PHYSICAL REVIEW E VOLUME 50, NUMBER 6 DECEMBER 1994

Quantum kinetic theory of irreversible thermodynamics: Low-density gases

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(Received 23 February 1994; revised manuscript received 1 July 1994)

A quantum theory of irreversible thermodynamics is developed for a system of dilute quantum particles in terms of an irreversible kinetic equation for the density matrix, which is assumed to have a structure similar to the Boltzmann-Nordheim-Uehling-Uhlenbeck equation. The local balance equations for conserved variables (mass, momentum, and energy) and the evolution equations for nonconserved variables are derived directly from the density matrix. They have the same mathematical structures as the corresponding classical equations. It is shown that the local entropy differential consists of a compensation differential and an energy dissipation term that depends on the path of irreversible processes in the macroscopic variable space, as in the case of the corresponding classical system. The statistical definition of temperature for nonequilibrium systems and its operational meaning are discussed in detail. The extended hydrodynamic equations are presented, which attend the theory of irreversible processes and are consistent with the H theorem. Application of the theory is briefly discussed.

PACS number(s): 05.30.−d, 05.20.Dd, 05.70.Ln

I. INTRODUCTION

The theories of transport phenomena in macroscopic systems of gases and liquids are mostly formulated in the phase space within the framework of classical mechanics, but transport phenomena in semiconductors and small quantum devices at low temperatures usually require quantum mechanical treatments. When faced with such a problem, one either relies on the density matrix approach, wherein the density matrix is calculated quantum mechanically by some approximate means [1], or uses the Wigner distribution function or its equivalent, semiclassical distribution functions [2,3], to calculate the desired transport properties. Furthermore, despite the fact that macroscopic phenomena, either quantum or classical, must be subjected to the requirements of the thermodynamic laws, attention is not usually paid to these requirements when quantum transport properties are calculated in such theories. If transport processes occur near equilibrium so that a linear theory is adequate, such requirements are usually met even if precautionary measures are not taken. However, if the processes occur far removed from the linear regime as in many cases of phenomena in semiconductors and small quantum devices at high field gradients, the aforementioned thermodynamic requirements are not automatically satisfied and a thermodynamically consistent theory of nonlinear transport processes will not be ensured unless special care is exercised to satisfy the requirements of the thermodynamic laws. The kind of theory we are alluding to here has been developed for transport phenomena in classical systems [3] that can be sufficiently well described within the framework of classical mechanics. In this paper, we remove the restriction of classical mechanics and extend the classical theory into the quantum domain when the density of the system is sufficiently low so that the statistical correlations arising from the interactions between the particles are negligible. On this ground, we will assume that the singlet density matrices are sufficient for a statistical description of the system (e.g., consisting of dilute quantum gases or charges or phonons or photons, etc.) and that the singlet distribution functions obey a set of irreversible (time-reversal symmetry breaking) kinetic equations. These kinetic equations may be approximately justified from the quantum Liouville (von Neumann) equation as traditionally done in statistical mechanics or simply postulated as is done, for example, in the quantum semigroup theory [4] of irreversible processes. In either one of these approaches, it is necessary to formulate a theory of transport processes in a way consistent with the thermodynamic laws and the end results would be the same. Here we will take an approach akin to the quantum semigroup theory, but with the irreversibility imposed, as a postulate, on the time-reversal symmetry breaking collision term in the kinetic equations. In this paper, we show that a theory of irreversible thermodynamics can be erected with the kinetic equations postulated. A theory of transport processes will be presented and applied to transport phenomena in semiconductors in a sequel.

In Sec. II we present kinetic equations for density matrices together with definitions of necessary symbols for discussions in the subsequent sections. The entropy will be defined statistically and its time derivative will be calculated by means of the kinetic equations postulated. In Sec. III various balance equations for mass, mass fractions, momentum, and internal energy will be derived in local form. They will be shown to be in the same form as in the classical theory. The evolution equations for the nonconserved variables (fluxes) will be also derived from the kinetic equations postulated together with the local entropy balance equation derived. In Sec. IV discussions

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are given on the statistical definition of temperature for quantum gases in equilibrium and nonequilibrium. On the basis of the definition of temperature for nonequilibrium systems, differential forms will be derived for the entropy. The results of this section provide the basis on which to build the thermodynamics of irreversible processes in the quantum fluids considered. In Sec. V a discussion is given on the form of transition probability together with a brief discussion on how to apply the theory to study transport processes. Since the details of the theory of transport processes will be followed up with applications to semiconductor problems, this part of discussion will be brief. Concluding remarks are also given in this section.

II. KINETIC EQUATIONS

Let us denote the singlet density matrix for a particle of species a in the system by $\mathbf{f}_a$. The system is assumed to consist of r components. There are N_a particles of species a in volume V. The global number density then is N_a/V and the total number density is N/V, where $N=N_1+N_2+\cdots+N_r$. If the density is sufficiently low, the statistical correlations are negligible between the particles. Under this assumption, the density matrix for the whole system consisting of the r components is given by

$$\mathbf{f}=\prod_{a=1}^{r}\mathbf{f}_a \ . \tag{2.1}$$

This system is assumed to be subjected to an external field $\mathbf{F}$, which is uniform in space at least over the distance of interparticle interaction, but may change in time with a characteristic frequency. The external force on a particle of species a will be denoted by $\mathbf{F}_a$. The potential energy operator corresponding to this force will be denoted by $\mathfrak{V}_a$. It will be assumed that this potential energy varies very slowly over the range of interparticle interactions so that it does not affect particle collisions. The Hamiltonian operator $\mathbf{H}_a$ for a particle of the species a thus may be written as

$$\mathbf{H}_a=\mathbf{H}_a^0+\mathfrak{V}_a \ , \tag{2.2}$$

where $\mathbf{H}_a^0$ is the kinetic energy operator for a particle of species a:

$$\mathbf{H}_a^0=p_a^2/2m_a \tag{2.3}$$

with $p_a^2\equiv\mathbf{p}_a\cdot\mathbf{p}_a$ and m_a denoting the mass of species a. This assumption should be taken with the understanding that although the interparticle correlations are absent at the statistical level so that the statistical correlation functions are neglected on account of the density being low, the particles collide with each other through interparticle interaction forces at the few-particle dynamical level. This few-particle dynamics is relevant to the collision term in the kinetic equations presented later. The density matrix $\mathbf{f}_a$ is assumed to normalize to N_a:

$$\mathrm{Tr}\,\mathbf{f}_a=N_a \ , \tag{2.4}$$

where Tr is taken over the states of a particle of the species a. The local number density of the species a is then given by

$$\mathrm{Tr}[\delta(\mathbf{r}_a-\mathbf{r})\mathbf{f}_a]=n_a \ . \tag{2.4$'$}$$

Statistical averages of dynamical variables can be computed by means of he density matrix introduced:

$$\overline{A}_a(r,t)=\mathrm{Tr}[\,\mathbf{A}_a\delta(\mathbf{r}_a-\mathbf{r})\mathbf{f}_a(t)]\equiv\langle\,\mathbf{A}_a\delta(\mathbf{r}_a-\mathbf{r})\mathbf{f}_a(t)\rangle \ , \tag{2.5}$$

where $\mathbf{A}_a$ is the microscopic expression for a dynamical variable pertaining to a particle of the species a. The vector $\mathbf{r}_a$ is the position vector of a particle of the species a and $\mathbf{r}$ is the position vector in a suitable fixed coordinate system. Henceforth, the delta function will be abbreviated as $\delta_a\equiv\delta(\mathbf{r}_a-\mathbf{r})$.

In the quantum semigroup theory [4] of irreversible processes the density matrix is assumed to obey a linear kinetic equation, such as the quantum Pauli master equation, which is irreversible in the sense that the motion of the system is associated with a unidirectional time flow, and then consequences of such an equation are formally examined. However, irreversible thermodynamics has not been formulated therewith. We take up this subject here with a nonlinear kinetic equation.

Such a linear evolution equation for the density matrix is a special case of a class of kinetic equations with time-reversal symmetry breaking built into them. A well-known example for such a nonlinear evolution equation would be the quantum version of the Boltzmann equation. This viewpoint toward the semigroup equations suggests that one may assume a class of evolution equations, namely, kinetic equations, for the density matrix of the system that satisfy a set of conditions such as the existence of conservation laws of mass, momentum, and energy in addition to the H theorem necessary for constructing the entropy for the system. In the past study [3] in classical systems, it was found sufficient to assume a classical kinetic equation meeting such conditions and formulate a theory of irreversible processes. In such an approach the precise form for the kinetic equation was not required until transport processes were investigated case by case, which then would require a more explicit form for the collision term in the kinetic equation in question. Thus the viewpoint taken for this approach to macroscopic properties of the system is comparable to the formal theory (i.e., analytical dynamics) of few-body mechanics wherein either Newtonian equations of motion or quantum equations of motion are assumed with an interaction force replaceable with a suitable form, depending on the nature of the problem, and formal aspects of the theory are studied. To elaborate on what is said here in the case of irreversible thermodynamics, we may assume that the density matrix $\mathbf{f}_a$ obeys the irreversible kinetic equation

$$\partial_t\mathbf{f}_a-(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a]=\mathfrak{R}[\mathbf{f}_a] \ , \tag{2.6}$$

where $[\mathbf{H}_a,\mathbf{f}_a]$ is a commutator with $\mathbf{H}_a$ denoting the Hamiltonian operator of a particle of species a and $\mathfrak{R}[\mathbf{f}_a]$ stands for the collision term whose collision invariants are mass, momentum, and energy and which breaks the time-reversal symmetry and thus is responsible for the kinetic equation (2.6) being irreversible, more specifically, satisfying the *H* theorem. The first condition gives rise to the conservation laws of mass, momentum, and energy and the second condition ensures an *H* theorem to be satisfied so that a theory of irreversible processes can be constructed on it. This collision term is the replaceable part of the evolution equation for $\mathbf{f}_a$ mentioned earlier in allusion to the Newtonian or quantum equations of motion for few-particle dynamics. Explicit models for the collision term should be constructed such that they meet the aforementioned requirements on it and yield an accurate interpretation of the experimental data on transport properties of interest. Therefore, we regard the role of the theory of transport processes as that of elucidating the collision term in the kinetic equation in this approach. The point is, if the aim is to develop a formal theory of irreversible thermodynamics, it is not necessary to explicitly specify $\mathfrak{R}[\mathbf{f}_a]$ except for the conditions mentioned earlier.

However, as a preparation for the future studies on quantum transport properties in mind, we assume for $\mathfrak{R}[\mathbf{f}_a]$ the following Boltzmann-Nordheim-Uehling-Uhlenbeck (BNUU) model [5–9] in this work:

$$\mathfrak{R}[\mathbf{f}_a]=\sum_b^r \operatorname*{Tr}_{(b,a',b')}\{W_{ab}^{(\varepsilon)}[\mathbf{f}'_a\mathbf{f}'_b(1+\varepsilon_a\mathbf{f}_a)(1+\varepsilon_b\mathbf{f}_b)$$
$$-\mathbf{f}_a\mathbf{f}_b(1+\varepsilon_a\mathbf{f}'_a)(1+\varepsilon_b\mathbf{f}'_b)]\}\ , \quad (2.7)$$

where ε_a is 1 for bosons, -1 for fermions, and 0 for Boltzmann particles, and $W_{ab}^{(\varepsilon)}\equiv W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}'_a\mathbf{k}'_b)$ is the transition probability given in terms of suitably symmetrized scattering operators describing the collision process from the initial state $(\mathbf{k}_a,\mathbf{k}_b)$ to the final state $(\mathbf{k}'_a\mathbf{k}'_b)$. Here $\mathbf{k}_a$, etc. denote wave number vectors. The prime denotes the post-collision value of the parameter or the quantity in question. The subscripts [e.g., (b,a',b')] to Tr mean that the traces are to be taken over the quantum states pertaining to the particles corresponding to the subscripts. Here the subscripts a and b are used dually to denote both the species and the quantum state of the particle involved. The density matrices in (2.7) are assumed to be diagonal in coordinate representation, namely, $\mathbf{f}_a=f_a(\mathbf{r},\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$, etc. The transition probabilities obey symmetry relations $W_{ab}^{(\varepsilon)}=W_{ba}^{(\varepsilon)}$ and $W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}'_a\mathbf{k}'_b)=W^{(\varepsilon)}(\mathbf{k}'_a\mathbf{k}'_b|\mathbf{k}_a\mathbf{k}_b)$. The first relation is for the symmetry with respect to interchange of particle species and the second relation expresses the microscopic reversibility of the collision events under the reversal of the processes $(\mathbf{k}_a,\mathbf{k}_b)\rightarrow(\mathbf{k}'_a,\mathbf{k}'_b)$ to $(\mathbf{k}'_a,\mathbf{k}'_b)\rightarrow(\mathbf{k}_a,\mathbf{k}_b)$ and vice versa. These two symmetry properties of $W_{ab}^{(\varepsilon)}$ are sufficient for a thermodynamically consistent theory of irreversible processes in dilute quantum systems as will be shown. More detailed forms will be required for $W_{ab}^{(\varepsilon)}$ for elucidation of transport processes in comparison with experiment, but since our main interest in this work is not in transport processes, it is beyond the scope of this work and therefore we defer it to a future work.

It is useful to observe that the factors $(1+\varepsilon_a\mathbf{f}_a)(1+\varepsilon_b\mathbf{f}_b)$ and $(1+\varepsilon_a\mathbf{f}'_a)(1+\varepsilon_b\mathbf{f}'_b)$ appearing in (2.7) may be regarded as approximate forms for the pair correlation functions for the quantum particles in the post-collision and the pre-collision state, respectively. Such particle correlations arise from the quantum effect, namely, quantum attractions in the case of bosons and quantum repulsions (Pauli exclusion principle) in the case of fermions, inherent to quantum particles. Such correlations are absent in the case of classical Boltzmann particles for which the doublet density matrix (distribution function) is simply a product of two singlet density matrices (distribution functions) in the low-density limit. In this sense, a gas of quantum particles is not ideal in the manner a gas of the Boltzmann particles is. Note in this connection that the equations of state for quantum gases [10] are not in the form of the ideal gas equation of state holding for the Boltzmann gas. In fact, the quantum gases have virial coefficients owing to the correlations arising from the quantum mechanical effects.

It is easy to show that the BNUU form of the collision term $\mathfrak{R}[\mathbf{f}_a]$ satisfies the following general conditions, mentioned earlier, that must be met by the collision integral of an irreversible kinetic equation.

(i) It is such that the conservation laws of mass, momentum, and energy follow from the kinetic equation (2.6). In other words, if $\mathbf{A}_a$ stands for the quantum mechanical operator for mass or momentum or energy, then $\mathfrak{R}[\mathbf{f}_a]$ is such that $\mathbf{A}_a$ is a collision invariant:

$$\mathrm{Tr}(\mathbf{A}_a\mathfrak{R}[\mathbf{f}_a])=\langle\mathbf{A}_a\mathfrak{R}[\mathbf{f}_a]\rangle=0 \quad (2.8a)$$

or, in local form,

$$\mathrm{Tr}\{\mathbf{A}_a\delta(\mathbf{r}_a-\mathbf{r})\mathfrak{R}[\mathbf{f}_a]\}=\langle\mathbf{A}_a\delta(\mathbf{r}_a-\mathbf{r})\mathfrak{R}[\mathbf{f}_a]\rangle=0\ . \quad (2.8a')$$

(ii) The *H* theorem is satisfied by the kinetic equation postulated. In the case of the collision integral given in (2.7), this condition demands, and is fully met by, the inequality

$$-\mathrm{Tr}\{[\ln\mathbf{f}_a-\ln(1+\varepsilon_a\mathbf{f}_a)]\mathfrak{R}[\mathbf{f}_a]\}$$
$$=\mathrm{Tr}\{\ln(\varepsilon_a+\mathbf{f}_a^{-1})\mathfrak{R}[\mathbf{f}_a]\}\geq 0\ , \quad (2.8b)$$

the equality holding at equilibrium only. Thus the equilibrium solution $\mathbf{f}_{a_{\mathrm{eq}}}$ to the kinetic equation (2.6) is defined by

$$\mathrm{Tr}\{\ln(\varepsilon_a+\mathbf{f}_{a_{\mathrm{eq}}}^{-1})\mathfrak{R}[\mathbf{f}_{a_{\mathrm{eq}}}]\}=0\ . \quad (2.9)$$

We will return to this equation later and find out the explicit form for $\mathbf{f}_{a_{\mathrm{eq}}}$. It is shown in Appendix A that the BNUU model satisfies these conditions.

If the collision term is set equal to zero, then (2.6) becomes the Liouville–von Neumann equation for the singlet density matrix $\mathbf{f}_a$, which is nondissipative and time-reversal invariant. The presence of the dissipative and time-reversal symmetry breaking collision term in the kinetic equation is essential for describing irreversible processes in macroscopic systems and by postulating such a kinetic equation we are elevating it to the status of a fundamental evolution equation for mesoscopic description of macroscopic systems. The question of the origin of irreversibility therefore is not asked in this approach. A principal aim of this work is to formulate a thermodynamically consistent theory of macroscopic processes for a class of quantum systems.

The *H* theorem, for $\mathfrak{R}[\mathbf{f}_a]$ given in (2.7), motivates us to define the entropy of the global system by the formula

$$S(t)=-k_B\sum_a^r \mathrm{Tr}[\mathbf{f}_a \ln \mathbf{f}_a-\varepsilon_a(1+\varepsilon_a\mathbf{f}_a)\ln(1+\varepsilon_a\mathbf{f}_a)]\ . \tag{2.10}$$

We remark that the term entropy used here does not mean the entropy used by Clausius in the context of equilibrium thermodynamics to which the entropy in (2.10) reduces only at equilibrium. We simply tolerate this overlapping usage of terms out of deference to the tradition in the kinetic theory of gases. We hope to rectify it when the basic concepts of irreversible thermodynamics are taken up for careful analysis elsewhere. In the meantime we will use the term as it is. The *H* theorem then is expressed as the inequality

$$\frac{dS}{dt}\geq 0\ . \tag{2.11}$$

To show that this theorem is satisfied by the kinetic equation (2.6) with (2.7) satisfying condition (ii) on the collision term, it is necessary to establish the evolution equation for $\ln \mathbf{f}_a$ and $\ln(1+\varepsilon_a\mathbf{f}_a)$ since the density matrix is a quantum operator. To this end, we quickly review some of the mathematical identities for operators and their time derivatives in quantum mechanics.

Let us consider two operators $\mathbf{x}$ and $\mathbf{y}$ which do not commute. If operator $\mathbf{z}$ is such that

$$e^{\mathbf{x}}e^{\mathbf{y}}=e^{\mathbf{z}}\ , \tag{2.12}$$

then

$$\mathbf{z}=\mathbf{x}+\mathbf{y}+\tfrac{1}{2}[\mathbf{x},\mathbf{y}]+\tfrac{1}{3}[[\mathbf{x},\mathbf{y}],\mathbf{y}]+\cdots\ . \tag{2.13}$$

If the l nested commutators $[[\cdots[[\mathbf{x},\mathbf{y}],\mathbf{y}],\ldots,\mathbf{y}],\mathbf{y}]$, where the $\mathbf{y}$'s appear l times within the commutators, are abbreviated by $\{\mathbf{x},\mathbf{y}^l\}\equiv[[\cdots[[\mathbf{x},\mathbf{y}],\mathbf{y}],\ldots,\mathbf{y}],\mathbf{y}]$, then we may write $\mathbf{z}$ in the form

$$\mathbf{z}=\mathbf{x}+\mathbf{y}+\sum_{l\geq 1}\frac{1}{l+1}\{\mathbf{x},\mathbf{y}^l\}\ . \tag{2.13'}$$

In addition to this relation, the following relation will be useful in our calculations:

$$e^{-\mathbf{x}}\mathbf{y}e^{\mathbf{x}}=\sum_{l=0}^{\infty}\frac{1}{l!}\{\mathbf{y},\mathbf{x}^l\}\ . \tag{2.14}$$

Applying this relation, we obtain

$$e^{-\mathbf{x}}\left[\mathbf{y}\frac{\partial}{\partial\mathbf{x}}\right]e^{\mathbf{x}}=\sum_{l=0}^{\infty}\frac{1}{l!}\left\{\left[\mathbf{y}\frac{\partial}{\partial\mathbf{x}}\right],\mathbf{x}^l\right\}\ . \tag{2.15}$$

Since $\{[\mathbf{y}(\partial/\partial\mathbf{x})],\mathbf{x}^l\}=\{\mathbf{y},\mathbf{x}^{l-1}\}$ for $l\geq 1$, $\{[\mathbf{y}(\partial/\partial\mathbf{x})],\mathbf{x}^0\}=0$, and $\{\mathbf{y},\mathbf{x}^0\}=\mathbf{y}$, we find

$$e^{-\mathbf{x}}\left[\mathbf{y}\frac{\partial}{\partial\mathbf{x}}\right]e^{\mathbf{x}}=\sum_{l=1}^{\infty}\frac{1}{l!}\{\mathbf{y},\mathbf{x}^{l-1}\}=\left\{\mathbf{y},\frac{e^{\mathbf{x}}-1}{\mathbf{x}}\right\}\ . \tag{2.16}$$

By using the identity $\{\{\mathbf{y},\mathbf{x}^l\},\mathbf{x}^m\}=\{\mathbf{y},\mathbf{x}^{l+m}\}$, we easily find

$$\begin{aligned}\left[\left[\mathbf{y}\frac{\partial}{\partial\mathbf{x}}\right]e^{\mathbf{x}}\right]e^{-\mathbf{x}}&=e^{\mathbf{x}}\left\{\mathbf{y},\frac{e^{\mathbf{x}}-1}{\mathbf{x}}\right\}e^{-\mathbf{x}}\\&=\left\{\mathbf{y},\frac{1-e^{-\mathbf{x}}}{\mathbf{x}}\right\}\ .\end{aligned} \tag{2.17}$$

The following lemma due to Magnus [11] holds.

Let $\mathbf{P}$ and $\mathbf{Q}$ such that $\mathbf{PQ}=1$ and $\{\mathbf{y},\mathbf{P}\}=\mathbf{z}$. Then, $\mathbf{y}=\{\mathbf{z},\mathbf{Q}\}$ and vice versa.

The aforementioned mathematical identities are useful in the following calculations.

Let the operator $\mathfrak{F}$ be defined such that

$$\mathbf{f}_a=\exp(\mathfrak{F})\ . \tag{2.18}$$

Then, the evolution equation for $\mathfrak{F}$ is obtained by using the identities given earlier. First, we note

$$\begin{aligned}\frac{\partial}{\partial t}\exp(\mathfrak{F})&=\left[\frac{\partial\mathfrak{F}}{\partial t}\frac{\partial}{\partial\mathfrak{F}}\right]\exp(\mathfrak{F})\\&=\left\{\frac{\partial\mathfrak{F}}{\partial t},\frac{1-\exp(-\mathfrak{F})}{\mathfrak{F}}\right\}\exp(\mathfrak{F})\\&=(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a]+\mathfrak{R}[\mathbf{f}_a]\ .\end{aligned} \tag{2.19}$$

Applying the Magnus lemma to this equation, we obtain

$$\begin{aligned}\frac{\partial\mathfrak{F}}{\partial t}\exp(\mathfrak{F})=&\left\{(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a],\frac{\mathfrak{F}}{1-\exp(-\mathfrak{F})}\right\}\\&+\left\{\mathfrak{R}[\mathbf{f}_a],\frac{\mathfrak{F}}{1-\exp(-\mathfrak{F})}\right\}\ .\end{aligned} \tag{2.20}$$

That is, written in terms of $\mathbf{f}_a$,

$$\begin{aligned}\left[\frac{\partial}{\partial t}\ln\mathbf{f}_a\right]\mathbf{f}_a=&\left\{(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a],\frac{\ln\mathbf{f}_a}{1-\exp(-\ln\mathbf{f}_a)}\right\}\\&+\left\{\mathfrak{R}[\mathbf{f}_a],\frac{\ln\mathbf{f}_a}{1-\exp(-\ln\mathbf{f}_a)}\right\}\ .\end{aligned} \tag{2.21a}$$

By applying to this formula the Bernoulli expansion [12]

$$\frac{\tau}{e^{\tau}-1}=\sum_{l=0}^{\infty}\frac{B_l}{l!}\tau^l\ ,$$

where B_l are the Bernoulli numbers $B_0=1$, $B_1=-\frac{1}{2}$, $B_2=\frac{1}{6}$, $B_4=-\frac{1}{30}$, $B_6=\frac{1}{42}$, etc. and $B_{2l+1}=0$ $(l\geq 1)$, we obtain

$$\left[\frac{\partial}{\partial t}\ln\mathbf{f}_a\right]\mathbf{f}_a=(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a]+\mathfrak{R}[\mathbf{f}_a]+\sum_{l=1}^{\infty}\frac{B_l}{l!}\{(i\hbar)^{-1}[\mathbf{H}_a,\mathbf{f}_a]+\mathfrak{R}[\mathbf{f}_a],(-\ln\mathbf{f}_a)^l\}\ . \tag{2.21a'}$$

A similar calculation can be made for $\ln(1+\varepsilon_a\mathbf{f}_a)$ to obtain the equation

$$\left[\frac{\partial}{\partial t}\ln(1+\varepsilon_a\mathbf{f}_a)\right](1+\varepsilon_a\mathbf{f}_a)=(i\hbar)^{-1}\left\{[\mathbf{H}_a,(1+\varepsilon_a\mathbf{f}_a)],\frac{\ln(1+\varepsilon_a\mathbf{f}_a)}{1-\exp[-\ln(1+\varepsilon_a\mathbf{f}_a)]}\right\}+\left\{\mathfrak{R}[\mathbf{f}_a],\frac{\ln(1+\varepsilon_a\mathbf{f}_a)}{1-\exp[-\ln(1+\varepsilon_a\mathbf{f}_a)]}\right\}\ . \tag{2.21b}$$

By differentiating (2.10) with time and using this result, we obtain

$$\begin{aligned}\frac{dS}{dt}=&-k_B(i\hbar)^{-1}\sum_a^r\mathrm{Tr}\{\ln f_a[\mathbf{H}_a,\mathbf{f}_a]-\varepsilon_a\ln(1+\varepsilon_a\mathbf{f}_a)[\mathbf{H}_a,(1+\varepsilon_a f_a)]\}-k_B\sum_a^r\mathrm{Tr}\{[\ln\mathbf{f}_a-\ln(1+\varepsilon_a\mathbf{f}_a)]\mathfrak{R}[\mathbf{f}_a]\}\\&-k_B(i\hbar)^{-1}\sum_a^r\mathrm{Tr}\left\{[\mathbf{H}_a,\mathbf{f}_a],\frac{\ln\mathbf{f}_a}{1-\exp(-\ln\mathbf{f}_a)}\right\}-k_B\sum_a^r\mathrm{Tr}\left\{\mathfrak{R}[\mathbf{f}_a],\frac{\ln f_a}{1-\exp(-\ln\mathbf{f}_a)}\right\}\\&+(i\hbar)^{-1}k_B\sum_a^r\mathrm{Tr}\left\{[\mathbf{H}_a,(1+\varepsilon_a\mathbf{f}_a)],\frac{\varepsilon_a\ln(1+\varepsilon_a\mathbf{f}_a)}{1-\exp[-\ln(1+\varepsilon_a f_a)]}\right\}+k_B\sum_a^r\mathrm{Tr}\left\{\mathfrak{R}[\mathbf{f}_a],\frac{\varepsilon_a\ln(1+\varepsilon_a\mathbf{f}_a)}{1-\exp[-\ln(1+\varepsilon_a\mathbf{f}_a)]}\right\}\ .\end{aligned} \tag{2.22}$$

The last four terms on the right-hand side can be shown to vanish and the first term also vanishes at the boundary of the system. Therefore, we have

$$\begin{aligned}\frac{dS}{dt}&=-k_B\sum_a^r\mathrm{Tr}\{[\ln\mathbf{f}_a-\ln(1+\varepsilon_a\mathbf{f}_a)]\mathfrak{R}[\mathbf{f}_a]\}\\&=k_B\sum_a^r\mathrm{Tr}\{\ln(\varepsilon_a+\mathbf{f}_a^{-1})\mathfrak{R}[\mathbf{f}_a]\}\geq 0\end{aligned} \tag{2.23}$$

since $\mathfrak{R}[\mathbf{f}_a]$ satisfies condition (ii) imposed on the collision term as shown in Appendix A. We note that

$$\mathrm{Tr}[\mathbf{H}_a,\mathbf{f}_a]=0,\quad \mathrm{Tr}(\mathfrak{R}[\mathbf{f}_a])=0\ ,$$

$$\mathrm{Tr}\{[\mathbf{H}_a,\mathbf{f}_a],P(\ln\mathbf{f}_a)\}=0,\quad \mathrm{Tr}\{\mathfrak{R}[\mathbf{f}_a],P(\ln\mathbf{f}_a)\}=0\ ,$$

where $P(\ln\mathbf{f}_a)$ is a function of $\ln\mathbf{f}_a$. These identities have been used to obtain (2.23) from (2.22). Equation (2.23) will be put into a local form later when local evolution equations are derived for macroscopic variables.

III. EVOLUTION EQUATIONS FOR MACROSCOPIC VARIABLES

Statistical mechanical averages of dynamical variables can be identified with macroscopic variables and their evolution equations can be derived from the kinetic equation (2.6) with (2.7) postulated. These evolution equations for macroscopic variables then are used to construct a theory of irreversible processes in a way consistent with the thermodynamic laws with the help of the H theorem or equivalently the entropy balance equation derived from (2.22). Their derivations follow the same procedure as for their classical counterparts, but are much more involved mathematically because of the noncommutativity of the operators involved. Nevertheless, the final mathematical structures of the evolution equations obtained turn out to be the same as the classical evolution equations, except that the statistical definitions of the macroscopic quantities are quantum mechanical. It must be remarked, however, that when carefully worked out, the statistical averages of macroscopic quantities do have quantum corrections to their classical analogs.

A. Conservation laws: Balance equations of conserved variables

The local mass density $\rho(\mathbf{r},t)$ at position $\mathbf{r}$ and time t is defined by [13]

$$\rho(\mathbf{r},t)=\sum_{a=1}^r\mathrm{Tr}[m_a\delta(\mathbf{r}_a-\mathbf{r})\mathbf{f}_a(t)]\ . \tag{3.1}$$

The mass density of species a may also be defined by

$$\rho_a(\mathbf{r},t)=\mathrm{Tr}[m_a\delta(\mathbf{r}_a-\mathbf{r})\mathbf{f}_a(t)]\ . \tag{3.2}$$

This suggests that

$$\rho(\mathbf{r},t)=\sum_{a=1}^r\rho_a(\mathbf{r},t)\ . \tag{3.3}$$

It is also convenient to define mass fractions

$$c_a=\rho_a(\mathbf{r},t)/\rho(\mathbf{r},t)\ , \tag{3.4}$$

which normalizes to unity by definition. By differentiating (3.1) with time and using the kinetic equation (2.6) and the aforementioned condition on the collision term, we obtain the equation of continuity. Since this derivation is a prototype of the procedure used for deriving evolution equations in the present theory, we take this example as an illustration. The time derivative of (3.1) is given by

$$\partial_t\rho=\mathrm{Tr}\left[\sum_{a=1}^{r} m_a\delta(\mathbf{r}_a-\mathbf{r})\partial_t\mathbf{f}_a\right]$$
$$=(i\hbar)^{-1}\mathrm{Tr}\left[\sum_{a=1}^{r} m_a\delta(\mathbf{r}_a-\mathbf{r})[\mathbf{H}_a,\mathbf{f}_a]\right]$$
$$+\mathrm{Tr}\left[\sum_{a=1}^{r} m_a\delta(\mathbf{r}_a-\mathbf{r})\Re[\mathbf{f}_a]\right] . \tag{3.5}$$

The second term on the right-hand side vanishes owing to the condition on the collision term $\Re[\mathbf{f}_a]$. By using the cyclic property of the trace of operator products $\mathrm{Tr}(ABC)=\mathrm{Tr}(BCA)=\mathrm{Tr}(CAB)$, the first term of the right-hand side of (3.5) can be written as

$$\mathrm{Tr}\{m_a\delta(\mathbf{r}_a-\mathbf{r})[\mathbf{H}_a,\mathbf{f}_a]\}$$
$$=-\mathrm{Tr}\{[\mathbf{H}_a,m_a\delta_a]\mathbf{f}_a\}$$
$$=-(i\hbar/2)\nabla\cdot\mathrm{Tr}[(p_a\delta_a{}_+\delta_a\mathbf{p}_a)\mathbf{f}_a] . \tag{3.6}$$

The second equality arises as follows: By the commutation relation $[\mathbf{r}_a,\mathbf{p}_a]=-(\mathbf{p}_a\mathbf{r}_a)$, where the parentheses mean that $\mathbf{p}_a$ operates on $\mathbf{r}_a$ only, we obtain

$$2m_a[\mathbf{H}_a,\delta_a]\mathbf{f}_a=[p_a^2,\delta_a]\mathbf{f}_a$$
$$=(\mathbf{p}_a\cdot[\mathbf{p}_a,\delta_a]+[\mathbf{p}_a,\delta_a]\cdot\mathbf{p}_a)\mathbf{f}_a$$
$$=[\mathbf{p}_a\cdot(\mathbf{p}_a\delta_a)+(\mathbf{p}_a\delta_a)\cdot\mathbf{p}_a]\mathbf{f}_a .$$

Now, by using the property of the delta function

$$\nabla_i\delta(\mathbf{r}_i-\mathbf{r})=-\nabla\delta(r_i-\mathbf{r}) ,$$

where $\nabla_i=\partial/\partial r_i$ and $\nabla=\partial/\partial\mathbf{r}$, we arrive at the second equality in (3.6). Therefore, with the definition of mean velocities $\mathbf{u}_a$ and $\mathbf{u}$ by the formulas

$$\rho_a\mathbf{u}_a(\mathbf{r},t)=\mathrm{Tr}[\tfrac{1}{2}(\mathbf{p}_a\delta_a+\delta_a p_a)\mathbf{f}_a] \tag{3.7a}$$

$$\rho\mathbf{u}(\mathbf{r},t)=\sum_{a=1}^{r}\rho_a\mathbf{u}_a(\mathbf{r},t) , \tag{3.7b}$$

we obtain the equation of continuity (mass balance equation)

$$\partial_t\rho=-\nabla\cdot\rho\mathbf{u} . \tag{3.8}$$

It must be noted that the definition of average velocity $\mathbf{u}_a$ involves a symmetrized product of $\mathbf{p}_a$ and δ_a and this appearance of a symmetrized product is a natural consequence of quantum mechanics. Mori [13(b)] and Dahler [13(c)] used such symmetrized products for momentum and energy densities. See also Ref. [13(e)]. In Refs. [13(b)] and [13(c)] the statistical averaging of the equations, however, is not taken and the kinetic equation does not appear. The Heisenberg representation is used for the operators in their calculations. The present method is similar to the one used in Ref. [13(e)]. In the present paper a larger set of evolution equations is derived than in Ref. [13(e)] together with the entropy balance equation, which serves as the starting point for a thermodynamic theory of irreversible processes. We point out that various symmetrized products of momenta and a δ function appear naturally when the evolution equations for macroscopic variables are sequentially derived step by step starting from the equation of continuity.

We now define the peculiar velocity operator $\mathbf{C}_a$ by

$$\mathbf{C}_a=\mathbf{p}_a/m_a-\mathbf{u} .$$

Then, the diffusion flux $\mathbf{J}_a$ of species a is defined by

$$\mathbf{J}_a=\mathrm{Tr}[\tfrac{1}{2}m_a(\mathbf{C}_a\delta_a+\delta_a\mathbf{C}_a)\mathbf{f}_a] . \tag{3.9}$$

It is important to note that the velocity $\mathbf{u}$ acts as a classical variable as any other macroscopic averaged variables and thus commutes with the delta function δ_a and other quantum mechanical operators. All other mean continuum macroscopic variables are classical in that sense. With this definition and the definition of the substantial time derivative $d_t=\partial_t+\mathbf{u}\cdot\nabla$, we obtain from (3.8) the mass fraction balance equation

$$\rho d_t c_a=-\nabla\cdot\mathbf{J}_a . \tag{3.10}$$

It is assumed that there is no chemical reaction in the system.

By differentiating (3.7) with time, using the kinetic equation (2.6) and applying the same procedure as for the equation of continuity, we obtain the momentum balance equation

$$\rho d_t\mathbf{u}=-\nabla\cdot\mathbf{P}+\rho\mathbf{F}(\mathbf{r},t) , \tag{3.11}$$

where $\mathbf{P}$ is the stress tensor defined by

$$P_{\beta\gamma}=\sum_{a=1}^{r}(\mathbf{P}_a)_{\beta\gamma}$$
$$=\sum_{a=1}^{r}\mathrm{Tr}[\tfrac{1}{4}m_a(C_{a\beta}C_{a\gamma}\delta_a+C_{a\beta}\delta_a C_{a\gamma}$$
$$+C_{a\gamma}\delta_a C_{a\beta}+\delta_a C_{a\beta}C_{a\gamma})\mathbf{f}_a] , \tag{3.12}$$

$$\rho\mathbf{F}=\sum_{a}^{r}\rho_a\mathbf{F}_a=-\sum_{a=1}^{r}\mathrm{Tr}[\delta_a(\nabla_a\mathfrak{B})\mathbf{f}_a]\equiv\sum_{a=1}^{r}\mathrm{Tr}(\delta_a\mathcal{F}_a\mathbf{f}_a) . \tag{3.13}$$

Here $\mathbf{F}_a$ is the external force per mass of species a at position r and $\mathbf{F}$ is the mean external force per mass at r. Note that $\mathcal{F}_a=-\nabla_a\mathfrak{B}$ for a particle of species a located at $\mathbf{r}_a$. The greek subscripts β and γ in (3.12) refer to the Cartesian components of the vectors and the tensors involved and greek subscripts will henceforth be reserved for such purpose throughout this paper. Note that the peculiar velocity product in (3.12) is symmetrized owing to the noncommutativity of the operators involved. These symmetrized products give rise to quantum effect terms in the macroscopic variables associated with them.

The internal energy is intimately related to the stress tensor. Therefore, the formula (3.12) for the stress tensor suggests that the internal energy be defined by the formula

$$\rho\mathcal{E}(\mathbf{r},t)=\sum_{a=1}^{r}\mathrm{Tr}[\tfrac{1}{8}m_a(\mathbf{C}_a\cdot\mathbf{C}_a\delta_a+2\mathbf{C}_a\delta_a\cdot\mathbf{C}_a$$
$$+\delta_a\mathbf{C}_a\cdot\mathbf{C}_a)\mathbf{f}_a] . \tag{3.14}$$

On application of the procedure used for deriving the aforementioned balance equations for mass and momentum, this definition gives rise to the energy balance equations as follows:

$$\rho d_t \mathcal{E} = -\nabla\cdot\mathbf{Q} - \mathbf{P}:\nabla\mathbf{u} + \sum_a^r \mathbf{J}_a\cdot\mathbf{F}_a \ . \tag{3.15}$$

Here Q is the heat flux defined by

$$\begin{aligned}\mathbf{Q} &= \sum_{a=1}^r \mathbf{Q}_a \\ &= \sum_{a=1}^r \mathrm{Tr}[\tfrac{1}{16} m_a (C_a^2 \mathbf{C}_a \delta_a + C_a^2 \delta_a \mathbf{C}_a + 2\mathbf{C}_a \mathbf{C}_a \delta_a \cdot \mathbf{C}_a \\ &\quad + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a \mathbf{C}_a + \mathbf{C}_a \delta_a C_a^2 + \delta_a C_a^2 \mathbf{C}_a) \mathbf{f}_a] \ . \end{aligned} \tag{3.16}$$

We note that these balance equations have exactly the same mathematical structures as the balance equations appearing in the classical theory, except that this time the statistical mechanical definitions of the macroscopic variables are quantum mechanical and hence include quantum effects through the symmetrized operator products and the density matrix.

B. Evolution equations for nonconserved variables

On differentiation of (3.9), (3.12), and (3.16) with time and use of the kinetic equation (2.6), we obtain the evolution equations for $\mathbf{J}_a$, $\mathbf{P}$, and $\mathbf{Q}$. In the case of a mixture, it is more convenient to derive evolution equations for species components $\mathbf{P}_a$ and $\mathbf{Q}_a$ from their statistical definitions:

$$\begin{aligned}\mathbf{P}_{a\beta\gamma} = \mathrm{Tr}[\tfrac{1}{4} m_a (& C_{a\beta} C_{a\gamma} \delta_a + C_{a\beta} \delta_a C_{a\gamma} \\ & + C_{a\gamma} \delta_a C_{a\beta} + \delta_a C_{a\beta} C_{a\gamma}) \mathbf{f}_a] \ ,\end{aligned} \tag{3.17}$$

$$\begin{aligned}\mathbf{Q}_a = \mathrm{Tr}[\tfrac{1}{16} m_a (& C_a^2 \mathbf{C}_a \delta_a + C_a^2 \delta_a \mathbf{C}_a + 2\mathbf{C}_a \mathbf{C}_a \delta_a \cdot \mathbf{C}_a \\ & + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a \mathbf{C}_a + \mathbf{C}_a \delta_a C_a^2 + \delta_a C_a^2 \mathbf{C}_a) \mathbf{f}_a] \ .\end{aligned} \tag{3.18}$$

The results are as follows. With the definitions $\hat{\mathbf{P}}_a = \mathbf{P}_a/\rho$, $\hat{\mathbf{Q}}_a = \mathbf{Q}_a/\rho$, and $\hat{\mathbf{J}}_a = \mathbf{J}_a/\rho$,

$$\begin{aligned}\rho d_t \hat{\mathbf{P}}_a = & -\nabla\cdot\bar{\boldsymbol{\psi}}_a^{(1)} - [(d_t\mathbf{u} - \mathbf{F}_a)\mathbf{J}_a + \mathbf{J}_a(d_t\mathbf{u} - \mathbf{F}_a)] \\ & - [\mathbf{P}_a \cdot \nabla\mathbf{u} + (\nabla\mathbf{u})^t \cdot \mathbf{P}_a^t] + \Lambda_a^{(s)} \ ,\end{aligned} \tag{3.19}$$

$$\begin{aligned}\rho d_t \hat{\mathbf{Q}}_a = & -\nabla\cdot\bar{\boldsymbol{\psi}}_a^{(3)} - (\mathbf{P}_a - p_a \boldsymbol{\delta})\cdot(d_t\mathbf{u} - \mathbf{F}_a) \\ & - \varphi_a^{(3)}:\nabla\mathbf{u} - \mathbf{Q}_a \cdot \nabla\mathbf{u} + \Lambda_a^{(h)} \ ,\end{aligned} \tag{3.20}$$

$$\rho d_t \mathbf{J}_a = -\nabla\cdot\mathbf{P}_a - \rho_a(d_t\mathbf{u} - \mathbf{F}_a) - \mathbf{J}_a \cdot \nabla U + \Lambda_a^{(d)} \ . \tag{3.21}$$

Here the superscript t means the transpose of the tensor, $\boldsymbol{\delta}$ denotes the unit second-rank tensor, and various other symbols are defined by the statistical expressions

$$\begin{aligned}\bar{\psi}_{a\beta\gamma\varepsilon}^{(1)} = \mathrm{Tr}\{\tfrac{1}{8} m_a [& C_{a\beta} C_{a\gamma} C_{a\varepsilon} \delta_a + C_{a\beta} C_{a\gamma} \delta_a C_{a\varepsilon} + C_{a\beta} \delta_a C_{a\gamma} C_{a\varepsilon} + \delta_a C_{a\beta} C_{a\gamma} C_{a\varepsilon} \\ & + C_{a\beta} C_{a\varepsilon} \delta_a C_{a\gamma} + C_{a\varepsilon} C_{a\gamma} \delta_a C_{a\beta} + C_{a\gamma} \delta_a C_{a\beta} \delta_a C_{a\varepsilon} + C_{a\varepsilon} \delta_a C_{a\gamma} C_{a\beta}] \mathbf{f}_a\} \ ,\end{aligned} \tag{3.22}$$

$$\begin{aligned}\bar{\psi}_{a\beta\gamma}^{(3)} = \mathrm{Tr}\{\tfrac{1}{32} m_a [& C_{a\beta} C_{a\gamma} C_{a\varepsilon}^2 \delta_a + C_{a\beta} C_{a\gamma} \delta_a C_{a\varepsilon}^2 + C_{a\beta} \delta_a C_{a\gamma} C_{a\varepsilon}^2 + \delta_a C_{a\beta} C_{a\gamma} C_{a\varepsilon}^2 + C_{a\beta} C_{a\varepsilon}^2 \delta_a C_{a\gamma} \\ & + C_{a\gamma\beta} C_{a\varepsilon}^2 \delta_a C_{a\beta} + C_a^2 \delta_a C_{a\beta} C_{a\gamma} + C_{a\gamma} \delta_a C_{a\beta} C_{a\varepsilon}^2 + 2C_{a\beta} C_{a\gamma} C_{a\varepsilon} \delta_a C_{a\varepsilon} \\ & + 2C_{a\beta} C_{a\varepsilon} \delta_a C_{a\varepsilon} C_{a\gamma} + 2C_{a\gamma} C_{a\varepsilon} \delta_a C_{a\varepsilon} C_{a\beta} + 2C_{a\varepsilon} \delta_a C_{a\varepsilon} C_{a\beta} C_{a\gamma}] \mathbf{f}_a\} \ ,\end{aligned} \tag{3.23}$$

$$\varphi_{a\beta\gamma\varepsilon}^{(3)} = \bar{\psi}_{a\beta\gamma\varepsilon}^{(1)} \ , \tag{3.24}$$

$$\Lambda_{a\alpha\beta}^{(s)} = \mathrm{Tr}\{\tfrac{1}{4} m_a (C_{a\alpha} C_{a\beta} \delta_a + C_{a\alpha} \delta_a C_{a\beta} + C_{a\beta} \delta_a C_{a\alpha} + \delta_a C_{a\alpha} C_{a\beta}) \Re[\mathbf{f}_a]\} \ , \tag{3.25}$$

$$\Lambda_a^{(h)} = \mathrm{Tr}\{\tfrac{1}{16} m_a (C_a^2 \mathbf{C}_a \delta_a + C_a^2 \delta_a \mathbf{C}_a + 2\mathbf{C}_a \mathbf{C}_a \delta_a \cdot \mathbf{C}_a + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a \mathbf{C}_a + \mathbf{C}_a \delta_a C_a^2 + \delta_a C_a^2 \mathbf{C}_a) \Re[\mathbf{f}_a]\} \ , \tag{3.26}$$

$$\Lambda_a^{(d)} = \mathrm{Tr}\{\tfrac{1}{2} m_a (\mathbf{C}_a \delta_a + \delta_a \mathbf{C}_a) \Re[\mathbf{f}_a]\} \ . \tag{3.27}$$

We reiterate that $\bar{\psi}_{a\beta\gamma\varepsilon}^{(1)}$ and $\bar{\psi}_{a\beta\gamma}^{(3)}$ are the $\beta\gamma\varepsilon$ and $\beta\gamma$ components of third- and second-rank tensors $\bar{\boldsymbol{\psi}}_a^{(1)}$ and $\bar{\boldsymbol{\psi}}_a^{(3)}$, respectively. We again find that these evolution equations for fluxes are in the same mathematical forms as for the corresponding evolution equations in the classical theory, except that the macroscopic variables therein are quantum mechanically defined. Nevertheless, these are new results for quantum systems. In order to cast these evolution equations into the constitutive equations for observables measured in the laboratory and more suitable for formulating irreversible thermodynamics, we introduce the following macroscopic variables:

$$\Pi_a = \mathbf{P}_a - \tfrac{1}{3}(\mathbf{P}_a:\boldsymbol{\delta})\boldsymbol{\delta} \ , \tag{3.28a}$$

$$\Delta_a = \tfrac{1}{3}(\mathbf{P}_a:\boldsymbol{\delta}) - p_a \ , \tag{3.28b}$$

$$\mathbf{Q}_a' = \mathbf{Q}_a - \hat{h}_a \mathbf{J}_a \ , \tag{3.29}$$

where p_a is the pressure whose statistical definition will be given later at a more appropriate stage and $\hat{h}_a$ is the enthalpy per mass of species a: $\hat{h}_a = \mathcal{E}_a + p_a v_a$ with $v_a = \rho_a^{-1}$. Equations (3.28a) and (3.28b) mean that the stress tensor $\mathbf{P}_a$ is decomposable into the form

$$\mathbf{P}_a = \Pi_a + \Delta_a \boldsymbol{\delta} + p_a \boldsymbol{\delta} \ . \tag{3.30}$$

It is convenient to define the following abbreviations for the symmetrized molecular expressions appearing in the stress tensor and the heat flux:

$$\bar{\mathbf{h}}_{a\beta\gamma}^{(1)}=\tfrac{1}{4}m_a[C_{a\beta}C_{a\gamma}\delta_a+C_{a\beta}\delta_a C_{a\gamma}+C_{a\gamma}\delta_a C_{a\beta}+\delta_a C_{a\beta}C_{a\gamma}$$
$$-\tfrac{1}{3}(C_{a\varepsilon}^2\delta_a+C_{a\varepsilon}\delta_a C_{a\varepsilon}$$
$$+C_{a\varepsilon}\delta_a C_{a\varepsilon}+\delta_a C_{a\varepsilon}^2)\delta_{\beta\gamma}]\ , \tag{3.31}$$

$$\bar{\mathbf{h}}_a^{(2)}=[\tfrac{1}{12}m_a(C_a^2\delta_a+\mathbf{C}_a\delta_a\cdot\mathbf{C}_a+\mathbf{C}_a\delta_a\cdot\mathbf{C}_a+\delta_a C_a^2)$$
$$-(p_a/\rho_a)m_a\delta_a]\ , \tag{3.32}$$

$$\bar{\mathbf{h}}_a^{(3)}=[\tfrac{1}{16}m_a(C_a^2\mathbf{C}_a\delta_a+C_a^2\delta_a\mathbf{C}_a+2\mathbf{C}_a\mathbf{C}_a\delta_a\cdot\mathbf{C}_a$$
$$+2\mathbf{C}_a\delta_a\cdot\mathbf{C}_a\mathbf{C}_a+\mathbf{C}_a\delta_a C_a^2+\delta_a C_a^2\mathbf{C}_a)$$
$$-\tfrac{1}{2}\hat{h}_a m_a(\mathbf{C}_a\delta_a+\delta_a\mathbf{C}_a)]\ , \tag{3.33}$$

$$\bar{\mathbf{h}}_a^{(4)}=\tfrac{1}{2}m_a(\mathbf{C}_a\delta_a+\delta_a\mathbf{C}_a)\ , \tag{3.34}$$

where $\delta_{\beta\gamma}$ is a Kronecker delta and the Einstein summation convention is used for repeated greek indices. These definitions of moments motivate us to define the following:

$$\psi_{a\beta\gamma\varepsilon}^{(1)}=\bar{\psi}_{a\beta\gamma\varepsilon}^{(1)}-\tfrac{1}{3}\bar{\psi}_{a\sigma\sigma\varepsilon}^{(1)}\delta_{\beta\gamma}$$
$$=\mathrm{Tr}[\tfrac{1}{2}(\bar{\mathbf{h}}_{a\beta\gamma}^{(1)}C_{a\varepsilon}+C_{a\varepsilon}\bar{\mathbf{h}}_{a\beta\gamma}^{(1)})\mathbf{f}_a]\ , \tag{3.35}$$

$$\psi_{a\varepsilon}^{(2)}=\tfrac{1}{3}\bar{\psi}_{a\beta\beta\varepsilon}^{(1)}-(p_a/\rho_a)\mathbf{J}_{a\varepsilon}$$
$$=\mathrm{Tr}\{[\tfrac{1}{2}(\bar{\mathbf{h}}_{a\beta\beta}^{(1)}C_{a\varepsilon}+C_{a\varepsilon}\bar{\mathbf{h}}_{a\beta\beta}^{(1)})$$
$$-\tfrac{1}{2}(p_a/\rho_a)m_a(\mathbf{C}_a\delta_a+\delta_a C_a)]\mathbf{f}_a\}\ ,$$
$$=\mathrm{Tr}[\tfrac{1}{2}(\bar{\mathbf{h}}_a^{(2)}C_{a\varepsilon}+C_{a\varepsilon}\bar{\mathbf{h}}_a^{(2)})\mathbf{f}_a]\ , \tag{3.36}$$

$$\psi_{a\beta\gamma}^{(3)}=\bar{\psi}_{a\beta\gamma}^{(3)}-\hat{h}_a P_{a\beta\gamma}$$
$$=\mathrm{Tr}[\tfrac{1}{2}(\bar{\mathbf{h}}_{a\beta}^{(3)}C_{a\gamma}+C_{a\gamma}\bar{\mathbf{h}}_{a\beta}^{(3)})\mathbf{f}_a]\ . \tag{3.37}$$

With the molecular moments $\bar{\mathbf{h}}_a^{(1)}$, etc. defined earlier, we define the dissipative terms

$$\Lambda_a^{(k)}=\mathrm{Tr}(\bar{\mathbf{h}}_a^{(k)}\mathfrak{R}[\mathbf{f}_a])\quad(k=1,2,3,4,\ldots) \tag{3.38}$$

and the corresponding kinematic terms

$$\mathbf{Z}_a^{(k)}=(i\hbar)^{-1}\mathrm{Tr}[\tfrac{1}{2}m_a C_a^2,\mathbf{f}_a\bar{h}_a^{(k)}]$$
$$+\mathrm{Tr}\left[\mathbf{f}_a\left[\frac{\partial}{\partial t}\bar{\mathbf{h}}_a^{(k)}-(i\hbar)^{-1}[\mathbf{H}_a,\bar{\mathbf{h}}_a^{(k)}]\right]\right]$$
$$(k=1,2,3,4,\ldots)\ . \tag{3.39}$$

When the first term on the right-hand side of (3.39) is calculated a little further, the kinematic term may be written as

$$\mathbf{Z}_a^{(k)}=-\nabla\cdot\boldsymbol{\psi}_a^{(k)}+\mathrm{Tr}\left[\mathbf{f}_a\left[\frac{\partial}{\partial t}\bar{\mathbf{h}}_a^{(k)}-(i\hbar)^{-1}[\mathbf{H}_a,\bar{\mathbf{h}}_a^{(k)}]\right]\right]\ . \tag{3.39$'$}$$

Note that $\boldsymbol{\psi}_a^{(k)}$ $(k\le 3)$ are defined in (3.35)–(3.37). Calculated explicitly in terms of macroscopic variables, these kinematic terms are as follows:

$$\mathbf{Z}_a^{(1)}=-\nabla\cdot\boldsymbol{\psi}_a^{(1)}-[(d_t\mathbf{u}-\mathbf{F}_a)\mathbf{J}_a]^{(2)}$$
$$-2[\Pi_a\cdot\boldsymbol{\gamma}]^{(2)}-[\Pi_a,\omega]-\tfrac{2}{3}\Pi_a\nabla\cdot\mathbf{u}\ , \tag{3.40}$$

$$\mathbf{Z}_a^{(2)}=-\nabla\cdot\boldsymbol{\psi}_a^{(2)}-\tfrac{2}{3}(d_t\mathbf{u}-\mathbf{F}_a)\cdot\mathbf{J}_a-p_a d_t\ln(p_a v^{5/3})$$
$$-\tfrac{2}{3}\Pi_a{:}\gamma-\tfrac{2}{3}\Delta_a\nabla\cdot\mathbf{u}-\nabla\cdot(\mathbf{J}_a p_a/\rho_a)\ , \tag{3.41}$$

$$\mathbf{Z}_a^{(3)}=-\nabla\cdot\boldsymbol{\psi}_a^{(3)}-(\mathbf{P}_a-p_a\delta)\cdot(d_t\mathbf{u}-\mathbf{F}_a)$$
$$-\varphi_a^{(3)}{:}\nabla\mathbf{u}-\mathbf{Q}_a'\cdot\nabla\mathbf{u}-\mathbf{J}_a d_t\hat{h}_a-\mathbf{P}_a\cdot\nabla\hat{h}_a\ , \tag{3.42}$$

$$\mathbf{Z}_a^{(4)}=-\nabla\cdot\mathbf{P}_a-\rho_a(d_t\mathbf{u}-\mathbf{F}_a)-\mathbf{J}_a\cdot\nabla\mathbf{u}\ . \tag{3.43}$$

Here various symbols are defined by

$$\boldsymbol{\gamma}=\tfrac{1}{2}[\nabla\mathbf{u}+(\nabla\mathbf{u})^t]-\tfrac{1}{3}\delta\nabla\cdot\mathbf{u}\ ,$$

$$\omega=\tfrac{1}{2}[\nabla\mathbf{u}-(\nabla\mathbf{u})^t]\ ,$$

$$[\Pi_a,\omega]=\Pi_a\omega-\omega\Pi_a\ .$$

The evolution equations for $\Pi_a=\rho\hat{\Pi}_a$, $\Delta_a=\rho\hat{\Delta}_a$, $\mathbf{Q}_a'=\rho\hat{\mathbf{Q}}_a'$, $\mathbf{J}_a=\rho\hat{\mathbf{J}}_a$, and so on are then as follows:

$$\rho d_t\hat{\Pi}_a=\mathbf{Z}_a^{(1)}+\Lambda_a^{(1)}\ , \tag{3.44a}$$

$$\rho d_t\hat{\Delta}_a=\mathbf{Z}_a^{(2)}+\Lambda_a^{(2)}\ , \tag{3.44b}$$

$$\rho d_t\hat{\mathbf{Q}}_a'=\mathbf{Z}_a^{(3)}+\Lambda_a^{(3)}\ , \tag{3.44c}$$

$$\rho d_t\hat{\mathbf{J}}_a=\mathbf{Z}_a^{(4)}+\Lambda_a^{(4)}\ , \tag{3.44d}$$

etc., which will be simply represented by the equation

$$\rho d_t\hat{\mathbf{\Phi}}_a^{(k)}=Z_a^{(k)}+\Lambda_a^{(k)}\quad(k\ge 1)\ . \tag{3.44$'$}$$

Here the dissipative terms $\Lambda_a^{(k)}$ can be obtained from (3.25)–(3.27) by using the definitions of $\bar{\mathbf{h}}_{a\beta\gamma}^{(1)}$, etc. in (3.31)–(3.34); in fact, $\Lambda_a^{(4)}=\Lambda_a^{(d)}$. These evolution equations for fluxes Π_a, Δ_a, $\mathbf{Q}_a'$, and $\mathbf{J}_a$ are constitutive equations which characterize the nonequilibrium constitution of the material and irreversible processes therein. It must be noted that their mathematical structures are the same as the constitutive equations in the classical theory [3], except for the definitions of the macroscopic variables involved. Since the quantum system obeys the same macroscopic evolution equations as the classical system, this result is important for irreversible thermodynamics of the quantum system of interest here. Together with the conservation laws—balance equations for conserved variables (3.8), (3.10), (3.11), and (3.15)—the flux evolution equations (3.44a)–(3.44d) form the set of extended hydrodynamic equations describing irreversible processes in the system. These extended hydrodynamic equations reduce to the Navier-Stokes, Fourier, and Fick equations near equilibrium.

Before closing this subsection, we would like to make the following remark regarding (3.44d). This constitutive equation may be recast in a form which is closer to the classical equation of motion for the center of mass for species a. By transferring the $d_t\mathbf{u}$ term to the left and making use of the definition of diffusion flux

$$\mathbf{J}_a = \rho_a(\mathbf{u}_a - \mathbf{u}) , \tag{3.45}$$

which follows from the statistical definition of $\mathbf{J}_a$ (3.9), we obtain from (3.44d)

$$\rho_a d_t \mathbf{u}_a = \rho_a \mathbf{F}_a - (\nabla\cdot\mathbf{P}_a + \mathbf{J}_a\cdot\nabla\mathbf{u} + \mathbf{J}_a d_t \ln c_a) + \Lambda_a^{(4)} . \tag{3.46}$$

The term of the left-hand side is the acceleration, whereas the first term on the right-hand side is the force on the center of mass of species a; the first term in the parentheses, namely, $-\nabla\cdot\mathbf{P}_a$, gives rise to the thermodynamic driving force which, to the lowest-order approximation, is proportional to the mass fraction gradient, or the gradient of the chemical potential; and the last term $\Lambda_a^{(4)}$, the dissipative term, is related to the friction term to the lowest order since it is proportional to the diffusion flux itself with the proportionality constant being the friction constant. Therefore, (3.46) is similar to the Langevin equation, except that there is no fluctuating noise term unless one is prepared to assert that the second group of terms in the parentheses on the right-hand side of (3.46) is a fluctuating noise term. This identification, however, is not necessary in the present theory since a theory of transport processes can be satisfactorily constructed with the identification with a thermodynamic force mentioned. Equation (3.46) differs from the momentum balance equation appearing in the balance equation approach of Lei *et al.* [14], who obtained the equation by a perturbation method for the density matrix.

C. Entropy balance equation

The evolution equations for conserved and nonconserved variables presented earlier are subject to the constraint of the entropy principle, that is, the H theorem. Since the evolution equations are local, it is necessary to have the entropy constraint also in local form and such a local form is the balance equation for entropy. To derive it, it is first necessary to define an entropy density at position $\mathbf{r}$ and time t. We define the entropy density by

$$S(t) = \int_V d\mathbf{r}\, \rho \mathcal{S}(\mathbf{r},t) . \tag{3.47}$$

Comparison of this with the statistical definition of $S(t)$ in (2.10) yields the statistical formula for the entropy density

$$\begin{aligned} \rho\mathcal{S}(\mathbf{r},t) &= -k_B \sum_a^r \mathrm{Tr}[\mathbf{f}_a\{\delta_a \ln \mathbf{f}_a\} \\ &\qquad - \varepsilon_a(1+\varepsilon_a\mathbf{f}_a)\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}] \\ &= k_B \sum_a^r \mathrm{Tr}[\mathbf{f}_a\{\delta_a \ln(\varepsilon_a + \mathbf{f}_a^{-1})\} \\ &\qquad + \varepsilon_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}] , \end{aligned} \tag{3.48}$$

where the delta function δ_a is symmetrized with the logarithmic functions of $\mathbf{f}_a$ since the distribution function is generally a function of momentum. It is convenient to define

$$\mathfrak{J}_a = \varepsilon_a \mathbf{f}_a^{-1} \ln(1+\varepsilon_a\mathbf{f}_a) , \tag{3.49a}$$

$$\mathfrak{C} = \ln(\varepsilon_a + \mathbf{f}_a^{-1}) . \tag{3.49b}$$

By differentiating the formula (3.48) for the entropy density and using the kinetic equation together with the mathematical identities leading to (2.22) and (2.23), we obtain the entropy balance equation

$$\rho d_t \mathcal{S}(\mathbf{r},t) = -\nabla\cdot\mathbf{J}_s(\mathbf{r},t) + \sigma_{\mathrm{ent}}(\mathbf{r},t) , \tag{3.50}$$

where the entropy flux $\mathbf{J}_s$ and the entropy production σ_{ent} are given, respectively, by

$$\begin{aligned} \mathbf{J}_s(\mathbf{r},t) = k_B \sum_a^r \mathrm{Tr}(\tfrac{1}{2}[C_a\{(\mathfrak{C}_a + \mathfrak{J}_a)\delta_a\} \\ + \{(\mathfrak{C}_a + \mathfrak{J}_a)\delta_a\}C_a]\mathbf{f}_a) , \end{aligned} \tag{3.51}$$

$$\sigma_{\mathrm{entr}}(\mathbf{r},t) = -k_B \sum_a^r \mathrm{Tr}(\{\mathfrak{C}_a\delta_a\}\mathfrak{R}[\mathbf{f}_a]) . \tag{3.52}$$

The definition of the entropy production in (3.52) follows straightforwardly from the production term in (2.23) $k_B \sum_a^r \mathrm{Tr}\{\ln(\varepsilon_a + \mathbf{f}_a^{-1})\mathfrak{R}[\mathbf{f}_a]\}$, which we recover on integrating (3.52) over the volume of the system. The definition of the entropy flux $\mathbf{J}_s(\mathbf{r},t)$ in (3.51) arises as follows. First, observe that it stems from the first term on the right-hand side of (2.22). After symmetrizing the logarithmic factors with δ_a, the said term can be manipulated into the divergence form

$$
\begin{aligned}
&-k_B(i\hbar)^{-1}\mathrm{Tr}(\{\delta_a \ln \mathbf{f}_a\}[\mathbf{H}_a,\mathbf{f}_a]-\varepsilon_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}[\mathbf{H}_a,(1+\varepsilon_a\mathbf{f}_a)]) \\
&\quad = k_B(i\hbar)^{-1}\mathrm{Tr}([\mathbf{H}_a,\{\delta_a \ln \mathbf{f}_a\}]\mathbf{f}_a-\varepsilon_a[\mathbf{H}_a,\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}](1+\varepsilon_a\mathbf{f}_a)) \\
&\quad = (i\hbar)^{-1}\mathrm{Tr}\left[\frac{1}{2m_a}[p_a^2,\{\delta_a \ln \mathbf{f}_a\}]\mathbf{f}_a-\varepsilon_a\frac{1}{2m_a}[p_a^2,\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}](1+\varepsilon_a\mathbf{f}_a)\right] \\
&\quad = (i\hbar)^{-1}\mathrm{Tr}\Bigg[\frac{1}{2m_a}(\mathbf{p}_a\cdot[\mathbf{p}_a,\{\delta_a \ln \mathbf{f}_a\}]+[\mathbf{p}_a,\{\delta_a \ln \mathbf{f}_a\}]\cdot\mathbf{p}_a)\mathbf{f}_a \\
&\qquad\qquad -\varepsilon_a\frac{1}{2m_a}(\mathbf{p}_a\cdot[\mathbf{p}_a,\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}]+[\mathbf{p}_a,\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}]\cdot\mathbf{p}_a)(1+\varepsilon_a\mathbf{f}_a)\Bigg] \\
&\quad = (i\hbar)^{-1}\mathrm{Tr}\Bigg[\frac{1}{2m_a}[\mathbf{p}_a\cdot(\mathbf{p}_a\{\delta_a \ln \mathbf{f}_a\})+(\mathbf{p}_a\{\delta_a \ln \mathbf{f}_a\})\cdot\mathbf{p}_a]\mathbf{f}_a \\
&\qquad\qquad -\varepsilon_a\frac{1}{2m_a}(\mathbf{p}_a\cdot[\mathbf{p}_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}]+[\mathbf{p}_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}]\cdot\mathbf{p}_a)(1+\varepsilon_a\mathbf{f}_a)\Bigg] \\
&\quad = \boldsymbol{\nabla}\cdot\mathrm{Tr}\Bigg[\frac{1}{2m_a}(\mathbf{p}_a\{\delta_a \ln \mathbf{f}_a\}+\{\delta_a \ln \mathbf{f}_a\}\mathbf{p}_a)\mathbf{f}_a \\
&\qquad\qquad -\varepsilon_a\frac{1}{2m_a}[\mathbf{p}_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}+\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}\mathbf{p}_a](1+\varepsilon_a\mathbf{f}_a)\Bigg] \\
&\quad = -\boldsymbol{\nabla}\cdot[k_B\,\mathrm{Tr}(\tfrac{1}{2}[\mathbf{C}_a\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\}+\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\}\mathbf{C}_a]\mathbf{f}_a)+\mathbf{u}k_B\,\mathrm{Tr}[\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\}\mathbf{f}_a]]\,. \qquad (3.53)
\end{aligned}
$$

Therefore, summing this equation over species we obtain the divergence term in the entropy balance equation

$$
\begin{aligned}
\boldsymbol{\nabla}\cdot(\mathbf{J}_s+\rho\mathcal{S}\mathbf{u})=\boldsymbol{\nabla}\cdot\sum_a^r[k_B\,\mathrm{Tr}(\tfrac{1}{2}[\mathbf{C}_a\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\} \\
+\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\}\mathbf{C}_a]f_a) \\
+\mathbf{u}k_B\,\mathrm{Tr}[\{(\mathfrak{C}_a+\mathfrak{F}_a)\delta_a\}\mathbf{f}_a]]\,.
\end{aligned}
\qquad (3.54)
$$

In the fourth equality of (3.53), $(\mathbf{p}_a\{\delta_a \ln \mathbf{f}_a\})$ means that $\mathbf{p}_a$ operates on $\{\delta_a \ln \mathbf{f}_a\}$ only and similarly for $[\mathbf{p}_a\{\delta_a \ln(1+\varepsilon_a\mathbf{f}_a)\}]$. For the fifth equality the property of the derivative of a delta function is used. Note that if the distribution function vanishes at the boundaries of the system, then this divergence term, when integrated over the volume, does not contribute to the time derivative of the entropy (dS/dt). This was the result we used for (2.23).

IV. NONEQUILIBRIUM CANONICAL FORM FOR THE DENSITY MATRIX AND IRREVERSIBLE THERMODYNAMICS

To make the extended hydrodynamic equations derived in the preceding section useful for the study of macroscopic irreversible processes, it is necessary to be more explicit about the flux dependence of the dissipation terms $\Lambda_a^{(k)}$ and the entropy production as well as the entropy flux. This aim cannot be achieved unless an explicit form is used for the collision term $\mathfrak{R}[\mathbf{f}_a]$ in the kinetic equation. Nevertheless, there still are some aspects of irreversible thermodynamics which we can uncover without using an explicit form for the collision term. We will first take up this line of study, since then the results we obtain thereby will be deemed general, not being subordinated to a particular model taken for the collision term. The BNUU models for the collision term will be explicitly used and then a theory of transport processes can be developed with the dissipation terms calculated with the model for the collision term in a sequel to this work.

A. Equilibrium solution of the kinetic equation

The equilibrium solution of the kinetic equation has been defined in connection with the H theorem as a density matrix satisfying (2.9). Since only the collision invariants such as mass, momentum, and energy satisfy (2.9) by condition 1 on $\mathfrak{R}[\mathbf{f}_a]$, it follows that $\ln(\varepsilon_a+\mathbf{f}_{a_{\mathrm{eq}}}^{-1})$ must be a linear combination of the collision invariants. Thus it is possible to write $\mathbf{f}_{a_{\mathrm{eq}}}$ in the form

$$\mathbf{f}_{a_{\mathrm{eq}}}=[\exp[\beta_e(\mathbf{H}_a-\mu_a^e)]-\varepsilon_a]^{-1}\,, \qquad (4.1)$$

where μ_a^e is the normalization factor determined by the equation

$$n_a=\mathrm{Tr}\{\delta_a[\exp\beta_e(\mathbf{H}_a-\mu_a^e)-\varepsilon_a]^{-1}\} \qquad (4.2)$$

and β_e is a parameter to be determined shortly. Substitution of (4.1) into (2.10) yields the equilibrium entropy S_e:

$$S_e=k_B\beta_e\left[E_e+p_eV-\sum_a^r\hat{\mu}_a^e N_a\right]\,, \qquad (4.3)$$

where

$$\hat{\mu}_a^e = \mu_a^e / m_a \ , \tag{4.4a}$$

$$E_e = \sum_a^r \mathrm{Tr}(\mathbf{H}_a \mathbf{f}_{a_{\mathrm{eq}}}) \ , \tag{4.4b}$$

$$p_e V = -\beta_e^{-1} \sum_a^r \mathrm{Tr}\{\varepsilon_a \ln[1 - \varepsilon_a \exp\beta_e(\mu_a^e - \mathbf{H}_a)]\} \ . \tag{4.4c}$$

Identifying E_e, p_e, and S_e with the thermodynamic internal energy, pressure, and thermodynamic entropy, respectively, and thus μ_a^e with the thermodynamic chemical potential according to the general methodology in the Gibbs ensemble theory, we are led to conclude that β_e is related to the absolute temperature of the system by the following relation:

$$\beta_e = 1/k_B T_e \ , \tag{4.5}$$

where T_e is the absolute temperature for the system in thermal equilibrium. This procedure of identifying β_e with the inverse $k_B T_e$ may be done by means of the entropy differential, but the final result obtained thereby will be the same. The equilibrium solution (4.1), namely, the canonical density matrix for quantum particles (i.e., Bose-Einstein or Fermi-Dirac density matrix), is unique since there is only one linear combination of collision invariants possible for $\ln(\varepsilon_a + \mathbf{f}_{a_{\mathrm{eq}}}^{-1})$, and this uniqueness is a necessary consequence of the H theorem. The point we would like to emphasize here is that although it is not necessary to explicitly specify the collision term $\mathfrak{R}[\mathbf{f}_a]$ to obtain unique equilibrium solution, a kinetic equation satisfying the H theorem is essential to obtain a unique equilibrium solution. Equilibrium thermodynamic functions can be calculated from the equilibrium canonical density matrix (4.1).

B. Nonequilibrium canonical form for the density matrix

The nonequilibrium density matrix $\mathbf{f}_a$ can be constructed in a form similar to the equilibrium canonical matrix in (4.1). The reasoning behind such a construction is that, first of all, it is necessary to have the entropy production in a simple bilinear form similar to the form in the classical theory if its physical interpretation as the seat of energy dissipation is to remain the same as in the classical kinetic theory. Since the statistical formula for the entropy production contains $\ln(\varepsilon_a + \mathbf{f}_a^{-1})$, the only way to obtain a simple bilinear form for the entropy production is to express $\mathbf{f}_a$ in a canonical form as in (4.1). However, the meanings of the parameters such as β_e and μ_a^e in (4.1) cannot remain the same and require generalizations. The nonequilibrium canonical form for $\mathbf{f}_a$ is expected to include a parameter related to the temperature since even the thermal state of a nonequilibrium system must be characterized by a temperature or its spatial distribution. Therefore, it will be required to define the temperature of the nonequilibrium system. But its definition must be operational, that is, the nonequilibrium temperature must be directly measurable or given in terms of directly measurable quantities. To prepare for such a statistical definition [15], we first define the statistical temperature for the system in equilibrium. For quantum systems we define T_e by the statistical formula

$$\tfrac{3}{2}\zeta_e k_B T_e = \sum_a^r \mathrm{Tr}[\tfrac{1}{8} m_a (C_a^2 \delta_a + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a + \delta_a C_a^2) \mathbf{f}_{a_{\mathrm{eq}}}] \Big/ \sum_a^r \mathrm{Tr}(\delta_a \mathbf{f}_{a_{\mathrm{eq}}}) \ , \tag{4.6}$$

where ζ_e is a homogeneous zero-order function of μ_a^e and β_e^{-1} or, put in other words, a function of reduced variable $\bar{\mu}_a^e = \mu_a^e / m_a T_e = \hat{\mu}_a^e / T_e$ only. This reduced variable $\bar{\mu}_a^e$ is homogeneous zero degree of $\hat{\mu}_a^e$ and T_e. In the case of classical gases, $\zeta_e = 1$. This parameter ζ_e is the correction for the equipartition law in quantum theory. In (4.6) the factor $\frac{1}{8}$ is decomposable into the factors $\frac{1}{4}$ and $\frac{1}{2}$, the former accounting for the symmetrization of $\mathbf{C}_a$ and δ_a and the latter being a factor in the kinetic energy. Equation (4.6) says that the mean kinetic energy of a particle is first-degree homogeneous in $k_B T_e$. This property is true regardless of whether the particle is classical or quantum.

Since $\mathbf{f}_a$ is looked for in a canonical form similar to (4.1), we now define the nonequilibrium temperature by the statistical formula

$$\tfrac{3}{2}\zeta k_B T = \sum_a^r \mathrm{Tr}[\tfrac{1}{8} m_a (C_a^2 \delta_a + 2\mathbf{C}_a \cdot \delta_a \mathbf{C}_a + \delta_a C_a^2) \mathbf{f}_a] \Big/ \sum_a^r \mathrm{Tr}(\delta_a \mathbf{f}_a) \ . \tag{4.7}$$

In this statistical formula, the left-hand side is an abbreviation of the right-hand side, which has no other operational meaning than it is a mean kinetic energy of the system in a nonequilibrium state. It is essential for making the ensuing theory something more than a symbolism to give it a thermodynamic operational meaning. The thermodynamic operational meaning of the parameter T is fixed by its correspondence to the local equilibrium temperature $T_e(\mathbf{r},t)$, which is made dependent on position and time and determined thermodynamically at position $\mathbf{r}$ in the system and at time t; to make this position and time dependence clear and distinguish the equilibrium T_e from the local equilibrium T_e, we have made $\mathbf{r}$ and t explicit in T_e. To be more precise, we take a sufficiently small volume around position $\mathbf{r}$ at time t which contains a sufficiently large number of particles as to make a statistical mechanical method applicable. This small volume is locally in equilibrium with a temperature probe (i.e., thermometer) of a sufficiently small size, which is calibrated to the absolute thermodynamic scale. This local temperature is in fact the contact temperature for the volume element at $\mathbf{r}$ and t of interest. This contact temperature gives the just defined nonequilibrium temperature a thermodynamic operational meaning when it is matched with the contact temperature, namely $T_e(\mathbf{r},t)$ at position $\mathbf{r}$ and t as is done below. It must be remarked that this use of local equilibrium temperature does not mean that the whole system is in equilibrium; rather it means that the temperature at $\mathbf{r}$ and t of the nonequilibrium system is the contact temperature of the volume element at $\mathbf{r}$ and at time t, which is measured with the ideal gas thermometer in the absolute temperature scale. The temperature T is defined and given an operational meaning such that

$$\zeta=\frac{\sum_{a}^{r}\mathrm{Tr}[\frac{1}{8}(z_a^2\delta_a+2\mathbf{z}_a\cdot\delta_a\mathbf{z}_a+\delta_a z_a^2)\mathbf{f}_a(\mathbf{z}_a)]}{\sum_{a}^{r}\mathrm{Tr}[\delta_a\mathbf{f}_a(\mathbf{z}_a)]}$$

$$=\frac{\sum_{a}^{r}\mathrm{Tr}[\frac{1}{8}(z_a^2\delta_a+2\mathbf{z}_a\cdot\delta_a\mathbf{z}_a+\delta_a z_a^2)\mathbf{f}_{a_{\mathrm{eq}}}(\mathbf{z}_a)]}{\sum_{a}^{r}\mathrm{Tr}[\delta_a\mathbf{f}_{a_{\mathrm{eq}}}(\mathbf{z}_a)]}=\zeta_e\ , \tag{4.8}$$

where $z_a=(m_a\beta)^{1/2}\mathbf{C}_a$ for ζ in the first line and $z_a=(m_a\beta_e)^{1/2}\mathbf{C}_a$ for ζ_e in the second line. In addition to this, the internal energy, momentum, and density satisfy the matching conditions. The internal energy is matched with the local equilibrium internal energy $\mathscr{E}=\mathscr{E}_e$, where $\mathscr{E}_e$ is the internal energy computed by means of $\mathbf{f}_{a_{\mathrm{eq}}}$. That is,

$$\rho\mathscr{E}=\sum_{a}^{r}\mathrm{Tr}[\tfrac{1}{8}m_a(C_a^2\delta_a+2\mathbf{C}_a\delta_a\cdot\mathbf{C}_a+\delta_a C_a^2)\mathbf{f}_a]$$

$$=\sum_{a}^{r}\mathrm{Tr}[\tfrac{1}{8}m_a(C_a^2\delta_a+2\mathbf{C}_a\delta_a\cdot\mathbf{C}_a+\delta_a C_a^2)\mathbf{f}_{a_{\mathrm{eq}}}]=\rho_e\mathscr{E}_e\ . \tag{4.9a}$$

For the rest of the matching conditions, we impose the following on the mean velocity and mass density:

$$\rho\mathbf{u}=\sum_{a}^{r}\mathrm{Tr}[\tfrac{1}{2}(p_a\delta_a+\delta_a\mathbf{p}_a)\mathbf{f}_a]$$

$$=\sum_{a}^{r}\mathrm{Tr}[\tfrac{1}{2}(\mathbf{p}_a\delta_a+\delta_a\mathbf{p}_a)\mathbf{f}_{a_{\mathrm{eq}}}]=\rho_e\mathbf{u}\ , \tag{4.9b}$$

$$\rho=\sum_{a}^{r}\mathrm{Tr}(m_a\delta_a\mathbf{f}_a)=\sum_{a}^{r}\mathrm{Tr}(m_a\delta_a\mathbf{f}_{a_{\mathrm{eq}}})=\rho_e\ . \tag{4.9c}$$

These matching conditions follow necessarily and sufficiently for the conserved variables from the kinetic equation postulated if the system is spatially homogeneous since the mass, momentum, and kinetic energy are collision invariants of $\Re[\mathbf{f}_a]$ in the kinetic equation. It can be shown by using the same method as in Ref. [3]. The matching condition on the mean mass densities may be replaced with a similar condition on the number densities:

$$n=\sum_{a}^{r}\mathrm{Tr}(\delta_a\mathbf{f}_a)=\sum_{a}^{r}\mathrm{Tr}(\delta_a\mathbf{f}_{a_{\mathrm{eq}}})=n_e\ . \tag{4.9c$'$}$$

Under these matching conditions and (4.8) the temperatures match:

$$T=T_e(\mathbf{r},t) \tag{4.10}$$

and thus T is given a physical meaning as the position- and time-dependent local absolute temperature $T_e(\mathbf{r},t)$ at $\mathbf{r}$ and t. These matching conditions are essential for making operational the formalism of irreversible thermodynamics presented below.

The nonequilibrium density matrix must be constructed such that these matching conditions (4.8)–(4.9c) are satisfied and the parameters T and ρ in the nonequilibrium density matrix are endowed with thermodynamic operational meanings. To implement this strategy, we construct the local reference density matrix $\mathbf{f}_a^0$ involving T, ρ_a, and μ_a^e such that

$$\mathbf{f}_a^0=[\exp\beta(\mathbf{H}_a^0-\mu_a^0)-\varepsilon_a]^{-1}\quad(\beta=1/k_BT)\ , \tag{4.11a}$$

where β is the nonequilibrium parameter defined by the left-hand side of (4.9a) and given the thermodynamic operational meaning by the right-hand side of (4.10), and similarly for μ_a^0 by the normalization of $\mathbf{f}_a^0$

$$n_a=\mathrm{Tr}(\delta_a\mathbf{f}_a^0)\ . \tag{4.11b}$$

Finally, $\mathbf{H}_a^0=\frac{1}{2}m_aC_a^2$. On the basis of β and μ_a^0 so determined, the nonequilibrium density matrix $\mathbf{f}_a$ is looked for in the form

$$\mathbf{f}_a=[\exp\beta(\mathbf{H}_a^0+\mathbf{H}_a^1-\mu_a)-\varepsilon_a]^{-1}\ . \tag{4.12}$$

This is the nonequilibrium canonical form for the quantum gas of interest to which we have alluded earlier. Here μ_a is the normalization factor of $\mathbf{f}_a$ defined by the relation

$$n_a=\mathrm{Tr}\{\delta_a[\exp\beta(\mathbf{H}_a^0+\mathbf{H}_a^1-\mu_a)-\varepsilon_a]^{-1}\} \tag{4.13}$$

and $\mathbf{H}_a^1$ is the nonequilibrium correction to be determined. It is a function of $\mathbf{p}_a$ to be determined such that the density matrix in (4.12) is consistent with the H theorem. This will be the subject of discussion in this section.

Let us first introduce a weight function ω_a such that

$$\omega_a=(2\pi)^{-3/2}\exp(-\tfrac{1}{2}x_a^2)\ , \tag{4.14a}$$

where

$$\mathbf{x}_a=(m_a\beta)^{1/2}\mathbf{C}_a\ . \tag{4.14b}$$

This function ω_a will be the weight function for an orthogonal set $\{\mathscr{H}^{(k)}(x_a)\colon k\geq 1\}$ of tensor Hermite polynomials. With the subscript a omitted from the argument, a few leading elements of the set are

$$\mathscr{H}^{(0)}(\mathbf{x})=1,\quad \mathscr{H}_a^{(1)}(\mathbf{x})=x_a\ ,$$

$$\mathscr{H}_{\alpha\beta}^{(2)}(\mathbf{x})=x_\alpha x_\beta-\delta_{\alpha\beta}\ , \tag{4.14c}$$

$$\mathscr{H}_{\alpha\beta\gamma}^{(3)}(\mathbf{x})=x_\alpha x_\beta x_\gamma-\delta_{\alpha\beta}x_y-\delta_{\alpha\gamma}x_\beta-\delta_{\beta\gamma}x_\alpha\ ,$$

etc. The properties of these orthogonal polynomials are discussed in Refs. [16] and [17] to which the reader is referred. It is sufficient for our purpose here to note that these polynomials are orthogonal in the following sense:

$$\mathrm{Tr}[\delta_a\mathscr{H}_i^{(k)}(\mathbf{x}_a)\mathscr{H}_j^{(m)}(\mathbf{x}_a)\omega_a(\mathbf{x}_a)]=\delta_{km}\delta_{ij}^k\ , \tag{4.14d}$$

where $i=(i_1,i_2,\ldots,i_k)$ and $j=(j_1,j_2,\ldots,j_m)$ and δ_{ij}^k

stands for the sum of all nonredundant permuted products of k Kronecker deltas whose subscripts are composed of indices drawn one each from the sets $i=(i_1,i_2,\ldots,i_k)$ and $j=(j_1,j_2,\ldots,j_m)$. This orthogonality relation looks different from the orthogonality relations of classical orthogonal polynomials, but it is easy to see that they are the same if the momentum representation is used for the quantities involved. Another way to see it is to use the Fourier transform method together with the Wigner distribution functions; see Ref. [15(a)]. This method easily transforms (4.14d) into the same form as the classical expression.

Since the local equilibrium can be treated as the reference state, it is reasonable to construct the nonequilibrium density matrix on the local equilibrium density matrix $\mathbf{f}_a^0$. Therefore, we are motivated to look for an expansion of $\mathbf{f}_a-\mathbf{f}_a^0$ in a series. By using the weighting function $\omega_a(\mathbf{x}_a)=(2\pi)^{-3/2}\exp(-\beta\mathbf{H}_a^0)$, we expand $\mathbf{f}_a$ in the form

$$\begin{aligned}\mathbf{f}_a&=\mathbf{f}_a^0+\exp[-\beta(\mathbf{H}_a^0-\mu_a^0)]\sum_{k\ge1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\\&=\mathbf{f}_a^0+(2\pi)^{-3/2}\exp(\beta\mu_a^0)\omega_a(\mathbf{x}_a)\sum_{k\ge1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\ .\end{aligned}\tag{4.15}$$

The normalization conditions (4.11b) and (4.13) demand

$$\mathrm{Tr}\left\{\delta_a\omega_a(\mathbf{x}_a)\sum_{k\ge1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right\}=0\ .$$

This expansion (4.15) is a quantum version of the classical Grad moment expansion [16] to which it reduces if the gas obeys the Boltzmann statistics, namely, if $\varepsilon_a=0$. We also remark that this expansion is consistent with the matching conditions in (4.9) and (4.8) since $\mathbf{f}_{a_{\mathrm{eq}}}$ may be replaced by $\mathbf{f}_a^0$. Thus, if the collision invariants are collectively denoted by ϕ, then the matching conditions may be expressed by $\langle\phi(\mathbf{f}_a-\mathbf{f}_a^0)\rangle=0$, which is evidently satisfied by the expansion (4.15) because of the orthogonality relation (4.14d). Therefore, the nonequilibrium canonical form (4.12) is consistent with the matching conditions since it is constructed from (4.15), as will be shown shortly. We take this approach of using expansion (4.15) since this expansion is easier to construct in a way consistent with the matching conditions than the nonequilibrium canonical form (4.12), although the latter is best suited for formulating a theory of irreversible thermodynamics. Thus the strategy is to deduce the nonequilibrium canonical form from the quantum Grad expansion (4.15) constructed such that the matching conditions are satisfied. We will show how to construct the nonequilibrium canonical form (4.12).

First, the expansion coefficients $A_a^{(k)}$ in (4.15) may be determined in terms of macroscopic variables. For this purpose, we first define

$$\Theta_a^{(k)}=\mathrm{Tr}[\delta_a\mathcal{H}^{(k)}(\mathbf{x}_a)\mathbf{f}_a]\ ,\tag{4.16a}$$

$$\varTheta_a^{(k)}=\mathrm{Tr}[\delta_a\mathcal{H}^{(k)}(\mathbf{x}_a)\mathbf{f}_a^0]\ .\tag{4.16b}$$

On multiplying $\delta_a\mathcal{H}^{(k)}(\mathbf{x}_a)$ by (4.16), taking the trace, and using the orthogonality of the tensor Hermite polynomials, we obtain the desired relation of the expansion coefficient to the macroscopic variables just defined in (4.16):

$$A_{aj}^{(k)}\delta_{ij}^k=(2\pi)^{-3/2}\exp(-\beta\mu_a^0)[\Theta_{ai}^{(k)}-\varTheta_{ai}^{(k)}]\ .\tag{4.17}$$

The macroscopic variables $\Theta_a^{(k)}$ are linearly related to $\Phi_a^{(k)}$ introduced earlier since the set $\{\bar{h}_a^{(k)}\}$ defined in (3.31)–(3.34) is linearly related to the set of $\{\mathcal{H}^{(k)}(\mathbf{x}_a)\}$. Therefore, $\Theta_a^{(k)}$ and thus $A_a^{(k)}$ can be determined from $\Phi_a^{(k)}$, which obey the evolution equations (3.44′).

We now observe that the nonequilibrium canonical form (4.12) may be rearranged to the form

$$\exp\beta(\mathbf{H}_a^0+\mathbf{H}_a^1-\mu_a)=\varepsilon_a+\mathbf{f}_a^{-1}\ ,\tag{4.12′}$$

and on taking logarithm of (4.12′), substituting (4.16) for $\mathbf{f}_a^{-1}$, and rearranging the terms, it is possible to relate $\mathbf{H}_a^1$ to $A_a^{(k)}$ as follows:

$$\begin{aligned}\beta(\mathbf{H}_a^1-\Delta\mu_a)&\\&=-\ln\left[1+(1+\varepsilon_a\mathbf{f}_a^0)^{-1}\sum_{k\ge1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\\&\quad+\ln\left[1+\varepsilon_a\mathbf{f}_a^0(1+\varepsilon_a\mathbf{f}_a^0)^{-2}\sum_{k\ge1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\ ,\end{aligned}\tag{4.18}$$

where

$$\Delta\mu_a=\mu_0'-\mu_a^0\tag{4.19}$$

with $\mu_0'=\mu_a-\mathfrak{B}_a$ and the following relations have been used:

$$(1+\varepsilon_a\mathbf{f}_a^0)^{-1}=1-\varepsilon_a\exp[-\beta(\mathbf{H}_a^0-\mu_a^0)]\ ,$$

$$\begin{aligned}\varepsilon_a\mathbf{f}_a^0(1+\varepsilon_a\mathbf{f}_a^0)^{-2}&=\varepsilon_a\exp[-\beta(\mathbf{H}_a^0-\mu_a^0)]\\&\quad\times\{1-\varepsilon_a\exp[-\beta(\mathbf{H}_a^0-\mu_a^0)]\}\ .\end{aligned}$$

One may then determine $\mathbf{H}_a^1$ in (4.13) from (4.18) by using (4.17) for $A_a^{(k)}$ and the orthogonality relation (4.14d) as will be shown presently.

The ε_a-dependent terms in (4.18) the quantum corrections. On setting $\varepsilon_a=0$, we recover the classical result [7]. Here it is important to remark that μ_a is essentially the chemical potential of the system subject to an external field (e.g., the electrochemical potential if the external field is electrical) and therefore $\mu_a^m\equiv\mu_a-\mathfrak{B}_a$ is the matter part of the chemical potential. Equation (4.12) gives $\mathfrak{C}_a$ in (3.49b) a more explicit form:

$$\mathfrak{C}_a=\beta(\mathbf{H}_a^0+\mathbf{H}_a^1-\mu_a')\ .\tag{4.20}$$

The relation (4.18) suggests that $\mathbf{H}_a^1$ is expressible in terms of the complete set $\{\mathcal{H}^{(k)}(x_a)\colon k\ge1\}$. Therefore, we expand $\mathbf{H}_a^1$ into a series of $\mathcal{H}^{(k)}(\mathbf{x}_a)$ ($k\ge1$) and determined the expansion coefficients. Thus we write

$$\mathbf{H}_a^1=\sum_{k\ge1}Y_a^{(k)}\mathcal{H}_a^{(k)}\ .\tag{4.21}$$

The expansion coefficients $Y_a^{(k)}$ depend on macroscopic variables only. They may be determined as follows. On substitution of (4.21) into (4.18) and using the orthogonality relations (4.14d), we obtain a pair of equations relating $Y_a^{(k)}$ and $A_a^{(k)}$:

$$Y_{aj}^{(k)}\delta_{ij}^{k}=-\beta^{-1}\mathrm{Tr}\left[\omega(\mathbf{x}_a)\delta_a\mathcal{H}_i^{(k)}(\mathbf{x}_a)\ln\left[1+(1+\varepsilon_a\mathbf{f}_a^0)^{-1}\sum_{k\geq 1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\right]$$

$$+\beta^{-1}\mathrm{Tr}\left[\omega(\mathbf{x}_a)\delta_a\mathcal{H}_i^{(k)}(\mathbf{x}_a)\ln\left[1+\varepsilon_a\mathbf{f}_a^0(1+\varepsilon_a\mathbf{f}_a^0)^{-2}\sum_{k\geq 1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\right]\,, \tag{4.22a}$$

$$\Delta\mu_a=\beta^{-1}\mathrm{Tr}\left[\omega(\mathbf{x}_a)\delta_a\ln\left[1+(1+\varepsilon_a\mathbf{f}_a^0)^{-1}\sum_{k\geq 1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\right]$$

$$-\beta^{-1}\mathrm{Tr}\left[\omega(\mathbf{x}_a)\delta_a\ln\left[1+\varepsilon_a\mathbf{f}_a^0(1+\varepsilon_a\mathbf{f}_a^0)^{-2}\sum_{k\geq 1}A_a^{(k)}\mathcal{H}^{(k)}(\mathbf{x}_a)\right]\right]\,. \tag{4.22b}$$

It is a matter of computing the right-hand sides of these equations to find $\{Y_a^{(k)}:\,k\geq 1\}$ in terms of $\{A_a^{(k)}:\,k\geq 1\}$. This problem is akin to the calculation of the partition function in equilibrium statistical mechanics. We assume that such a calculation is done in principle. These equations then make it possible to construct a nonequilibrium canonical form (4.12), given the quantum Maxwell-Grad expansion, in a way consistent with the matching conditions on the nonequilibrium density matrix and the condition on temperature. However, the set $\{\mathcal{H}^{(k)}(\mathbf{x}_a):\,k\geq 1\}$ is not directly related to the observables used in the measurements of transport processes. We have seen that the set motivated by such observables consists of $\{\bar{h}_a^{(k)}:\,k\geq 1\}$ given in (3.31)–(3.34). In view of this, we construct the following set:

$$\mathbf{h}_a^{(1)}=m_a(\mathbf{C}_a\mathbf{C}_a-\tfrac{1}{3}\delta C_a^2)\,, \tag{4.23a}$$

$$\mathbf{h}_a^{(2)}=\tfrac{1}{3}m_aC_a^2-p_a/n_a\,, \tag{4.23b}$$

$$\mathbf{h}_a^{(3)}=m_a(\tfrac{1}{2}C_a^2\mathbf{C}_a-\hat{h}_a\mathbf{C}_a)\,, \tag{4.23c}$$

$$\mathbf{h}_a^{(4)}=m_a\mathbf{C}_a\,, \tag{4.23d}$$

etc. Here $\hat{h}_a$ is the enthalpy per mass of species a and

$$p_a=\beta^{-1}\mathrm{Tr}[\delta_a\varepsilon_a\ln(1+\varepsilon_a\mathbf{f}_a)]\,. \tag{4.23e}$$

This is the statistical definition of p_a introduced in Sec. III. We assume that these suitably arranged polynomials form a complete set $\{h_a^{(k)}:\,k\geq 1\}$. These polynomials are tensor Hermite polynomials [16,17] of $\mathbf{C}_a$ and may be expressed as linear combinations of $\mathcal{H}^{(k)}(\mathbf{x}_a)$ introduced earlier. For example,

$$\mathbf{h}_a^{(1)}=k_BT[\mathcal{H}^{(2)}(\mathbf{x}_a)-\tfrac{1}{3}\delta\mathcal{H}_{\alpha\alpha}^{(2)}(\mathbf{x}_a)]\,, \tag{4.24a}$$

$$\mathbf{h}_a^{(2)}=k_BT[\tfrac{1}{3}\mathcal{H}_{\alpha\alpha}^{(2)}(\mathbf{x}_a)-\mathcal{L}_a] \tag{4.24b}$$

$$\mathbf{h}_a^{(3)}=\tfrac{1}{2}k_BT(k_BT/m_a)^{1/2}[\mathcal{H}_{\alpha\alpha}^{(3)}(\mathbf{x}_a)-\mathscr{h}_a\mathcal{H}^{(1)}(\mathbf{x}_a)]\,, \tag{4.24c}$$

$$\mathbf{h}_a^{(4)}=(m_ak_BT)^{1/2}\mathcal{H}^{(1)}(\mathbf{x}_a)\,, \tag{4.24d}$$

etc., where the Einstein summation convention is used for repeated subscripts for Cartesian components and

$$\mathcal{L}_a=p_a/n_ak_BT-1\,,\qquad \mathscr{h}_a=2(m_a/k_BT)\hat{h}_a-5\,. \tag{4.25}$$

Note that for classical systems $\mathcal{L}_a=\mathscr{h}_a=0$, but for quantum systems these quantities may be given in series of the Planck constant or the virial coefficients proportional to powers of $\hbar$. The set (4.23) becomes $\bar{\mathbf{h}}_a^{(k)}$: $k=1,2,3,4,\ldots\}$ when suitably symmetrized on multiplication of delta function δ_a to the terms on the right-hand side:

$$\bar{\mathbf{h}}_a^{(k)}=\{\mathbf{h}_a^{(k)}\delta_a\}\,. \tag{4.23$'$}$$

The tensorial set $\{\mathbf{h}_a^{(k)}\}$ is a quantum mechanical operator version of the complete set used in the classical version of the modified moment method [3]. The leading members of the polynomial set presented here are clearly orthogonal to each other either for symmetry reason or by construction.

It is more convenient to expand $\mathbf{H}_a^1$ in the measurement-motivated set $\{h_a^{(k)}:\,k\geq 1\}$ than the tensorial set $\{\mathcal{H}^{(k)}:\,k\geq 1\}$. Thus we expand

$$\mathbf{H}_a^1=\sum_{k\geq 1}X_a^{(k)}h_a^{(k)} \tag{4.26}$$

and the nonequilibrium density matrix is then written in the form

$$\mathbf{f}_a=\left[\exp\beta\left[\mathbf{H}_a^0+\sum_{k\geq 1}X_a^{(k)}h_a^{(k)}-\mu_a\right]-\varepsilon_a\right]^{-1}\,. \tag{4.27}$$

Here $\mathbf{X}_a^{(k)}$ are vectors or tensors depending only on macroscopic variables which determine the time and position dependence of the density matrix $\mathbf{f}_a$. The polynomials $\mathbf{h}_a^{(k)}$ are conjugate vectors or tensors depending on momenta. The expansion coefficients $X_a^{(k)}$ are now determined from $Y_a^{(k)}$ already given in terms of $A_a^{(k)}$ by the relation

$$\sum_{k\geq 1}\mathrm{Tr}[\delta_a\omega_a(\mathbf{x}_a)\mathcal{H}_i^{(k)}(\mathbf{x}_a)h_{aj}^{(l)}]X_{aj}^{(l)}=Y_{aj}^{(l)}\delta_{ij}^{l}\,. \tag{4.28}$$

This equation is easily obtained by equating (4.21) and (4.26) and making use of the orthogonality relation (4.14d). This set of algebraic equations determine $X_a^{(k)}$ in terms of macroscopic variables $\Phi_a^{(k)}$ $(k\geq 1)$ through the chain of equations (4.22a), (4.22b), (4.17), and (4.24). Since we do not need the explicit formulas for the relations of $X_a^{(k)}$ to $\Phi_a^{(k)}$ in this paper, we will not dwell on them. We use the nonequilibrium canonical form (4.27) to construct a theory of irreversible processes in the following. We emphasize, however, that the expansion (4.26), equivalent to (4.21), is not essential for constructing a basic mathematical structure of thermodynamics of irreversible processes since one can obtain such a structure in terms of variables $\Theta_a^{(k)}$ instead of variables $\Phi_a^{(k)}$.

In this connection note that $\Theta_a^{(k)}$ are linearly related to $\Phi_a^{(k)}$, as is clear from relations in (4.24). Finally, we remark that the nonequilibrium canonical form leaves the H theorem satisfied regardless of the approximation taken for $Y_a^{(k)}$ or $X_a^{(k)}$. It is one of the most powerful aspects of the nonequilibrium canonical form. This statement is easily verified by using (A2) in Appendix A.

Before we proceed further, we pause to examine the significance entailed by the nonequilibrium canonical form (4.27) or (4.12) with (4.21). Since $\mathfrak{C}_a$ in (4.20) was originally defined as an operator consisting of a complete set of operators in the Hilbert space for the system, the representation of $\mathfrak{C}_a$ in (4.20) with $\mathbf{H}_a^1$ expanded as in either (4.21) or (4.26) is a projection of the Hilbert space $\mathfrak{C}_a$ onto the space of macroscopic variables consisting of $\mathbf{X}_a^{(k)}$ or $Y_a^{(k)}$. This projection is accompanied by a contraction of information and nonbijective. The thermodynamic consequence of this contraction of information will be clarified later when we will have calculated the entropy and related differentials.

On substitution of the nonequilibrium canonical form (4.27) into the statistical expression for the entropy production, the following more insightful form for the entropy production follows:

$$\sigma_{\text{ent}}=T^{-1}\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)}\Lambda_a^{(k)} \;. \tag{4.29}$$

This form is identical with the entropy production in the classical theory. This bilinear form made up of $\mathbf{X}_a^{(k)}$, which appears in the density matrix $\mathbf{f}_a$, and $\Lambda_a^{(k)}$, which is the dissipation term in the evolution equation for $\hat{\Phi}_a^{(k)}$, gives a physically transparent interpretation for the entropy production that the energy of the system dissipates from a useful to a less useful form through a dissipative evolution of nonconserved variables $\hat{\Phi}_a^{(k)}$ (i.e., fluxes) and consequently the dissipation terms $\Lambda_a^{(k)}$ of the flux evolution equations are the seat of energy dissipation in the system. This interpretation would not have been possible if the density matrix $\mathbf{f}_a$ were given in a form other than that in (4.27). A similar comment can be given for the entropy flux represented below. We also find the entropy flux in the form

$$\mathbf{J}_s=T^{-1}\sum_a^r (\mathbf{Q}_a-\hat{\mu}_a\mathbf{J}_a)+T^{-1}\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)}\psi_a^{(k)}+J_{\text{sq}} \;, \tag{4.30a}$$

$$J_{\text{sq}}=k_B\sum_a^r \text{Tr}[\tfrac{1}{2}(\mathbf{C}_a\delta_a+\delta_a\mathbf{C}_a)\varepsilon_a \ln(1+\varepsilon_a\mathbf{f}_a)] \;, \tag{4.30b}$$

which is also in the same form as for the classical theory except for the quantum contribution $\mathbf{J}_{\text{sq}}$.

In view of the same mathematical structures of the entropy balance equation, the entropy flux, the entropy production, and the flux evolution equations as those for the classical system, the entropy balance equation is, as in the classical theory, expected to be, and indeed is, in the form

$$d_t\mathcal{S}=d_t\Psi-\hat{\sigma}_L \;, \tag{4.31}$$

where $d_t\Psi$ is the compensation differential [3] given by

$$\begin{aligned} d_t\Psi &= T^{-1}\left[d_t\mathcal{E}+pd_tv-\sum_a^r \hat{\mu}_a d_t c_a+\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} d_t\hat{\Phi}_a^{(k)}\right] \\ &= T^{-1}\left[d_t\mathcal{E}_{\text{ex}}+pd_tv-\sum_a^r \hat{\mu}_a^{\text{ex}} d_t c_a \right.\\ &\qquad \left. +\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} d_t\hat{\Phi}_a^{(k)}\right] \;, \end{aligned} \tag{4.32}$$

$$\begin{aligned}\hat{\sigma}_L=-(\rho T)^{-1}\sum_a^r [&\mathbf{\Pi}_a\!:\!\nabla\mathbf{u}+\Delta_a\nabla\cdot\mathbf{u}+\mathbf{Q}_a\cdot\nabla\ln T \\ &+\mathbf{J}_a\cdot(T\nabla\bar{\mu}_a^e-\mathbf{F}_a)] \;, \end{aligned} \tag{4.33}$$

where

$$\mathcal{E}_{\text{ex}}=\mathcal{E}+\sum_a^r c_a\hat{\mathfrak{B}}_a \;, \tag{4.34}$$

$$\hat{\mu}_a^{\text{ex}}=\hat{\mu}_a+\hat{\mathfrak{B}}_a,\;\; \hat{\mu}_a^{e'}=\hat{\mu}_a^e-\hat{\mathfrak{B}}_a \;\; (\hat{\mathfrak{B}}_a=\mathfrak{B}_a/m_a) \;. \tag{4.35}$$

Therefore, $\hat{\mu}_a^{\text{ex}}$ is seen as the chemical potential of species a subject to the external field. Thus, if the external field is electrical, then $\hat{\mu}_a^{\text{ex}}$ is the electrochemical potential. The other symbols in these equations are

$$\Phi_a^{(k)}=\rho\hat{\Phi}_a^{(k)}=\text{Tr}(\bar{\mathbf{h}}_a^{(k)}\mathbf{f}_a) \;, \tag{4.36}$$

with $\bar{\mu}_a^e=\hat{\mu}_a^e/T$. The derivation of (4.31) is given in Appendix B. It must be noted that by the matching conditions taken in (4.9), the Gibbs-Duhem relation can be written

$$\sum_a^r c_a d_t\bar{\mu}_a^e=\mathcal{E}d_t(1/T)+vd_t(p_e/T) \;. \tag{4.37}$$

This relation, used to derive (4.31), follows from (4.11a) and (4.3) and the equilibrium Gibbs relation for the entropy that follows from the latter. Therefore, from the standpoint of irreversible thermodynamics, the matching conditions introduced are essential and, without them, the parameters appearing in (4.31) and (4.32) do not have operational thermodynamic meanings, rendering (4.31) and (4.32) to be an empty mathematical symbolism. Note that the compensation differential $d_t\Psi$ is in the same form as for the classical theory. It is reasonable that the mathematical structure of the theory of irreversible processes is the same for both quantum and classical systems since irreversible thermodynamics is a description at the continuum macroscopic level of many-particle systems and macroscopic variables *per se* are not quantum mechanical, although they are the statistical averages of quantum mechanical operators computed with a quantum mechanical density matrix.

As in the classical theory, one can draw the conclusion that the entropy differential $d_t\mathcal{S}$ is not an exact differential in the macroscopic variable space $\mathfrak{C}$ spanned by $\mathcal{E},v,c_a$, and $\hat{\Phi}_a^{(k)}$, $1\leq a\leq r$, $k\geq 1$ because $\hat{\sigma}_L$ does not vanish away from equilibrium. The balance equation for Ψ can be obtained from (4.31) and (3.51) together with the expressions (4.29) and (4.30) for the entropy flux and the entropy production

$$\rho d_t \Psi = -\nabla \cdot \left[T^{-1} \sum_a^r (\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a) + T^{-1} \sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \psi_a^{(k)} + \mathbf{J}_{\mathrm{sq}} \right] + \hat{\sigma}_L + T^{-1} \sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \mathbf{\Lambda}_a^{(k)} . \quad (4.38)$$

Therefore, if one is inclined to regard the compensation function ψ as an extended form of the Clausius entropy, then the corresponding extended entropy flux should be defined by

$$\mathbf{J}_{\mathrm{comp}} = T^{-1} \sum_a^r (\mathbf{Q}_a - \hat{\mu}_a \mathbf{J}_a) + T^{-1} \sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \psi_a^{(k)} + \mathbf{J}_{\mathrm{sq}} \quad (4.39)$$

and the extended entropy production by

$$\sigma_{\mathrm{comp}} = \hat{\sigma}_L + T^{-1} \sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \mathbf{\Lambda}_a^{(k)} . \quad (4.40)$$

The implications of this balance equation need further elaboration, especially with regard to the second law of thermodynamics, and it will be done elsewhere in the future.

V. DISCUSSION AND CONCLUDING REMARKS

The principal aim of this paper is in formulating a formal theory of irreversible processes in dilute quantum gases by using the density matrix. It is found that the mathematical structure of irreversible thermodynamics for quantum gases remains the same as for the classical gases, except for the statistical definitions of macroscopic variables made in terms of the density matrix and symmetrized operators and a contribution to the entropy arising as a quantum correction. Various authors [13] showed in the literature that the balance equations for conserved variables (conservation laws) have the same forms as their classical counterparts. Therefore, it is not too surprising that the structure of irreversible thermodynamics should have the same structure as the classical theory. Nevertheless, it hitherto has remained undemonstrated even with a particular model and this paper achieves the goal, at least, in a partial measure with a special model. The theory of transport processes remains to be developed. The present mathematical formalism can serve as the starting point of such a theory. The fact that the mathematical structure of the macroscopic evolution equations for the present quantum system remains the same as for the classical systems clearly suggests that the theory of quantum transport processes will be parallel to the classical counterpart. We will report on it in the near future.

Irreversible thermodynamics is necessarily formal in structure since it is a theoretical framework within which all macroscopic processes must be described in conformation to the thermodynamic principles. For this reason we have deliberately tried to remain formal, especially with regards to the transition probability $W_{ab}^{(\varepsilon)}$, except for some general symmetry conditions that it must satisfy. These symmetry relations are sufficient for proving the H theorem and the Onsager reciprocal relations for phenomenological coefficients (transport coefficients) and thus for making the theory of irreversible processes formulated consistent with the thermodynamic laws. When a specific form is used for $W_{ab}^{(\varepsilon)}$ for a given dynamical system, it is possible to describe the irreversible process of interest for the system in question. Elucidation of $W_{ab}^{(\varepsilon)}$ for dynamical systems falls in the category of studies in transport processes in the system and thus is outside the scope of the question addressed in this work, namely, the theoretical structure of irreversible thermodynamics. Such studies have been already made as applications of the present theory to transport phenomena, such as magnetoconductivities in a quantum wire [18], in semiconductors subjected to a large external field. Applications to other aspects of semiconductor phenomena will be reported in the near future.

To help the reader grasp the applicability of the present theory, we indicate that the transition probability $W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b')$ for the collision process $(\mathbf{k}_a,\mathbf{k}_b) \to (\mathbf{k}_a',\mathbf{k}_b')$ may be given in terms of the transition matrix element $T(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b')$ obeying the quantum mechanical Lippmann-Schwinger equation for scattering [20]:

$$W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b') = (2\pi/\hbar)|T(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b') + P_{ab}T(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b')|^2 \times \delta(E_{ab}-E_{ab}')\delta(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_a'-\mathbf{k}_b') , \quad (5.1)$$

where P_{ab} is the symmetrization operator which gives rise to an appropriately symmetrized transition matrix element with a plus sign for boson or a minus sign for fermions attached to it. The right-hand side of (5.1) is basically proportional to the differential cross section for the collision process $(\mathbf{k}_a,\mathbf{k}_b) \to (\mathbf{k}_a',\mathbf{k}_b')$, which clearly satisfies the microscopic reversibility. The transition matrix element can be in principle determined from the Schrödinger equation or the Lippmann-Schwinger equation [19] once the interaction potential is assumed for the process. We note that the microscopic reversibility satisfied by $W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b')$, namely,

$$W^{(\varepsilon)}(\mathbf{k}_a\mathbf{k}_b|\mathbf{k}_a'\mathbf{k}_b') = W^{(\varepsilon)}(\mathbf{k}_a'\mathbf{k}_b'|\mathbf{k}_a\mathbf{k}_b) , \quad (5.2)$$

gives rise to symmetry relations between collision bracket integrals [3] arising from the collision integral $\Re[\mathbf{f}_a]$ and thus ultimately to the Onsager reciprocal relations between transport coefficients. Such relations can be shown explicitly and in a straightforward manner by developing theory of transport processes on the basis of the extended hydrodynamic equations presented here, if the procedure described in Ref. [3] is followed. Lack of space does not permit us to dwell in detail on this subject here, which does not involve anything new as far as the methodology is concerned. Therefore, we simply present the result for a special case where only diffusions are present. Without loss of generality of the essential point we will confine the discussion to a linear process. In this case, it can be shown that the dissipation term for diffusion is approximated by the linear form

$$\Lambda_a^{(4)} = -(\beta g)^{-1} \sum_{b=1}^{r} \mathfrak{R}_{ab} \rho_b^{-1} \mathbf{J}_b \ , \tag{5.3}$$

where the collision bracket integral $\mathfrak{R}_{ab}$ is given by

$$\begin{aligned} \mathfrak{R}_{aa} = {} & \tfrac{1}{4}\beta^2 g \operatorname{Tr}[(\bar{h}_a^{(4)} + \bar{h}_{a'}^{(4)} - \bar{h}_{a'}^{(4)*} - \bar{h}_a^{(4)*})(h_a^{(4)} + h_{a'}^{(4)} - h_a^{(4)} - h_{a'}^{(4)}) W_{aa'}^{(\varepsilon)} \mathbf{f}_a^0 \mathbf{f}_{a'}^0 Q_{aa'}] \\ & + \sum_{b \neq a} \tfrac{1}{2}\beta^2 g \operatorname{Tr}[(\bar{h}_a^{(4)} - \bar{h}_{a'}^{(4)})(h_b^{(4)} - h_b^{(4)}) W_{ab}^{(\varepsilon)} \mathbf{f}_a^0 \mathbf{f}_b^0 Q_{ab}] \ , \end{aligned} \tag{5.4a}$$

$$\mathfrak{R}_{ab} = \tfrac{1}{2}\beta^2 g \operatorname{Tr}[(\bar{h}_a^{(4)} - \bar{h}_{a'}^{(4)})(h_b^{(4)} - h_b^{(4)}) W_{ab}^{(\varepsilon)} \mathbf{f}_a^0 \mathbf{f}_b^0 Q_{ab}] \quad (a \neq b) \ , \tag{5.4b}$$

where

$$Q_{ab} = [(1-\varepsilon_a \mathbf{f}_a^0)(1-\varepsilon_b \mathbf{f}_b^0)]^{-2} \ . \tag{5.5}$$

In (5.3) we have used the approximation $X_a^{(4)} = -\mathbf{J}_a/\rho_a$. The trace in (5.4) is taken for particles a and b and the asterisk means the post-collision value and the prime on a means another particle of species a. The parameter g is defined by $g = (m\beta)^{1/2}/(nd)^2$, where m is the mean mass and d is the mean size parameter of the particles. On substitution (5.3) into (3.46) or (3.44d), we obtain the diffusion flux evolution equation from which the diffusion coefficients can be extracted. Clearly, the collision bracket integrals (5.4b) satisfy the Onsager reciprocal relations because of the symmetry properties of $W_{ab}^{(\varepsilon)}$ postulated.

It was mentioned earlier in Sec. IV that the nonequilibrium canonical form (4.27) or (4.12) with the expansion (4.21) is a projection of the Hilbert space density matrix or, more precisely, a resummation of the projection (4.15), that is, the quantum Maxwell-Grad moment expansion. We emphasize that the quantum Maxwell-Grad moment expansion is not a pure Hilbert space density matrix, but a hybrid of Hilbert space operators and conjugate macroscopic variables. This manner of dually expressing the density matrix in two different spaces, one representing fine-grained states of the system and the other the average states of the system at the macroscopic level, exacts a cost from the entropy density. The cost is that the entropy is not a state function in the macroscopic variable space chosen. However, the situation is not too serious for the theory of irreversible processes since there still exists a state function in the chosen macroscopic space on which irreversible thermodynamics can be built, that is, the compensation function and its differential. There is much work to be done in the theory of irreversible thermodynamics along the line suggested by the theory presented here.

We reiterate that the parameter $T = (k_B\beta)^{-1}$ in (4.27) and (4.32) is the absolute temperature at position **r** in the system and at time t, and this is due to the matching conditions discussed earlier. The integrability [20] of the differential $d_t\Psi$ implies that Ψ can be constructed in terms of such T among other variables relevant to the nonequilibrium system of interest. It must be recalled that the notion of contact temperature, which is the temperature of the heat reservoir in contact locally with the system, plays a role in this identification of T with the local absolute temperature, and with the temperature T so identified, $d_t\Psi$ can be used for developing irreversible thermodynamics parallel to equilibrium thermodynamics.

APPENDIX A: THE *H* THEOREM FOR THE BNUU MODEL

In this appendix we show the BNUU model satisfies the condition (2.8a) and (2.8b) required of the collision term $\mathfrak{R}[\mathbf{f}_a]$. On multiplication of collision invariant operator A_a to $\mathfrak{R}[\mathbf{f}_a]$, summation over species, and taking trace, we find

$$\sum_{a}^{r} \operatorname*{Tr}_{(a)} A_a \mathfrak{R}[\mathbf{f}_a] = \tfrac{1}{4} \sum_{a}^{r} \sum_{b}^{r} \operatorname*{Tr}_{(ab)} \{(A_a + A_b - A_a' - A_b') W_{ab}^{(\varepsilon)} [\mathbf{f}_a' \mathbf{f}_b' (1+\varepsilon_a \mathbf{f}_a)(1+\varepsilon_b \mathbf{f}_b) - \mathbf{f}_a \mathbf{f}_b (1+\varepsilon_a \mathbf{f}_a')(1+\varepsilon_b \mathbf{f}_b')]\} = 0 \tag{A1}$$

since $A_a + A_b - A_a' - A_b' = 0$ by the fact that A_a, etc. are collision invariants. Thus condition (2.8a) is satisfied. Proceeding similarly with multiplication of $\ln(\varepsilon_a + \mathbf{f}_a^{-1})$ by $\mathfrak{R}[\mathbf{f}_a]$, we obtain

$$\begin{aligned} & \sum_{a}^{r} \operatorname*{Tr}_{(a)} \{\ln(\varepsilon_a + \mathbf{f}_a^{-1}) \mathfrak{R}[\mathbf{f}_a]\} \\ & = \tfrac{1}{4} \sum_{a}^{r} \sum_{b}^{r} \operatorname*{Tr}_{(ab)} \left\{ W_{ab}^{(\varepsilon)} \ln \left[\frac{\mathbf{f}_a' \mathbf{f}_b' (1+\varepsilon_a \mathbf{f}_a)(1+\varepsilon_b \mathbf{f}_b)}{\mathbf{f}_a \mathbf{f}_b (1+\varepsilon_a \mathbf{f}_a')(1+\varepsilon_b \mathbf{f}_b')} \right] [\mathbf{f}_a' \mathbf{f}'(1+\varepsilon_a \mathbf{f}_a)(1+\varepsilon_b \mathbf{f}_b) - \mathbf{f}_a \mathbf{f}_b (1+\varepsilon_a \mathbf{f}_a')(1+\varepsilon_b \mathbf{f}_b')] \right\} \geq 0 \ . \end{aligned} \tag{A2}$$

This is the H theorem for the BNUU model.

APPENDIX B: DERIVATION OF THE DIFFERENTIAL FORM FOR ENTROPY

In this appendix we present the derivation of the differential form for the entropy density in (4.31). Since the external field is assumed to be homogeneous, the field contribution to the Hamiltonian $\mathbf{H}_a$ may be absorbed into the normalization factor μ_a. Thus we define $\mu'_a = \mu_a - \mathfrak{B}_a$. With this definition, the density matrix $\mathbf{f}_a$ may be written as

$$\mathbf{f}_a = [\exp\beta(\mathbf{H}_a^0 + \mathbf{H}_a^1 - \mu'_a) - \varepsilon_a]^{-1} \ . \tag{B1}$$

On substitution of this form into (3.51) [see (3.49) for the definitions of $\mathfrak{F}$ and $\mathfrak{C}_a$], we obtain (4.30), for $\mathbf{J}_s$,

$$\mathbf{J}_s = T^{-1}\sum_a^r (\mathbf{Q}_a - \hat{\mu}'_a \mathbf{J}_a) + T^{-1}\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \psi_a^{(k)} + \mathbf{J}_{\text{sq}} \ , \tag{B2a}$$

$$\mathbf{J}_{\text{sq}} = k_B \sum_a^r \text{Tr}\tfrac{1}{2}[C_a\{\delta_a \varepsilon_a \ln(1+\varepsilon_a \mathbf{f}_a)\} + \{\delta_a \varepsilon_a \ln(1+\varepsilon_a \mathbf{f}_a)\}\mathbf{C}_a] \ . \tag{B2b}$$

The entropy production is given by (4.29):

$$\sigma_{\text{ent}} = T^{-1}\sum_a^r \sum_{k\geq 1} \mathbf{X}_a^{(k)} \Lambda_a^{(k)} \ . \tag{B3}$$

These quantities form the entropy balance equation in the form

$$\rho \frac{d}{dt}\mathcal{S} = -\nabla\cdot\mathbf{J}_s + \sigma_{\text{ent}} \tag{B4}$$

as a local representation of the H theorem since $\sigma_{\text{ent}} \geq 0$, the equality holding valid only at equilibrium.

The dissipation terms $\Lambda_a^{(k)}$, $\mathbf{Q}_a$, and $\mathbf{J}_a$ can be eliminated from the entropy balance equation (B4) if the evolution equation (3.44) for $\Phi_a^{(k)}$, the energy balance equation (3.15), and the mass fraction balance equation (3.10) are used. The entropy balance equation is then cast into the form

$$\begin{aligned} d_t\mathcal{S} = {} & T^{-1}\left[d_t\mathcal{E} + p d_t v - \sum_a^r \mu'_a d_t c_a \sum_a^r \sum_{k\geq 1} X_a^{(k)} d_t \hat{\Phi}_a^{(k)} \right] + (\rho T)^{-1}\sum_a^r [\Pi_a : \nabla\mathbf{u} + \Delta_a \nabla\cdot\mathbf{u} + \mathbf{Q}_a\cdot\nabla\ln T + \mathbf{J}_a\cdot(T\nabla\bar{\mu}'_a - \mathbf{F}_a)] \\ & -\rho^{-1}\left[\nabla\cdot\left[\sum_a^r \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \boldsymbol{\psi}_a^{(k)} \right] + \sum_a^r \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \mathbf{Z}_a^{(k)} \right] , \end{aligned} \tag{B5}$$

where $\bar{\mu}'_a = \boldsymbol{\bar{\mu}}'_a / t$ and $\overline{X}_a^{(k)} = X_a^{(k)}/T$.

By using the definition of $\mathbf{Z}_a^{(k)}$, it is possible to show

$$\nabla\cdot\left[\sum_a^r \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \psi_a^{(k)} \right] + \sum_a^r \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \mathbf{Z}_a^{(k)} = -\Phi_a^{(k)} d_t \overline{\mathbf{X}}_a^{(k)} + \sum_a^r \text{Tr}\left[\mathbf{f}_a \left\{ \frac{\partial}{\partial t} \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \overline{\mathbf{h}}_a^{(k)} - (i\hbar)^{-1}\left[\mathbf{H}_a, \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \overline{\mathbf{h}}_a^{(k)} \right] \right\} \right] . \tag{B6}$$

The second term on the right-hand side can be rewritten as

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \overline{\mathbf{h}}_a^{(k)} - (i\hbar)^{-1}\left[\mathbf{H}_a, \sum_{k\geq 1} \overline{\mathbf{X}}_a^{(k)} \overline{\mathbf{h}}_a^{(k)} \right] = {} & \frac{\partial}{\partial t}(\Delta\bar{\mu}'_a \delta_a) - (i\hbar)^{-1}[\mathbf{H}_a, \Delta\bar{\mu}'_a \delta_a] \\ & + k_b \left\{ \frac{\partial}{\partial t}\delta_a \ln\left[\frac{\varepsilon_a + \mathbf{f}_a^{-1}}{\varepsilon_a + (\mathbf{f}_a^0)^{-1}} \right] - (i\hbar)^{-1}\left[\mathbf{H}_a, \delta_a \ln\left[\frac{\varepsilon_a + \mathbf{f}_a^{-1}}{\varepsilon_a + (\mathbf{f}_a^0)^{-1}} \right] \right] \right\} . \end{aligned} \tag{B7}$$

The first two terms on the right-hand side, when substituted into (B6), give rise to the formula

$$\rho \sum_a^r c_a d_t \Delta\bar{\mu}'_a + \sum_a^r \mathbf{J}_a\cdot\nabla(\Delta\bar{\mu}'_a) \ . \tag{B8}$$

Since the equation

$$\sum_{a}^{r} c_a d_t \bar{\mu}_a^{e'} = \mathcal{E} d_t(1/T) + v d_t(p_e/T) \tag{B9}$$

holds, for which the matching conditions on energy and density are used, on substitution of this equation into (B8), we obtain

$$\rho \sum_{a}^{r} c_a d_t \bar{\mu}_a' - \mathcal{E} d_t(1/T) - v d_t(p_e/T) + \sum_{a}^{r} \mathbf{J}_a \cdot \nabla(\Delta_a \bar{\mu}_a') \, . \tag{B10}$$

The last term in (B7), when summed over species and taken trace, can be recast into the form

$$\rho d_t[(p-p_e)v/T] - \nabla \cdot \mathbf{J}_{\mathrm{sq}} = k_B \sum_{a}^{r} \mathrm{Tr} \left\{ \frac{\partial}{\partial t} \delta_a \ln \left[\frac{\varepsilon_a + \mathbf{f}_a^{-1}}{\varepsilon_a + (\mathbf{f}_a^0)^{-1}} \right] - (i\hbar)^{-1} \left[\mathbf{H}_a, \delta_a \ln \left[\frac{\varepsilon_a + \mathbf{f}_a^{-1}}{\varepsilon_a + (\mathbf{f}_a^0)^{-1}} \right] \right] \right\} , \tag{B11}$$

where the pressures are defined by the statistical formulas

$$p_a = \beta^{-1} \mathrm{Tr}[\delta_a \varepsilon_a \ln(1+\varepsilon_a \mathbf{f}_a)] \quad \left[p = \sum_{a}^{r} p_a \right] , \tag{B12a}$$

$$p_{a^e} = \beta_e^{-1} \mathrm{Tr}[\delta_a \varepsilon_a \ln(1+\varepsilon_a \mathbf{f}_a^0)] \quad \left[p_e = \sum_{a}^{r} p_{a^e} \right] . \tag{B12b}$$

Note that β_e in p_e can be replaced with β by the temperature matching condition and therefore p and p_e are multiplied by the same T^{-1} in (B11). Combining these results, we obtain the desired results

$$d_t \mathcal{S} = d_t \Psi - \hat{\sigma}_L \tag{B13}$$

for the entropy balance equation.

[1] *Physics of Hot Electron Transport in Semiconductors,* edited by C. S. Ting (World Scientific, Singapore, 1992).

[2] B. C. Eu, J. Chem. Phys. **80**, 2123 (1984).

[3] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics* (Wiley, New York, 1992).

[4] G. Lindblad, *Non-Equilibrium Entropy and Irreversibility* (Reidel, Dordrecht, 1983).

[5] L. W. Nordheim, Proc. R. Soc. London Ser. A **119**, 689 (1928).

[6] E. A. Uehling and G. E. Uhlenbeck, Phys. Rev. **43**, 552 (1932).

[7] H. Mori and S. Ono, Prog. Theor. Phys. Jpn. **8**, 327 (1952).

[8] H. Mori, Prog. Theor. Phys. Jpn. **9**, 473 (1953).

[9] S. Ono, Prog. Theor. Phys. Jpn. **12**, 113 (1954).

[10] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon, London, 1958).

[11] W. Magnus, Commun. Pure Appl. Math. **7**, 649 (1954).

[12] A. Erdelyi, *Higher Transcendental Functions* (McGraw-Hill, New York, 1955), Vol. 2.

[13] For derivations of conservation laws for quantum systems, see, for example, (a) J. H. Irving and R. W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951); (b) H. Mori, Phys. Rev. **112**, 1829 (1958); (c) J. S. Dahler, *ibid.* **129**, 1464 (1963); (d) R. F. Snider and K. S. Lewchuk, J. Chem. Phys. **46**, 3163 (1967); (e) J. W. Dufty and C. S. Kim (unpublished).

[14] See, Lei *et al.*, in *Physics of Hot Electron Transport in Semiconductors* (Ref. [1]), pp. 1–130.

[15] Tolman's generalized equipartition theorem [R. C. Tolman, Phys. Rev. **11**, 261 (1918)] is suggested as a statistical definition of temperature in a recent paper by V. J. Menon and D. C. Agrawal, J. Phys. A **25**, 4517 (1992). It, however, does not define temperature unambiguously since the average of the temperature operator (θ in their notation) is not a simple function of absolute temperature. Tolman's generalized equipartition theorem is nothing but a rearrangement of the normalization condition for the distribution function. As such, it is devoid of the physical meaning inherent to the notion of temperature, that is, a measure of the average kinetic energy.

[16] See, for example, H. Grad, Commun. Pure Appl. Math. **2**, 331 (1949).

[17] B. C. Eu and Y. G. Ohr, Physica A **202**, 321 (1994).

[18] K. Mao, M. P. Chaubey, and B. C. Eu (unpublished).

[19] M. L. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964).

[20] M. Chen and B. C. Eu, J. Math. Phys. **34**, 3012 (1993).