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Irreversible thermodynamics of multicomponent fluids and its statistical mechanics basis

R. F. Snider[*]
Department of Chemistry, University of British Columbia, Vancouver, Canada V6T 1Z1

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The irreversible thermodynamics of a multicomponent fluid is reviewed. This includes a discussion of the role of individual component fluxes. It is argued that their differences vanish on the same time scale as that which establishes local thermodynamic equilibrium and thus do not play an independent role in fluid dynamics, but only arise in response to gradients in conserved thermodynamic variables. The contributions to the energy flux are examined and it is argued that there should be explicit contributions associated with the various component fluxes, which are not mentioned in standard kinetic theory presentations. Three different thermodynamic perspectives are discussed as to their form, with the respective equations for the entropy flux and production described and contrasted. The Onsager reciprocal relations are considered to be a consequence of the single-valuedness of the entropy production with the chemical potential gradients as the driving forces for diffusion. These are specialized to ideal gas mixtures using the component density gradients associated with Fick's laws and to using the mole fraction gradients that are standardly used in gas kinetic theory. The ideal gas Onsager relations are identical to those deduced from the Boltzmann equation. Irving and Kirkwood's statistical mechanics treatment of the evolution equations of a one-component fluid [J. Chem. Phys. **18**, 817 (1950)] is generalized to multicomponent fluids and agrees with the thermodynamic perspective that treats the energy transfers as reversible.

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I. INTRODUCTION

A. Background

Irreversible thermodynamics involves treating a system as having thermodynamic properties which are, by definition, in equilibrium and also as having time dependent properties which are out of equilibrium. It is important to understand how and under what conditions this dichotomy of properties can occur in the real world. For gases, the classification of three different distance scales for dynamical behavior (equivalently time scales by using the mean particle speed to relate distance and time scales) as elucidated by Bogoliubov [1] (see also Uhlenbeck's [2] presentation of Bogoliubov's work) provides a perspective for understanding how this can be. This can also be adapted to liquids. Bogoliubov's classification is to contrast the range of a collision (which is of the order of the range of the intermolecular potential, $\approx 3\times10^{-8}$ cm for N_2) with the mean free path (distance traveled between collisions $\approx 7\times10^{-6}$ cm for N_2 at 1 atm and 300 °K) and, third, the fluid dynamic changes over the range of centimeters to kilometers (such as the flow of air from a punctured balloon to variations in the atmosphere). In liquids the difference between the first two vanishes since the particles are always interacting. But it is the large difference between the mean free path and the fluid flow properties that allows collisions to create a "local" thermodynamic equilibrium while the thermodynamic variables describing the local behavior can vary from one position to another in the fluid. For a gas, this difference is well described by the Boltzmann equation and its Chapman-Enskog solution to give the equations of fluid dynamics [3–5]. The same difference is assumed to be valid in liquids but there is no clear standard theory to use since there are multiparticle collisions which defy simple analysis. This difference in local equilibrium versus spatial variation is fundamental to the description of fluid dynamics, specifically that fluid flow properties are driven by spatial variations, in particular by gradients of the parameters describing the local equilibria, and where irreversible thermodynamics can be useful in understanding its properties in laminar flow. Another way of describing this situation is to identify the collisional and between collisional motions as using individual particle variables, which is thus microscopic motion, while the fluid flow uses mean particle variables for their description and is thus macroscopic motion.

Any fluid involves a tremendous number of particles; for example, air under standard conditions has a density of $\approx 10^{19}$ molecules per cm^3. Thus there are an enormous number of variables for the particle description of the fluid. These variables can be organized in different ways into what variables are treated as macroscopic, and which microscopic. This has an advantage of allowing a more detailed or cruder description of the system, but also the disadvantage of deciding what variables give the best description. It is how a particular variable varies with respect to the different distance scales that determines whether that variable should be classified as macroscopic or microscopic. Variables that undergo changes during collisions vary on the short distance scale and get averaged over by the large collision rate so these microscopic variables have small average values. Those variables that

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[*] rfsnider@shaw.ca

do not vary during collisions then dominate the behavior of the fluid at this scale. Another way of expressing this is to recognize these are the variables that are conserved during collisions. Since collisions involve particle dynamics, these are also the variables that, when applied to all particles in the system, are also conserved. This language emphasizes gas behavior, but in liquids the same type of behavior occurs, namely that variables that are conserved in few-particle dynamics are related to macroscopically conserved variables and it is these variables that dominate fluid dynamic behavior.

Recent treatments of the irreversible thermodynamics of multicomponent fluids [6,7] tend to add the component flow velocities ($\mathbf{v}_\alpha$ for component α) as fluid variables. It is shown in Sec. VI that collisions transfer momentum from one component to another so that only the mean momentum remains after the collision regime is passed and thus are averaged over in the approach to local thermodynamic equilibrium at the collision rate governed by the mean free path so the different component velocities should not be treated as macroscopic variables; rather only their average (the stream velocity) is a macroscopic variable.

B. Methodology

In the absence of external forces the equations of fluid dynamics are based on the conservation equations for mass, momentum, and energy, and for multicomponent systems, on the conservation of each chemical component, ignoring chemical reactions. Chemical reactions add complications due to the requirement that they need specification of the mechanism for each chemical reaction, which varies greatly from one reaction to another. Thus chemical reactions are best discussed for each special case and thus not included in the general presentation given here. As already mentioned, some presentations of irreversible thermodynamics include the component fluxes as thermodynamic variables. These are not conserved since momentum is transferred from one component to another and so do not fit into the above description of fluid dynamics. That this transfer rate is of the same order as the collision rate implies that such quantities arise only on a time scale before local thermodynamic equilibrium is attained and so are averaged over before the fluid dynamic time scale and thus are irrelevant extra variables to be considered in the fluid dynamics time scale. Such an argument is presented in Sec. VI, based on a simple estimate using the Boltzmann equation for a gas mixture. For this reason it is only the above mentioned conserved variables that are treated in the bulk of this paper.

The conservation equations are integrated together by assuming the fluid is in local thermodynamic equilibrium; that is, the thermodynamic variables are position ($\mathbf{r}$) dependent and also time (t) dependent since the system is evolving with time, so that the equations of thermodynamics can be applied at each specific position and time. However, the conservation equations involve the rate of change of the equilibrium thermodynamic variables and in general require nonequilibrium variables for their description. Thus the description of the fluid must involve both the (local) equilibrium variables and nonequilibrium variables which are presumably small in some sense to allow the local equilibrium thermodynamic relations to be valid. That is, there is some sense of a fast time scale to allow thermodynamic equilibrium to be locally attained and of a slower time scale for the description of the transfer of conserved variables between the different regions of the fluid. It is an inherent assumption that such a distinction can be made so that the equations of fluid dynamics have a local equilibrium structure. Shock waves strain this assumption and probably violate this separation of time scales. Here only the laminar flow described by fluid dynamics is addressed.

The first law of thermodynamics states that energy is conserved and attributes any change in the internal energy $\mathcal{U}$ of a system to heat and/or work transferred to the system from its surroundings. For a small volume of fluid in its rest frame, hereafter referred to as an element of fluid, this means the transfers of energy from its neighboring fluid elements. Work is associated with changes in the mechanical properties of the system while heat is associated with nonmechanical changes, usually attributed to random motions (fluctuations) or to changes in the probabilities of the states of the mechanical energies constituting the physical nature of the system. For a system in thermodynamic equilibrium, heat is related to the entropy $\mathcal{S}$ change of the system. This relation is written

$$d\mathcal{U} = Td\mathcal{S} - PdV + \sum_\alpha \mu_\alpha dN_\alpha, \tag{1}$$

where T, P, and V are the temperature, pressure, and volume of the system while μ_α and N_α are the chemical potential and number of molecules of component α. The volume and the numbers of particles are mechanical variables so $-PdV$ and $\sum_\alpha \mu_\alpha dN_\alpha$ are elements of mechanical and chemical work while $Td\mathcal{S}$ is heat. Fluid dynamics usually assumes that the thermodynamics of the system is extensive, namely that $\mathcal{U}$, $\mathcal{S}$, and the N_α are proportional to the volume V. This allows the first law to be rewritten as

$$d(\rho U) = Td(\rho S) + \sum_\alpha \mu_\alpha dn_\alpha, \tag{2}$$

where ρ is the mass density, U and S are the internal energy and entropy per unit of mass, while n_α is the number density of component α. Note that now no PdV term appears since this equation is for unit volume and the only work terms that explicitly appear are the chemical work terms. Since the mass density ρ plays a major role in fluid dynamics, Eq. (2) is the appropriate form for the first law of thermodynamics when discussing multicomponent fluids.

The equations of change are rationalized by the nature of a typical conservation law in Sec. II. For mass, momentum, and component densities the conservation equations are straightforward and not controversial but the expression for the energy flux is subject to different interpretations. Since the fluid is in motion the energy of a fluid element has a kinetic energy of motion (convective energy) as well as internal energy. The energy transferred by this motion from one position of a fluid element to another is easily identified as associated with the motion itself and with the momentum flux. These convective dependent energy transfers are well recognized as contributors to the energy flux. The conductive (convective independent) energy transfers analogous to the changes in internal energy changes of Eq. (2) are standardly lumped into one contribution to the energy flux and usually labeled as heat.

This mistreats the chemical work energy as a separate method of energy transfer. It is the objective of this paper to identify and consider the consequences of the energy carried by the differing velocities of the components. These are referred to as the chemical energy fluxes.

Three different ways of thermodynamically treating the conductive contributions to the energy flux are discussed. Their subsequent consequences for the entropy equation of change and entropy production are compared after all three have been presented. Linear relations between fluxes and generalized forces lead to the entropy production being expressed as a quadratic form in the generalized forces. The single-valuedness of this quadratic form implies the proper form for the Onsager relations, in particular between the different diffusion coefficients. Section III specializes these relations to ideal gas mixtures where the independent thermodynamic variables are taken as the temperature, component densities, and the stream velocity. Reference to the results obtained from solving the Boltzmann equation [8] are made and shown to be the same Onsager relations. Section IV continues with the properties of an ideal gas, but uses the temperature, pressure, mole fractions, and stream velocity as the independent variables. Again the properties of solving the Boltzmann equation [3,4,8] are referred to and also compared to the Sec. III results. It is shown that the two sets of diffusion constants are different with different symmetry relations but consistent with each other associated with their different definitions. Section V extends the statistical mechanical derivation of the equations of change of a fluid by Irving and Kirkwood [9] to multicomponent mixtures. This verifies that the proper form for the energy carried by the chemical fluxes is obtained thermodynamically by treating the energy transfer as a reversible process. A discussion of the consequences of this analysis is given in Sec. VII. As already mentioned, Sec. VI presents an estimate of the momentum transfer rate between components and its consequences.

II. GENERAL IRREVERSIBLE THERMODYNAMICS OF A FLUID SYSTEM

A. Conservation equations

If ρY is the density of a (mechanical) conserved quantity, then the only way an amount of Y in a volume element can change with time t is by means of the flux $\mathbf{J}_Y$ through the surface of the volume element. Written in differential form, the conservation equation for Y is

$$\frac{\partial \rho Y}{\partial t} = -\boldsymbol{\nabla}\cdot\mathbf{J}_Y. \tag{3}$$

In the absence of external influences (gravity, electromagnet, etc.) mass, momentum, and energy are conserved variables in a fluid. Ignoring also the possibility of chemical reactions, each component of a multicomponent mixture is also conserved. The effects of any of these processes (external influences and/or reactions) can be added but are not considered here. Angular momentum is another conserved quantity but its treatment is complicated by the question of choosing where the axis of rotation of the fluid is to be placed. Such questions are of import when internal angular momentum states (spin and/or molecular rotation) of the molecules are present and will not be discussed here (see Refs. [10–12] for initial treatments of such systems).

The flux of the mass density $\rho(\mathbf{r}, t)$ at position $\mathbf{r}$ and time t is the momentum density $\rho\mathbf{v}_0$, which defines the stream velocity $\mathbf{v}_0$. Thus the conservation equation of mass, also known as the equation of continuity, is

$$\frac{\partial \rho}{\partial t} = -\boldsymbol{\nabla}\cdot(\rho\mathbf{v}_0) \quad \text{or} \quad \frac{D\rho}{Dt} = -\rho\boldsymbol{\nabla}\cdot\mathbf{v}_0, \tag{4}$$

where $\mathbf{v}_0$ is the mass average (stream) velocity and

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v}_0\cdot\boldsymbol{\nabla} \tag{5}$$

is the substantial (barycentric) time derivative.

The mass density $\rho(\mathbf{r}, t)$ as a function of the position $\mathbf{r}$ and time t is a major property of a fluid. Relative to that, the internal energy per unit volume is written here as ρU, with position and time dependence understood but not explicitly expressed. Assuming the fluid element can be considered in local thermodynamic equilibrium, $\rho U(\rho S, \{n_\alpha\})$ is a thermodynamic characteristic function of entropy per unit volume ρS and the set of c (number of components) particle densities $\{n_\alpha\}$ with fundamental equation (2) defining the temperature T and set of chemical potentials $\{\mu_\alpha\}$. Note that there is no mechanical (PdV) work term since this equation has been written for unit volume of fluid while $\mu_\alpha dn_\alpha$ is the element of chemical work done on the system by inserting dn_α molecules of α per unit volume. $Td(\rho S)$ is the element of "reversible" heat added to the system. Note also that only intensive variables are involved in this equation and ρU depends on $c+1$ independent variables. On the basis that all thermodynamic variables are either intensive or extensive, the identity

$$\sum_\alpha n_\alpha\mu_\alpha = \rho(U - TS) + P \tag{6}$$

is valid. Note that the derivation of this last equation depends on explicitly using the volume in order to integrate over the extensive variables and thus is deduced from Eq. (1) rather than from Eq. (2).

In the absence of chemical reactions, the number of particles of each component is conserved so each component satisfies a conservation equation of the form (written here for component α)

$$\frac{Dn_\alpha}{Dt} = -n_\alpha\boldsymbol{\nabla}\cdot\mathbf{v}_0 - \boldsymbol{\nabla}\cdot(n_\alpha\overline{\mathbf{V}}_\alpha), \tag{7}$$

with $\overline{\mathbf{V}}_\alpha$ known as the diffusion velocity of component α. Identifying the mass density as

$$\rho = \sum_\alpha n_\alpha m_\alpha, \tag{8}$$

the diffusion velocities satisfy the sum rule

$$\sum_\alpha n_\alpha m_\alpha\overline{\mathbf{V}}_\alpha = 0, \tag{9}$$

and so describe the "conductive" motion of the components relative to the "convective" velocity $\mathbf{v}_0$. The combination $n_\alpha\overline{\mathbf{V}}_\alpha$ will be variously labeled as the component flux, particle flux, chemical flux, or material flux since these labels provide different associations as to what this flux represents in different applications.

Momentum is also conserved, so its conservation equation is

$$\frac{\partial \rho \mathbf{v}_0}{\partial t} = -\nabla \cdot [\rho \mathbf{v}_0 \mathbf{v}_0 + \mathsf{P}], \tag{10}$$

where the momentum flux is given as a sum of a convective contribution $\rho \mathbf{v}_0 \mathbf{v}_0$ associated with the momentum carried by the fluid flow (stream velocity) and a conductive contribution P associated with the microscopic random motions of the molecules. P is standardly referred to as the pressure tensor and sometimes as (minus) the stress tensor. Another way of writing the above equation is

$$\rho \frac{D\mathbf{v}_0}{Dt} = -\nabla \cdot \mathsf{P}. \tag{11}$$

Finally there is the conservation of energy and this requires some elaboration. First, the total energy per unit mass, $E = U + \mathbf{v}_0^2/2$, involves the convective as well as the internal energy. It is the total energy that is conserved so its equation of change is of conservation type,

$$\frac{\partial \rho E}{\partial t} = -\nabla \cdot \mathbf{J}_E, \tag{12}$$

namely, the energy density changes only via energy flux from other elements of the fluid via work done on the system or heat transferred from its surroundings (namely, the neighboring fluid elements). The following describes three thermodynamic perspectives of how this can be written.

1. All purely conductive energy flux is heat

Convection (equivalently, the mass flux) carries energy so the energy flux due to convection is $\rho E \mathbf{v}_0$. The momentum flux also carries energy via the force transferred to the surface of a fluid element. But since the convective contributions to the energy flux have already been accounted for, it is only the conductive part of the momentum flux that should be added, namely, with a contribution $\mathsf{P} \cdot \mathbf{v}_0$. Note the $\mathbf{v}_0$ arises as the rate of change of convective energy with respect to the momentum, namely, $(\partial \rho \mathbf{v}_0^2/2/\partial \rho \mathbf{v}_0)_\rho$. These are the only energy flux contributions that involve $\mathbf{v}_0$; hence other contributions are conductive and labeled as $\mathbf{q}$. This is the symbol standardly used for heat flux so this association is inherently made. Some presentations explicitly make this association whereas others carefully avoid this name and consider that $\mathbf{q}$ can include many different contributions. But if all conductive energy fluxes are lumped together then the entropy flux and production also have all these contributions lumped together rather than playing different roles in the approach to equilibrium, in effect acting as if they are heat (see Sec. II B). Thus the term heat is used here as a simple label and the total energy flux vector in this perspective is written as

$$\mathbf{J}_E = \rho E \mathbf{v}_0 + \mathsf{P} \cdot \mathbf{v}_0 + \mathbf{q}. \tag{13}$$

This is the expression for the energy flux that appears in most of the literature, in particular Refs. [3–5,11].

An elegant method of obtaining this result is described by McLennan [12]. He examines the changes to the equations of change (4), (10), and (12) due to Galilean transformations and the particular relation between them in the laboratory frame and in the rest frame moving with the stream velocity. He also specializes these to the case where the latter is in thermal equilibrium and identifies which quantities have nonvanishing equilibrium values and those which do not. In particular the diffusion velocities and the heat flux (which he only identifies as the energy flux in the local rest frame rather than calling it heat) vanish at equilibrium. The pressure tensor has both an isotropic equilibrium pressure and nonequilibrium contributions.

2. Energy flux has chemical work contributions

The first perspective makes no explicit reference to the energy carried by the different components. Since different components have different thermal energies and moreover move at different diffusion velocities, the energy flux should be dependent on how the internal energy U is affected by the changing composition during fluid flow. An obvious way of accounting for these effects is to look at Eq. (2). The entropy change is associated with reversible heat while the energy change due to composition changes depend on the chemical potentials. Thus Eq. (13) is replaced by

$$\mathbf{J}_E = \rho E \mathbf{v}_0 + \mathsf{P} \cdot \mathbf{v}_0 + \sum_\alpha \mu_\alpha n_\alpha \overline{\mathbf{V}}_\alpha + \mathbf{q} \tag{14}$$

since $n_\alpha \overline{\mathbf{V}}_\alpha$ is the conductive flux of component α. The quantities dependent on the stream velocity remain the same while the heat flux is now associated with the entropy change. This is what the author used in Ref. [8].

3. Energy flux is reversible

As mentioned in the Introduction, the fluid is assumed to be in local thermodynamic equilibrium with a small nonequilibrium aspect. Thus the major effects are to be carried out in a reversible manner, and nonequilibrium aspects only arise in allowing changes to occur. Within this approach the surface of a fluid element and the contact between fluid elements are to be treated as if they are in thermodynamic equilibrium, namely, at constant temperature, pressure, and chemical potentials since these define thermal, mechanical, and chemical equilibrium. The stream velocity is also constant since this defines the particular local rest frame. The manner in which the energy density varies with component density is then

$$\begin{aligned}\left(\frac{\partial \rho E}{\partial n_\alpha}\right)_{T,P,\{\mu_\alpha\},\mathbf{v}_0} &= \left(\frac{\partial \rho U}{\partial n_\alpha}\right)_{T,P,\{\mu_\alpha\}} \\ &= T\left(\frac{\partial \rho S}{\partial n_\alpha}\right)_{T,P,\{\mu_\alpha\}} \\ &\quad + \mu_\alpha = T s_\alpha + \mu_\alpha = h_\alpha.\end{aligned} \tag{15}$$

This has dropped the convective energy density and then used Eq. (2) with the identification of the partial molar entropy s_α and enthalpy h_α. Thus the “conductive” energy flux carried by the component α flux is

$$\sum_\alpha n_\alpha h_\alpha \overline{\mathbf{V}}_\alpha. \tag{16}$$

Combining these contributions together and adding the heat flux $\mathbf{q}$ gives the energy flux as

$$\mathbf{J}_E = \rho E\mathbf{v}_0 + \mathsf{P}\cdot\mathbf{v}_0 + \sum_\alpha n_\alpha h_\alpha \overline{\mathbf{V}}_\alpha + \mathbf{q}. \tag{17}$$

With this form for the energy flux, the equation for the conservation of energy (12) can be written in terms of the substantial time derivative of U as

$$\begin{aligned}\rho\frac{DU}{Dt} &= \rho\frac{DE}{Dt} - \rho\mathbf{v}_0\cdot\frac{D\mathbf{v}_0}{Dt}\\ &= -\mathsf{P}:(\nabla\mathbf{v}_0)^t - \nabla\cdot\left[\sum_\alpha n_\alpha h_\alpha\overline{\mathbf{V}}_\alpha + \mathbf{q}\right],\end{aligned} \tag{18}$$

where superscript t denotes the transpose of the second-order tensor. The analogous equations for the other perspectives for the energy flux are obtained by setting $h_\alpha = 0$ for the first perspective and $h_\alpha = \mu_\alpha$ for the second.

B. Entropy equation of change and the phenomenological equations

The rate of change of the entropy per unit mass, S, is related to the internal energy change via Eq. (2), which is expressed in terms of the substantial time derivatives as

$$\begin{aligned}\rho T\frac{DS}{Dt} &= \rho\frac{DU}{Dt} + (U - TS)\frac{D\rho}{Dt} - \sum_\alpha \mu_\alpha\frac{Dn_\alpha}{Dt}\\ &= \rho\frac{DU}{Dt} + \left[\sum_\alpha n_\alpha\mu_\alpha - P\right]\frac{1}{\rho}\frac{D\rho}{Dt}\\ &\quad - \sum_\alpha \mu_\alpha\frac{Dn_\alpha}{Dt},\end{aligned} \tag{19}$$

with the second form using Eq. (6). Inserting the results of Eqs. (4), (11), and (18) into this equation and extensive rearrangement lead to

$$\begin{aligned}\rho T\frac{DS}{Dt} &= -(\mathsf{P} - P\mathsf{U}):(\nabla\mathbf{v}_0)^t\\ &\quad - \nabla\cdot\left[\sum_\alpha n_\alpha(h_\alpha - \mu_\alpha)\overline{\mathbf{V}}_\alpha + \mathbf{q}\right]\\ &\quad - \sum_\alpha n_\alpha\overline{\mathbf{V}}_\alpha\cdot\nabla\mu_\alpha,\end{aligned} \tag{20}$$

where U is the second order tensor identity. With the help of the relation $\mu_\alpha = h_\alpha - Ts_\alpha$, the equation for the time dependence of the entropy can be expressed as

$$\rho\frac{DS}{Dt} = -\nabla\cdot\left[\sum_\alpha n_\alpha s_\alpha\overline{\mathbf{V}}_\alpha + \frac{\mathbf{q}}{T}\right] + \sigma_3, \tag{21}$$

representing the entropy transferred through the boundary of a fluid element in terms of the sum of the component entropies transferred due to the chemical fluxes plus the standard expression for the entropy change as the heat flux divided by the temperature. The entropy production σ_3 (labeled with 3 since this arises from perspective 3 for the energy flux) is given by

$$\begin{aligned}T\sigma_3 &= -\left[\sum_\alpha n_\alpha s_\alpha\overline{\mathbf{V}}_\alpha + \frac{\mathbf{q}}{T}\right]\cdot\nabla T - \sum_\alpha n_\alpha\overline{\mathbf{V}}_\alpha\cdot\nabla\mu_\alpha\\ &\quad - (\mathsf{P} - P\mathsf{U}):(\nabla\mathbf{v}_0)^t.\end{aligned} \tag{22}$$

Lavenda [13] has an equation similar to Eq. (21) but with a notation based on a different background so its equivalence is not clear.

For perspective 1 for the energy flux, the time dependence of the entropy is

$$\rho\frac{DS}{Dt} = -\nabla\cdot\left[\frac{\mathbf{q} - \sum_\alpha n_\alpha\mu_\alpha\overline{\mathbf{V}}_\alpha}{T}\right] + \sigma_1 \tag{23}$$

with

$$\begin{aligned}T\sigma_1 &= -\left(\mathbf{q} - \sum_\alpha n_\alpha\mu_\alpha\overline{\mathbf{V}}_\alpha\right)\cdot\nabla\ln T\\ &\quad - \sum_\alpha n_\alpha\overline{\mathbf{V}}_\alpha\cdot\nabla\mu_\alpha - (\mathsf{P} - P\mathsf{U}):(\nabla\mathbf{v}_0)^t.\end{aligned} \tag{24}$$

This is equivalent to the form appearing in Ref. [11].

For perspective 2 for the energy flux, the time dependence of the entropy is

$$\rho\frac{DS}{Dt} = -\nabla\cdot\frac{\mathbf{q}}{T} + \sigma_2 \tag{25}$$

with

$$\begin{aligned}T\sigma_2 &= -\mathbf{q}\cdot\nabla\ln T - \sum_\alpha n_\alpha\overline{\mathbf{V}}_\alpha\cdot\nabla\mu_\alpha\\ &\quad -(\mathsf{P} - P\mathsf{U}):(\nabla\mathbf{v}_0)^t.\end{aligned} \tag{26}$$

This is what was considered in Ref. [8].

Clearly the entropy flux (the term whose divergence is taken in the entropy equation) differs due to the different versions of the energy flux as does the term involving the temperature gradient in the entropy production. But the purely convective term (proportional to $\nabla\mathbf{v}_0$) and the purely diffusion terms (proportional to $\nabla\mu_\alpha$) in the entropy production are the same for all versions. As to the structure of the entropy production, this has the well known form of being a sum of products of fluxes times gradients, the latter acting as generalized forces for the fluxes. Standard practice is to assume that the fluxes are linearly dependent on the forces while Curie's principle [11] states that the (transport) coefficients (being the linear coefficients in this relation) must have the symmetry (under space inversion as well as rotational properties) of the fluid. Here the fluid is taken as being in isotropic equilibrium, so this means any relation between flux and force must be rotationally invariant. If the fluid is acted upon by an external force (for example, by gravity or magnetic field) then its associated symmetry must be taken into account. Here these possibilities are ignored. Since the convective term involves second order tensors while all of the other fluxes and forces are vectors, this leads to an immediate separation between these two sets of quantities. In particular, the nonequilibrium part of the pressure tensor has the form

$$\mathsf{P} - P\mathsf{U} = -2\eta[\nabla\mathbf{v}_0]^{(2)} - \kappa\nabla\cdot\mathbf{v}_0\mathsf{U}, \tag{27}$$

where η and κ are the shear and bulk viscosities while $[\nabla\mathbf{v}_0]^{(2)} \equiv (1/2)[\nabla\mathbf{v}_0 + (\nabla\mathbf{v}_0)^t] - (1/3)\nabla\cdot\mathbf{v}_0\mathsf{U}$ is the symmetric traceless part of the stream velocity gradient. The separation into two terms is associated with irreducible representations of the three-dimensional rotation group, equivalently into quadrupole and scalar parts of $\nabla\mathbf{v}_0$. Group theory-wise, there could also be an antisymmetric part of $\nabla\mathbf{v}_0$ which is proportional to the vorticity $\nabla\times\mathbf{v}_0$, but this arises only when angular momentum is important, as in rotational relaxation problems or turbulence, and is not considered here. References [10–12] have some discussion about the former.

The other fluxes and forces appearing in the entropy production are all vectors so the heat and chemical fluxes are coupled. Emphasizing perspective 3, the phenomenological equations are written

$$n_\alpha\overline{\mathbf{V}}_\alpha = -\sum_\beta \mathfrak{D}_{\alpha\beta}\nabla\mu_\beta - \mathfrak{D}_\alpha^T\nabla\ln T \tag{28}$$

and

$$\mathbf{q} + \sum_\alpha n_\alpha T s_\alpha\overline{\mathbf{V}}_\alpha = -\lambda_\mu\nabla T - \sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha. \tag{29}$$

Note that the notation parallels that used in Ref. [8] and the diffusion constants appearing here do not have the standard units since the chemical potential gradients appear rather than the particle density gradients in these equations. Connection to the standard density gradients and Fick's law is made in Sec. III when discussing an ideal gas as the fluid, while here it is the natural set of variables that is used for describing thermodynamic equilibrium. From Eq. (22) the entropy production is

$$\begin{aligned} T\sigma &= \left[\lambda_\mu\nabla T + \sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha\right]\cdot\nabla\ln T + \sum_{\alpha\beta}\mathfrak{D}_{\alpha\beta}\nabla\mu_\beta\cdot\nabla\mu_\alpha + \sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha\cdot\nabla\ln T + \left[2\eta[\nabla\mathbf{v}_0]^{(2)} + \kappa\nabla\cdot\mathbf{v}_0\mathsf{U}\right] : \nabla\mathbf{v}_0 \\ &= \frac{\lambda_\mu}{T}(\nabla T)^2 + \frac{2}{T}\sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha\cdot\nabla T + \sum_{\alpha\beta}\mathfrak{D}_{\alpha\beta}\nabla\mu_\beta\cdot\nabla\mu_\alpha + 2\eta[\nabla\mathbf{v}_0]^{(2)} : [\nabla\mathbf{v}_0]^{(2)} + \kappa(\nabla\cdot\mathbf{v}_0)^2. \end{aligned} \tag{30}$$

The second law of thermodynamics states that entropy increases for spontaneous processes, and implies that the entropy increase drives spontaneity. Thus the entropy production must be positive. Since the above equation is quadratic in the gradients, the square terms must have positive coefficients, implying that λ_μ, η, and κ must be positive, and the diffusion matrix $\mathfrak{D}_{\alpha\beta}$ is required to be positive. It is also possible to write the first three terms as a sum of two square terms, which implies a constraint on the c-dimensional vector $\mathfrak{D}_\alpha^T$. Since the entropy production determines the nature of how spontaneity occurs, the symmetry of the purely diffusion quadratic form implies that the matrix $\mathfrak{D}_{\alpha\beta}$ is symmetric. This is one of the Onsager relations [14]. Another symmetry relation is that $\mathfrak{D}_\alpha^T$ determines both the thermal diffusion as in Eq. (28) and the diffusion thermal effect in Eq. (29) since there is equal contribution to the entropy production from these processes. Of course, that they appear with equal coefficients has been helped by the choice of how the phenomenological relations have been written and is predicated on the uniqueness of the entropy production in that it can have only one set of terms that are proportional to each of $\nabla\mu_\alpha\cdot\nabla\ln T$. It is also of importance to note that Eqs. (9) and (28) imply that both the diffusion and thermal diffusion constants satisfy sum rules, namely,

$$\sum_\alpha m_\alpha\mathfrak{D}_{\alpha,\beta} = 0, \quad \sum_\alpha m_\alpha\mathfrak{D}_\alpha^T = 0. \tag{31}$$

For perspective 1 for the energy flux, the linear relations between the vectorial fluxes and forces can be written as Eq. (28) for the diffusion velocities and

$$\mathbf{q} - \sum_\alpha n_\alpha\mu_\alpha\overline{\mathbf{V}}_\alpha = -\lambda_\mu\nabla T - \sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha. \tag{32}$$

The same phenomenological coefficients are used here as for perspective 3, but their meanings are to be associated with the definitions used in perspective 1. Interestingly, the equation for the entropy production is identical to Eq. (30). Perspective 2 has a similar result, with phenomenological equations (28) and

$$\mathbf{q} = -\lambda_\mu\nabla T - \sum_\alpha \mathfrak{D}_\alpha^T\nabla\mu_\alpha, \tag{33}$$

also resulting in Eq. (30) for the entropy production.

Thus all versions have the same properties for the phenomenological coefficients and it is only the different equations for the heat flux that occur, and then only how $\mathbf{q}$ varies with the diffusion velocities. Further discussion on the various ways of expressing the energy flux is given in Sec. VII.

It is noted that the diffusion constants are standardly defined in terms of the particle flux being driven by density gradients or mole fraction gradients rather than by the gradients of the chemical potentials. This requires expanding the chemical potential gradients in terms of either temperature and density gradients or temperature and mole fraction gradients. Such expansions are not done here in general but the two following sections do this for an ideal monatomic gas mixture and make connections to the kinetic theory of ideal gases and the standard Boltzmann equation.

III. TEMPERATURE, DENSITY VARIABLES FOR AN IDEAL MIXTURE OF MONATOMIC GASES

For an ideal monatomic gas mixture, the chemical potential of component α is

$$\begin{aligned}\mu_\alpha &= kT\ln\left(\frac{n_\alpha h^3}{(2\pi m_\alpha kT)^{3/2}}\right)\\ &= kT\ln\left(\frac{n_\alpha}{n}\frac{Ph^3}{kT(2\pi m_\alpha kT)^{3/2}}\right),\end{aligned} \tag{34}$$

where h is Planck's constant and k is Boltzmann's constant. The first version is appropriate when the temperature and the particle densities are independent, whereas the second version is expressed for the case in which the pressure and temperature are both treated as independent variables, with the mole fraction giving the concentration dependence. It is the first form that is emphasized in this section and has the advantage that all components are treated equally and that diffusion is described by Fick's laws, whereas when using the mole fractions, one component must be chosen to have its mole fraction dependent on the mole fractions of the others. The standard presentations of gas kinetic theory [3–5] only cursorily mention irreversible thermodynamics so no connection to an analysis like that given in Sec. II appears. Rather the emphasis is on the Boltzmann equation and its solution. Section IV uses the second form (using the mole fractions) and makes connection to the formalism used in these presentations which arises naturally when solving the Boltzmann equation for the transport coefficients. Here the first form of Eq. (34) is used so that the independent variables are T, $\{n_\alpha\}$. This set of variables was first introduced (as best as this author knows) in Ref. [8]. That paper is on solving the Boltzmann equation and both sets of variables are used in that paper to obtain molecular expressions for the various transport coefficients. Since Sec. V shows that perspective 3 for the energy flux is what statistical mechanics predicts, both Secs. III and IV are restricted to using only that choice. Since Ref. [8] uses perspective 2 for the energy flux there are minor differences between what is presented here and what appears in that paper. Section IV also discusses the relation between the two different sets of diffusion coefficients associated with the different sets of independent variables, namely, the component densities versus the mole fractions.

From the first form of Eq. (34), the gradient of the chemical potential is

$$\nabla\mu_\alpha = \left(\frac{\mu_\alpha}{T} - \frac{3}{2}k\right)\nabla T + \frac{kT}{n_\alpha}\nabla n_\alpha \tag{35}$$

and the entropy production for the vectorial fluxes is, from Eq. (22),

$$\begin{aligned}T\sigma = &-\left[\mathbf{q} + \sum_\alpha n_\alpha\left(h_\alpha - \frac{3}{2}kT\right)\overline{\mathbf{V}}_\alpha\right]\cdot\nabla\ln T\\ &-kT\sum_\alpha \overline{\mathbf{V}}_\alpha\cdot\nabla n_\alpha.\end{aligned} \tag{36}$$

Again $T\sigma$ is a sum of products of fluxes times forces, which identifies the combinations of terms which are to be the fluxes corresponding to the generalized forces being the temperature and component density gradients. The corresponding linear phenomenological equations for these fluxes are written as

$$\begin{aligned}\mathbf{q}_n &\equiv \mathbf{q} + \sum_\alpha\left(h_\alpha - \frac{3}{2}kT\right)n_\alpha\overline{\mathbf{V}}_\alpha\\ &= -\lambda_n\nabla T - kT\sum_\alpha \mathcal{D}^T_\alpha\nabla n_\alpha\end{aligned} \tag{37}$$

and

$$n_\alpha\overline{\mathbf{V}}_\alpha = -n_\alpha\mathcal{D}^T_\alpha\nabla\ln T - \sum_\beta\mathcal{D}_{\alpha,\beta}\nabla n_\beta. \tag{38}$$

The phenomenological coefficients associated with the cross effects between diffusion and heat conduction have been written as $n_\alpha\mathcal{D}^T_\alpha$ in order to conform with more standard notation, as have the diffusion constants $\mathcal{D}_{\alpha\beta}$ corresponding to Fick's first law. In comparison with the formulas of the last section emphasizing the chemical potential gradients, these quantities are

$$n_\alpha\mathcal{D}^T_\alpha = \mathfrak{D}^T_\alpha + \sum_\beta\mathfrak{D}_{\alpha,\beta}\left(\mu_\beta - \frac{3}{2}kT\right) \tag{39}$$

and

$$\mathcal{D}_{\alpha\beta} = \frac{kT\mathfrak{D}_{\alpha\beta}}{n_\beta}. \tag{40}$$

Since $\mathfrak{D}_{\alpha\beta}$ is symmetric, this implies

$$\mathcal{D}_{\alpha\beta}n_\beta = kT\mathfrak{D}_{\alpha\beta} = kT\mathfrak{D}_{\beta\alpha} = \mathcal{D}_{\beta\alpha}n_\alpha, \tag{41}$$

which is also equivalent to

$$\frac{1}{n_\alpha}\mathcal{D}_{\alpha\beta} = \frac{1}{n_\beta}\mathcal{D}_{\beta\alpha} \tag{42}$$

as the Onsager reciprocal relations for the diffusion coefficients. Reference [8] shows that this symmetry is also obtained when calculating the gas transport coefficients from the Boltzmann equation. Note that the only difference between what is written here and in Ref. [8] is that h_α here is replaced by μ_α there in Eqs. (36) and (37). Thus in particular, all properties of the diffusion matrix are the same. These phenomenological coefficients also satisfy the sum rules

$$\sum_\alpha n_\alpha m_\alpha\mathcal{D}^T_\alpha = 0 \quad\text{and}\quad \sum_\alpha m_\alpha\mathcal{D}_{\alpha\beta} = 0, \tag{43}$$

arising from the sum rule of Eq. (9). Note that the diffusion matrix $\mathcal{D}_{\alpha\beta}$ is not symmetric whereas $\mathfrak{D}_{\alpha\beta}$ is. The contributions to the thermal conductivity are related according to

$$\begin{aligned}\lambda_n = \lambda_\mu &+ \frac{2}{T}\sum_\alpha\mathfrak{D}^T_\alpha\left(\mu_\alpha - \frac{3}{2}kT\right)\\ &+ \frac{1}{T}\sum_{\alpha,\beta}\left(\mu_\alpha - \frac{3}{2}kT\right)\mathfrak{D}_{\alpha\beta}\left(\mu_\beta - \frac{3}{2}kT\right).\end{aligned} \tag{44}$$

In terms of these phenomenological coefficients, the entropy production is

$$\begin{aligned}T\sigma = &\frac{\lambda_n}{T}(\nabla T)^2 + 2\eta[\nabla\mathbf{v}_0]^{(2)}:[\nabla\mathbf{v}_0]^{(2)} + \kappa(\nabla\cdot\mathbf{v}_0)^2\\ &+ kT\sum_{\alpha,\beta}\frac{\mathcal{D}_{\alpha\beta}}{n_\alpha}\nabla n_\beta\cdot\nabla n_\alpha + 2k\sum_\alpha\mathcal{D}^T_\alpha\nabla n_\alpha\cdot\nabla T\end{aligned}$$

$$
\begin{aligned}
&= \frac{\lambda_n}{T}\left[\nabla T + \frac{kT}{\lambda_n}\sum_\alpha \mathcal{D}_\alpha^T \nabla n_\alpha\right]^2 \\
&\quad + kT\sum_{\alpha\beta}\left[\frac{\mathcal{D}_{\alpha\beta}}{n_\alpha} - \frac{k}{\lambda_n}\mathcal{D}_\alpha^T\mathcal{D}_\beta^T\right]\nabla n_\alpha\cdot\nabla n_\beta \\
&\quad + 2\eta[\nabla \mathbf{v}_0]^{(2)} : [\nabla \mathbf{v}_0]^{(2)} + \kappa(\nabla\cdot\mathbf{v}_0)^2. \qquad (45)
\end{aligned}
$$

The positivity of the entropy production shows that λ_n must be positive and that the matrix $\mathcal{D}_{\alpha\beta}/n_\alpha - k\mathcal{D}_\alpha^T\mathcal{D}_\beta^T/\lambda_n$ must be symmetric positive semidefinite. Analogous conditions are applicable to the quantities in the previous section, but were not written out there. Other comments on the properties of the phenomenological coefficients can be found in Ref. [8].

IV. TEMPERATURE, MOLE FRACTIONS, AND PRESSURE VARIABLES FOR AN IDEAL GAS MIXTURE

From the second version of Eq. (34) the gradient of the chemical potential is

$$
\nabla\mu_\alpha = \left(\frac{\mu_\alpha}{T} - \frac{5}{2}k\right)\nabla T + kT\nabla\ln x_\alpha + kT\nabla\ln P, \qquad (46)
$$

where $x_\alpha \equiv n_\alpha/n$ is the mole fraction of component α. The standard method of gas kinetic theory [3–5] introduces the quantities

$$
\mathbf{d}_\alpha \equiv \nabla x_\alpha + (x_\alpha - \rho_\alpha)\nabla\ln P \qquad (47)
$$

as the driving forces for diffusion, where $\rho_\alpha = m_\alpha n_\alpha/\rho$ is the mass fraction of component α. Following this method of treating mixtures, the gradient of the chemical potential is expressed in terms of the $\mathbf{d}_\alpha$ instead of the mole fraction gradients, thus

$$
\begin{aligned}
\nabla\mu_\alpha &= \left(\frac{\mu_\alpha}{T} - \frac{5}{2}k\right)\nabla T + \frac{kT}{x_\alpha}\mathbf{d}_\alpha + \left(\frac{kT\rho_\alpha}{x_\alpha}\right)\nabla\ln P \\
&= \left(\frac{\mu_\alpha}{T} - \frac{5}{2}k\right)\nabla T + \frac{kT}{x_\alpha}\mathbf{d}_\alpha + \frac{m_\alpha}{\rho}\nabla P. \qquad (48)
\end{aligned}
$$

Substituting this into the entropy production, Eq. (22), gives

$$
\begin{aligned}
T\sigma = &-\left[\mathbf{q} + \sum_\alpha n_\alpha\left(h_\alpha - \frac{5}{2}kT\right)\overline{\mathbf{V}}_\alpha\right]\cdot\nabla\ln T \\
&- P\sum_\alpha \overline{\mathbf{V}}_\alpha\cdot\mathbf{d}_\alpha - (\mathsf{P} - P\mathsf{U}) : \nabla\mathbf{v}_0. \qquad (49)
\end{aligned}
$$

The sum rule (9) eliminates the ∇P term arising from the chemical potential gradients. This is appropriate since ∇P is one of the driving forces for the stream velocity (see the momentum conservation equation), whereas the variables responsible for irreversibility are all conductive, namely, relative to the motion of the fluid as a whole. The above expression for the entropy production is linear in the gradients $\nabla\ln T$, $\mathbf{d}_\alpha$, and the stream velocity gradient with corresponding fluxes involving $\mathbf{q}$, $n_\alpha\overline{\mathbf{V}}_\alpha$ and $\mathsf{P} - P\mathsf{U}$. The linear phenomenological equations relating fluxes to forces are written here for an energy flux including both the heat flux $\mathbf{q}$ and an appropriate energy flux carried by the particle fluxes

$$
\mathbf{q}_P \equiv \mathbf{q} + \sum_\alpha n_\alpha\left(h_\alpha - \frac{5}{2}kT\right)\overline{\mathbf{V}}_\alpha = -\lambda_P\nabla T - P\sum_\alpha \mathbb{D}_\alpha^T\mathbf{d}_\alpha, \qquad (50)
$$

the conductive particle fluxes

$$
n_\alpha\overline{\mathbf{V}}_\alpha = -n_\alpha\sum_\beta \mathbb{D}_{\alpha\beta}\mathbf{d}_\beta - n_\alpha\mathbb{D}_\alpha^T\nabla\ln T, \qquad (51)
$$

and Eq. (27) for the pressure tensor. The choice of prefactors in these equations is so that they conform to the usage in Ref. [4]. For an ideal monatomic gas, the molar enthalpy is $5kT/2$ so the term added to the heat flux vanishes and makes $\mathbf{q}_P = \mathbf{q}$. Thus there is a formal difference with what is given in Ref. [8] for $\mathbf{q}$ for this set of variables. With the above expressions for the fluxes the entropy production is the quadratic in gradients expression

$$
T\sigma = \frac{\lambda_P}{T}(\nabla T)^2 + P\sum_{\alpha\beta}\mathbb{D}_{\alpha\beta}\mathbf{d}_\alpha\cdot\mathbf{d}_\beta + \frac{2P}{T}\sum_\alpha \mathbb{D}_\alpha^T\mathbf{d}_\alpha\cdot\nabla T + 2\eta[\nabla\mathbf{v}_0]^{(2)} : [\nabla\mathbf{v}_0]^{(2)} + \kappa(\nabla\cdot\mathbf{v}_0)^2. \qquad (52)
$$

Now it would be nice to predict properties of the transport coefficients from the required (by the second law of thermodynamics) positivity of the entropy production but it is noted that $\sum_\alpha \mathbf{d}_\alpha = 0$ implies that the $\mathbf{d}_\alpha$ are not all independent so that the $(c \times c)$-dimensional diffusion matrix is multiplied by a matrix $\mathbf{d}_\alpha\cdot\mathbf{d}_\beta$ which is equivalent to a matrix with at most only $(c-1)\times(c-1)$ independent elements. Thus not all elements of the $\mathbb{D}$ matrix appear in the entropy production. Similarly, not all elements $\mathbb{D}_\alpha^T$ of the component vector $\mathbb{D}^T$ appear. This leaves a question as to what properties can be deduced from the entropy production.

Actually the situation is a bit more complicated than what was given above. The sum rule, Eq. (9), implies the sum rules

$$
\sum_\alpha n_\alpha m_\alpha \mathbb{D}_\alpha^T = 0, \qquad \sum_\alpha n_\alpha m_\alpha \mathbb{D}_{\alpha\beta} = 0. \qquad (53)
$$

Thus as component vectors, $\mathbf{d}$ and $\mathbb{D}^T$ are orthogonal to different vectors, and so are $\mathbf{d}$ and the diffusion matrix. This does not help to clarify what properties can be deduced from the entropy production.

That the $\mathbf{d}_\alpha$ are not independent causes problems in solving the Boltzmann equation for the transport coefficients. Waldmann [3] solved this, and Chapman and Cowling [4] copied his method, by rewriting $\mathbf{d}_\alpha$ as

$$
\mathbf{d}_\alpha = \frac{1}{P}(\nabla P_\alpha - \rho_\alpha\nabla P) = \frac{1}{P}\sum_\beta(\delta_{\alpha\beta} - \rho_\alpha)\nabla P_\beta \qquad (54)
$$

and using the partial pressures $P_\alpha = x_\alpha P$ as c independent quantities. This method is equivalent [8] to the independent particle density approach to solving the Boltzmann equation, which is based on the variables introduced in Sec. III, and the solution shows that $\mathbb{D}$ is a symmetric matrix. Here the same rewriting of $\mathbf{d}_\alpha$ is applied to the phenomenological equations and to the equation for the entropy production. From Eqs. (50) and (51) the phenomenological equations are

$$\mathbf{q}_P = -\lambda_P \nabla T - \sum_\alpha \mathbb{D}^T_\alpha \nabla P_\alpha, \tag{55}$$

which uses one of the sum rules (53) and

$$\overline{\mathbf{V}}_\alpha = -\frac{1}{P}\sum_\beta \mathbb{D}_{\alpha\beta}[\nabla P_\beta - \rho_\beta \nabla P] - \mathbb{D}^T_\alpha \nabla \ln T. \tag{56}$$

Since the total pressure should not affect the conductive fluxes, the ∇P term is nonphysical and thus set equal to zero! This is equivalent to assuming $\sum_\beta \mathbb{D}_{\alpha\beta} n_\beta m_\beta$ vanishes, which is equivalent to assuming that the matrix $\mathbb{D}$ is symmetric in regards to the second sum rule of Eq. (53). As a consequence of these forms for the phenomenological equations, the entropy production is

$$\begin{aligned} T\sigma &= -\mathbf{q}_P \cdot \nabla \ln T - \sum_\alpha \overline{\mathbf{V}}_\alpha \cdot \nabla P_\alpha - (\mathsf{P} - P\mathsf{U}) : \nabla \mathbf{v}_0 \\ &= \frac{\lambda_P}{T}(\nabla T)^2 + \frac{1}{P}\sum_{\alpha\beta} \mathbb{D}_{\alpha\beta} \nabla P_\beta \cdot \nabla P_\alpha + 2\sum_\alpha \mathbb{D}^T_\alpha \nabla P_\alpha \cdot \nabla \ln T + 2\eta[\nabla \mathbf{v}_0]^{(2)} : [\nabla \mathbf{v}_0]^{(2)} + \kappa(\nabla \cdot \mathbf{v}_0)^2. \end{aligned} \tag{57}$$

Writing the first three terms as a sum of squares shows that λ_P is positive for a spontaneous process and $\mathbb{D}_{\alpha\beta} - P\mathbb{D}^T_\alpha \mathbb{D}^T_\beta/(\lambda_P T)$ must be a symmetric positive matrix, again for a spontaneous process. The latter is a stronger constraint on the diffusion matrix $\mathbb{D}$ than merely being symmetric, as required to eliminate the ∇P term in Eq. (56). As was mentioned earlier, the symmetry of the diffusion matrix $\mathbb{D}$ was noted [3,4,8] as a result when solving the Boltzmann equation.

Comparison of Eqs. (38) and (56) with the expansion $P_\beta = n_\beta kT$ shows that the diffusion and thermal diffusion coefficients of Secs. III and IV are related by

$$\mathcal{D}_{\alpha\beta} = x_\alpha \mathbb{D}_{\alpha\beta} \quad \text{and} \quad \mathcal{D}^T_\alpha = \mathbb{D}^T_\alpha + \sum_\beta \mathbb{D}_{\alpha\beta} x_\beta. \tag{58}$$

These relationships were also found [8] when solving the Boltzmann equation. Similarly a comparison of Eqs. (37) and (55) shows that the thermal conductivities are related by

$$\lambda_P = \lambda_n - k\sum_\alpha n_\alpha \left(2\mathcal{D}^T_\alpha - \sum_\beta \mathcal{D}_{\beta\alpha}\right) \tag{59}$$

and also confirms the relationship between the thermal diffusion coefficients. This relation also appears in Ref. [8], where λ_P is labeled as λ'. Thus the phenomenological coefficients are the same in that paper as what appears here but the difference arises in the meaning of $\mathbf{q}$, namely, there $\mathbf{q}_{\text{there}} = \mathbf{q}_{\text{here}} + \sum_\alpha n_\alpha T s_\alpha \overline{\mathbf{V}}_\alpha$, corresponding to perspective 2 for the energy flux that is used there, whereas perspective 3 is used here [note the difference in entropy equations (25) and (21)]. See Sec. VII for further discussion of the differences.

V. CONSERVATION EQUATIONS VIA STATISTICAL MECHANICS

A. General comments and notation

The time evolution of the appropriate classical mechanical observables are presented first. Connection with the time evolution of the expectation values of these observables requires a choice of distribution function. The connection with irreversible thermodynamics implies that an equilibrium distribution function should be dominant, but the time dependence also requires a nonequilibrium contribution which is added to the equilibrium distribution function as a perturbation. This reflects the nature of the local equilibrium and the linear (hence relatively small) position gradients that drive a fluid's motion in laminar flow. On the basis that the particles interact with only pair additive forces, only one and two-particle distribution functions are needed with appropriate perturbation functions to account for the nonequilibrium aspects of the fluid motion.

The one-component analog of this presentation was given by Irving and Kirkwood [9] based on the Liouville equation for the time dependence of the N-particle distribution function. An extension to the multicomponent case was attempted by Bennett and Curtiss [15] but emphasizing Bogoliubov's [1] treatment for extending the Boltzmann equation to include density corrections. Their treatment thus assumes that the pair distribution factors into a product of singlets, which is not assumed here. Their treatment is also questionable since they use the relative and mean positions of a pair of particles rather than the relative and center of mass positions when referring to the dynamics of a pair of particles.

Since the objective here is to relate to the irreversible thermodynamic treatment of the fluid, the densities of pair particle observables such as the potential energy are attributed to lie equally divided at the positions of the two particles. In contrast, Irving and Kirkwood [9] place all the density at the center of mass position. The reason for the present choice is that thermodynamics emphasizes the properties (such as energy) of the system as attributed to the individual particles and where they are in the fluid; thus the present assignment of where a potential resides is closer to the thermodynamic assignment.

Individual particles are labeled numerically: $1, 2, \ldots$, or in general by $j, k, \ldots$. A lot of the general formalism needs no further designation as to the nature of the particles. The components are labeled by lower case greek letters, as in the previous sections, and to apply the general formalism to a multicomponent system requires designating a component label to each particle. This is done with a component identifier such as $\mathcal{P}_1^\alpha$, which says that particle 1 is of component α. Only translational degrees of freedom are used in this paper, with $\mathbf{r}_j, \mathbf{p}_j$ labeling the position and momentum of particle j and its mass by m_j, needed because of the different masses of the different components. When it comes to pairs of particles, the total mass of the pair is designated by $M_{jk} = m_j + m_k$ while the relative mass is $\mu_{jk} = m_j m_k / M_{jk}$. Correspondingly, the center of mass position and momentum are denoted by

$$\mathbf{R}_{jk} \equiv \frac{m_j \mathbf{r}_j + m_k \mathbf{r}_k}{M_{jk}}, \quad \mathbf{P}_{jk} \equiv \mathbf{p}_j + \mathbf{p}_k, \tag{60}$$

while the relative position and momentum are denoted by

$$\mathbf{r}_{jk} \equiv \mathbf{r}_j - \mathbf{r}_k, \quad \mathbf{p}_{jk} \equiv \frac{m_k \mathbf{p}_j - m_j \mathbf{p}_k}{M_{jk}}. \tag{61}$$

B. Conservation equations

The mass density $\rho(\mathbf{r})$ at macroscopic position $\mathbf{r}$ is the expectation value

$$\rho(\mathbf{r}) = \left\langle \sum_j m_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle. \tag{62}$$

Its time dependence is obtained using Newton's equations in the form

$$\begin{aligned}\frac{\partial \rho}{\partial t} &= \left\langle \left[\sum_k \left(\frac{\mathbf{p}_k}{m_k} \cdot \frac{\partial}{\partial \mathbf{r}_k} + \mathbf{F}_k \cdot \frac{\partial}{\partial \mathbf{p}_k} \right) \right] \sum_j m_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &= \left\langle \sum_j \mathbf{p}_j \cdot \frac{\partial}{\partial \mathbf{r}_j} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &= -\nabla \cdot \left\langle \sum_j \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \equiv -\nabla \cdot (\rho \mathbf{v}_0),\end{aligned} \tag{63}$$

where $\nabla \equiv \partial / \partial \mathbf{r}$ is the derivative with respect to the macroscopic position and $\mathbf{v}_0(\mathbf{r})$ is identified as the mass average (stream) velocity at $\mathbf{r}$. The time dependence of these variables is not indicated, but understood, while the $\mathbf{r}$ dependence is also often not explicitly indicated. $\mathbf{F}_k$ is the intermolecular force acting on particle k. In the following this is assumed to be from pair particle interactions through the potentials $\varphi_{k\ell}(r_{k\ell})$ between molecules k and ℓ and dependent on the distance $r_{k\ell}$ between the centers of mass of the pair of molecules.

The number density n_α of a typical component α at $\mathbf{r}$ is similarly expressed as

$$n_\alpha(\mathbf{r}) = \left\langle \sum_j \mathcal{P}_j^\alpha \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle, \tag{64}$$

where $\mathcal{P}_j^\alpha$ is the selection operator that selects only those molecules j which are of component α. Its time dependence is obtained in the same way as above, namely,

$$\begin{aligned}\frac{\partial n_\alpha}{\partial t} &= \left\langle \left[\sum_k \left(\frac{\mathbf{p}_k}{m_k} \cdot \frac{\partial}{\partial \mathbf{r}_k} + \mathbf{F}_k \cdot \frac{\partial}{\partial \mathbf{p}_k} \right) \right] \sum_j \mathcal{P}_j^\alpha \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &= \left\langle \sum_j \mathcal{P}_j^\alpha \frac{\mathbf{p}_j}{m_j} \cdot \frac{\partial}{\partial \mathbf{r}_j} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &= -\nabla \cdot \left\langle \sum_j \mathcal{P}_j^\alpha \frac{\mathbf{p}_j}{m_j} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &\equiv -\nabla \cdot (n_\alpha [\mathbf{v}_0 + \overline{\mathbf{V}}_\alpha]),\end{aligned} \tag{65}$$

with the diffusion velocity $\overline{\mathbf{V}}_\alpha$ used to describe the velocity of component α relative to the stream velocity. The above conservation equations are the same as discussed in Sec. II and have the same properties as discussed there while giving the particle interpretation of them.

The rate of change of momentum density $\rho \mathbf{v}_0$ is obtained in a similar manner but now involves a role for the intermolecular forces. The obvious first step is

$$\begin{aligned}\frac{\partial \rho \mathbf{v}_0}{\partial t} &= \left\langle \left[\sum_\ell \frac{\mathbf{p}_\ell}{m_\ell} \cdot \frac{\partial}{\partial \mathbf{r}_\ell} + \sum_{\ell,k} \mathbf{F}_{\ell k} \cdot \frac{\partial}{\partial \mathbf{p}_\ell} \right] \sum_j \mathbf{p}_j \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &= -\nabla \cdot \left\langle \sum_j \frac{\mathbf{p}_j \mathbf{p}_j}{m_j} \delta(\mathbf{r}_j - \mathbf{r}) \right\rangle \\ &\quad + \frac{1}{2} \left\langle \sum_{j\ell} \mathbf{F}_{j\ell} [\delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_\ell - \mathbf{r})] \right\rangle.\end{aligned} \tag{66}$$

This uses the antisymmetry of the force, namely, that the force on particle ℓ due to interaction with particle j is minus the force on particle j due to interaction with particle ℓ, specifically $\mathbf{F}_{\ell j} = -\mathbf{F}_{j\ell}$. The macroscopic position of the pair $j\ell$ is placed at the position of one of the particles, so expanding the difference in delta functions about this reference position gives

$$\begin{aligned}\delta(\mathbf{r}_j - \mathbf{r}) - \delta(\mathbf{r}_\ell - \mathbf{r}) &= \delta(\mathbf{r}_j - \mathbf{r}) - (\mathbf{r}_{\ell j} + \mathbf{r}_j - \mathbf{r}) \\ &= \mathbf{r}_{\ell j} \cdot \nabla \delta(\mathbf{r}_j - \mathbf{r}) + O(\nabla^2),\end{aligned} \tag{67}$$

which leads to the equation for the conservation of momentum,

$$\frac{\partial \rho \mathbf{v}_0}{\partial t} = -\nabla \cdot (\rho \mathbf{v}_0 \mathbf{v}_0 + \mathsf{P}). \tag{68}$$

The momentum flux has been written as the sum over the convective momentum flux $\rho \mathbf{v}_0 \mathbf{v}_0$ and the conductive momentum flux

$$\begin{aligned}\mathsf{P}(\mathbf{r}) \equiv \Bigg\langle & \sum_j \left[\frac{(\mathbf{p}_j - m_j \mathbf{v}_0)(\mathbf{p}_j - m_j \mathbf{v}_0)}{m_j} \right] \delta(\mathbf{r}_j - \mathbf{r}) \\ & + \frac{1}{4} \sum_{j\ell} \mathbf{r}_{j\ell} \mathbf{F}_{j\ell} [\delta(\mathbf{r}_j - \mathbf{r}) + \delta(\mathbf{r}_\ell - \mathbf{r}) + O(\nabla)] \Bigg\rangle,\end{aligned} \tag{69}$$

commonly referred to as the pressure tensor. Note that the potential contribution has been written so as to reflect the symmetry between the two interacting particles. This expression for the pressure tensor, and the heat flux vector to be presented in the following, is an extension of the treatment by Irving and Kirkwood [9] to use the particle positions as where the quantity is placed macroscopically. Details of the separation of the kinetic contribution to the momentum flux into convective and conductive contributions involves adding and subtracting $m_j \mathbf{v}_0$ to each momentum and reorganizing the result, namely,

$$\begin{aligned}\left\langle\sum_j \frac{\mathbf{p}_j\mathbf{p}_j}{m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle &= \left\langle\sum_j \frac{(\mathbf{p}_j-m_j\mathbf{v}_0+m_j\mathbf{v}_0)(\mathbf{p}_j-m_j\mathbf{v}_0+m_j\mathbf{v}_0)}{m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle \\ &= \left\langle\sum_j \frac{(\mathbf{p}_j-m_j\mathbf{v}_0)(\mathbf{p}_j-m_j\mathbf{v}_0)}{m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle + \left\langle\sum_j m_j\mathbf{v}_0\mathbf{v}_0\delta(\mathbf{r}_j-\mathbf{r})\right\rangle \\ &\quad + \left\langle\sum_j [(\mathbf{p}_j-m_j\mathbf{v}_0)\mathbf{v}_0+\mathbf{v}_0(\mathbf{p}_j-m_j\mathbf{v}_0)]\delta(\mathbf{r}_j-\mathbf{r})\right\rangle \end{aligned} \tag{70}$$

with the terms in the last line vanishing on identifying the expectation values. Note that there is no need to introduce component labels in the equation of change for the momentum so the expressions are relatively simple.

Last, there are the expressions for the energy density and its rate of change. The expectation value for the energy is calculated from the expression

$$\rho E(\mathbf{r}) \equiv \rho\left(U+\frac{1}{2}v_0^2\right) = \left\langle\sum_j \frac{\mathbf{p}_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r}) + \frac{1}{4}\sum_{jk}\varphi_{jk}(r_{jk})[\delta(\mathbf{r}_j-\mathbf{r})+\delta(\mathbf{r}_k-\mathbf{r})]\right\rangle. \tag{71}$$

As for the pressure tensor, the potential contribution is written so as to be symmetric in the two interacting particles. Note that different components may generally have different potential expressions, hence the labeling of the potential φ, but all components have the general expression for the energy so no component labeling is required at this point. Also note that the kinetic part of the energy density can be written as

$$\left\langle\sum_j \frac{\mathbf{p}_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle = \left\langle\sum_j \frac{(\mathbf{p}_j-m_j\mathbf{v}_0)^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle + \frac{1}{2}\rho\mathbf{v}_0^2, \tag{72}$$

following the same procedure as used in the expression for the kinetic part of the momentum flux to separate into conductive and convective contributions. The rate of change of energy density is given by

$$\begin{aligned}\frac{\partial\rho E}{\partial\mathbf{r}} &= \left\langle\left[\sum_\ell \frac{\mathbf{p}_\ell}{m_\ell}\cdot\frac{\partial}{\partial\mathbf{r}_\ell} + \sum_{\ell,h}\mathbf{F}_{\ell h}\cdot\frac{\partial}{\partial\mathbf{p}_\ell}\right]\left[\sum_j \frac{\mathbf{p}_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r}) + \frac{1}{4}\sum_{jk}\varphi_{jk}(r_{jk})[\delta(\mathbf{r}_j-\mathbf{r})+\delta(\mathbf{r}_k-\mathbf{r})]\right]\right\rangle \\ &= -\boldsymbol{\nabla}\cdot\left\langle\left[\sum_j \frac{\mathbf{p}_j}{m_j}\frac{\mathbf{p}_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r}) + \frac{1}{4}\sum_{j\ell}\varphi_{j\ell}\left(\frac{\mathbf{p}_j}{m_j}\delta(\mathbf{r}_j-\mathbf{r})+\frac{\mathbf{p}_\ell}{m_\ell}\delta(\mathbf{r}_\ell-\mathbf{r})\right)\right]\right\rangle \\ &\quad + \frac{1}{4}\left\langle\sum_{j\ell}\frac{\partial\varphi_{j\ell}}{\partial\mathbf{r}_{j\ell}}\cdot\left(\frac{\mathbf{p}_j}{m_j}-\frac{\mathbf{p}_\ell}{m_\ell}\right)(\delta(\mathbf{r}_j-\mathbf{r})+\delta(\mathbf{r}_\ell-\mathbf{r}))\right\rangle + \left\langle\sum_{j\ell}\mathbf{F}_{j\ell}\cdot\frac{\mathbf{p}_j}{m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle. \end{aligned} \tag{73}$$

In the divergence term an initial separation into convective and conductive contributions is accomplished by adding and subtracting $\mathbf{v}_0$ from the vectorial velocities while particle symmetrization of the last term and combining it with the second to last term allow that combination to be expanded to first order in $\boldsymbol{\nabla}$, specifically

$$\begin{aligned}\frac{\partial\rho E}{\partial t} &= -\boldsymbol{\nabla}\cdot\left[\rho E\mathbf{v}_0 + \left\langle\sum_j \frac{\mathbf{p}_j-m_j\mathbf{v}_0}{m_j}\frac{p_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r}) + \frac{1}{4}\sum_{j\ell}\varphi_{j\ell}\left(\frac{\mathbf{p}_j-m_j\mathbf{v}_0}{m_j}\delta(\mathbf{r}_j-\mathbf{r})+\frac{\mathbf{p}_\ell-m_\ell\mathbf{v}_0}{m_\ell}\delta(\mathbf{r}_\ell-\mathbf{r})\right)\right\rangle\right] \\ &\quad - \boldsymbol{\nabla}\cdot\left\langle\frac{1}{4}\sum_{j\ell}\mathbf{r}_{j\ell}\mathbf{F}_{j\ell}\cdot\left(\frac{\mathbf{p}_j}{m_j}\delta(\mathbf{r}_j-\mathbf{r})+\frac{\mathbf{p}_\ell}{m_\ell}\delta(\mathbf{r}_\ell-\mathbf{r})\right)\right\rangle. \end{aligned} \tag{74}$$

This shows that the equation of change for the energy is in the form of a conservation equation.

The purely kinetic energy term in the expression for the energy flux can be rewritten

$$\begin{aligned}\left\langle\sum_j \frac{\mathbf{p}_j-m_j\mathbf{v}_0}{m_j}\frac{p_j^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle &= \left\langle\sum_j \frac{\mathbf{p}_j-m_j\mathbf{v}_0}{m_j}\left[\frac{(\mathbf{p}_j-m_j\mathbf{v}_0)^2}{2m_j}+(\mathbf{p}_j-m_j\mathbf{v}_0)\cdot\mathbf{v}_0+\frac{1}{2}m_j\mathbf{v}_0^2\right]\delta(\mathbf{r}_j-\mathbf{r})\right\rangle \\ &= \left\langle\sum_j \frac{\mathbf{p}_j-m_j\mathbf{v}_0}{m_j}\frac{(\mathbf{p}_j-m_j\mathbf{v}_0)^2}{2m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle + \left\langle\sum_j \frac{(\mathbf{p}_j-m_j\mathbf{v}_0)(\mathbf{p}_j-m_j\mathbf{v}_0)}{m_j}\delta(\mathbf{r}_j-\mathbf{r})\right\rangle\cdot\mathbf{v}_0, \end{aligned} \tag{75}$$

with the $\mathbf{v}_0^2$ term vanishing on taking expectation values since it has the structure

$$\frac{1}{2}\mathbf{v}_0^2\sum_j\langle(\mathbf{p}_j-m_j\mathbf{v}_0)\delta(\mathbf{r}_j-\mathbf{r})\rangle=\frac{1}{2}\mathbf{v}_0^2[\rho\mathbf{v}_0-\rho\mathbf{v}_0]=0 \tag{76}$$

according to Eqs. (62) and (64) while the term linear in $\mathbf{v}_0$ is recognized as the kinetic contribution to the pressure tensor times the stream velocity, $\mathsf{P}_K\cdot\mathbf{v}_0$ [see Eq. (69)]. The remaining term in Eq. (75) is cubic in $\mathbf{p}_j-m_j\mathbf{v}_0$ and vanishes in thermal equilibrium (a Maxwellian in how the velocity differs from the stream velocity); thus it represents a nonequilibrium effect.

So far, no detail of the form of the distribution functions used to evaluate the expectation values has been made since the previously mentioned expectation values are all assigned by definition. But now some knowledge of their form is needed. Essentially the fluid dynamic system is assumed to be in local equilibrium with small deviations associated with the gradients of the densities of mass, temperature, stream velocity, and the component densities. For the energy equation, and also the pressure tensor, only one- and two-particle properties are involved. Thus it is the singlet and pair distribution functions that are needed. At equilibrium, these are well known, being the Maxwellian for a singlet and the product of Maxwellians times the radial distribution function for a pair, specifically

$$f_1^{(1,0)\alpha}(\mathbf{r}_1,\mathbf{p}_1)=\frac{n_\alpha\mathcal{P}_1^\alpha}{(2\pi m_1kT)^{3/2}}e^{-(\mathbf{p}_1-m_1\mathbf{v}_0)^2/2m_1kT} \tag{77}$$

and

$$f_{12}^{(2,0)\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2)=f_1^{(1,0)\alpha}f_2^{(1,0)\beta}g_{12}(r_{12},T), \tag{78}$$

where the component densities, temperature, and stream velocity are position dependent at the corresponding particle position and also assumed time dependent. Technically, the radial distribution function $g(r)$ should be the sum of two terms, each localized at the position of one of the particles with a factor of 1/2. The diffusion velocities vanish at local equilibrium so there needs to be (small) nonequilibrium perturbation terms added to these distribution functions, namely,

$$f_1^{(1)\alpha}=f_1^{(1,0)\alpha}\big[1+\phi_1^\alpha(\mathbf{r}_1,\mathbf{p}_1)\big] \tag{79}$$

and

$$f_{12}^{(2)\alpha\beta}=f_{12}^{(2,0)\alpha\beta}\big[1+\phi_1^\alpha+\phi_2^\beta+\Phi_{12}^{\alpha\beta}(\mathbf{r}_1\cdots\mathbf{p}_2)\big]. \tag{80}$$

Note that the dependence on the temperature, stream velocity and component densities, and/or their gradients are not explicitly displayed in these perturbation terms. These expressions reflect the form of the distribution functions, and only those aspects of these quantities needed for identifying the various contributions to the energy flux are discussed here. Specifically no attempt is made to formulate a theory for the calculation of the perturbations. In this regard, for an ideal gas only the singlet is needed and the perturbation can be calculated by an appropriate solution of the Boltzmann equation [3–5,8]. The author knows of no calculation of Φ.

To connect the distribution functions with the expectation formalism used to derive the conservation equations, the phase space functions are expressed in the expectation formalism as

$$f_1^{(1)\alpha}(\mathbf{r}_1,\mathbf{p}_1)\equiv\left\langle\sum_j\mathcal{P}_j^\alpha\delta(\mathbf{r}_1-\mathbf{r}_j)\delta(\mathbf{p}_1-\mathbf{p}_j)\right\rangle \tag{81}$$

and

$$\begin{aligned}f_{12}^{(2)\alpha\beta}(\mathbf{r}_1\mathbf{r}_2\mathbf{p}_1\mathbf{p}_2)\equiv\Bigg\langle\sum_{j\ell}&\mathcal{P}_j^\alpha\mathcal{P}_\ell^\beta\delta(\mathbf{r}_1-\mathbf{r}_j)\delta(\mathbf{p}_1-\mathbf{p}_j)\\&\times\delta(\mathbf{r}_2-\mathbf{r}_\ell)\delta(\mathbf{p}_2-\mathbf{p}_\ell)\Bigg\rangle.\end{aligned} \tag{82}$$

Note that the sums over particles of each component are reflected in the densities appearing in the $f^{(1,0)}$'s of Eq. (77).

Since the diffusion velocities are nonequilibrium one-particle properties they must be determined by the perturbations ϕ_j^α; specifically this perturbation must contain a term that is "equivalent" to $[(\mathbf{p}_j-m_j\mathbf{v}_0)/kT]\cdot\overline{\mathbf{V}}_\alpha$ since the expectation value from Eq. (68) is

$$\begin{aligned}n_\alpha\overline{\mathbf{V}}_\alpha&=\left\langle\sum_j\mathcal{P}_j^\alpha\left(\frac{\mathbf{p}_j}{m_j}-\mathbf{v}_0\right)\delta(\mathbf{r}_j-\mathbf{r})\right\rangle\\&=\iint\mathcal{P}_1^\alpha\left(\frac{\mathbf{p}_1}{m_1}-\mathbf{v}_0\right)\delta(\mathbf{r}_1-\mathbf{r})f_1^{(0)\alpha}[1+\phi_1^\alpha]d\mathbf{r}_1d\mathbf{p}_1\\&=\iint\mathcal{P}_1^\alpha\left(\frac{\mathbf{p}_1}{m_1}-\mathbf{v}_0\right)\delta(\mathbf{r}_1-\mathbf{r})f_1^{(0)\alpha}\\&\qquad\times\frac{\mathbf{p}_1-m_1\mathbf{v}_0}{kT}\cdot\overline{\mathbf{V}}_\alpha d\mathbf{r}_1d\mathbf{p}_1=n_\alpha\overline{\mathbf{V}}_\alpha.\end{aligned} \tag{83}$$

The sum over j is inappropriate when using the distribution function since the density appears explicitly as n_α in the distribution function so the count over the number of particles of component α is already taken into account. Note that this does not evaluate the perturbation, or $\overline{\mathbf{V}}_\alpha$, but only indicates what term is needed in order to make the perturbation consistent with the presence of a finite diffusion velocity.

In the actual calculation of the diffusion velocities the perturbations do not contain the diffusion velocities themselves but rather have terms proportional to the chemical potential gradients and the temperature gradient which contribute to the diffusion velocities. The above "equivalence" shows that such contributions are linear in the respective $(\mathbf{p}_j-m_j\mathbf{v}_0)/kT$ multiplying the appropriate gradient. As is now to be discussed is the separation of the conductive energy flux into that carried by the diffusion fluxes and by the heat flux, these must be independent and thus the part of the perturbations that contribute to the heat flux must be appropriately orthogonal to the part that contributes to the diffusion fluxes. This is what is done when solving the Boltzmann equation for the transport coefficients but is only hinted at in this presentation.

But the calculation of the expectation value of the energy flux is affected by the presence of this perturbation of the local equilibrium distribution function. Specifically, the cubic term in the kinetic energy flux, Eq. (75), has the contribution to its α component

$$\iint \mathcal{P}_1^{\alpha} \frac{(\mathbf{p}_1 - m_1\mathbf{v}_0)(\mathbf{p}_1 - m_1\mathbf{v}_0)^2}{2m_1^2}\delta(\mathbf{r}_1 - \mathbf{r}) f_1^{(0)\alpha}\left[1 + \frac{\mathbf{p}_1 - m_1\mathbf{v}_0}{kT}\cdot\overline{\mathbf{V}}_\alpha\right] d\mathbf{p}_1 d\mathbf{r}_1 = \frac{5}{2} n_\alpha kT \overline{\mathbf{V}}_\alpha. \tag{84}$$

It is noted that this flux is proportional to the component's kinetic part of the enthalpy. This term should be subtracted from the cubic term before associating the remainder with the kinetic heat flux $\mathbf{q}_K$. Collecting together the various contributions from the purely kinetic energy flux gives

$$\begin{aligned}\left\langle \sum_j \frac{\mathbf{p}_j - m_j\mathbf{v}_0}{m_j}\frac{p_j^2}{2m_j}\delta(\mathbf{r}_j - \mathbf{r})\right\rangle &= \left\langle \sum_j \frac{\mathbf{p}_j - m_j\mathbf{v}_0}{m_j}\left[\frac{(\mathbf{p}_j - m_j\mathbf{v}_0)^2}{2m_j} - \frac{5}{2}kT\right]\delta(\mathbf{r}_j - \mathbf{r})\right\rangle + \sum_\alpha \frac{5}{2}n_\alpha kT\overline{\mathbf{V}}_\alpha + \mathsf{P}_K\cdot\mathbf{v}_0 \\ &= \mathbf{q}_K + \sum_\alpha \frac{5}{2}n_\alpha kT\overline{\mathbf{V}}_\alpha + \mathsf{P}_K\cdot\mathbf{v}_0. \end{aligned} \tag{85}$$

The first term can be recognized as the typical kinetic contribution to the heat flux $\mathbf{q}_K$ when calculating the thermal conductivity from the Boltzmann equation [3–5].

The third term in the expression for the energy flux in Eq. (74) is recognized as the potential energy flux. Use of the above discussed contribution to the one-particle perturbation evaluates the momentum dependence of the expression for the potential energy flux, leaving the remaining position dependence to be evaluated to its local equilibrium value as long as that exists. For particle j,

$$\overline{\varphi}_{j\ell} = \frac{1}{2}\iint \varphi_{j\ell}(r_{j\ell})g_{j\ell}(r_{j\ell})\delta(\mathbf{r}_j - \mathbf{r})d\mathbf{r}_j d\mathbf{r}_\ell \tag{86}$$

is its mean particle potential energy due to its interaction with particle ℓ with the 1/2 associated with giving particle j half of the potential energy, and positioned at the position of particle j. Note that the potential and radial distribution function are particle labeled since these functions are dependent on the component labels of the particles which are assigned to the particle label. The contribution to the energy flux from such terms is the sum over all pairs of particles,

$$\sum_\alpha n_\alpha\overline{\varphi}_\alpha\overline{\mathbf{V}}_\alpha = \sum_\alpha\sum_{j\ell}\mathcal{P}_j^\alpha\overline{\varphi}_{j\ell}\overline{\mathbf{V}}_\alpha. \tag{87}$$

Note that the sum over ℓ includes all particles of all components.

The remaining part of the third term in Eq. (74) contributes to the heat flux. This involves the correlation of position and momentum so is determined by the pair perturbation Φ. But the form for the dynamical function for this must not contribute to the particle flux contributions, Eq. (87), since these are already accounted for. This can be ensured by subtracting out the mean potential energy, in a form equivalent to what is done for the kinetic energy. But this is complicated by the varied behavior of $\overline{\varphi}$ associated with the different components. Thus this contribution to the heat flux is identified as

$$\mathbf{q}_{\varphi 1} \equiv \frac{1}{2}\left\langle \sum_\alpha\sum_{j\ell}\mathcal{P}_j^\alpha[\varphi_{j\ell} - \overline{\varphi}_{j\ell}]\left(\frac{\mathbf{p}_j}{m_j} - \mathbf{v}_0\right)\delta(\mathbf{r}_j - \mathbf{r})\right\rangle. \tag{88}$$

Finally there is the second line in Eq. (74). It is first noticed that $\mathbf{v}_0$ should be subtracted and added to each momentum vector with the separate $\mathbf{v}_0$ term immediately recognized as involving the potential part of the pressure tensor, Eq. (69), so that contribution to the energy flux is $\mathsf{P}_\varphi\cdot\mathbf{v}_0$. The remainder involves the combination $\mathbf{p}_j - m_j\mathbf{v}_0$ type of terms, which has contributions proportional to the diffusion velocities, typically for component α through a ϕ perturbation according to the following:

$$\begin{aligned}&\frac{1}{2}\sum_{\alpha\beta}\mathcal{P}_1^\alpha\mathcal{P}_2^\beta\iiiint \mathbf{r}_{12}\mathbf{F}_{12}\cdot\frac{\mathbf{p}_1 - m_1\mathbf{v}_0}{m_1}\delta(\mathbf{r}_1 - \mathbf{r})f_{12}^{(2,0)\alpha\beta}\frac{\mathbf{p}_1 - m_1\mathbf{v}_0}{kT}\cdot\overline{\mathbf{V}}_\alpha d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 \\ &\quad = \frac{1}{2}\sum_{\alpha\beta}\mathcal{P}_1^\alpha\mathcal{P}_2^\beta n_\alpha n_\beta\iint \mathbf{r}_{12}\mathbf{F}_{12}g_{\alpha\beta}(r_{12})\delta(\mathbf{r}_1 - \mathbf{r})d\mathbf{r}_1 d\mathbf{r}_2\cdot\overline{\mathbf{V}}_\alpha = \sum_\alpha P_\varphi^\alpha\overline{\mathbf{V}}_\alpha\end{aligned} \tag{89}$$

with P_φ^α the potential contribution to the pressure associated with component α, the equilibrium part of the α component part of the pressure tensor. Subtracting the above terms from the energy flux given by the second line of Eq. (74), it is recognized that there is also a contribution to the heat flux given by

$$\mathbf{q}_{\varphi 2} = \frac{1}{2}\left\langle \sum_\alpha\sum_{j\ell}\mathcal{P}_j^\alpha\mathbf{r}_{j\ell}\mathbf{F}_{j\ell}\cdot\left(\frac{\mathbf{p}_j - m_j\mathbf{v}_0}{m_j} - \overline{\mathbf{V}}_\alpha\right)\delta(\mathbf{r}_j - \mathbf{r})\right\rangle. \tag{90}$$

Combining together the various contributions to the energy flux of Eq. (74), the total energy flux is

$$\rho E\mathbf{v}_0 + \mathsf{P}\cdot\mathbf{v}_0 + \sum_\alpha \left[\frac{5}{2}n_\alpha kT + n_\alpha\overline{\varphi}_\alpha + P_\varphi^\alpha\right]\overline{\mathbf{V}}_\alpha + \mathbf{q}_K$$
$$+\mathbf{q}_{\varphi 1} + \mathbf{q}_{\varphi 2} = \rho E\mathbf{v}_0 + \mathsf{P}\cdot\mathbf{v}_0 + \sum_\alpha h_\alpha\overline{\mathbf{V}}_\alpha + \mathbf{q}, \quad (91)$$

where the various heat flux contributions have been combined into $\mathbf{q}$ while the partial molar enthalpy h_α is the sum of the (per particle) kinetic contributions $5kT/2$ (associated with the kinetic internal energy $3kT/2$ and kinetic pressure kT) plus the potential internal energy $\overline{\varphi}_\alpha$ and the potential contribution to the partial pressure P_φ^α. This is perspective 3 in Sec. II, Eq. (17), for the energy flux $\mathbf{J}_E$.

VI. COMPONENT MOMENTUM EVOLUTION VIA THE BOLTZMANN EQUATION

This discussion is based on the Boltzmann equation keeping only those terms which are considered as representing the meaning and evolution of the mean momentum of the individual components. Explicitly, the local equilibrium momentum distribution function for component α describes the probability per unit volume of a particle's momentum. It is written here as

$$f_1^{(1,0)\alpha} = \frac{n_\alpha\mathcal{P}_1^\alpha}{(2\pi m_1 kT)^{3/2}}e^{(\mathbf{p}_1 - m_1\mathbf{v}_\alpha)^2/2m_1kT} \quad (92)$$

rather than Eq. (77), having the component velocity $\mathbf{v}_\alpha$ rather than the stream velocity $\mathbf{v}_0$. In particular the momentum density of component α is

$$\rho_\alpha\mathbf{v}_\alpha \equiv n_\alpha m_\alpha\mathbf{v}_\alpha = \int \mathbf{p}_1 f_1^{(1,0)\alpha}d\mathbf{p}_1. \quad (93)$$

This is the interpretation that this paper uses as to the meaning that each component has its own mean velocity, as used in Refs. [6,7] in the treatment of extended irreversible thermodynamics. It implies that each component separately reaches a local thermodynamic equilibrium; but if that was the case, should each component have its own particular temperature as well? The object of this section is to argue that this is inconsistent with local equilibrium, specifically that different components collide and thus transfer momentum and energy between the different components, with the consequence that, since collisions dominate the approach to thermal equilibrium, there is only one local (stream) velocity and temperature for a gas that is in thermal equilibrium. Nonequilibrium properties driven by inhomogeneities [specifically by the gradients in the (local) thermodynamic variables] arise in fluid flow and perturb the component velocities as well as their densities and energies from their local equilibrium values and it is the competition between the inhomogeneities and the collisions that is reflected in the equations of fluid flow. It is not the purpose of this section to discuss the latter (aspects of that are addressed in the previous sections of this paper), but the last comment was added to emphasize the perspective of the difference played by the collisions and the inhomogeneities.

The Boltzmann equation describes the evolution of the one-particle distribution function due to free motion and binary collisions. Explicitly this is written for classical mechanics as

$$P_j^\alpha\left[\frac{\partial f_j}{\partial t} + \frac{\mathbf{p}_j}{m_j}\cdot\nabla f_j\right]$$
$$= \sum_\beta P_j^\alpha P_k^\beta \iiint [f_j'f_k' - f_jf_k]\frac{p_{jk}}{\mu_{jk}}bdbd\epsilon d\mathbf{p}_k, \quad (94)$$

where collisions of particle j of component α with a typical particle k of component β, for all β, including $\beta = \alpha$, are included. A prime designates the incoming momenta $\mathbf{p}_j'$, $\mathbf{p}_k'$ for a binary collision, while $\mathbf{p}_j$, $\mathbf{p}_k$ are the corresponding outgoing momenta. See one of the classic references [3–5] for more information on the meaning and structure of the Boltzmann equation. b is the impact parameter (the miss distance in relative coordinates between the centers of mass of the particles if there was no interaction between the particles) and ϵ is the angle of orientation of $\mathbf{b}$ around the outgoing relative momentum $\mathbf{p}_{jk}$. $\mathbf{b}$ (as a two-dimensional vector) lies in the plane perpendicular to $\mathbf{p}_{jk}$. The relative and center of mass momenta are related to the individual particle momenta by

$$\mathbf{p}_{jk} = \frac{m_k\mathbf{p}_j - m_j\mathbf{p}_k}{M_{jk}} \quad \text{and} \quad \mathbf{P}_{jk} = \mathbf{p}_j + \mathbf{p}_k, \quad (95)$$

where $M_{jk} = m_j + m_k$ is the total mass of the pair of particles while $\mu_{jk} = m_jm_k/M_{jk}$ is the reduced mass of the pair. It may also be of use to note that, due to conservation of angular momentum, the collision occurs in the plane determined by $\mathbf{p}_{jk}$ and $\mathbf{b}$.

On multiplying Eq. (94) by $\mathbf{p}_j$ and integrating over $\mathbf{p}_j$, the equation of change for the momentum density of α can be written as

$$\frac{\partial\rho_\alpha\mathbf{v}_\alpha}{\partial t} + \nabla\cdot(n_\alpha kT\mathsf{U} + \rho_\alpha\mathbf{v}_\alpha\mathbf{v}_\alpha) = \sum_\beta \mathbf{C}_{\alpha\beta}. \quad (96)$$

The free motion contribution is analogous to the free motion part of Eqs. (82)–(86) and using Eq. (92) while the collision integral $\mathbf{C}_{\alpha\beta}$ describes the transfer of momentum between components. In detail the collision integral for components α and β is

$$\mathbf{C}_{\alpha\beta} = P_j^\alpha P_k^\beta \iiiint \mathbf{p}_j[f_j'f_k' - f_jf_k]\frac{p_{jk}}{\mu_{jk}}bdbd\epsilon d\mathbf{p}_kd\mathbf{p}_j \quad = P_j^\alpha P_k^\beta \iiiint \frac{1}{2}(\mathbf{p}_j - \mathbf{p}_j')[f_j'f_k' - f_jf_k]\frac{p_{jk}}{\mu_{jk}}bdbd\epsilon d\mathbf{p}_kd\mathbf{p}_j,$$

where the second form has made use of the collision inversion symmetry of the Boltzmann collision kernel (which is due to the time reversal and spatial inversion symmetry of classical mechanics) which interchanges the incoming and outgoing momenta. Since the center of mass momentum $\mathbf{P}_{jk}$ is unaffected by the collision it is appropriate to change the momentum integrals into those for the center of mass and relative motion. This involves the relation for the differentials $d\mathbf{p}_kd\mathbf{p}_j = d\mathbf{P}_{jk}d\mathbf{p}_{jk}$ and for the energy factors that appear in the exponents in the distribution functions:

$$\frac{(\mathbf{p}_j - m_j\mathbf{v}_\alpha)^2}{2m_j} + \frac{(\mathbf{p}_k - m_k\mathbf{v}_\beta)^2}{2m_k} = \frac{(\mathbf{P}_{jk} - m_j\mathbf{v}_\alpha - m_k\mathbf{v}_\beta)^2}{2M_{jk}} + \frac{(\mathbf{p}_{jk} - \mu_{jk}[\mathbf{v}_\alpha - \mathbf{v}_\beta])^2}{2\mu_{jk}}. \tag{97}$$

The inversion of the momentum relations (95) implies $\mathbf{p}_j = \mathbf{p}_{jk} + (m_j/M_{jk})\mathbf{P}_{jk}$ and since $\mathbf{P}'_{jk} = \mathbf{P}_{jk}$ by momentum conservation, the factor $\mathbf{p}_j - \mathbf{p}'_j$ reduces to $\mathbf{p}_{jk} - \mathbf{p}'_{jk}$. Thus $\mathbf{C}_{\alpha\beta}$ becomes

$$\begin{aligned}\mathbf{C}_{\alpha\beta} = {} & P_j^\alpha P_k^\beta \frac{n_\alpha n_\beta}{2(2\pi m_j kT)^{3/2}(2\pi m_k kT)^{3/2}} \iiint (\mathbf{p}_{jk} - \mathbf{p}'_{jk})[e^{-(\mathbf{p}'_{jk}-\mathbf{p}_{\alpha\beta})^2/2\mu_{jk}kT} - e^{-(\mathbf{p}_{jk}-\mathbf{p}_{\alpha\beta})^2/2\mu_{jk}kT}] \\ & \times \frac{p_{jk}}{\mu_{jk}} b\,db\,d\epsilon\,d\mathbf{p}_{jk} \int e^{-(\mathbf{P}_{jk} - m_j\mathbf{v}_\alpha - m_k\mathbf{v}_\beta)^2/2M_{jk}kT} d\mathbf{P}_{jk},\end{aligned} \tag{98}$$

where $\mathbf{p}_{\alpha\beta} \equiv \mu_{\alpha\beta}(\mathbf{v}_\alpha - \mathbf{v}_\beta)$ is introduced as a convenient notation. The separation of the center of mass integral from the others is done since it is the same for the incoming and outgoing factors in the collision integral and thus factors out from the other terms. Its integral is evaluated as $(2\pi M_{jk}kT)^{3/2}$.

A more elaborate estimation of this integral can be made but for simplicity only the small mean velocity difference case is considered here, that is, to terms linear in $\mathbf{p}_{\alpha\beta}$. Thus to first order in $\mathbf{p}_{\alpha\beta}$ and using the conservation of energy in a collision, equivalently that $(\mathbf{p}'_{jk})^2 = (\mathbf{p}_{jk})^2$, the momentum transfer collision integral simplifies to

$$\mathbf{C}_{\alpha\beta} = P_j^\alpha P_k^\beta \frac{n_\alpha n_\beta}{2(2\pi \mu_{jk} kT)^{3/2}} \left[\iiint \frac{(\mathbf{p}_{jk} - \mathbf{p}'_{jk})(\mathbf{p}'_{jk} - \mathbf{p}_{jk})}{\mu_{jk}kT} e^{-(\mathbf{p}_{jk})^2/2\mu_{jk}kT} \frac{p_{jk}}{\mu_{jk}} b\,db\,d\epsilon\,d\mathbf{p}_{jk}\right] \cdot \mathbf{p}_{\alpha\beta}. \tag{99}$$

By spherical symmetry, since the integral now involves no vector that is not integrated over, the integral must be rotationally invariant and thus proportional to the rotational identity U. This allows $\mathbf{C}_{\alpha\beta}$ to be written as

$$\mathbf{C}_{\alpha\beta} = -\mathbf{p}_{\alpha\beta} P_j^\alpha P_k^\beta \frac{n_\alpha n_\beta}{6\mu_{jk}^2 kT(2\pi\mu_{jk}kT)^{3/2}} \iiint (\mathbf{p}'_{jk} - \mathbf{p}_{jk})^2 e^{-(\mathbf{p}_{jk})^2/2\mu_{jk}kT} p_{jk} b\,db\,d\epsilon\,d\mathbf{p}_{jk} \equiv -\mathbf{p}_{\alpha\beta} C_{\alpha\beta}. \tag{100}$$

Note the minus sign and the introduction of the positive scalar collision integral which is also symmetric to the exchange of α and β. Now the square of the momentum difference is

$$(\mathbf{p}'_{jk} - \mathbf{p}_{jk})^2 = 2p_{jk}^2(1 - \cos\chi), \tag{101}$$

where χ is the angle of deflection (the angle between incoming and outgoing relative momenta) and the conservation of energy has been used to get only one relative momentum magnitude. The integral over the impact parameter b can be replaced by an integral over χ, specifically $b\,db = \sigma \sin\chi\, d\chi$, where σ is the differential cross section. This simplifies the collision integral to

$$\begin{aligned}C_{\alpha\beta} = {} & P_j^\alpha P_k^\beta \frac{n_\alpha n_\beta}{3\mu_{jk}^2 kT(2\pi\mu_{jk}kT)^{3/2}} \iiint \mathbf{p}_{jk}^2(1 - \cos\chi) \\ & \times e^{-(\mathbf{p}_{jk})^2/2\mu_{jk}kT} p_{jk}\sigma \sin\chi\, d\chi\, d\epsilon\, d\mathbf{p}_{jk}.\end{aligned} \tag{102}$$

This is valid for any interaction potential and has used only the approximation that this is first order in $\mathbf{p}_{\alpha\beta}$ as well as the interpretation that it is the distribution function of Eq. (92) that represents the assumption of having local component momentum densities.

The hard sphere is the simplest potential to use to evaluate the collision dynamics since its differential cross section is $\sigma = a_{\alpha\beta}^2/4$, where $a_{\alpha\beta}$ is the mean diameter of the pair of colliding particles, equivalently the sum of their radii, and the total cross section is $\pi a_{\alpha\beta}^2$. Analytically evaluating the fivefold integral (there are two angles and a magnitude to integrate for the vector $\mathbf{p}_{jk}$), the collision integral reduces to

$$C_{\alpha\beta} = \frac{4n_\alpha n_\beta \pi a_{\alpha\beta}^2}{3}\sqrt{\frac{8kT}{\pi\mu_{\alpha\beta}}}. \tag{103}$$

This can be recognized as 4/3 times the collision rate between particles α and β.

Dropping the gradient terms in Eq. (96) and recognizing that ρ_α changes only due to gradient terms [compare Eq. (68)], the rate of change of $\mathbf{v}_\alpha$ is determined by

$$\rho_\alpha \frac{\partial \mathbf{v}_\alpha}{\partial t} = \sum_\beta \mathbf{C}_{\alpha\beta} = -\sum_\beta \mathbf{p}_{\alpha\beta} C_{\alpha\beta}. \tag{104}$$

The analogous equation for component β is

$$\rho_\beta \frac{\partial \mathbf{v}_\beta}{\partial t} = -\sum_\gamma \mathbf{p}_{\beta\gamma} C_{\beta\gamma} = \sum_\gamma \mathbf{p}_{\gamma\beta} C_{\gamma\beta}. \tag{105}$$

The last term reflects the component antisymmetry of $\mathbf{p}_{\gamma\beta}$ and symmetry of $\mathbf{C}_{\gamma\beta}$. Rather than attempt to organize all the gains and losses of component mean velocities, consider a binary mixture having only components α and β. Then the rate of change of the difference in mean component velocities is

$$\begin{aligned}\frac{\partial(\mathbf{v}_\alpha - \mathbf{v}_\beta)}{\partial t} & = -\left[\frac{1}{\rho_\alpha} + \frac{1}{\rho_\beta}\right]\mathbf{p}_{\alpha\beta} C_{\alpha\beta} \\ & = -\frac{4(\rho_\alpha + \rho_\beta)\pi a_{\alpha\beta}^2}{3M_{\alpha\beta}}\sqrt{\frac{8kT}{\pi\mu_{\alpha\beta}}}(\mathbf{v}_\alpha - \mathbf{v}_\beta) \\ & \equiv -\frac{(\mathbf{v}_\alpha - \mathbf{v}_\beta)}{\tau_{\alpha\beta}}.\end{aligned} \tag{106}$$

Thus the difference in mean velocity components decays with a rate constant $1/\tau_{\alpha\beta}$ determined as the product of an effective density $(\rho_\alpha + \rho_\beta)/M_{\alpha\beta}$, a total cross section $\pi a_{\alpha\beta}^2$, and the mean relative speed of the colliding pair of particles. This rate constant is $4/3$ times the collision rate of α with β except for a difference in which density is relevant for which equilibration process.

Since collisions determine whether a local thermodynamic equilibrium is obtained, part of this local equilibrium state is the equality of all component mean velocities, specifically then at the local stream velocity.

VII. DISCUSSION

It has been emphasized how important the different distance scales (equivalently time scales since these are related by the mean particle speed) are in describing the dynamics of a fluid. Specifically the collision rate is much faster than the evolution of the fluid flow which is driven by the gradients of the thermodynamic variables that parametrize the local equilibrium state of the fluid. It is the fast collision rate that is responsible for the local thermodynamic equilibrium. This analysis was first emphasized by Bogoliubov [1] but does not appear to be generally appreciated. In particular, many authors (e.g., Refs. [6,7]) consider that the mean component velocities should play a detailed role in fluid dynamics, but these are all equilibrated to the stream velocity by collisions so it is argued here that only the stream velocity is of importance in the analysis of the fluid flow regime. Section VI gives an explicit derivation of how this equilibration occurs. This is also consistent with the notion that only collision invariants are of importance in describing the state of local thermodynamic equilibrium. Note that it is these same variables that are conserved for fluid motion as a whole (ignoring interactions with any surroundings) and used as the base for the equations of fluid dynamics.

The conservation equations for mass, momentum, energy, and components have been reviewed with an examination of what contributes to the fluxes of these conserved quantities. It is only the form of the energy flux that is questioned with the notion that energy is mechanically carried by the fluxes of mass, momentum, and components as well as transferred by a heat flux. This is where the difference between heat and work comes in, with the latter associated with mechanical motion while the former is associated with nonmechanical energy changes, usually attributed to changes in the probabilities of the different states of the particles making up the system. Mass and momentum are immediately identified as mechanical quantities, but changing the number of particles of a component is also a mechanical change, often thought of as a chemical change, but still of a mechanical nature. Unfortunately the energy carried by component fluxes is usually not identified as such but considered as a form of heat. This appears inconsistent in concept. From an irreversible thermodynamic viewpoint the amount of energy carried by a component flux should be decided by a thermodynamic argument. A thermodynamic argument used by the author in a previous paper gave this as the chemical potential. It was the object of verifying this that the general statistical mechanical formulation of a multicomponent mixture was examined, as done in Sec. V. This shows that the appropriate quantity is the partial molar enthalpy rather than the chemical potential. On rethinking the thermodynamic situation, the notion that treating the fluxes from one fluid element to another as being reversible processes gives this result. It is believed that this thermodynamic rationale is true and has not been explicitly stated previously. The consequences of the differing thermodynamic arguments have been contrasted for the form of the equation for the entropy density, Sec. II B. If one looks at the solution of the Boltzmann equation for the heat flux as carried out in the classic literature [3–5], one of the terms is the component sum of $5kT/2$ times the particle flux. This factor is there identified as the enthalpy and consequently used in engineering applications [16] and often referred to as enthalpy diffusion. Its importance in contributing to the energy flux has recently been emphasized [17]. The above arguments imply that this quantity is mislabeled and should be treated as a form of work flux rather than as part of the heat flux. It is also acknowledged that if the equations of change for the independent component fluxes are considered, these lead to an explicit enthalpy diffusion contribution to the energy flux as clearly done by Ramshaw [6], but these equations are an unnecessary detail for describing the subsequent evolution of the fluid.

The gradients of the chemical potential are used for the general treatment of diffusion but for an ideal gas mixture these are specialized to the concentration gradients and Fick's law in Sec. III, and to the $\mathbf{d}_\alpha$ involving mole fraction and/or partial pressure gradients in Sec. IV. These give rise to different sets of diffusion constants with different symmetry properties but are shown to be transformable into each other, respecting their different definitions and manner of application.

The data that support the findings of this study are available within the article and the references.

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