The *H* Theorem and Irreversible Thermodynamics

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Following a method first introduced by Prigogine, the *H* theorem is written as the law of increase of entropy for a slightly inhomogeneous gas. It is shown that the local rate of entropy production for such a gas is simply a homogeneous quadratic form of the generalized forces associated with the various irreversible processes with coefficients possessing all the properties of the phenomenological coefficients of irreversible thermodynamics. The local rate of entropy production is explicitly evaluated for a simple monatomic gas and is compared with the corresponding expression of irreversible thermodynamics.

1. INTRODUCTION

The *H* theorem introduced by Boltzmann[1] in this famous 1872 memoir is still regarded as one of the outstanding achievements of the human mind in perceiving natural phenomena. Although there were objections to the generalization of the *H* theorem to polyatomic gases, these objections have been circumvented first quantum mechanically by Stueckelberg[2] and Waldmann[3] utilizing the unitariety of the scattering matrix, and recently classically by Cercignani and Lampis[4] using time reversal invariance of the equations of motion.

The *H* theorem is simply a statement of the universal law of the increase of entropy for a gas in terms of the binary collisions of its constituents. Almost all of the natural processes observed in our universe are known to follow this principle of increase of entropy, and no indication has ever been made that violates this principle. However, as it occurs most of the natural phenomena are often studied macroscopically by utilizing the

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phenomenological laws of irreversible thermodynamics. The H theorem is usually used not as a beginning principle, but rather as a principle which is treated as a constraint in obtaining certain properties pertaining to the microscopic world in the study of irreversible processes.[5,6]

The first detailed study of the H theorem as a beginning principle for the law of increase of entropy was made by Prigogine.[7] In this treatise Prigogine shows in detail a comparison between the Gibbs formula and the requirements of the kinetic theory of gases and ends in expressions for the entropy production of various irreversible processes using the Chapman–Enskog[8,9] approximation for the distribution function. Since then, the compatibility between the laws of irreversible thermodynamics and the results of the kinetic theory have been further studied in detail (Lifshitz and Pitaevskii,[5] Woods,[6] Rumer and Ryvkin,[10] de Groot and Mazur,[11] etc.). More recently van Beijeren and Ernst[12] have suggested for the distribution function a modified Enskog equation, particularly important for mixtures of hard spheres, which leads to transport coefficients that are in complete agreement with the laws of irreversible thermodynamics. What is not discussed in all of these references is how the entropy production through the H theorem becomes a quadratic form of the generalized forces where the kinetic coefficients that satisfy all the requirements of the phenomenological coefficients of irreversible thermodynamics can be readily obtained.

It is the purpose of this study to show that the H theorem in conjunction with the Boltzmann equation can be used more widely as the fundamental equation of irreversible thermodynamics for even systems that are far from equilibrium and that it is equivalent to the Gibbs equation in expressing the local rate of entropy production as the sum of the products of generalized forces and conjugate generalized fluxes. Moreover for the weakly nonequilibrium state of the gas under consideration, the linear phenomenological laws between generalized fluxes and generalized forces of irreversible thermodynamics can be readily obtained from the solution of the Boltzmann equation in conjunction with the H theorem ensuring all the properties of the phenomenological coefficients.

In this study following Prigogine[7] the H theorem is written for a slightly inhomogeneous gas expressing the local rate of entropy production. The Chapman–Enskog[8,9] or Hilbert[13,14] solution of the Boltzmann equation is used to show that the local rate of entropy production is simply a homogeneous quadratic form of the generalized forces with coefficients satisfying Onsager's principle[15] and all the pertaining properties. Finally the local rate of entropy production for a simple monatomic gas is evaluated explicitly and is compared with the corresponding expression of irreversible thermodynamics.

Only single-component gases are considered in this paper.

2. THE *H*-THEOREM FOR A SLIGHTLY INHOMOGENEOUS GAS

We consider Boltzmann's *H* theorem in the absence of any external field for the nonequilibrium state of a single-component gas characterized by the distribution function $f(\mathbf{v}, \mathbf{x}, t)$ at point $\mathbf{x}$ and time t:

$$\frac{dH}{dt} = \int \ln f J(f)\, d^3v \leqslant 0 \tag{2.1}$$

where $J(f)$ is the collision integral given by

$$J(f) = \int w'(f'f_1' - ff_1)\, d^3v'\, d^3v_1'\, d^3v_1 \tag{2.2}$$

H is the Boltzmann *H* function defined as

$$H \equiv \int f \ln f\, d^3v \tag{2.3}$$

$\mathbf{v}, \mathbf{v}_1$ and $\mathbf{v}', \mathbf{v}_1'$ denote the atomic (or molecular) velocities before and after a binary collision, respectively,

$$f = f(\mathbf{v}, \mathbf{x}, t) \qquad f' = f(\mathbf{v}', \mathbf{x}, t)$$
$$f_1 = f(\mathbf{v}_1, \mathbf{x}, t) \qquad f_1' = f(\mathbf{v}_1', \mathbf{x}, t)$$

and $w' = w(\mathbf{v}, \mathbf{v}_1 \to \mathbf{v}', \mathbf{v}_1')$ is the transition probability from a state $(\mathbf{v}, \mathbf{v}_1)$ to a state $(\mathbf{v}', \mathbf{v}_1')$ in a binary collision. The total entropy *S* of the gas is related to the Boltzmann *H* function, except for an additive constant, by the famous relation

$$S = -k \int H\, d^3x \tag{2.4}$$

where k is Boltzmann's constant.[2] Consequently the *H* theorem given by (2.1) together with (2.4) can be conveniently written as

$$\frac{dS}{dt} = \frac{1}{2} \int w' ff_1(z \ln z - z - 1)\, d^4\Gamma\, d^3x \geqslant 0$$

where

$$z \equiv \frac{f'f_1'}{ff_1} \qquad \text{and} \qquad d^4\Gamma \equiv d^3v\, d^3v_1\, d^3v'\, d^3v_1'$$

[2] From now on we set $k = 1$ for convenience until a later discussion.

expressing the law of increase of entropy as worked out in detail in Lifshitz and Pitaevskii.[5] If we denote the local rate of entropy production in unit volume by σ_S, we can then state the H theorem as

$$\sigma_S = \frac{1}{2} \int w' f f_1 (z \ln z - z - 1) \, d^4\Gamma \geqslant 0 \qquad (2.5)$$

Following the method first introduced by Prigogine,[7] we now consider a slightly inhomogeneous gas characterized by the distribution function

$$f = f_L(1 + \phi) \qquad (2.6)$$

where $\phi = \phi(\mathbf{v}, \mathbf{x}, t)$ satisfies the condition $|\phi| \ll 1$ and where f_L is the local Maxwellian corresponding to a state of local equilibrium given by

$$f_L = n \left(\frac{m}{2\pi T} \right)^{3/2} \exp\left[-\frac{m}{2T} (\mathbf{v} - \mathbf{u})^2 \right] \qquad (2.7)$$

In (2.7), n is the number density, $\mathbf{u}$ is the gross velocity field, T is the temperature field (measured in energy units), and m is the atomic or molecular mass. Since ϕ is small compared to unity, it follows that z can be approximated by

$$z \approx \frac{1 + \phi' + \phi'_1}{1 + \phi + \phi_1} \approx 1 - (\phi + \phi_1 - \phi' - \phi'_1)$$

where we have used the Maxwellian property

$$f_L f_{L1} = f'_L f'_{L1}$$

Similarly $\ln z$ can be approximated by

$$\ln z \approx -(\phi + \phi_1 - \phi' - \phi'_1) - 1/2(\phi + \phi_1 - \phi' - \phi'_1)^2$$

Substitution from above for z and $\ln z$ and from (2.6) for f into (2.5) yields to a good approximation

$$\sigma_S = \frac{1}{4} \int w' f_L f_{L1} (\phi + \phi_1 - \phi' - \phi'_1)^2 \, d^4\Gamma \geqslant 0 \qquad (2.8)$$

Equation (2.8) is the statement of Boltzmann's H theorem written for the local rate of entropy production of a slightly inhomogeneous gas and is in complete agreement with equation (3.6) of Prigogine[7] written for a single component gas. The function ϕ in (2.8) should be such that the distribution function f given by (2.6) satisfies the Boltzmann equation. It can easily be

verified that the equality holds only when ϕ vanishes, and by virtue of (2.6) the entropy production vanishes for a state of local equilibrium characterized by the distribution function f_L given by (2.7). However, it is important to note that f_L itself does not satisfy the Boltzmann equation unless n, T and $\mathbf{u}$ are constants (the uniform state of the gas). Consequently entropy production vanishes for a gas in the uniform state as deduced by Boltzmann.

3. THE LINEAR KINETIC LAWS OF TRANSPORT PROCESSES, THE KINETIC COEFFICIENTS AND ONSAGER'S PRINCIPLE

To proceed further with Boltzmann's *H* theorem stated as the law of increase of entropy for a slightly inhomogeneous gas, we acquire information about the function ϕ. As already mentioned in Section 2, the function ϕ should be such that the distribution function f given by (2.6) satisfies the Boltzmann equation. If we consider the Chapman–Enskog[8,9] or Hilbert[13,14] expansions to the Boltzmann equation for a slightly inhomogeneous gas, we may to a good approximation identify ϕ from the second approximation to the distribution function of these expansions. In this case ϕ satisfies an inhomogeneous linear integral equation the solution of which can be written as

$$\phi = \sum_r \beta_{(r)} X^{(r)} + C_1 + \mathbf{C} \cdot (\mathbf{v} - \mathbf{u}) + C_2(\mathbf{v} - \mathbf{u})^2 \qquad (3.1)$$

where C_1, $\mathbf{C}$, and C_2 are some functions of $\mathbf{x}$ and t (it follows that C_1, $\mathbf{C}$, and C_2 vanish in the Chapman–Enskog solution and are functions of $\mathbf{x}$ only in the steady Hilbert solution), $\beta_{(r)}$ are functions of n, T, and $(\mathbf{v} - \mathbf{u})$, and $X^{(r)}$ are the generalized forces describing the deviation from equilibrium of the associated various nonequilibrium processes. It is worthwhile to note that $\beta_{(r)}$ and $X^{(r)}$ can be tensors of any order (scalars, vectors, second-order tensors, etc.). For instance, for thermal conduction $X_i^{(T)} = (\partial/\partial x_i)(1/T)$ corresponding to the ith component of a vector and for viscous dissipation $X_{ik}^{(u)} = (1/T)(\partial u_i/\partial x_k)$ corresponding to the (ik)th component of a second-order tensor. Moreover $\beta_{(r)}$ and $X^{(r)}$ must be tensors of the same order since ϕ is a scalar function.

Substitution from (3.1) into (2.8) and utilizing the conservation laws of a binary collision yield a homogeneous quadratic form of the generalized forces for the local rate of entropy production:

$$\sigma_S = \sum_r Y^{(r)} X^{(r)} = \sum_{r,s} L_{rs} X^{(r)} X^{(s)} \geqslant 0 \qquad 3.2)$$

where we have defined $Y^{(r)}$ as the generalized fluxes conjugate to the generalized forces $X^{(r)}$ and related to them by

$$Y^{(r)} = \sum_s L_{rs} X^{(s)} \tag{3.3}$$

and where L_{rs} are defined by

$$L_{rs} = \frac{1}{4} \int w' f_L f_{L1} (\beta_{(r)} + \beta_{(r)1} - \beta'_{(r)} - \beta'_{(r)1})$$

$$\times (\beta_{(s)} + \beta_{(s)1} - \beta'_{(s)} - \beta'_{(s)1}) d^4 \Gamma \tag{3.4}$$

The generalized forces $X^{(r)}$ are proportional to the gradients of temperature and velocity (and of any probable deriving quantity of the related nonequilibrium process) describing the weakly nonequilibrium state of the gas. Thus, the generalized fluxes given by (3.3) are simply linear combinations of such gradients. Consequently equation (3.3) describes the linear kinetic laws of transport processes for a slightly inhomogeneous gas. It follows that both $X^{(r)}$ and $Y^{(r)}$ vanish in the uniform state of the gas and by virtue of (3.2) the entropy production also vanishes for the uniform (equilibrium) state of the gas.

The coefficients L_{rs} which connect the generalized forces to the generalized fluxes and which are given by (3.4) are called the kinetic coefficients. It follows directly from (3.4) that

$$L_{rs} = L_{sr} \tag{3.5}$$

i.e., the kinetic coefficients L_{rs} satisfy Onsager's principle.[15] The reason behind (3.5) should be sought in the principle of detailed balancing already contained in the H theorem. Moreover if we set $r = s$ in (3.4), we obtain

$$L_{rr} = \frac{1}{4} \int w' f_L f_{L1} (\beta_{(r)} + \beta_{(r)1} - \beta'_{(r)} - \beta'_{(r)1})^2 d^4 \Gamma \geqslant 0 \tag{3.6}$$

Another relation between the kinetic coefficients can be obtained by simply applying the Schwartz inequality for integrals to (3.4), which yields

$$L_{rr} L_{ss} \geqslant (L_{rs})^2 \tag{3.7}$$

The kinetic coefficients L_{rs} defined by (3.4) (with $r \neq s$) give the coupling between the irreversible processes described microscopically by $\beta_{(r)}$ and $\beta_{(s)}$. If $\beta_{(r)}$ and $\beta_{(s)}$ are such that certain orthogonality relations hold in the form

$$\int w' f_L f_{L1} \beta_{(r)} (\beta_{(s)} + \beta_{(s)1} - \beta'_{(s)} - \beta'_{(s)1}) d^4 \Gamma = 0 \tag{3.8}$$

then by definition the corresponding kinetic coefficient L_{rs} vanishes. Equation (3.8) is simply a mathematical statement of the Curie–Prigogine principle.[16–18] This principle is particularly important for an isotropic medium. Since no isotropic tensor of odd order can be constructed, it follows that (3.8) is automatically satisfied in an isotropic medium when the sum of the orders of the tensors $\beta_{(r)}$ and $\beta_{(s)}$ is an odd integer. This is in fact the reason for the decoupling between the irreversible processes of thermal conduction and viscous dissipation of a simple monatomic gas discussed in detail below.

4. THE *H*-THEOREM FOR THE ENTROPY PRODUCTION OF A SIMPLE MONATOMIC GAS

For a simple monatomic gas the transition probability can be described by

$$w' d^3 v' \, d^3 v_1' = g \, d\sigma$$

where

$$g = |\mathbf{v} - \mathbf{v}_1| = |\mathbf{v}' - \mathbf{v}_1'|$$

and $d\sigma$ is the differential cross section in a binary collision. Thus, expression (2.8) for the local rate of entropy production of a slightly inhomogeneous gas becomes

$$\sigma_S = \tfrac{1}{4} \int f_L f_{L1} (\phi + \phi_1 - \phi' - \phi_1')^2 g \, d\sigma \, d^3 v \, d^3 v_1 \geqslant 0 \qquad (4.1)$$

for a simple monatomic gas. The function ϕ as mentioned in Section 3 can be obtained from the Chapman–Enskog[8,9,19] or Hilbert[13,14] solution of the Boltzmann equation for a simple monatomic gas:

$$\phi = -\frac{1}{nT^2} \zeta_i \frac{\partial T}{\partial x_i} - \frac{1}{nT} \tau_{ij} D_{ij} + C_1 + \mathbf{C} \cdot (\mathbf{v} - \mathbf{u}) + C_2 (\mathbf{v} - \mathbf{u})^2 \qquad (4.2)$$

where

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

and ζ_i and τ_{ij} are defined through the linear integral equations

$$I\zeta_i = [\tfrac{1}{2} m (\mathbf{v} - \mathbf{u})^2 - \tfrac{5}{2} T](v_i - u_i) \qquad (4.3)$$

$$I\tau_{ij} = m[(v_i - u_i)(v_j - u_j) - \tfrac{1}{3} \delta_{ij} (\mathbf{v} - \mathbf{u})^2] \qquad (4.4)$$

satisfying the orthogonality conditions

$$\int \Psi_\alpha \zeta_i f_L \, d^3v = 0 \qquad (4.5)$$

$$\int \Psi_\alpha \tau_{ij} f_L \, d^3v = 0 \qquad (4.6)$$

Ψ_α being any of the summational invariants 1, $(\mathbf{v} - \mathbf{u})$ and $\frac{1}{2}m(\mathbf{v} - \mathbf{u})^2$. The linear integral operator I which appears in (4.3) and (4.4) is defined by

$$I\psi \equiv \frac{1}{n} \int f_{L1}(\psi + \psi_1 - \psi' - \psi_1') g \, d\sigma \, d^3v_1 \qquad (4.7)$$

where ψ is any function of the atomic velocity $\mathbf{v}$.

Substitution from (4.2) for ϕ into (3.1) and utilizing the conservation laws of a binary collision together with the Curie–Prigogine principle for a simple monatomic gas yield the following expression for the local rate of entropy production:

$$\sigma_S = \frac{1}{4n^2T^4} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_j} \int f_L f_{L1}(\zeta_i + \zeta_{i1} - \zeta_i' - \zeta_{i1}')$$

$$\times (\zeta_j + \zeta_{j1} - \zeta_j' - \zeta_{j1}') g \, d\sigma \, d^3v \, d^3v_1$$

$$+ \frac{1}{4n^2T^2} D_{ij} D_{kl} \int f_L f_{L1}(\tau_{ij} + \tau_{ij1} - \tau_{ij}' - \tau_{ij1}')$$

$$\times (\tau_{kl} + \tau_{kl1} - \tau_{kl}' - \tau_{kl1}') g \, d\sigma \, d^3v \, d^3v_1 \qquad (4.8)$$

If we now identify the generalized forces for thermal conduction and viscous dissipation by

$$X_i^{(T)} = \frac{\partial}{\partial x_i}\left(\frac{1}{T}\right) = -\frac{1}{T^2}\frac{\partial T}{\partial x_i} \qquad (4.9)$$

$$X_{ij}^{(u)} = \frac{1}{T} D_{ij} \qquad (4.10)$$

we can define the kinetic coefficients for thermal conduction and viscous dissipation in the form

$$L_{ij}^{(T)} \equiv \frac{1}{4n^2} \int f_L f_{L1}(\zeta_i + \zeta_{i1} - \zeta_i' - \zeta_{i1}')$$

$$\times (\zeta_j + \zeta_{j1} - \zeta_j' - \zeta_{j1}') g \, d\sigma \, d^3v \, d^3v_1 \qquad (4.11)$$

and

$$L_{ijkl}^{(u)} = \frac{1}{4n^2} \int f_L f_{L1}(\tau_{ij} + \tau_{ij1} - \tau'_{ij} - \tau'_{ij1})$$

$$\times (\tau_{kl} + \tau_{kl1} - \tau'_{kl} - \tau'_{kl1})g \, d\sigma \, d^3v \, d^3v_1 \qquad (4.12)$$

and the conjugate generalized fluxes as

$$Y_i^{(T)} \equiv L_{ij}^{(T)} X_j^{(T)} \qquad (4.13)$$

and

$$Y_{ij}^{(u)} \equiv L_{ijkl}^{(u)} X_{lk}^{(u)} \qquad (4.14)$$

so that the entropy production σ_S given by (4.8) becomes the sum of the products of generalized forces and conjugate generalized fluxes:

$$\sigma_S = Y_i^{(T)} X_i^{(T)} + Y_{ij}^{(u)} X_{ji}^{(u)} \geq 0 \qquad (4.15)$$

It is readily evident that the kinetic coefficients given for thermal conduction by (4.11) and for viscous dissipation by (4.12) satisfy all the requirements imposed by irreversible thermodynamics discussed in detail in Section 3. Consequently the *H* theorem incorporated with the solution of the Boltzmann equation defines the kinetic coefficients in a rather natural way.

Further simplifications arise if one considers isotropy. It follows that in an isotropic medium one can define two parameters λ and η (to be identified later) by the relations

$$L_{ij}^{(T)} = \lambda T^2 \delta_{ij} \qquad (4.16)$$

and

$$L_{ijkl}^{(u)} = \eta T(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \tfrac{2}{3}\delta_{ij}\delta_{kl}) \qquad (4.17)$$

Substituting from (4.16) and (4.17) for $L_{ij}^{(T)}$ and $L_{ijkl}^{(u)}$ into (4.11) and (4.12) and utilizing (4.7) together with an integral theorem in kinetic theory, we obtain the following expressions for the two parameter λ and η:

$$\lambda = \frac{1}{3nT^2} \int f_L \zeta_i I \zeta_i \, d^3v \qquad (4.18)$$

$$\eta = \frac{1}{10nT} \int f_L \tau_{ij} I \tau_{ij} \, d^3v \qquad (4.19)$$

Substitution from (4.16) and (4.17) for the kinetic coefficients and from (4.9) and (4.10) for the generalized forces into (4.13) and (4.14) yields the conjugate generalized fluxes:

$$Y_i^{(T)} = -\lambda \frac{\partial T}{\partial x_i} \qquad \text{(Fourier's law)} \qquad (4.20)$$

and

$$Y_{ij}^{(u)} = 2\eta(D_{ij} - \tfrac{1}{3}D_{kk}\delta_{ij}) \qquad \text{(Stokes' law)} \qquad (4.21)$$

where λ and η are given by (4.18) and (4.19). From (4.20) and (4.21), we can now identify the parameters λ and η as the thermal conductivity and the shear viscosity, respectively. Equation (4.18) for the thermal conductivity λ and equation (4.19) for the shear viscosity η are in complete agreement with the corresponding formulas obtained through the direct definition of fluxes in the Chapman–Enskog[8,9,19] or Hilbert[14] theories.

Finally by substituting from (4.9) and (4.10) for the generalized forces and from (4.20) and (4.21) for the conjugate generalized fluxes into (4.15), we obtain an expression for the local rate of entropy production of a slightly inhomogeneous simple monatomic gas:

$$\sigma_S = \frac{\lambda}{T^2} \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} + \frac{2\eta}{T} (D_{ik}D_{ik} - \tfrac{1}{3}D_{ii}D_{kk}) \geqslant 0 \qquad (4.22)$$

Moreover it can be shown by utilizing equations (4.11), (4.12), (4.16), and (4.17) that

$$\lambda > 0 \qquad \text{and} \qquad \eta > 0 \qquad (4.23)$$

5. ENTROPY PRODUCTION IN IRREVERSIBLE THERMODYNAMICS

The local rate of entropy production $\hat{\sigma}_S^3$ in irreversible thermodynamics is given by the expression

$$\hat{\sigma}_S = \sum_r \hat{Y}^{(r)} \hat{X}^{(r)} \geqslant 0 \qquad (5.1)$$

where $\hat{X}^{(r)}$ are the generalized forces and $\hat{Y}^{(r)}$ are the conjugate generalized fluxes. Equation (5.1) is simply a result of the Gibbs equation together with

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[3] We have used the notation (^) for the phenomenological quantities of irreversible thermodynamics to merely distinguish them from the corresponding kinetic quantities.

the local state assumption (for details one may refer to Prigogine,[17] Katchalsky and Curran,[18] and de Groot[20]). For systems with small deviations from equilibrium, the flux–force relations can be taken linear, i.e.,

$$\hat{Y}^{(r)} = \sum_s \hat{L}_{rs} \hat{X}^{(s)} \tag{5.2}$$

where $\hat{L}_{rs}$ are called the phenomenological coefficients. With (5.2), the local rate of entropy production becomes a homogeneous quadratic form of the generalized forces $\hat{X}^{(r)}$:

$$\hat{\sigma}_S = \sum_{r,s} \hat{L}_{rs} \hat{X}^{(r)} \hat{X}^{(s)} \geqslant 0 \tag{5.3}$$

Expression (5.3) has the same form of the kinetic result (3.2) with the phenomenological coefficients $\hat{L}_{rs}$ possessing the same properties of the kinetic coefficients L_{rs} described in detail in Section 3. Thus, the phenomenological quantities can differ from the corresponding kinetic quantities only by a multiplicative constant which can be identified from the appropriate choice of units of measurement.

For the irreversible processes of thermal conduction and viscous dissipation, we may phenomenologically identify the generalized forces and the corresponding conjugate generalized fluxes as below:

$$\hat{X}_i^{(T)} = \frac{\partial}{\partial x_i} \left(\frac{1}{\hat{T}} \right) = -\frac{1}{\hat{T}^2} \frac{\partial \hat{T}}{\partial x_i} \tag{5.4}$$

$$\hat{X}_{ik}^{(u)} = \frac{1}{\hat{T}} D_{ik} \equiv \frac{1}{2\hat{T}} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right) \tag{5.5}$$

$$\hat{Y}_i^{(T)} = -\kappa \frac{\partial \hat{T}}{\partial x_i} = \kappa \hat{T}^2 \frac{\partial}{\partial x_i} \left(\frac{1}{\hat{T}} \right) \tag{5.6}$$

$$\hat{Y}_{ik}^{(u)} = 2\mu \left(D_{ik} - \frac{1}{3} D_{jj} \delta_{ik} \right) + \mu_1 D_{jj} \delta_{ik} \tag{5.7}$$

where u_i is the ith component of the gross velocity field, $\hat{T}$ is the thermodynamic temperature measured in $°K$, and κ, μ, and μ_1 denote the thermal conductivity, the shear viscosity and the bulk viscosity of the gas, respectively. In particular for a simple monatomic gas it can be shown that

$$\mu_1 = 0 \tag{5.8}$$

Thus, the local rate of entropy production for a simple monatomic gas in irreversible thermodynamics can be evaluated by simply substituting from

Eqs. (5.4)–(5.7) for generalized forces and fluxes together with (5.8) into (5.1) to give

$$\hat{\sigma}_S = \frac{\kappa}{\hat{T}^2} \frac{\partial \hat{T}}{\partial x_i} \frac{\partial \hat{T}}{\partial x_i} + \frac{2\mu}{\hat{T}} \left(D_{ik} D_{ik} - \frac{1}{3} D_{ii} D_{kk} \right) \geqslant 0 \qquad (5.9)$$

Moreover it follows from the inequality sign of (5.9) that

$$\kappa > 0 \qquad \text{and} \qquad \mu > 0 \qquad\qquad (5.10)$$

6. THE KINETIC AND THERMODYNAMIC TEMPERATURES

The thermodynamic temperature $\hat{T}$ used in Section 5 was chosen to be measured in °K, whereas the kinetic temperature T was chosen to be masured in energy units (by setting $k = 1$). By comparing (5.9) and (4.22) for the local rate of entropy production of a slightly inhomogeneous simple monatomic gas, we note that σ_S and $\hat{\sigma}_S$ essentially have the same form and differ only by a multiplicative constant. If we choose the kinetic and thermodynamic temperatures to be related by

$$T = k\hat{T} \qquad\qquad (6.1)$$

where $k = 1.3806 \times 10^{-16}$ ergs/°K is Boltzmann's constant, we can show that the expressions (5.9) and (4.22) become identical when

$$\hat{\sigma}_S = k\sigma_S, \qquad \kappa = k\lambda, \qquad \text{and} \quad \mu = \eta \qquad (6.2)$$

7. CONCLUDING REMARKS

The H theorem following a method first introduced by Prigogine[7] is written for the local rate of entropy production of a slightly inhomogeneous gas. The simultaneous treatment of the H theorem and of the Boltzmann equation for a slightly inhomogeneous gas yields the linear kinetic laws of transport processes. In this case the entropy production becomes a homogeneous quadratic form of the generalized forces with the kinetic coefficients possessing all the properties of the phenomenological coefficients of irreversible thermodynamics.

In the present study by identifying the generalized forces responsible for the considered irreversible processes, we have defined the conjugate generalized fluxes and the kinetic coefficients through the H theorem using a solution of the Boltzmann equation. We have further illuminated that the definition of the kinetic coefficients by this method seems to be the most natural way since (i) Onsager's principle[15] follows by definition, (ii) the

condition for the kinetic coefficient $L_{rr} \geqslant 0$ follows by definition, (iii) the inequality between the kinetic coefficients

$$L_{rr} L_{ss} \geqslant (L_{rs})^2$$

follows directly by applying Schwartz inequality for integrals, and (iv) the Curie–Prigogine principle[16-18] can be discussed in a more natural way.

In addition we have shown that the Hilbert[13,14] and Chapman–Enskog[8,9] solutions of the Boltzmann equation yield the same local rate of entropy production for a slightly inhomogeneous gas. Finally by comparing the results of the present method with the results of irreversible thermodynamics, we have reached the conclusion that kinetic theory and the Gibbs equation essentially yield the same results for small deviations from equilibrium, in agreement with Prigogine.[7]

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