{\mathsf{E}}}}), \hat{B}_j(\mathbf{U}_j\mathbf{U}_j : \mathring{\bar{\bar{\mathsf{E}}}})]\right\}
\end{aligned} \tag{42}$$

4. THE PHENOMENOLOGICAL EQUATIONS

The first-order phenomenological equations which relate the first-order fluxes to the forces are obtained by introducing the solutions (24) for the first-order distribution functions into the definitions of the fluxes (7)–(9):

$$\mathbf{J}_q^{*(1)} = -L_{qq}\frac{1}{T^2}\operatorname{grad} T - \sum_{k=1}^{N-1} L_{qk}\mathbf{R}_k\frac{1}{T} \tag{43}$$

where

$$\mathbf{J}_q{}^* \equiv \mathbf{J}_q - \sum_j h_j\mathbf{J}_j, \qquad \mathbf{J}_i^{(1)} = -L_{iq}\frac{1}{T^2}\operatorname{grad} T - \sum_{k=1}^{N-1} L_{ik}\mathbf{R}_k\frac{1}{T} \tag{43a}$$

$$\mathsf{\Pi}^{(1)} = -(L/T)\mathring{\bar{\bar{\mathsf{E}}}} \equiv -2\eta\mathring{\bar{\bar{\mathsf{E}}}} \tag{43b}$$

These equations are identical with those of the macroscopic theory of irreversible thermodynamics. They also agree with the Curie principle, in that the fluxes are coupled only with forces of the same tensorial order.

The phenomenological coefficients L relating the fluxes and forces in the phenomenological equations (43) are functionals of the functions A_i, D_{ik}, and B_i. They are listed in Appendix A.

Using the principle of microscopic reversibility, which can be expressed(4) in the form

$$W(\mathbf{k}_{ij}|\mathbf{k}'_{ij};\ |\mathbf{u}_{ij}|) = W(-\mathbf{k}'_{ij}|-\mathbf{k}_{ij};\ |\mathbf{u}_{ij}|) \tag{44}$$

it can be shown that, within the framework of the kinetic theory, the Onsager reciprocity relations

$$L_{qk} = L_{kq}; \qquad L_{ik} = L_{ki} \tag{45}$$

are valid between the first-order phenomenological coefficients even for nonlinear irreversible processes and for processes between states not in local equilibrium.

The second-order phenomenological equations can be obtained by introducing the solutions for the second-order distribution functions into the definitions of the fluxes. This can be done without getting an explicit solution for $\phi^{(2)}$ but only by using the right-hand side of Eq. (29) (Ref. 2, §15.3). The fluxes are given by

$$\mathbf{J}_q^{*(2)} = KT\sum_i \int A_i \mathbf{U}_i Y_i \, \mathbf{dU}_i \tag{46}$$

$$\begin{aligned} \mathbf{J}_i^{(2)} &= KT\frac{\rho}{\rho_N}\sum_{k=1}^{N-1}\int D_{ik}\mathbf{U}_i Y_i \, \mathbf{dU}_i, \qquad i = 1, 2, \ldots, N-1 \\ \mathbf{J}_i^{(2)} &= KT\frac{\rho}{\rho - \rho_N}\sum_{k=1}^{N-1}\int D_{ik}\mathbf{U}_i Y_i \, \mathbf{dU}_i, \qquad i = N \end{aligned} \tag{47}$$

$$\Pi^{(2)} = KT\sum_i \int B_i \mathbf{U}_i {}^\circ\mathbf{U}_i \, \mathbf{dU}_i \tag{48}$$

Only $N - 1$ diffusion fluxes are independent, since their sum must vanish.

Since integrals of odd functions of the components of the velocities U_i vanish, the terms of Eq. (40) do not contribute to the fluxes and to the pressure tensor, the even terms in Eq. (42) do not contribute to the fluxes, and the odd terms in Eq. (41) do not contribute to the pressure tensor. Therefore the heat and diffusion fluxes are obtained by introducing (41) into (46) and (47), and the pressure tensor by introducing (42) into (48). It can be shown also that the first term in Eq. (41) does not contribute to the heat flux; furthermore, it does not contribute to the diffusion flux in a binary mixture.[2,3] However, in the general case of a multicomponent system this term does make a contribution. It can be rearranged by making use of Eq. (43b):

$$-\frac{f_i^{(0)}m_i}{\rho KT}\mathbf{U}_i\cdot\mathrm{Div}\,\Pi^{(1)} = 2\frac{f_i^{(0)}m_i}{\rho KT}\mathbf{U}_i\cdot\left\{\left[\frac{\partial\eta}{\partial T}\,\mathrm{grad}\,T + \sum_j \frac{\partial\eta}{\partial n_j}\frac{\rho_j}{KT}(\mathrm{grad}\,\mu_j)_T\right]\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \eta\,\mathrm{Div}\,\overset{\circ}{\overline{\overline{\mathsf{E}}}}\right.$$

The phenomenological equations are given by

$$\begin{aligned}\mathbf{J}_q^{*(2)} = {} & \Theta_{v,T}(\mathrm{div}\,\mathbf{v})\,\mathrm{grad}\,T + \sum_{k=1}^{N-1}\Theta_{v,k}(\mathrm{div}\,\mathbf{v})\mathbf{R}_k \\ & + \Theta_{t,T}\left(\frac{d_0}{dt}\,\mathrm{grad}\,T - \mathsf{E}\cdot\mathrm{grad}\,T\right) \\ & + \sum_{k=1}^{N-1}\Theta_{t,k}\left(\frac{d_0}{dt}\mathbf{R}_k - \mathsf{E}\cdot\mathbf{R}_k\right) + \Theta_{T,E}\,\mathrm{grad}\,T\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \sum_{k=1}^{N-1}\Theta_{k,E}\mathbf{R}_k\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} \\ & + \sum_j \Theta_{n_j,E}(\mathrm{grad}\,\mu_j)_T\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \Theta_{E'}\,\mathrm{Div}\,\overset{\circ}{\overline{\overline{\mathsf{E}}}}\end{aligned} \tag{49}$$

$$\begin{aligned}\mathbf{J}_i^{(2)} = {} & \Delta_{iv,T}(\mathrm{div}\,\mathbf{v})\,\mathrm{grad}\,T + \sum_{k=1}^{N-1}\Delta_{iv,k}(\mathrm{div}\,\mathbf{v})\mathbf{R}_k \\ & + \Delta_{it,T}\left(\frac{d_0}{dt}\,\mathrm{grad}\,T - \mathsf{E}\cdot\mathrm{grad}\,T\right) \\ & + \sum_{k=1}^{N-1}\Delta_{it,k}\left(\frac{d_0}{dt}\mathbf{R}_k - \mathsf{E}\cdot\mathbf{R}_k\right) + \Delta_{iT,E}\,\mathrm{grad}\,T\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \sum_{k=1}^{N-1}\Delta_{ik,E}\mathbf{R}_k\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} \\ & + \sum_j \Delta_{in_j,E}(\mathrm{grad}\,\mu_j)_T\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \Delta_{iE'}\,\mathrm{Div}\,\overset{\circ}{\overline{\overline{\mathsf{E}}}}, \qquad i = 1, 2, \ldots, N\end{aligned} \tag{50}$$

$$\begin{aligned}\Pi^{(2)} = {} & \Omega_{v,E}(\mathrm{div}\,\mathbf{v})\overset{\circ}{\overline{\overline{\mathsf{E}}}} + \Omega_{t,E}\left(\frac{d_0}{dt}\overset{\circ}{\overline{\overline{\mathsf{E}}}} - 2\overset{\circ}{\overline{\overline{\mathsf{E}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}}}}\right) \\ & + \Omega_{T,T}\,\overset{\circ}{\overline{\overline{\mathrm{grad}\,T\,\mathrm{grad}\,T}}} \\ & + \sum_{k=1}^{N-1}\Omega_{k,T}\overset{\circ}{\overline{\overline{\mathbf{R}_k\,\mathrm{grad}\,T}}} + \sum_j \Omega_{T,n_j}\,\overset{\circ}{\overline{\overline{\mathrm{grad}\,T(\mathrm{grad}\,\mu_j)_T}}} \\ & + \sum_{k=1}^{N-1}\sum_{l=1}^{N-1}\Omega_{k,l}\overset{\circ}{\overline{\overline{\mathbf{R}_k\mathbf{R}_l}}} + \sum_j\sum_{k=1}^{N-1}\Omega_{k,n_j}\overset{\circ}{\overline{\overline{\mathbf{R}_k(\mathrm{grad}\,\mu_j)_T}}} \\ & + \Omega_{E,E}\overset{\circ}{\overline{\overline{\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}}}} + \Omega_{T'}\,\overset{\circ}{\overline{\overline{\mathrm{Grad}\,\mathrm{grad}\,T}}} + \sum_{k=1}^{N-1}\overset{\circ}{\overline{\overline{\mathrm{grad}\,\mathbf{R}_k}}}\Omega_k\end{aligned} \tag{51}$$

All the phenomenological coefficients appearing in Eqs. (49)–(51) depend on the local properties (temperature and composition) and are expressed by functionals of the functions $\hat{A}_i$, $\hat{D}_{ik}$, and $\hat{B}_i$. They are listed in Appendix A.

Let us examine the significance of the various terms appearing in the second-order phenomenological equations (49)–(51). The vectorial fluxes of heat and diffusion depend on all second-order vectorial combinations of the forces (binary products and differentials), with scalar coefficients. The symmetric and traceless second-order pressure tensor depends similarly on the forces. Thus the Curie principle is obviously valid. It should be noticed that additional independent forces appear in the second-order equations, namely the gradients of the chemical potentials. These forces do not appear independently in the first-order equations. Moreover, all the elements of the velocity gradient tensor affect the second-order equations, including the trace div $\mathbf{v}$ and the antisymmetric part, while only the symmetric traceless part $\overset{\circ}{\overline{\overline{\mathsf{E}}}}$ appears in the first-order equations.

The second-order phenomenological equations (49)–(51) demonstrate coupling effects between phenomena which are not coupled through the first order relations: The velocity gradient tensor affects the heat and diffusion fluxes and the pressure tensor depends on the gradients of the temperature and the chemical potentials.

Phenomenological relations between some of the second-order coefficients exist, as can be shown by Eqs. (A.13) and (A.33); and (A.24) and (A.34):

$$\Theta_{E'} = T\Omega_{T'} \tag{52}$$

$$\sum_{k=1}^{N-1} \Omega_{k'} = -\Delta_{NE'} \tag{53}$$

Since the Nth component can be chosen arbitrarily, the relation (53) is applicable to all the coefficients $\Delta_{iE'}$.

As an estimate of the values of the phenomenological coefficients, the results for a simple Maxwellian gas are shown. The calculations of the coefficients for this case become simpler since the contribution of the collision integrals C vanishes. The phenomenological equations for a single Maxwellian gas were obtained by Chapman and Cowling(2)

$$\begin{aligned}
\mathbf{J}_q^{*(2)} = {} & \frac{\eta^2}{\rho T}\frac{15}{4}\left(\frac{7}{2} - \frac{T}{\eta}\frac{d\eta}{dT}\right)(\operatorname{div}\mathbf{v}) \operatorname{grad} T \\
& + \frac{45}{8}\frac{\eta^2}{\rho T}\left(\frac{d_0}{dt}\operatorname{grad} T - \mathsf{E}\cdot\operatorname{grad} T\right) \\
& - 3\frac{\eta^2}{\rho p}\operatorname{grad} p\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}} + 3\frac{\eta^2}{\rho}\operatorname{Div}\overset{\circ}{\overline{\overline{\mathsf{E}}}} + 3\left(\frac{35}{4} + \frac{T}{\eta}\frac{d\eta}{dT}\right)\operatorname{grad} T\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}
\end{aligned} \tag{54}$$

$$\Pi^{(2)} = \frac{4}{3}\left(\frac{7}{2} - \frac{T}{\eta}\frac{d\eta}{dT}\right)\frac{\eta^2}{p}(\operatorname{div}\mathbf{v})\overset{\circ}{\overline{\overline{\mathsf{E}}}} + 2\frac{\eta^2}{p}\left(\frac{d_0}{dt}\overset{\circ}{\overline{\overline{\mathsf{E}}}} - 2\overset{\circ}{\overline{\overline{\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}}}}\right)$$

$$+ 3\frac{\eta^2}{\rho T}\overset{\circ}{\overline{\overline{\text{Grad grad } T}}} + \frac{\eta^2}{\rho T^2}\frac{3T}{\eta}\frac{d\eta}{dT}\overset{\circ}{\overline{\overline{\text{grad } T \text{ grad } T}}} + 8\frac{\eta^2}{p}\overset{\circ}{\overline{\overline{\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}}}} \quad (55)$$

where the force $(\text{grad } \mu)_T$ was replaced by $(1/\rho)$ grad p according to the Gibbs–Duhem equations. It is clearly seen that the phenomenological relation (52) is satisfied.

5. THE ENTROPY, ENTROPY FLUX, AND ENTROPY SOURCE

The entropy can be expanded into series by order of magnitude

$$\rho s = \rho s^{(0)} + \rho s^{(1)} + \rho s^{(2)} + \cdots \quad (56)$$

The values of each order of magnitude can be computed by Eqs. (15) and (19). Thus, $\rho s^{(0)}$, which is local-equilibrium entropy, is given by

$$\rho s^{(0)} = -K\sum_i \int f_i^{(0)}(\ln f_i^{(0)} - 1)\,\mathbf{du}_i \quad (57)$$

Obviously, $\rho s^{(0)}$ depends on the properties alone (and not on their gradients). Hence its character agrees with the classical entropy, e.g., it satisfies the Gibbs equation. The first-order entropy vanishes:

$$\rho s^{(1)} = -K\sum_i \int f_i^{(0)}\phi_i^{(1)} \ln f_i^{(0)}\,\mathbf{du}_i = 0 \quad (58)$$

The deviation from local equilibrium is expressed by the second-order entropy density:

$$\rho s^{(2)} = -\tfrac{1}{2}K\sum_i \int f_i^{(0)}[\phi_i^{(1)}]^2\,\mathbf{du}_i \leqslant 0 \quad (59)$$

which satisfies the condition that the entropy is maximum in equilibrium. The deviation from the state of equilibrium is clearly characterized by the gradients of the properties (temperature, composition, and barycentric velocity).

The first- and second-order entropy fluxes are obtained by introducing the series from (19) into the definition of $\mathbf{J}_s$, (16). It can be shown that $\mathbf{J}_s^{(1)}$ and $\mathbf{J}_s^{(2)}$ are given by

$$\mathbf{J}_s^{(1)} = (1/T)\left(\mathbf{J}_q^{(1)} - \sum_j \mu_j \mathbf{J}_j^{(1)}\right) \quad (60)$$

$$\mathbf{J}_s^{(2)} = (1/T)\left(\mathbf{J}_q^{(2)} - \sum_j \mu_j \mathbf{J}_j^{(2)}\right) - \tfrac{1}{2}K\sum_i \int \mathrm{U}_i f_i^{(0)}[\phi_i^{(1)}]^2\,\mathbf{dU}_i \quad (61)$$

The rate of entropy production can be evaluated by expanding $\ln f_i$ and the collision integrals in series:

$$C(f_i,f_j) = C^{(0)}(f_i,f_j) + C^{(1)}(f_i,f_j) + C^{(2)}(f_i,f_j) \tag{62}$$

where

$$C^{(r)}(f_i,f_j) = \sum_{r'} C(f_i^{(r')},f_j^{(r-r')}) \tag{63}$$

The following expressions are obtained for the entropy source ($\sigma^{(0)}$ vanishes, as mentioned above):

$$\sigma^{(1)} = -K\sum_i\sum_j\int \phi_i^{(1)}C^{(1)}(f_i,f_j)\,\mathbf{dU}_i \tag{64}$$

$$\begin{aligned}\sigma^{(2)} &= -K\sum_i\sum_j\int \phi_i^{(2)}C^{(1)}(f_i,f_j)\,\mathbf{dU}_i \\ &\quad + \tfrac{1}{2}K\sum_i\sum_j\int [\phi_i^{(1)}]^2C^{(1)}(f_i,f_j)\,\mathbf{dU}_i \\ &\quad - K\sum_i\sum_j\int \phi_i^{(1)}C^{(2)}(f_i,f_j)\,\mathbf{dU}_i \equiv \sigma_A^{(2)} + \sigma_B^{(2)} + \sigma_C^{(2)}\end{aligned} \tag{65}$$

When we introduce $C^{(1)}(f_i,f_j)$ from the Boltzmann equation into (64), the first-order entropy source becomes

$$\sigma^{(1)} = -\frac{1}{T^2}\,\mathbf{J}_q^{*(2)}\cdot\text{grad}\,T - \frac{1}{T}\sum_{i=1}^{N-1}\mathbf{J}_i^{(1)}\cdot\mathbf{R}_i - \frac{1}{T}\Pi^{(1)}:\mathsf{E} \tag{66}$$

Equations (58), (60), and (66) describe the first-order deviation from equilibrium, and can be applied to local equilibrium states. These results are equivalent to those of the linear macroscopic theory of irreversible thermodynamics.

The expression for $\rho s^{(2)}$ is obtained by introducing the solution (24) for $\phi_i^{(1)}$ into (59):

$$\begin{aligned}\rho s^{(2)} &= -c_T(\text{grad}\,T)^2 - \sum_{k=1}^{N-1} c_{Tk}\mathbf{R}_k\cdot\text{grad}\,T \\ &\quad - \sum_{j,k=1}^{N-1} c_{jk}\mathbf{R}_j\cdot\mathbf{R}_k - c_E\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}\end{aligned} \tag{67}$$

where the coefficients c depend on the temperature and composition and are listed in Appendix B. The condition $\rho s^{(2)} \leqslant 0$ imposes some relations among the coefficients c. These relations are given in a more convenient form if the following notations are used:

$$\mathbf{X}_j \equiv \mathbf{R}_j, \quad j = 1, 2, \ldots, N-1; \qquad \mathbf{X}_N = \operatorname{grad} T \tag{68}$$

Thus Eq. (67) reduces to

$$\rho s^{(2)} = -\sum_{i,j} c_{ij}^{*} \mathbf{X}_i \cdot \mathbf{X}_j - c_E \overset{\circ}{\bar{\bar{\mathsf{E}}}} \cdot \overset{\circ}{\bar{\bar{\mathsf{E}}}} \leqslant 0 \tag{69}$$

where

$$\begin{gathered} c_{ij}^{*} \equiv c_{ij}, \qquad i,j = 1, 2, \ldots, N-1 \\ c_{iN}^{*} = c_{Ni}^{*} \equiv \tfrac{1}{2} c_{Ti} \qquad c_{NN}^{*} \equiv c_T \end{gathered} \tag{70}$$

and the coefficients c must satisfy the conditions $c_E \geqslant 0$ and the matrix c_{ij}^{*} is positive definite. These conditions are, indeed, satisfied [as can be seen from eqs. (B.1)–(B.4) of Appendix B] because $[\phi_i^{(1)}]^2 \geqslant 0$,

All the coefficients c appearing in Eq. (67) are related to some of the phenomenological coefficients, as can be shown from the appropriate expressions in Appendices A and B:

$$\begin{gathered} T^2 c_T = \tfrac{1}{2} \Theta_{t,T}, \qquad T \sum_{k=1}^{N-1} c_{Tk} = \Delta_{Nt,T} \\ T \sum_{k=1}^{N-1} c_{jk} = \Delta_{Nt,j}, \qquad T_{c_E} = \tfrac{1}{2} \Omega_{t,E} \end{gathered} \tag{71}$$

As mentioned above, the Nth component is chosen arbitrarily. Thus, the second and third relations in (71) are applicable to all the coefficients $\Delta_{it,T}$ and $\Delta_{it,j}$.

The values of c_T and c_E for a simple Maxwellian gas are obtained by performing the integrations in Eqs. (B.1) and (B.4):

$$c_T = (45/16)\eta^2/\rho T^3; \qquad c_E = \eta^2/\rho T \tag{72}$$

The second-order entropy flux is obtained by using Eqs. (24) and (61).

$$\mathbf{J}_s^{(2)} = (1/T)\left(\mathbf{J}_q^{(2)} - \sum_j \mu_j \mathbf{J}_j^{(2)}\right) - \left(\Gamma_T \operatorname{grad} T \cdot \overset{\circ}{\bar{\bar{\mathsf{E}}}} + \sum_{k=1}^{N-1} \Gamma_k \mathbf{R}_k \cdot \overset{\circ}{\bar{\bar{\mathsf{E}}}}\right) \tag{73}$$

where the coefficients Γ_T and Γ_k are functions of the properties and are given in Eqs. (B.5) and (B.6). Comparing these expressions with some of those of Appendix A, we establish the following relations

$$\Gamma_T = -(1/T^2)\Omega_{T'} = -(1/T^3)\Theta_{E'}, \qquad \Gamma_k = -(1/T)\Omega_{k'} \tag{74}$$

and the value of Γ_T for a simple Maxwellian gas is found to be

$$\Gamma_T = 3\eta^2/pT^3 \tag{75}$$

It can be seen from Eq. (73) that the deviation of the second-order entropy flux from its value for processes between states of local equilibrium depends on the thermodynamic forces. It is interesting that whenever the barycentric velocity is uniform, the second-order entropy flux reduces to the local equilibrium value even for local nonequilibrium states.

Finally, the second-order entropy source is examined by evaluating the three integrals $\sigma_A^{(2)}$, $\sigma_B^{(2)}$, and $\sigma_C^{(2)}$ on the right-hand side of Eq. (65). The first integral is evaluated by a procedure similar to that used in deriving the expression (66) for $\sigma^{(1)}$. The result is also similar to (66):

$$\sigma_A^{(2)} = -\frac{1}{T^2}\,\mathbf{J}_q^{*(2)}\cdot\operatorname{grad} T - \frac{1}{T}\sum_{k=1}^{N-1}\mathbf{J}_k^{(2)}\cdot\mathbf{R}_k - \frac{1}{T}\Pi^{(2)} : \mathsf{E} \tag{76}$$

Since the second-order fluxes can be expressed by second-order combinations of the forces, the rate of entropy production can be described by third-order combinations of the forces. It will be demonstrated below that the other two integrals appearing in the expression for $\sigma^{(2)}$ contribute terms of the same character. The second integral in Eq. (65) is treated in a similar manner, i.e., by introducing $C^{(1)}(f_i, f_j)$ from the Boltzmann equation. The result is given by

$$\begin{aligned}\sigma_B^{(2)} &= \lambda_T(\operatorname{grad} T)(\operatorname{grad} T) : \overset{\circ}{\overline{\overline{\mathsf{E}}}} + \sum_{k=1}^{N-1}\lambda_{Tk}(\operatorname{grad} T)\mathbf{R}_k : \overset{\circ}{\overline{\overline{\mathsf{E}}}}\\ &\quad + \sum_{j,k=1}^{N-1}\lambda_{jk}\mathbf{R}_j\mathbf{R}_k : \overset{\circ}{\overline{\overline{\mathsf{E}}}} + \lambda_E\overset{\circ}{\overline{\overline{\mathsf{E}}}} : \overset{\circ}{\overline{\overline{(\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}})}}}\end{aligned} \tag{77}$$

where the coefficients λ are listed in Appendix B. The values of λ_T and λ_E for a simple Maxwellian gas are found to be

$$\lambda_T = (189/16)\eta^2/pT^3; \qquad \lambda_E = 4\eta^2/pT \tag{78}$$

The second-order collision integral is written explicitly from Eq. (63) as follows:

$$C^{(2)}(f_i, f_j) = C(f_i^{(2)}, f_j^{(0)}) + C(f_i^{(0)}, f_j^{(2)}) + C(f_i^{(1)}, f_j^{(1)}) \tag{79}$$

and is used to evaluate $\sigma_C^{(2)}$. The first two terms of the right-hand side of Eq. (79) contribute to $\sigma_C^{(2)}$ an expression identical to $\sigma_A^{(2)}$. The complete expression for $\sigma_C^{(2)}$ becomes, making use of Eq. (24),

$$
\begin{aligned}
\sigma_C^{(2)} = {} & \bigg\{ -\frac{1}{T^2}\,\mathbf{J}_q^{*(2)}\cdot\operatorname{grad} T - \frac{1}{T}\sum_{k=1}^{N-1} \mathbf{J}_k^{(2)}\cdot\mathbf{R}_k - \frac{1}{T}\,\Pi^{(2)} : \mathsf{E} \bigg\} \\
& + K \sum_{i,j} \int \bigg[\frac{A_i}{T} (\mathbf{U}_i\cdot\operatorname{grad} T) \\
& + \sum_{k=1}^{N-1} D_{ik}(\mathbf{U}_i\cdot\mathbf{R}_k)] \bigg] \bigg\{ C \bigg[\hat{A}_i(\mathbf{U}_i\cdot\operatorname{grad} T) \\
& + \sum_{l=1}^{N-1} \hat{D}_{il}(\mathbf{U}_i\cdot\mathbf{R}_l),\ \hat{B}_j(\mathbf{U}_j{}^\circ\mathbf{U}_j : \mathsf{E}) \bigg] \\
& + C \bigg[\hat{B}_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}),\ \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T) \\
& + \sum_{k=1}^{N-1} \hat{D}_{jk}(\mathbf{U}_j\cdot\mathbf{R}_k) \bigg] \bigg\} \, \mathbf{dU}_i \\
& + K \sum_{i,j} \int B_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}) C \bigg[\hat{A}_i(\mathbf{U}_i\cdot\operatorname{grad} T) \\
& + \sum_{k=1}^{N-1} \hat{D}_{ik}(\mathbf{U}_i\cdot\mathbf{R}_k),\ \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T) \\
& + \sum_{l=1}^{N-1} \hat{D}_{jl}(\mathbf{U}_j\cdot\mathbf{R}_l) \bigg] \, \mathbf{dU}_i \\
& + K \sum_{i,j} \int B_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}) C [\hat{B}_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}),\ \hat{B}_j(\mathbf{U}_j{}^\circ\mathbf{U}_j : \mathsf{E})] \, \mathbf{dU}_i
\end{aligned}
\tag{80}
$$

The second-order entropy production $\sigma^{(2)}$ becomes

$$
\begin{aligned}
\sigma^{(2)} & = \sigma_A^{(2)} + \sigma_B^{(2)} + \sigma_C^{(2)} \\
& = -2\bigg(\frac{1}{T^2}\,\mathbf{J}_q^{*(2)}\cdot\operatorname{grad} T + \frac{1}{T}\sum_{k=1}^{N-1} \mathbf{J}_k^{(2)}\cdot\mathbf{R}_k + \frac{1}{T}\,\Pi^{(2)} : \mathsf{E} \bigg) \\
& \quad + \Lambda_T \operatorname{grad} T \operatorname{grad} T : \overset{\circ}{\overline{\overline{\mathsf{E}}}} + \sum_{k=1}^{N-1} \Lambda_{Tk}(\operatorname{grad} T)\mathbf{R}_k : \overset{\circ}{\overline{\overline{\mathsf{E}}}} \\
& \quad + \sum_{j,k=1}^{N-1} \Lambda_{jk}\mathbf{R}_j\mathbf{R}_k : \overset{\circ}{\overline{\overline{\mathsf{E}}}} + \Lambda_E \overset{\circ}{\overline{\overline{\mathsf{E}}}} : (\overset{\circ}{\overline{\overline{\overset{\circ}{\overline{\overline{\mathsf{E}}}}\cdot\overset{\circ}{\overline{\overline{\mathsf{E}}}}}}})
\end{aligned}
\tag{81}
$$

where the coefficients Λ are listed in Appendix B. For a simple Maxwellian gas all contributions of the collision integrals vanish and the coefficients Λ_T and Λ_E reduce to λ_T and λ_E:

$$\Lambda_T = \lambda_T; \qquad \Lambda_E = \lambda_E \tag{82}$$

and their values are given by (78).

It should be noticed that $\sigma^{(2)}$ contains, in addition to the sum of flux-force products, a function of the forces which tends to zero as the system approaches local equilibrium.

The differential of $\sigma^{(2)}$ with respect to a coupled force yields an expression having the same force combination as that of the appropriate flux with different values of the coefficients. For example, the terms appearing in Eq. (49) for $\mathbf{J}_q^{*(2)}$ are obtained by differentiating $\sigma^{(2)}$ with respect to grad T. Even though the results obtained here are only qualitative, they suggest a way to predict the second-order effects occurring in nonlinear processes which are far enough from equilibrium.

6. DISCUSSION

One of the assumptions underlying most theories of nonequilibrium thermodynamics for irreversible processes(4) is that of local equilibrium. Since local equilibrium can be assumed only for processes in systems which are not too far from equilibrium, these processes can be described by linear phenomenological equations relating the thermodynamic fluxes and forces. Onsager reciprocity relations which exist between the coefficients of these equations are useful in calculating coefficients for the transport equations in cases where direct measurements are difficult.(5)

As mentioned above, the results of the first-order approximation of kinetic theory are compatible with the linear theory of irreversible thermodynamics. The first-order fluxes ($\mathbf{J}_q^{*(1)}$, $\mathbf{J}_i^{(1)}$ and $\overline{\Pi}^{(1)}$) are linear functions of the forces (grad T, $\mathbf{R}_k$ and Grad $\mathbf{v}$) and local equilibrium can be assumed. This approximation is valid (Ref. 2, Chapter 15) for small values of $l/L_{1,2}$, where l is the mean free path and L_1 and L_2 are scale lengths such that the gradients of the temperature and the scale mass velocity are T/L_1 and V/L_2 respectively.

For larger values of $l/L_{1,2}$ the first-order approximation fails to represent the processes, and further orders must be taken into account. Such cases may be encountered in systems with very low densities, when l becomes large, or in shock waves, where $L_{1,2}$ become small. In these systems, the assumption of local equilibrium is no longer valid. In fact, it was shown here that some relations between properties are not compatible with equilibrium thermodynamics. For example, the entropy now also depends on the temperature gradient [see Eqs. (24) and (59)].

In the present work, the second-order constitutive equations relating second-order fluxes to second-order forces were derived for multicomponents systems. Several relations between the transport coefficients in these equations were developed. Specifically, the relations between the second-order entropy, the entropy source, the entropy flux, and the thermodynamic fluxes and forces were established.

It should be also noted(2) that when the ratios $l/L_{1,2}$ approach unity, first- and second-order approximations may not be sufficient to describe the process, and additional orders may be required. Thus the range of utility of second-order along with first-order terms is limited to intermediate values of $l/L_{1,2}$: $0 \ll l/L_{1,2} \ll 1$. At the lower limit, first-order terms are sufficient, while at the higher limit, higher-order terms may be required.

APPENDIX A. PHENOMENOLOGICAL COEFFICIENTS

The first-order phenomenological coefficients L appearing in Eqs. (43) and (43a, b) are obtained by introducing the solution for $\phi_i^{(1)}$ into the definitions of the fluxes. Since the range of the integrals is over all possible values of the velocities between $-\infty$ and $+\infty$, integrals of odd functions of the velocities vanish. It is noted that A_i, D_{ik}, and B_i are even functions of the velocities because they depend on their absolute values. Use is also made of the integral theorems proved by Chapman and Cowling.(2)

The coefficients L_{qq} and L_{qk} appearing in Eq. (43) are obtained by introducing (24) into (7) and (8) and also using (14):

$$L_{qq} = \tfrac{1}{3}KT^2 \sum_i \int f_i^{(0)} A_i[(m_i U_i^2/2KT) - \tfrac{5}{2}]U_i^2\, \mathbf{dU}_i \tag{A.1}$$

$$L_{qk} = \tfrac{1}{3}KT \sum_i \int f_i^{(0)} D_{ik}[(m_i U_i^2/2KT) - \tfrac{5}{2}]U_i^2\, \mathbf{dU}_i \tag{A.2}$$

The coefficients L_{iq} and L_{ik} appearing in Eq. (43a) are similarly derived from Eqs. (24) and (7):

$$L_{iq} = \tfrac{1}{3}m_i T \int f_i^{(0)} A_i U_i^2\, \mathbf{dU}_i \tag{A.3}$$

$$L_{ik} = \tfrac{1}{3}m_i T \int f_i^{(0)} D_{ik} U_i^2\, \mathbf{dU}_i \tag{A.4}$$

Finally, the coefficient η is obtained from Eqs. (9) and (24):

$$\eta = (1/15) \sum_i m_i \int f_i^{(0)} B_i U_i^4\, \mathbf{dU}_i \tag{A.5}$$

The second-order phenomenological equations are derived by introducing the right-hand side of Eq. (29) into Eqs. (46)–(48). The second-order phenomenological coefficients appearing in the resulting phenomenological equations (49)–(51) are obtained in a manner similar to that used to determine the first-order coefficients.

The second-order heat flux $\mathbf{J}_q^{*(2)}$ is derived by introducing (40) into (46). The first term in Eq. (41) does not contribute to the heat flux; the other terms lead to the phenomenological coefficients appearing in Eq. (49). The following expressions are obtained for the phenomenological coefficients Θ:

$$\Theta_{v,T} = \frac{2}{9} KT \sum_i \int A_i \left(T \frac{\partial \hat{A}_i}{\partial T} + \frac{3}{2} \sum_j n_j \frac{\partial \hat{A}_i}{\partial n_j} + U_i^2 \frac{\partial \hat{A}_i}{\partial U_i^2} \right) U_i^2 \, \mathbf{dU}_i \tag{A.6}$$

$$\Theta_{v,k} = \frac{2}{9} KT \sum_i \int A_i \left(T \frac{\partial \hat{D}_{ik}}{\partial T} + \frac{3}{2} \sum_j n_j \frac{\partial \hat{D}_{ik}}{\partial n_j} + U_i^2 \frac{\partial \hat{D}_{ik}}{\partial U_i^2} \right) U_i^2 \, \mathbf{dU}_i \tag{A.7}$$

$$\Theta_{t,T} = -\frac{1}{3} KT \sum_i \int A_i \hat{A}_i U_i^2 \, \mathbf{dU}_i \tag{A.8}$$

$$\Theta_{t,k} = -\frac{1}{3} KT \sum_i \int A_i \hat{D}_{ik} U_i^2 \, \mathbf{dU}_i \tag{A.9}$$

$$\begin{aligned}\Theta_{T,E} = {} & -\frac{2}{15} KT \sum_i \int A_i \left(\frac{\partial \hat{B}_i}{\partial T} - 2 \frac{\partial \hat{A}_i}{\partial U_i^2} \right) U_i^4 \, \mathbf{dU}_i \\ & + KT \sum_i \overset{\sim}{\int} A_i \mathbf{U}_i \sum_j \{ C[\hat{A}_i(\mathbf{U}_i \cdot \mathrm{grad}\, T), \hat{B}_j(\mathbf{U}_j \mathbf{U}_j : \overset{\circ}{\overline{\overline{\mathrm{E}}}})] \\ & + C[\hat{B}_i(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\overline{\overline{\mathrm{E}}}}), \hat{A}_j(\mathbf{U}_j \cdot \mathrm{grad}\, T)] \} \, \mathbf{dU}_i \end{aligned} \tag{A.10}$$

$$\begin{aligned}\Theta_{k,E} = {} & -\frac{2}{3} KT \sum_i \int A_i \left[\left(\delta_{ik} - \frac{\rho_k}{\rho} \right) \left(\hat{B}_i + \frac{2}{5} U_i^2 \frac{\partial \hat{B}_i}{\partial U_i^2} \right) \right. \\ & \left. - \frac{2}{5} U_i^2 \frac{\partial \hat{D}_{ik}}{\partial U_i^2} \right] U_i^2 \, \mathbf{dU}_i \\ & + KT \sum_i \overset{\sim}{\int} A_i \mathbf{U}_i \sum_j \{ C[\hat{D}_{ik}(\mathbf{U}_i \cdot \mathbf{R}_k), \hat{B}_j(\mathbf{U}_j \mathbf{U}_j : \overset{\circ}{\overline{\overline{\mathrm{E}}}})] \\ & + C[\hat{B}_i(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\overline{\overline{\mathrm{E}}}}), \hat{D}_{jk}(\mathbf{U}_j \cdot \mathbf{R}_k)] \} \, \mathbf{dU}_i \end{aligned} \tag{A.11}$$

$$\Theta_{n_j,E} = -\frac{2}{3} KT \sum_i \int A_i \left[\delta_{ij} \left(\hat{B}_i + \frac{2}{5} U_i^2 \frac{\partial \hat{B}_i}{\partial U_i^2} \right) + \frac{1}{5} \frac{\rho_j}{KT} U_i^2 \frac{\partial \hat{B}_i}{\partial n_j} \right] U_i^2 \, \mathbf{dU}_i \tag{A.12}$$

$$\Theta_{E'} = -\frac{2}{15} KT \sum_i \int A_i \hat{B}_i U_i^4 \, \mathbf{dU}_i \tag{A.13}$$

where the tilde above the integral denotes the coefficient of the appropriate force combination appearing in the respective integral.

The phenomenological coefficients appearing in Eq. (50) for the diffusion fluxes are established in a similar way, by introducing (41) into (47). It is noted that the first term in Eq. (41) does have a contribution.

$$\Delta_{iv,T} = \frac{2}{9}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\left(T\,\frac{\partial\hat{A}_i}{\partial T} + \frac{3}{2}\sum_j n_j\,\frac{\partial\hat{A}_i}{\partial n_j} + U_i^2\,\frac{\partial\hat{A}_i}{\partial U_i^2}\right)U_i^2\,\mathbf{dU}_i \tag{A.14}$$

$$\Delta_{iv,k} = \frac{2}{9}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\left(T\,\frac{\partial\hat{D}_{ik}}{\partial T} + \frac{3}{2}\sum_j n_j\,\frac{\partial\hat{D}_{ik}}{\partial n_j} + U_i^2\,\frac{\partial\hat{D}_{ik}}{\partial U_i^2}\right)U_i^2\,\mathbf{dU}_i \tag{A.15}$$

$$\Delta_{it,T} = -\tfrac{1}{3}KT(\rho/\rho_N)\sum_{m=1}^{N-1}\int D_{im}\hat{A}_iU_i^2\,\mathbf{dU}_i \tag{A.16}$$

$$\Delta_{it,k} = -\tfrac{1}{3}KT(\rho/\rho_N)\sum_{m=1}^{N-1}\int D_{im}\hat{D}_{ik}U_i^2\,\mathbf{dU}_i = \Delta_{kt,i} \tag{A.17}$$

$$\begin{aligned}\Delta_{iT,E} = {} & \frac{2}{3}\,\frac{m_i}{\rho_N}\,\frac{\partial\eta}{\partial T}\sum_{m=1}^{N-1}\int D_{im}f_i^{(0)}U_i^2\,\mathbf{dU}_i \\ & - \frac{2}{15}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\overset{\sim}{\int} D_{im}\left(\frac{\partial\hat{B}_i}{\partial T} - 2\,\frac{\partial\hat{A}_i}{\partial U_i^2}\right)U_i^4\,\mathbf{dU}_i \\ & + KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\mathbf{U}_i\sum_j\{C[\hat{A}_i(\mathbf{U}_i\cdot\text{grad }T),\ \hat{B}_j(\mathbf{U}_j\mathbf{U}_j : \overset{\circ}{\overline{\overline{\mathsf{E}}}})\\ & + C[\hat{B}_i(\mathbf{U}_i\mathbf{U}_i : \overset{\circ}{\overline{\overline{\mathsf{E}}}}),\ \hat{A}_j(\mathbf{U}_j\cdot\text{grad }T)]\}\,\mathbf{dU}_i\end{aligned} \tag{A.18}$$

$$\begin{aligned}\Delta_{ik,E} = {} & -\frac{2}{3}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\left[\left(\delta_{ik} - \frac{\rho_k}{\rho}\right)\left(\hat{B}_i + \frac{2}{5}\,U_i^2\,\frac{\partial B_i}{\partial U_i^2}\right)\right. \\ & \left. - \frac{2}{5}\,U_i^2\,\frac{\partial\hat{D}_{ik}}{\partial U_i^2}\right]U_i^2\,\mathbf{dU}_i \\ & + KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\overset{\sim}{\int} D_{im}\mathbf{U}_i\sum_j\{C[\hat{D}_{ik}(\mathbf{U}_i\cdot\mathbf{R}_k),\ \hat{B}_j(\mathbf{U}_j\mathbf{U}_j : \overset{\circ}{\overline{\overline{\mathsf{E}}}}) \\ & + C[\hat{B}_i(\mathbf{U}_i\mathbf{U}_i : \overset{\circ}{\overline{\overline{\mathsf{E}}}}),\ \hat{D}_{jk}(\mathbf{U}_j\cdot\mathbf{R}_k)]\}\,\mathbf{dU}_i\end{aligned} \tag{A.19}$$

$$\begin{aligned}\Delta_{in_j,E} = {} & -\frac{2}{3}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\left[\frac{m_if_i^{(0)}}{\rho(KT)^2}\,\frac{\partial\eta}{\partial n_j}\right. \\ & \left. + \delta_{ij}\left(\hat{B}_i + \frac{2}{5}\,U_i^2\,\frac{\partial\hat{B}_i}{\partial U_i^2}\right) + \frac{1}{5}\,\frac{\rho_j}{KT}\,U_i^2\,\frac{\partial\hat{B}_i}{\partial n_j}\right]U_i^2\,\mathbf{dU}_i\end{aligned} \tag{A.20}$$

$$\Delta_{iE'} = -\frac{2}{3}\,KT\,\frac{\rho}{\rho_N}\sum_{m=1}^{N-1}\int D_{im}\left(\frac{m_if_i^{(0)}}{\rho KT}\,\eta + \frac{1}{5}\,\hat{B}_iU_i^2\right)U_i^2\,\mathbf{dU}_i \tag{A.21}$$

Equations (A.14)–(A.21) are for $i = 1, 2, \ldots, N - 1$; the coefficients for the Nth flux ($i = N$) are obtained by replacing ρ/ρ_N by $-\rho/(\rho - \rho_N)$ [see Eq. (47)]. Since the sum of all the fluxes vanishes, $\sum_j \mathbf{J}_j = 0$, the sum over i of every kind of coefficient Δ vanishes, too, e.g., $\sum_i \Delta_{iv,T} = 0$. This condition leads to the following relation:

$$\frac{\rho_N}{\rho}\left(\sum_{m=1}^{N-1} \Delta_{i[]} - \frac{\rho}{\rho_N}\frac{\rho - \rho_N}{\rho}\Delta_{N[]}\right) = -\Delta_{N[]} \tag{A.22}$$

Performing the operation indicated in Eq. (A.22) on Eqs. (A.16) and (A.21) for $\Delta_{it,T}$ and $\Delta_{iE'}$, the coefficients $\Delta_{Nt,T}$ and $\Delta_{NE'}$ are found to be

$$\Delta_{Nt,T} = \tfrac{1}{3}KT\sum_i \sum_{m=1}^{N-1} \int D_{im}\hat{A}_i U_i^2 \, \mathbf{dU}_i \tag{A.23}$$

$$\Delta_{NE'} = (2/15)KT\sum_i \sum_{m=1}^{N-1} \int D_{im}\hat{B}_i U_i^4 \, \mathbf{dU}_i \tag{A.24}$$

Finally, the phenomenological coefficients appearing in Eq. (51) for the second-order pressure tensor are obtained by introducing (42) into Eq. (48):

$$\Omega_{v,E} = \frac{4}{45}KT\sum_i \int B_i\left(T\frac{\partial \hat{B}_i}{\partial T} + \frac{3}{2}\sum_j n_j \frac{\partial \hat{B}_i}{\partial n_j} + U_i^2 \frac{\partial \hat{B}_i}{\partial U_i^2}\right) U_i^4 \, \mathbf{dU}_i \tag{A.25}$$

$$\Omega_{t,E} = -(2/15)KT\sum_i \int B_i\hat{B}_i U_i^4 \, \mathbf{dU}_i \tag{A.26}$$

$$\begin{aligned}\Omega_{T,T} = {} & -(2/15)KT\sum_i \int B_i(\partial\hat{A}_i/\partial T)U_i^4 \, \mathbf{dU}_i \\ & + KT\sum_i \tilde{\int} B_i \mathbf{U}_i{}^\circ\mathbf{U}_i C[\hat{A}_i(\mathbf{U}_i\cdot\operatorname{grad} T), \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T)] \, \mathbf{dU}_i\end{aligned} \tag{A.27}$$

$$\begin{aligned}\Omega_{k,T} = {} & -\frac{2}{15}KT\sum_i \int B_i\left[\frac{\partial\hat{D}_{ik}}{\partial T} + \left(\delta_{ik} - \frac{\rho_k}{\rho}\right)\frac{\partial \hat{A}_i}{\partial U_i^2}\right]U_i^4 \, \mathbf{dU}_i \\ & + KT\tilde{\sum_i} \int B_i \mathbf{U}_i{}^\circ\mathbf{U}_i \sum_j \{C[\hat{A}_i(\mathbf{U}_i\cdot\operatorname{grad} T), \hat{D}_{jk}(\mathbf{U}_j\cdot\mathbf{R}_k)] \\ & + C[\hat{D}_{ik}(\mathbf{U}_i\cdot\mathbf{R}_k), \hat{A}_j(\mathbf{U}_j\cdot\operatorname{grad} T)]\} \, \mathbf{dU}_i\end{aligned} \tag{A.28}$$

$$\Omega_{T,n_j} = -\frac{2}{15}KT\sum_i \int B_i\left(\frac{\rho_j}{KT}\frac{\partial \hat{A}_i}{\partial n_j} - 2\delta_{ij}\frac{\partial \hat{A}_i}{\partial U_i^2}\right)U_i^4 \, \mathbf{dU}_i \tag{A.29}$$

$$\Omega_{k,n_j} = -\frac{2}{15}KT\sum_i \int B_i\left(\frac{\rho_j}{KT}\frac{\partial \hat{D}_{ik}}{\partial n_j} - 2\delta_{ij}\frac{\partial \hat{D}_{ik}}{\partial U_i^2}\right)U_i^4 \, \mathbf{dU}_i \tag{A.30}$$

$$\Omega_{k,l} = -\frac{4}{15} KT \sum_i \int B_i \frac{\partial \hat{D}_{ik}}{\partial U_i^2} \left(\delta_{il} - \frac{\rho_l}{\rho}\right) U_i^4 \, \mathbf{dU}_i$$

$$+ KT \sum_i \tilde{\int} B_i \mathbf{U}_i {}^\circ \mathbf{U}_i \sum_j C[\hat{D}_{ik}(\mathbf{U}_i \cdot \mathbf{R}_k), D_{jl}(\mathbf{U}_j \cdot \mathbf{R}_l)] \, \mathbf{dU}_i \qquad \text{(A.31)}$$

$$\Omega_{E,E} = \frac{16}{105} KT \sum_i \int B_i \frac{\partial \hat{B}_i}{\partial U_i^2} U_i^6 \, \mathbf{dU}_i$$

$$+ KT \sum_i \tilde{\int} B_i \mathbf{U}_i {}^\circ \mathbf{U}_i \sum_j C[\hat{B}_i(\mathbf{U}_i \mathbf{U}_i : \overset{\circ}{\overline{\overline{\mathsf{E}}}}), \hat{B}_j(\mathbf{U}_j \mathbf{U}_j : \overset{\circ}{\overline{\overline{\mathsf{E}}}})] \, \mathbf{dU}_i \qquad \text{(A.32)}$$

$$\Omega_{T'} = -(2/15) KT \sum_i \int B_i \hat{A}_i U_i^4 \, \mathbf{dU}_i \qquad \text{(A.33)}$$

$$\Omega_{k'} = -(2/15) KT \sum_i \int B_i \hat{D}_{ik} U_i^4 \, \mathbf{dU}_i \qquad \text{(A.34)}$$

APPENDIX B. COEFFICIENTS APPEARING IN THE EXPRESSIONS FOR THE SECOND-ORDER ENTROPY, ENTROPY FLUX, AND ENTROPY SOURCES

The second-order entropy $\rho s^{(2)}$ is obtained by introducing (24) into (59). It is again noted that integrals of odd functions of the velocity U_i vanish, and the integral theorems mentioned in Appendix A are used again. The coefficients c appearing in Eq. (67) are found to be given by the following functionals:

$$c_T = \tfrac{1}{6}(K/T^2) \sum_i \int f_i^{(0)} A_i^2 U_i^2 \, \mathbf{dU}_i \qquad \text{(B.1)}$$

$$c_{Tk} = \tfrac{1}{3}(K/T) \sum_i \int f_i^{(0)} A_i D_{ik} U_i^2 \, \mathbf{dU}_i \qquad \text{(B.2)}$$

$$c_{jk} = \tfrac{1}{6} K \sum_i \int f_i^{(0)} D_{ij} D_{ik} U_i^2 \, \mathbf{dU}_i; \qquad c_{jk} = c_{kj} \qquad \text{(B.3)}$$

$$c_E = (1/15) K \sum_i \int f_i^{(0)} B_i^2 U_i^4 \, \mathbf{dU}_i \qquad \text{(B.4)}$$

The coefficients Γ appearing in the expression (73) for the second-order entropy flux $\mathbf{J}_s^{(2)}$ are obtained after introducing (24) into (61):

$$\Gamma_T = (2/15)(K/T^2) \sum_i \int A_i B_i f_i^{(0)} U_i^4 \, \mathbf{dU}_i \qquad \text{(B.5)}$$

$$\Gamma_k = (2/15) K \sum_i \int D_{ik} B_i f_i^{(0)} U_i^4 \, \mathbf{dU}_i \qquad \text{(B.6)}$$

The coefficients λ appearing in Eq. (77) are obtained after introducing the solution for $\phi_i^{(1)}$ from (24) and the first-order terms for $C^{(1)}(f_i, f_j)$ from the Boltzmann equation into the second integral on the right-hand side of Eq. (65):

$$\lambda_T = \frac{2}{15}\frac{K}{T^2}\sum_i \int \left(\frac{m_i U_i^2}{2KT} - \frac{5}{2}\right) f_i^{(0)} A_i B_i U_i^4 \, \mathbf{dU}_i$$

$$+ \frac{1}{15}\frac{1}{T^3}\sum_i m_i \int f_i^{(0)} A_i^2 U_i^4 \, \mathbf{dU}_i \tag{B.7}$$

$$\lambda_{Tk} = \frac{2}{15}\frac{K}{T^2}\sum_i \int \left(\frac{m_i U_i^2}{2KT} - \frac{5}{2}\right) f_i^{(0)} D_{ik} B_i U_i^4 \, \mathbf{dU}_i$$

$$+ \frac{2}{15}\frac{1}{T^3}\sum_i m_i \int f_i^{(0)} A_i B_i U_i^4 \, \mathbf{dU}_i \left(\delta_{ik} - \frac{\rho_k}{\rho}\right)$$

$$+ \frac{2}{15}\frac{1}{T^3}\sum_i m_i \int f_i^{(0)} A_i D_{ik} U_i^4 \, \mathbf{dU}_i \tag{B.8}$$

$$\lambda_{jk} = \frac{2}{15}\frac{1}{T}\sum_i m_i \int f_i^{(0)} B_i D_{ij} U_i^4 \, \mathbf{dU}_i \left(\delta_{ik} - \frac{\rho_k}{\rho}\right)$$

$$+ \frac{1}{15}\frac{1}{T}\sum_i m_i \int f_i^{(0} D_{ij} D_{ik} U_i^4 \, \mathbf{dU}_i \tag{B.9}$$

$$\lambda_E = \frac{4}{105}\frac{1}{T}\sum_i m_i \int f_i^{(0)} B_i^2 U_i^6 \, \mathbf{dU}_i \tag{B.10}$$

The coefficients Λ appearing in Eq. (81) are obtained from Eqs. (77) and (80):

$$\Lambda_T = \lambda_T + K \sum_{i,j} \overset{\sim}{\int} \frac{A_i}{T} (\mathbf{U}_i \cdot \mathrm{grad}\, T)$$

$$\times \{C[\hat{A}_i(\mathbf{U}_i \cdot \mathrm{grad}\, T), \hat{B}_j(\mathbf{U}_j{}^\circ\mathbf{U}_j : \mathsf{E})]$$

$$+ C[\hat{B}_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E}), \hat{A}_j(\mathbf{U}_j \cdot \mathrm{grad}\, T)]\} \, \mathbf{dU}_i$$

$$+ K \sum_{i,j} \overset{\sim}{\int} B_i(\mathbf{U}_i{}^\circ\mathbf{U}_i : \mathsf{E})$$

$$\times C[\hat{A}_i(\mathbf{U}_i \cdot \mathrm{grad}\, T), \hat{A}_j(\mathbf{U}_j \cdot \mathrm{grad}\, T)] \, \mathbf{dU}_i \tag{B.11}$$

$$
\begin{aligned}
\Lambda_{Tk} = \lambda_{Tk} &+ K \sum_{i,j} \tilde{\int} \frac{A_i}{T^2} (\mathbf{U}_i \cdot \mathrm{grad}\, T) \\
&\times \{C[\hat{D}_{ik}(\mathbf{U}_i \cdot \mathbf{R}_k), \hat{B}_j(\mathbf{U}_j \circ \mathbf{U}_j : \mathsf{E})] \\
&+ C[\hat{B}_i(\mathbf{U}_i \circ \mathbf{U}_i : \mathsf{E}), \hat{D}_{jk}(\mathbf{U}_j \cdot \mathbf{R}_k)]\}\, \mathbf{dU}_i \\
&+ \frac{K}{T} \sum_{i,j} \tilde{\int} D_{ik}(\mathbf{U}_i \cdot \mathbf{R}_k)\{C[\hat{A}_i(\mathbf{U}_i \cdot \mathrm{grad}\, T), \hat{B}_j(\mathbf{U}_j \circ \mathbf{U}_j : \mathsf{E})] \\
&+ C[\hat{B}_i(\mathbf{U}_i \circ \mathbf{U}_i : \mathsf{E}), \hat{A}_j(\mathbf{U}_j \cdot \mathrm{grad}\, T)]\}\, \mathbf{dU}_i
\end{aligned}
\tag{B.12}
$$

$$
\begin{aligned}
\Lambda_{lk} = \lambda_{lk} &+ K \sum_{i,j} \tilde{\int} D_{il}(\mathbf{U}_i \cdot \mathbf{R}_l) C[\hat{D}_{ik}(\mathbf{U}_i \cdot \mathbf{R}_k), \hat{B}_j(\mathbf{U}_j \circ \mathbf{U}_j : \mathsf{E})]\, \mathbf{dU}_i \\
&+ K \sum_{i,j} \tilde{\int} B_i(\mathbf{U}_i \circ \mathbf{U}_i : \mathsf{E}) C[\hat{D}_{il}(\mathbf{U}_i \cdot \mathbf{R}_l), \hat{D}_{jk}(\mathbf{U}_j \cdot \mathbf{R}_k)]\, \mathbf{dU}_i
\end{aligned}
\tag{B.13}
$$

$$
\Lambda_E = \lambda_E + K \sum_{i,j} \tilde{\int} B_i(\mathbf{U}_i \circ \mathbf{U}_i : \mathsf{E}) C[\hat{B}_i(\mathbf{U}_i \circ \mathbf{U}_i : \mathsf{E}), \hat{B}_j(\mathbf{U}_j \circ \mathbf{U}_j : \mathsf{E})]\, \mathbf{dU}_i
\tag{B.14}
$$

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