PHYSICAL REVIEW E **103**, 012127 (2021)

Nonequilibrium temperature, entropy production, and bulk viscosity of one-dimensional normal shock waves

Young Gie Ohr (오영기)[*]
Emeritus Professor, Paichai University, Daejeon, Republic of Korea

(Received 17 August 2020; revised 30 November 2020; accepted 3 December 2020; published 22 January 2021)

The nonequilibrium temperature in the kinetic theory of gases is reexamined and an alternative definition of the temperature in terms of the local equilibrium distribution function is proposed. The alternative definition introduces a new physical quantity, 'exoenergy,' which represents the nonequilibrium nature of thermodynamic systems. The internal energy equation is split into two equations, the temperature equation and the exoenergy equation. In order to rationalize the equation splitting, the nonequilibrium thermodynamics is considered introducing the nonequilibrium entropy phenomenologically. The proposed temperature equation resolves the overshooting anomaly of temperature profiles of the Monte Carlo data for one-dimensional normal shock waves. The exoenergy equation makes the theory self-consistent and gives the entropy production of shock waves in closed form. The theory gives a general form of the shock wave equation and the general relation of the bulk viscosity to the shear viscosity and the heat conductivity of dilute monatomic gases.

DOI: 10.1103/PhysRevE.103.012127

I. INTRODUCTION

It has been conventional in the kinetic theory of dilute gases [1,2] that the nonequilibrium local temperature $T(\mathbf{r},t)$ is defined by the average kinetic energy of molecules by using the velocity distribution function, whether the gas is at near-equilibrium or far from equilibrium, writing

$$\frac{3}{2}k_BT(\mathbf{r},t)=\frac{1}{n(\mathbf{r},t)}\int\frac{1}{2}mC^2f(\mathbf{v},\mathbf{r},t)d\mathbf{v},\tag{1}$$

where f is the distribution function, $\mathbf{v}$ is the molecular velocity, C is the magnitude of the peculiar velocity $\mathbf{C}=\mathbf{v}-\mathbf{u}(\mathbf{r},t)$, $\mathbf{u}$ is the local fluid velocity, m is the molecular mass, n is the local number density of gas molecules, and k_B is the Boltzmann constant. In the Monte Carlo simulation of nonequilibrium gases [3], the definition in Eq. (1) has been employed to produce the temperature. For the transport processes of liquids [4], the definition has also been applied. There seems to be a prevalent belief that the nonequilibrium local temperature should be defined like Eq. (1) in the kinetic theory of fluids.

According to the distribution function theory of equilibrium statistical mechanics, the temperature is derived as the form of Eq. (1) described in normal textbooks [5]. The nonequilibrium local temperature is a conceptual extension of the derivation in equilibrium statistical mechanics, assuming its validity by replacement of the equilibrium distribution function with the nonequilibrium one. However, the extension has the status of a postulate the validity of which remains to be further demonstrated, especially its limits.

The direct simulation Monte Carlo (DSMC) method for stationary one-dimensional (1D) normal shock waves shows a small overshooting temperature profile on the downstream side in the shock layer [6–9], when the Mach number is increased above a certain value. This is not due to a mathematical artifact of theory, but the result of atomistic dynamics. The temperature overshoot is a strange behavior, because the temperature gradient changes its sign within such a small distance of the shock layer, which amounts to a few mean free paths of gas molecules. Moreover, the sign change gives rise to a negative thermal conductivity. There were no proper explanations about this abnormal outcome, although there was a report that the overshoot is a matter of the definition of the nonequilibrium temperature [10].

Recently, a possible resolution of the anomaly has been suggested by the present author [11]. In the suggestion, the author postulated a temperature equation in a solely intuitive way and introduced a quantity termed 'exopressure,' which represents a deviation of the nonequilibrium pressure, i.e., one third of the trace of the pressure tensor, from the equilibrium hydrostatic pressure. The important result is the finite ratio of the bulk viscosity to the shear viscosity of dilute monatomic gases. Because it has been well recognized that the bulk viscosity is equal to 0 for dilute monatomic gases, the result is at variance with the conventional kinetic theory [12].

The definition in Eq. (1) has enforced that the bulk viscosity should be 0 for dilute monatomic gases. The pressure tensor P is written for the dilute gases [13]

$$\mathsf{P}(\mathbf{r},t)=\int m\mathbf{C}\mathbf{C}f(\mathbf{v},\mathbf{r},t)d\mathbf{v}.\tag{2}$$

It has been well understood that the pressure tensor should be split into a scalar hydrostatic part p and a viscous part $\mathbb{P}$. The p is regarded to be the equilibrium part of P, giving relation to the local temperature by the equation of state, $p=nk_BT$, for dilute gases. The nonequilibrium part $\mathbb{P}$ is again split into the trace part $\mathcal{P}$ and the traceless stress tensor Π. The $\mathcal{P}$ is

---

[*] ohr@pcu.ac.kr

related to the bulk viscosity, which is called the exopressure. The exopressure is the nonequilibrium part of the trace of P,

$$\mathsf{P} = (nk_BT + \mathcal{P})\delta + \Pi, \tag{3}$$

where δ is the second-order unit tensor. According to Eq. (1), it is apparent that $\mathcal{P} = 0$ by definition. In the previous work, it has been shown that the application of the postulated temperature equation to the energy conservation equation gives a nonvanishing $\mathcal{P}$, which gives a finite bulk viscosity together with monotonic temperature profiles without the overshooting.

The bulk viscosity has been disclosed only for polyatomic or dense fluids [12,14]. It is questionable whether the bulk viscosity of a dilute monatomic system is unmeasurable because it is too small, or because it does not exist in the nature. In order to answer this question, it may be inevitable to reexamine the definition of temperature in Eq. (1). There was an effort to conceptualize the nonequilibrium temperature from the thermodynamic viewpoint [15]. The present work addresses the kinetic theory, proposing an alternative definition, and then the thermodynamic aspect of the temperature is examined.

The shock condition of compressible fluids, i.e., the upstream should be supersonic while the downstream is subsonic, gives a finite entropy increase. Because the shock wave is essentially an adiabatic process, the entropy increase is equal to the total entropy production of the whole shock wave. It is important to study the physical mechanism of producing the entropy and evaluate the local entropy production within the layer. The spatial integration of local entropy production should coincide with the total entropy production if the theory is properly developed.

In the present work, it is attempted to look for the molecular basis of the temperature equation proposed in the previous work. In order to rationalize the equation in thermodynamics, the nonequilibrium thermodynamics is reformulated, because the equation does not comply with conventional theories. The nonequilibrium entropy is also defined in the reformulation, and the entropy balance equation is derived using the temperature equation. In order to see the validity of the proposal, it is applied to 1D stationary shock waves and analysis of the DSMC data. The obtained local entropy is compared with existing theories. The whole theory is restricted to dilute monatomic gases.

II. THE LOCAL EQUILIBRIUM

There seem to be some different understandings of the terminology of the local equilibrium of dilute gases. It is important to clarify the definition of it in the present work.

A. Phenomenological definitions

1. Thermodynamic definition

The local equilibrium is defined such that the thermodynamic quantities are functions of $(\mathbf{r}, t)$ but they comply with the equilibrium thermodynamic laws. The definition disregards whether or not the temperature gradient and the strain rate are present, if the local quantities obey equilibrium thermodynamics.

2. Fluid dynamic definition

The definition requires three balance equations, i.e., the continuity equation, the Euler equation, and the isentropic equation, in addition to the thermodynamic definition.

B. Microscopic definition

Let us write the Boltzmann equation in conventional notation,

$$\frac{\partial f}{\partial t} + v_s\nabla_s f = J, \tag{4}$$

for dilute monatomic gases, where repeated indices mean summation convention, J represents the collision integral, and $\nabla_s \equiv \partial/\partial r_s$. The H theorem states that

$$\int J \ln f d\mathbf{v} \leqslant 0. \tag{5}$$

According to the property of collision integral, the equality of Eq. (5) holds only when $\ln f$ is a linear combination of five collision invariants [1], i.e., the mass, three components of the momentum, and the kinetic energy of molecules,

$$\ln f = \ln f_0 = a + b_s v_s + cv^2, \tag{6}$$

which gives the Maxwell-Boltzmann distribution function under appropriate physical conditions.

Let us write the Boltzmann equation for f_0,

$$\frac{\partial f_0}{\partial t} + v_s\nabla_s f_0 = 0, \tag{7}$$

in which the collision integral vanishes obviously. The question is what the result is when f_0 in Eq. (6) is substituted into Eq. (7). The result is that only if the coefficients, a, b_i, and c, are such that the temperature gradient and the strain rate are 0 does f_0 satisfy Eq. (7), as shown in Appendix A. The temperature must be spatially uniform, and the fluid velocity should be the value at which the strain rate vanishes,

$$\nabla_i T = 0, \tag{8a}$$

$$\tfrac{1}{2}(\nabla_i u_j + \nabla_j u_i) - \tfrac{1}{3}\nabla_s u_s \delta_{ij} = 0. \tag{8b}$$

The present work defines this state as 'physical local equilibrium.' The terminology reflects the fact that the nonzero temperature gradient and the strain rates should give rise to a dissipative process and nonzero entropy production, which mean the system is no longer at local equilibrium. The equations for the physical local equilibrium stand for reversible changes of the system.

It is conventional to write the Maxwell-Boltzmann distribution function

$$f_0(\mathbf{v}, \mathbf{r}, t) = n\left(\frac{m}{2\pi k_BT}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2k_BT}|\mathbf{v} - \mathbf{u}|^2\right], \tag{9}$$

in which n, $\mathbf{u}$, and T are regarded as functions of $(\mathbf{r}, t)$, in contrast to the physical local equilibrium. The same is true for the phenomenological definitions of the local equilibrium. To clarify and distinguish the states, we define 'virtual local equilibrium' for the state where n, $\mathbf{u}$, and T are functions of $(\mathbf{r}, t)$ regardless of the temperature gradient and the strain rate, and their behaviors are described by the continuity equation, the Euler equation, and the isentropic equation, as well as the equilibrium thermodynamic laws. Apparently, there is no entropy production at the virtual local equilibrium. The virtual local equilibrium is a hypothetical state, because the temperature gradient and the strain rate should not necessarily vanish while the heat flux and the viscous pressure tensor should be 0, i.e., all the transport coefficients should be 0. The inviscid flow in the aerodynamic analyses assumes virtual local equilibrium [16].

III. NONEQUILIBRIUM TEMPERATURE

In order to look for the molecular basis of the temperature equation proposed in the previous work [11], the Boltzmann transport equation, (4), is employed. The solution of the Boltzmann equation may be written in factorized form, without loss of generality,

$$f(\mathbf{v},\mathbf{r},t) = f_0(\mathbf{v},\mathbf{r},t)g(\mathbf{v},\mathbf{r},t), \tag{10}$$

in which f_0 is the distribution function of the virtual local equilibrium in Eq. (9), and g represents a deviation of f from f_0, which accounts for the nonequilibrium nature of f. There is no special restriction on g. Individual theories may model the functional forms of g to evaluate f, however, the present work employs the DSMC data for a particular molecular model. Therefore, g no longer enters the present theory.

At the present moment, n, $\mathbf{u}$, and T in Eq. (9) are just mathematical functions of $(\mathbf{r},t)$. The n and $\mathbf{u}$ are assigned to the physical quantities by the definitions

$$n(\mathbf{r},t) = \int f(\mathbf{v},\mathbf{r},t)d\mathbf{v}, \tag{11}$$

the number density, and

$$\mathbf{u}(\mathbf{r},t) = \frac{1}{n(\mathbf{r},t)}\int \mathbf{v}f(\mathbf{v},\mathbf{r},t)d\mathbf{v}, \tag{12}$$

the gas flow velocity. Obviously,

$$\int (f-f_0)d\mathbf{v} = \int \mathbf{v}(f-f_0)d\mathbf{v} = 0. \tag{13}$$

As the temperature is defined in the equilibrium theory, it is interesting to extend the definition in terms of f_0 rather than f and examine its consequences,

$$\frac{3}{2}k_BT(\mathbf{r},t) = \frac{1}{n(\mathbf{r},t)}\int \frac{1}{2}mC^2 f_0(\mathbf{v},\mathbf{r},t)d\mathbf{v}. \tag{14}$$

The equation for the local temperature thus defined will have to be derived from the equation for f_0, not the equation for f. It should be noted that

$$\int \frac{1}{2}mC^2(f-f_0)d\mathbf{v} \neq 0. \tag{15}$$

The inequality prevents the use of the Chapman-Enskog method for the Boltzmann equation, since the solubility condition of the method, which stems from Hilbert's theorem [1,2], is given by

$$\int \frac{1}{2}mC^2(f-f_0)d\mathbf{v} = 0, \tag{16}$$

together with Eq. (13). The condition in Eq. (16) is deemed to be an overimposition on $f(\mathbf{v},\mathbf{r},t)$ as long as the temperature is defined by Eq. (14). The inequality in Eq. (15) is therefore regarded as a conservative idea to allow for $f(\mathbf{v},\mathbf{r},t)$ to be comprised of more physical ingredients, e.g., the bulk viscosity. Although there is no way to provide a fundamental justification of the idea, there may be a way to rationalize it considering the thermodynamics, which is discussed in the next section.

The hydrostatic pressure p is defined by

$$p(\mathbf{r},t) = \frac{1}{3}\int mC^2 f_0(\mathbf{v},\mathbf{r},t)d\mathbf{v}, \tag{17}$$

and the exopressure is defined by

$$\mathcal{P}(\mathbf{r},t) = \frac{1}{3}\int mC^2(f-f_0)d\mathbf{v}. \tag{18}$$

It is obvious that

$$p(\mathbf{r},t) = k_Bn(\mathbf{r},t)T(\mathbf{r},t), \tag{19}$$

the equation of state. The internal energy for monatomic dilute gases is defined by

$$\rho(\mathbf{r},t)U(\mathbf{r},t) = \int \frac{1}{2}mC^2 f(\mathbf{v},\mathbf{r},t)d\mathbf{v}, \tag{20}$$

where U is the internal energy per mass, and ρ is the mass density.

Let us introduce the 'exoenergy,' $\mathcal{E}$, defined by

$$\rho(\mathbf{r},t)\mathcal{E}(\mathbf{r},t) = \int \frac{1}{2}mC^2(f-f_0)d\mathbf{v}. \tag{21}$$

Then the internal energy is composed of two terms:

$$U = U_0 + \mathcal{E}, \tag{22}$$

where U_0 is the equilibrium part

$$U_0 = \frac{3}{2}\frac{k_BT}{m}, \tag{23}$$

and $\mathcal{E}$ is the nonequilibrium part. For dilute gases, the relation between the exopressure and the exoenergy can be written as

$$\mathcal{P} = \frac{2}{3}\rho\mathcal{E}. \tag{24}$$

For later use, we define the stress tensor Π and the heat flux vector $\mathbf{Q}$:

$$\Pi(\mathbf{r},t) = \int m\left(\mathbf{CC} - \frac{1}{3}C^2\delta\right)f(\mathbf{v},\mathbf{r},t)d\mathbf{v}, \tag{25a}$$

$$\mathbf{Q}(\mathbf{r},t) = \int \frac{1}{2}m\mathbf{C}C^2 f(\mathbf{v},\mathbf{r},t)d\mathbf{v}. \tag{25b}$$

Here, Π and $\mathbf{Q}$ are the quantities of the unit volume. The pressure tensor and its nonequilibrium viscous part given in Eqs. (2) and (3) are written as

$$\mathsf{P} = p\delta + \mathbb{P}, \tag{26a}$$

$$\mathbb{P} = \int m\mathbf{CC}(f-f_0)d\mathbf{v} = \mathcal{P}\delta + \Pi. \tag{26b}$$

It is straightforward to write the equations for ρ and $\mathbf{u}$, using the Boltzmann equation in Eq. (4),

$$\frac{\partial \rho}{\partial t} + \nabla_s(\rho u_s) = 0, \tag{27a}$$

$$\frac{\partial}{\partial t}(\rho u_i) + \nabla_s(\mathsf{P}_{si} + \rho u_s u_i) = 0, \tag{27b}$$

the continuity equation and the equation of motion, respectively.

The temperature equation can be derived by using the equation for f_0 in Eq. (7). Multiplying $\frac{1}{2}mv^2$ by both sides of Eq. (7) and integrating them,

$$\int \frac{1}{2}mv^2 \frac{\partial f_0}{\partial t} d\mathbf{v} + \int \frac{1}{2}mv^2 v_s \nabla_s f_0 d\mathbf{v} = 0. \tag{28}$$

Since $v^2 = C^2 + 2C_r u_r + u^2$, it is straightforward to get

$$\frac{\partial}{\partial t}\left(\frac{3}{2}nk_BT + \frac{1}{2}\rho u^2\right) + \nabla_s\left[u_s\left(\frac{5}{2}nk_BT + \frac{1}{2}\rho u^2\right)\right] = 0, \tag{29}$$

which is the proposed nonequilibrium temperature equation. Applying Eqs. (23) and (27) to Eq. (29), and using $p = nk_BT$, $\mathbb{P}_{rs} = \mathcal{P}\delta_{rs} + \Pi_{rs}$, the equation is rewritten,

$$\rho\frac{DU_0}{Dt} = -\mathsf{P}_{sr}\nabla_s u_r + \nabla_s(u_r\mathbb{P}_{rs}), \tag{30}$$

where $\frac{D}{Dt} \equiv \partial/\partial t + u_s\nabla_s$, the material derivative. The internal energy equation is derived using Eq. (4),

$$\rho\frac{DU}{Dt} = -\nabla_s Q_s - \mathsf{P}_{sr}\nabla_s u_r, \tag{31}$$

and the equation of exoenergy can be written by using Eqs. (22), (30), and (31),

$$\rho\frac{D\mathcal{E}}{Dt} = -\nabla_s Q_s - \nabla_s(u_r\mathbb{P}_{rs}). \tag{32}$$

Insofar as the equalities of Eq. (13) hold, it should also be possible to derive the equations for ρ and $\mathbf{u}$ from Eq. (7). The continuity equation takes the same form as Eq. (27a), however, the equation of motion gives the Euler equation,

$$\frac{\partial}{\partial t}(\rho u_i) + \nabla_s(p\delta_{si} + \rho u_s u_i) = 0, \tag{33}$$

which is the equation for the virtual local equilibrium. Although the role of Eq. (33) in nonequilibrium flows is not clear, it is apparent that the equation should participate in the process of onset of viscous flows from the physical local equilibrium state. The mathematical instability of viscous flow seems to suppress the role of Eq. (33) after the onset. In this respect, the derived Eq. (33) may be regarded as an 'equilibrium branch' of the equation of motion in the nonequilibrium flows, which becomes unstable after the onset of viscous flows.

There is also an equilibrium branch in the temperature equation. By multiplying $\frac{1}{2}mC^2$ by both sides of Eq. (7) and integrating them,

$$\begin{aligned}\int \frac{1}{2}mC^2\frac{\partial f_0}{\partial t}d\mathbf{v} &+ \int \frac{1}{2}mC^2 v_s\nabla_s f_0 d\mathbf{v}\\ &= \frac{\partial}{\partial t}\int \frac{1}{2}mC^2 f_0 d\mathbf{v} + \nabla_s\int \frac{1}{2}mC^2 v_s f_0 d\mathbf{v}\\ &\quad + (\nabla_s u_r)\int mC_r v_s f_0 d\mathbf{v},\end{aligned} \tag{34}$$

one obtains

$$\frac{\partial}{\partial t}\left(\frac{3}{2}nk_BT\right) + \nabla_s\left(u_s\frac{3}{2}nk_BT\right) + (\nabla_s u_s)nk_BT = 0. \tag{35}$$

Using the continuity equation (27a), Eq. (35) is rearranged to

$$\frac{D}{Dt}\ln\left(\frac{T^{\frac{3}{2}}}{n}\right) = 0. \tag{36}$$

It is noteworthy that the equilibrium branch of the temperature equation in Eq. (36) is an isentropic equation, which is also the equation for the virtual local equilibrium. It is regarded that the equilibrium branch of the temperature equation becomes mathematically unstable after the temperature gradient is developed by the onset of nonequilibrium flows.

IV. NONEQUILIBRIUM ENTROPY

The entropy is a concept of the equilibrium state. Its extension to nonequilibrium phenomena stems from the Clausius inequality and the Boltzmann H theorem [17]. It seems that the establishment of the second law is the main task in the nonequilibrium thermodynamics. On the other hand, the first law has been regarded as relatively less important, although the thermodynamics roots its foundation on the mechanical equivalent of heat. However, recent understandings of the time arrow of spontaneous changes in nonequilibrium phenomena [18–20] seem to enforce a reconsideration about the first law, i.e., the equivalence of heat and mechanical energy.

It has been well understood that the thermodynamic process involving nonequilibrium breaks the time reversal symmetry which the microscopic physics laws should follow. After taking the symmetry breaking as the nature itself, it may be the next step to reflect it properly in the thermodynamic laws [21,22]. Because the time translation symmetry is reflected by the energy conservation laws, the symmetry breaking should play its role in the energy equation. The first law of equilibrium thermodynamics describes the energy conservation, taking the thermal energy as a form of the internal energy as well as the mechanical energy. The mechanical energy change and its conservation in a specific process, whether reversible or irreversible, is essentially a reflection of the time translation symmetry, as in the microscopic laws. But the change of thermal energy is quite different from the mechanical part, which requires an additional law (the second law) for the direction of spontaneous irreversible change [22], whereas it is equivalent to the mechanical energy change in the reversible process. Therefore, it is regarded that the broken symmetry may be related to the anisotropy of heat flow.

It is interesting to split the internal energy equation for nonequilibrium processes into two parts, the equation for mechanical energy changes and the equation for heat flows, and examine their consequences considering the second law. Because the equilibrium thermodynamics is complete in the present form, the split equations should be combined in the original form in the physical local equilibrium state. Furthermore, it should be noted that the amount of work or heat flow in different processes may be different (i.e., inexact), even though each of the processes starts in the same initial state and terminates in the same final state. Both the heat and the work equations should be balanced by exact quantities whose changes are given by the differences in their initial and final states regardless of the detailed processes of the changes, which means that a new quantity should be introduced to make the heat and work be exact quantities. The new quantity must vanish in the physical local equilibrium state. In the following subsection, a possible formulation for the nonequilibrium first law is demonstrated realizing the above-mentioned idea.

A. The first law

Let us write the first law in the physical local equilibrium,

$$\frac{DU}{Dt} = \frac{\mathfrak{d}q}{\mathfrak{d}t} + \frac{\mathfrak{d}w}{\mathfrak{d}t}, \tag{37}$$

in which the inexactness of the infinitesimal heat flow and work is expressed by the Fraktur typeface. Considering the internal energy equation in Eq. (31), it is regarded that

$$\rho\frac{\mathfrak{d}q}{\mathfrak{d}t} = -\nabla_s Q_s, \tag{38a}$$

$$\rho\frac{\mathfrak{d}w}{\mathfrak{d}t} = -\mathsf{P}_{sr}\nabla_s u_r. \tag{38b}$$

Because the internal energy comprises the equilibrium and nonequilibrium parts in Eq. (22),

$$\frac{DU}{Dt} = \frac{DU_0}{Dt} + \frac{D\mathcal{E}}{Dt}. \tag{39}$$

Then the energy equation is split into two equations by using Eqs. (30) and (32):

$$\rho\frac{DU_0}{Dt} = \rho\frac{\mathfrak{d}w}{\mathfrak{d}t} + \nabla_s(u_r\mathbb{P}_{rs}), \tag{40}$$

the equation for mechanical energy change; and

$$\rho\frac{D\mathcal{E}}{Dt} = \rho\frac{\mathfrak{d}q}{\mathfrak{d}t} - \nabla_s(u_r\mathbb{P}_{rs}), \tag{41}$$

the equation for heat flow. Combining the split equations, the original energy equation is obtained. It is noteworthy that the terms $\nabla_s(u_r\mathbb{P}_{rs})$ in the split equations play roles to make the right-hand sides (RHSs) be exact differential, because the left-hand sides (LHSs) are regarded as exact differential.

The mechanical energy equation for dilute monatomic gases constitutes the temperature equation. The equation is meaningful only when $\mathcal{E} \neq 0$, which implies that split energy equations should be applied to dissipative irreversible processes. The state of $\mathcal{E} = 0$ corresponds to the physical local equilibrium, the equations for which are given in Eqs. (A6).

B. The equilibrium branch

The basic idea of the present theory is that when a macro system at equilibrium suffers from external operations (e.g., an external heat source or external force by piston movements), and when it should undergo the onset of nonequilibrium, a set of equations describing system behaviors, Eqs. (A6), furcates into branches. There are two kinds of branches. One is the stable nonequilibrium branch, which complies with the external operations generating entropy. The other is the unstable equilibrium branch, which goes underground without entropy production, keeping the values of intensive quantities consistent with the complying branch. The energy equation trifurcates at the onset: the isentropic equation, the equation for mechanical work, and the equation for heat flow. Among these, the isentropic equation is the unstable branch and the others are the stable. The equation of motion bifurcates: the Euler equation and the dissipative momentum balance equation. The Euler equation is the unstable branch. The continuity equation does not furcate.

The system in the nonequilibrium branch may be arbitrarily far from equilibrium and changes its state evolving in time according to stable balance equations. The unstable branch is at virtual local equilibrium, not physical local equilibrium. The evolution of the unstable branch is suppressed by the external operation, and it does not contribute to the irreversible process of the system if there happens to be no singular behavior.

The nonequilibrium local chemical potential, $\mu(\mathbf{r}, t)$, one of the intensive quantities, is defined by the fundamental thermodynamic equation for the nonequilibrium branch,

$$\mu = U + pV - TS, \tag{42}$$

in parallel to the equation for the equilibrium branch,

$$\mu_0 = U_0 + pV - TS_0, \tag{43}$$

where $V = 1/\rho$, the volume per mass, S is the local entropy per mass of the nonequilibrium system in the stable branch, and the subscript 0 designates the value of the virtual local equilibrium in the unstable branch. It is imposed that $\mu = \mu_0$ at steady state, and $\mu \neq \mu_0$ for a time-dependent transient state, while the other intensive quantities, T, ρ, and p, of the nonequilibrium branch are always equal to the values of the equilibrium branch whether steady or transient. Additional impositions to μ are such that if $\mu > \mu_0$, the system undergoes a change toward the local equilibrium decreasing μ until $\mu = \mu_0$, arriving at a new steady state or local equilibrium, and if $\mu < \mu_0$, then the system changes farther from the local equilibrium increasing μ until $\mu = \mu_0$, arriving at a new steady state.

At steady state, the unstable equilibrium branch is regarded as a conjugate pair of the stable nonequilibrium branch by the common intensive quantities and uncommon extensive quantities. The equations for ρ, $\mathbf{u}$, and T, in Sec. III, are rationalized by the above arguments.

C. Stationary nonequilibrium entropy

Considering Eq. (42), the stationary chemical potential is written in the form

$$\mu^{(s)} = U + pV - TS^{(s)}, \tag{44}$$

where the superscript (s)'s designate the steady-state values. Since $\mu^{(s)} = \mu_0$, by definition, and $U = U_0 + \mathcal{E}$, given in Eq. (22), the stationary entropy is obtained from Eqs. (43) and (44),

$$S^{(s)} = S_0 + \frac{\mathcal{E}}{T}, \tag{45}$$

which is the definition of the local stationary entropy, and S_0 is the local specific entropy of the equilibrium branch, given by the Sackur-Tetrode formula [5],

$$S_0 = \frac{k_B}{m} \ln\left(\frac{T^{\frac{3}{2}}}{\rho}\right) + \text{constant}. \tag{46}$$

In parallel to the equilibrium theory, the entropy differential of the equilibrium branch should be written by the Gibbs relation,

$$\frac{DS_0}{Dt} = \frac{1}{T}\frac{DU_0}{Dt} + \frac{p}{T}\frac{DV}{Dt}, \tag{47}$$

and the Gibbs-Duhem equation takes the form

$$\frac{D\mu_0}{Dt} = -S_0\frac{DT}{Dt} + V\frac{Dp}{Dt}, \tag{48}$$

because there is no entropy production in the equilibrium branch by definition. Substituting $S_0 = S^{(s)} - \mathcal{E}/T$ and $U_0 = U - \mathcal{E}$ into Eqs. (47) and (48), the nonequilibrium Gibbs relation,

$$\frac{D^{(s)}}{Dt}\left(S^{(s)} - \frac{\mathcal{E}}{T}\right) = \frac{1}{T}\frac{D^{(s)}}{Dt}(U - \mathcal{E}) + \frac{p}{T}\frac{D^{(s)}V}{Dt}, \tag{49}$$

and the nonequilibrium Gibbs-Duhem equation,

$$\frac{D^{(s)}\mu^{(s)}}{Dt} = -\left(S^{(s)} - \frac{\mathcal{E}}{T}\right)\frac{D^{(s)}T}{Dt} + V\frac{D^{(s)}p}{Dt}, \tag{50}$$

are obtained for the steady state, in which the stationary material derivative is designated by the superscript (s) defining $\frac{D^{(s)}}{Dt} \equiv u_r\nabla_r$.

D. The nonequilibrium steady state

The balance equations, (27), (29), and (32), take the forms at steady state

$$\nabla_r(\rho u_r) = 0, \tag{51a}$$

$$\nabla_r[\mathsf{P}_{ri} + \rho u_r u_i] = 0, \tag{51b}$$

$$\nabla_r\left[u_r\left(\frac{5}{2}nk_BT + \frac{1}{2}\rho u^2\right)\right] = 0, \tag{51c}$$

$$\nabla_r\left[\frac{3}{2}u_r\mathcal{P} + Q_r + u_s\mathbb{P}_{rs}\right] = 0. \tag{51d}$$

Equation (51c) can be further simplified using Eq. (51a),

$$u_r\nabla_r\left[\frac{5k_B}{m}T + u^2\right] = 0, \tag{52}$$

which is the relation between the temperature gradient and the gradient of the fluid velocity, giving

$$\frac{5k_B}{m}T + u^2 = \text{constant} \tag{53}$$

along the streamline of steady flow. Also, by applying $\mathbb{P}_{rs} = \mathcal{P}\delta_{rs} + \Pi_{rs}$, Eq. (51d) is rearranged to

$$\nabla_r\left[\frac{5}{2}u_r\mathcal{P} + Q_r + u_s\Pi_{rs}\right] = 0, \tag{54}$$

which gives the relation among $\mathcal{P}$, $\mathbf{Q}$, and Π at steady state.

The relation between T and u^2 in Eq. (53) has been obtained by splitting the internal energy equation as described thus far. In 1922, Becker [23] obtained the same relation without the split for 1D stationary normal shock waves, assuming that the viscosity and the heat conductivity are constants, and the Prandtl number, $\mathrm{Pr} = \frac{3}{4}$, which is defined by $\mathrm{Pr} \equiv c_p\eta/\kappa$, where c_p, η, and κ are the isobaric specific heat, the shear viscosity, and the heat conductivity, respectively. For dilute monatomic gases, $c_p = \frac{5}{2}k_B/m$, the Prandtl number gives

$$\frac{\kappa}{\eta} = \frac{10}{3}\frac{k_B}{m}, \tag{55}$$

whereas the ratio κ/η for monatomic ideal gases at near-equilibrium has been known as $\frac{15}{4}k_B/m$ [1], giving $\mathrm{Pr} = \frac{2}{3}$. Since the Prandtl number, $\mathrm{Pr} = \frac{3}{4}$, is a good approximation for the actual value, and the simple form of the energy equation in Eq. (53) makes the equation of motion in Eq. (51b) be of an analytically integrable form, there have been many efforts to analyze, extend, and modify Becker's work over about a hundred years [24–28].

In order to see what happens in Eq. (54) when $\mathrm{Pr} = \frac{3}{4}$, let us introduce the transport coefficients writing the constitutive relations for 1D shock waves,

$$\Pi_{xx} = -\frac{4}{3}\eta\frac{du_x}{dx}, \tag{56a}$$

$$\mathcal{P} = -\zeta\frac{du_x}{dx}, \tag{56b}$$

$$Q_x = -\kappa\frac{dT}{dx}, \tag{56c}$$

in which ζ is the bulk viscosity. Since

$$\frac{dT}{dx} = -\frac{2m}{5k_B}u_x\frac{du_x}{dx}, \tag{57}$$

from Eq. (53), it is obtained that

$$\zeta = \frac{2}{5}\left(\frac{2m}{5k_B}\kappa - \frac{4}{3}\eta\right), \tag{58}$$

from Eq. (54) for $du_x/dx \neq 0$. When $\kappa/\eta = \frac{15}{4}k_B/m$, it gives $\zeta = \eta/15$, as shown in the previous work [11], however, it is apparent that $\zeta = 0$ when $\kappa/\eta = \frac{10}{3}k_B/m$, which gives $\mathcal{P} = u_x\Pi_{xx} + Q_x = 0$, and thus Eq. (54) becomes null. This is the reason why the relation in Eq. (53) is obtainable without the splitting internal energy equation as Becker demonstrated.

In general, the transport coefficients are complicated functions of the temperature, and show deviations from the simple relations given by the Newton and Fourier laws, when the system is driven far from local equilibrium. The same is true for the behavior of κ and η within the shock layer, as argued by Wang Chang [29]. Therefore, the Prandtl number should apply to the upstream equilibrium or the downstrean equilibrium gases, for example,

$$\mathrm{Pr} = c_p^{(u)}\frac{\eta^{(u)}}{\kappa^{(u)}}, \tag{59}$$

where the superscript (u)'s designate upstream values. By manipulating Eq. (58) a bit,

$$\begin{aligned}\zeta &= \frac{2}{5}\eta^{(u)}\left(\frac{2m}{5k_B}\frac{\kappa}{\kappa^{(u)}}\frac{\kappa^{(u)}}{\eta^{(u)}} - \frac{4}{3}\frac{\eta}{\eta^{(u)}}\right)\\ &= \frac{2}{5}\eta^{(u)}\left(\frac{1}{\mathrm{Pr}}\frac{\kappa}{\kappa^{(u)}} - \frac{4}{3}\frac{\eta}{\eta^{(u)}}\right).\end{aligned} \tag{60}$$

When $\mathrm{Pr} = \frac{3}{4}$, the bulk viscosity takes the form

$$\zeta = \frac{8}{15}\eta^{(u)}\left(\frac{\kappa}{\kappa^{(u)}} - \frac{\eta}{\eta^{(u)}}\right), \tag{61}$$

where $\kappa/\kappa^{(u)} \neq \eta/\eta^{(u)}$, in general. This point is discussed further in Sec. VII.

E. Entropy production

Since the positivity of entropy production is consistent with the Clausius inequality, it has been conventional to demonstrate the second law by proving the positivity after derivation of the entropy balance equation. In the kinetic theory approach, the nonequilibrium entropy is defined by using the velocity distribution function and applies the H theorem for this purpose. In this approach, the H theorem is the bridge connecting the molecular theory to the second law of thermodynamics.

In the present formulation, the temperature equation takes the role of a bridge between the Boltzmann equation and the first law of thermodynamics. The entropy is defined phenomenologically, and the entropy balance equation is derived by using the temperature equation.

The entropy balance equation takes the form

$$\rho\frac{DS}{Dt} = -\nabla_r\mathcal{F}_r + \sigma, \tag{62}$$

where $\mathcal{F}_i$ and σ represent the entropy flux vector and the entropy production, respectively. The entropy equation for the virtual local equilibrium is derived from the equilibrium Gibbs relation, in Eq. (47), and using $p = nk_BT$,

$$\begin{aligned}\rho\frac{DS_0}{Dt} &= \rho\frac{1}{T}\frac{DU_0}{Dt} + \rho\frac{p}{T}\frac{DV}{Dt} &(63a)\\ &= \frac{3}{2}\frac{k_B}{m}\rho\frac{1}{T}\frac{DT}{Dt} - \frac{k_B}{m}\frac{D\rho}{Dt} &(63b)\\ &= \frac{k_B}{m}\rho\frac{D}{Dt}\ln\left(\frac{T^{\frac{3}{2}}}{\rho}\right), &(63c)\end{aligned}$$

which is to be the isentropic equation. The entropy balance equation for a nonequilibrium system can be derived from the nonequilibrium Gibbs relation in Eq. (49), at steady state,

$$\begin{aligned}\rho\frac{D^{(s)}S^{(s)}}{Dt} &= \rho\frac{1}{T}\frac{D^{(s)}}{Dt}(U-\mathcal{E}) + \rho\frac{p}{T}\frac{D^{(s)}V}{Dt} + \rho\frac{D^{(s)}}{Dt}\frac{\mathcal{E}}{T}\\ &= \frac{\rho}{T}\frac{D^{(s)}U_0}{Dt} - \frac{k_B}{m}\frac{D^{(s)}\rho}{Dt} + \rho\frac{D^{(s)}}{Dt}\frac{\mathcal{E}}{T}. &(64)\end{aligned}$$

Since

$$\rho\frac{D^{(s)}}{Dt}\frac{\mathcal{E}}{T} = \frac{\rho}{T}\frac{D^{(s)}\mathcal{E}}{Dt} - \frac{\rho\mathcal{E}}{T^2}\frac{D^{(s)}T}{Dt}, \tag{65}$$

using Eqs. (27a), (30), and (32) and $p = nk_BT$, it is obtained that

$$\rho\frac{D^{(s)}S^{(s)}}{Dt} = -\frac{1}{T}\nabla_rQ_r - \frac{1}{T}\mathbb{P}_{rs}\nabla_su_r - \frac{\rho\mathcal{E}}{T^2}\frac{D^{(s)}T}{Dt}. \tag{66}$$

Substituting $\frac{D^{(s)}}{Dt}T = u_r\nabla_rT$ into Eq. (66) and considering

$$\frac{1}{T}\nabla_rQ_r = \nabla_r\left(\frac{Q_r}{T}\right) + \frac{Q_r}{T^2}\nabla_rT, \tag{67}$$

the entropy balance equation at steady state is written in the form

$$\rho\frac{D^{(s)}S^{(s)}}{Dt} = -\nabla_r\mathcal{F}_r^{(s)} + \sigma^{(s)}, \tag{68}$$

where

$$\mathcal{F}_i^{(s)} = \frac{Q_i}{T}, \tag{69}$$

the steady-state local entropy flux, and

$$\sigma^{(s)} = -\frac{1}{T^2}(Q_r + \rho\mathcal{E}u_r)\nabla_rT - \frac{1}{T}\mathbb{P}_{rs}\nabla_ru_s, \tag{70}$$

the steady-state local entropy production per unit volume. The second law of thermodynamics requires that

$$\sigma^{(s)} > 0, \tag{71}$$

which should be verified for individual applications.

V. APPLICATION TO A 1D NORMAL SHOCK WAVE

A. Balance equations

In order to examine the validity of the postulated temperature equation and the entropy production, it is applied to the stationary 1D normal shock wave problem. Considering Eqs. (51), a set of balance equations for a 1D shock wave is written as

$$\frac{d}{dx}(\rho u_x) = 0, \tag{72a}$$

$$\frac{d}{dx}\left(\Pi_{xx} + \mathcal{P} + p + \rho u_x^2\right) = 0, \tag{72b}$$

$$\frac{d}{dx}\left[u_x\left(\frac{5}{2}p + \frac{1}{2}\rho u_x^2\right)\right] = 0, \tag{72c}$$

$$\frac{d}{dx}\left(\frac{5}{2}u_x\mathcal{P} + Q_x + u_x\Pi_{xx}\right) = 0. \tag{72d}$$

Applying the upstream equilibrium boundary condition at $x \to -\infty$, the stationary equations are integrated from $-\infty$ to a certain x,

$$\rho u_x = \rho^{(u)}u^{(u)}, \tag{73a}$$

$$\Pi_{xx} + \mathcal{P} + p + \rho u_x^2 = p^{(u)} + \rho^{(u)}(u^{(u)})^2, \tag{73b}$$

$$5u_xp + \rho u_x^3 = 5u^{(u)}p^{(u)} + \rho^{(u)}(u^{(u)})^3, \tag{73c}$$

$$5u_x\mathcal{P} + 2Q_x + 2u_x\Pi_{xx} = 0, \tag{73d}$$

where $\rho^{(u)}$, $u^{(u)}$, and $p^{(u)}$ are the upstream mass density, the x component of the upstream gas velocity, and the hydrostatic pressure of upstream gas, respectively. The downstream equilibrium values at $x \to \infty$ are obtained in terms of the upstream boundary conditions,

$$\rho^{(d)}u^{(d)} = \rho^{(u)}u^{(u)}, \tag{74a}$$

$$p^{(d)} + \rho^{(d)}(u^{(d)})^2 = p^{(u)} + \rho^{(u)}(u^{(u)})^2, \tag{74b}$$

$$5u^{(d)}p^{(d)} + \rho^{(d)}(u^{(d)})^3 = 5u^{(u)}p^{(u)} + \rho^{(u)}(u^{(u)})^3, \tag{74c}$$

where the superscript (d)'s denote the downstream values. It is convenient to express the values in dimensionless form. Let us define

$$\widetilde{\rho}^{(d)} \equiv \frac{\rho^{(d)}}{\rho^{(u)}}, \quad \widetilde{u}^{(d)} \equiv \frac{u^{(d)}}{u^{(u)}}, \quad \widetilde{T}^{(d)} \equiv \frac{T^{(d)}}{T^{(u)}}, \tag{75}$$

in which $T^{(u)}$ and $T^{(d)}$ are the upstream and the downstream temperatures, respectively. Since $p^{(d)} = k_B\rho^{(d)}T^{(d)}/m$ and $p^{(u)} = k_B\rho^{(u)}T^{(u)}/m$, the dimensionless values are obtained from Eqs. (74),

$$\widetilde{\rho}^{(d)} = \frac{4}{1+5p_0}, \quad \widetilde{u}^{(d)} = \frac{1+5p_0}{4},$$
$$\widetilde{T}^{(d)} = \frac{1}{16p_0}(3-p_0)(1+5p_0), \tag{76}$$

where p_0 is the dimensionless upstream pressure, which is related to the Mach number M as follows:

$$p_0 \equiv \frac{k_B T^{(u)}}{m(u^{(u)})^2} = \frac{3}{5M^2}. \tag{77}$$

B. Shock wave equation

Considering Eqs. (53) and (73c), it is apparent that

$$\frac{5k_B}{m}T + u_x^2 = \frac{5k_B}{m}T^{(u)} + \left(u^{(u)}\right)^2. \tag{78}$$

For later use, it is useful to write Eq. (78) in dimensionless form,

$$5p_0\widetilde{T} + \widetilde{u}^2 = 5p_0 + 1, \tag{79}$$

where $\widetilde{T} \equiv T/T^{(u)}$ and $\widetilde{u} \equiv u/u^{(u)}$.

In order to estimate the shock profiles, the shock equation should be derived. Substituting Eqs. (56a) and (56b) into the equation of motion, (73b), it is obtained that

$$\left(\frac{4}{3}\eta + \zeta\right)\frac{du_x}{dx} = p + \rho u_x^2 - p^{(u)} - \rho^{(u)}(u^{(u)})^2, \tag{80}$$

which constitutes the general form of the 1D normal shock wave equation. Because $p = nk_BT$ and T is given by Eq. (78), the shock equation in Eq. (80) is just a single ordinary differential equation for $u_x(x)$, provided that the shear and bulk viscosity are known. The bulk viscosity can be replaced by the heat conductivity if the relation in Eq. (58) is employed:

$$\frac{4}{3}\eta + \zeta = \frac{4}{5}\left(\eta + \frac{m}{5k_B}\kappa\right). \tag{81}$$

In general, the viscosity is a complicated function of the temperature and shows non-Newtonian behaviors when the system is driven far from equilibrium; care should be taken to apply the equation to strong shock waves.

C. Entropy production

The local entropy balance equation in Eq. (68) takes the form, in 1D shock waves,

$$\frac{d}{dx}\left(\rho u_x S^{(s)}\right) = -\frac{d}{dx}\left(\frac{Q_x}{T}\right) + \sigma^{(s)}, \tag{82}$$

where

$$\sigma^{(s)} = -\frac{1}{T^2}(Q_x + \rho\mathcal{E}u_x)\frac{dT}{dx} - \frac{1}{T}\mathbb{P}_{xx}\frac{du_x}{dx}, \tag{83}$$

in which the property of Eq. (72a) has been used. Using Eqs. (57) and (73d), $\rho\mathcal{E} = \frac{3}{2}\mathcal{P}$, and $\mathbb{P}_{xx} = \mathcal{P} + \Pi_{xx}$, it is obtained that

$$\sigma^{(s)} = -\frac{1}{T}\left(\frac{2mu_x^2}{5k_BT} + 1\right)\mathbb{P}_{xx}\frac{du_x}{dx}. \tag{84}$$

From Eq. (73b), we see that

$$\begin{aligned}\mathbb{P}_{xx} &= p^{(u)} - p + \rho^{(u)}(u^{(u)})^2 - \rho u_x^2 \\ &= \frac{k_BT^{(u)}}{m}\rho^{(u)} - \frac{k_BT}{m}\rho + \rho^{(u)}(u^{(u)})^2 - \rho u_x^2,\end{aligned} \tag{85}$$

and

$$\frac{\mathbb{P}_{xx}}{\rho^{(u)}(u^{(u)})^2} = p_0 + 1 - p_0\widetilde{\rho}\widetilde{T} - \widetilde{u}, \tag{86}$$

where $\widetilde{\rho} \equiv \rho/\rho^{(u)}$, and the property $\widetilde{\rho}\widetilde{u} = 1$ in Eq. (73a) has been used. Using Eqs. (76) and (79),

$$\frac{\mathbb{P}_{xx}}{\rho^{(u)}(u^{(u)})^2} = -\frac{4}{5\widetilde{u}}(\widetilde{u} - 1)(\widetilde{u} - \widetilde{u}^{(d)}), \tag{87}$$

which gives

$$\begin{aligned}&\frac{m}{k_B}\frac{\lambda^{(u)}\sigma^{(s)}}{\rho^{(u)}u^{(u)}} \\ &\quad = \frac{4}{\widetilde{u}}\frac{1 + 5p_0 + \widetilde{u}^2}{(1 + 5p_0 - \widetilde{u}^2)^2}(\widetilde{u} - 1)(\widetilde{u} - \widetilde{u}^{(d)})\frac{d\widetilde{u}}{d\widetilde{x}},\end{aligned} \tag{88}$$

where $\lambda^{(u)}$ is the mean free path of upstream molecules, and $\widetilde{x} \equiv x/\lambda^{(u)}$.

It is useful to note that

$$u^{(u)} = \sqrt{\frac{k_BT^{(u)}}{m}}\sqrt{\frac{m(u^{(u)})^2}{k_BT^{(u)}}} = p_0^{-\frac{1}{2}}\sqrt{\frac{k_BT^{(u)}}{m}}, \tag{89}$$

and the mean time between successive collisions of upstream molecules

$$\tau \equiv \lambda^{(u)}\sqrt{\frac{m}{k_BT^{(u)}}}. \tag{90}$$

Then the LHS of Eq. (88) can be rewritten as

$$\frac{m}{k_B}\frac{\lambda^{(u)}\sigma^{(s)}}{\rho^{(u)}u^{(u)}} = p_0^{\frac{1}{2}}\frac{\tau\sigma^{(s)}}{k_B}\frac{m}{\rho^{(u)}}. \tag{91}$$

Since $\sigma^{(s)}$ is the entropy production per unit volume, $\tau\sigma^{(s)}/k_B$ is the entropy produced during τ per unit volume in dimensionless entropy unit. Therefore, the local contribution of a molecule at x to the entropy creation during τ in entropy units at steady state, writing in $\Sigma^{(s)}$, takes the form

$$\Sigma^{(s)} \equiv \frac{\tau\sigma^{(s)}}{k_B}\frac{m}{\rho^{(u)}}$$
$$= \frac{4p_0^{-\frac{1}{2}}}{\widetilde{u}}\frac{1+5p_0+\widetilde{u}^2}{(1+5p_0-\widetilde{u}^2)^2}(\widetilde{u}-1)\big(\widetilde{u}-\widetilde{u}^{(d)}\big)\frac{d\widetilde{u}}{d\widetilde{x}}. \tag{92}$$

The transport coefficients for the entropy production are included in the term $d\widetilde{u}/d\widetilde{x}$, as shown in Eq. (80). It is obvious that $\Sigma^{(s)} > 0$, for

$$\widetilde{u}^{(d)} < \widetilde{u} < 1 \quad \text{and} \quad \frac{d\widetilde{u}}{d\widetilde{x}} < 0. \tag{93}$$

The local entropy change can be expressed by the nonequilibrium Gibbs relation in Eq. (49):

$$u_x\frac{d}{dx}S^{(s)} = u_x\frac{d}{dx}\frac{\mathcal{E}}{T} + \frac{1}{T}u_x\frac{d}{dx}(U-\mathcal{E}) + \frac{p}{T}u_x\frac{dV}{dx}. \tag{94}$$

Using $U-\mathcal{E} = U_0 = \frac{3}{2}k_BT/m$, $p = \rho k_BT/m$, and $V = 1/\rho$, it is simplified to

$$\frac{dS^{(s)}}{dx} = \frac{d}{dx}\frac{\mathcal{E}}{T} + \frac{3}{2}\frac{k_B}{m}\frac{1}{T}\frac{dT}{dx} - \frac{k_B}{m}\frac{1}{\rho}\frac{d\rho}{dx}. \tag{95}$$

The equation is further simplified:

$$\frac{dS^{(s)}}{dx} = \frac{d}{dx}\left(\frac{\mathcal{E}}{T} + \frac{3}{2}\frac{k_B}{m}\ln T - \frac{k_B}{m}\ln\rho\right). \tag{96}$$

Since $d(\rho u_xS^{(s)})/dx$ represents the entropy increasing rate per unit volume, the local entropy per mass, $S^{(s)}(x)$, can be evaluated by integration,

$$\int_{-\infty}^{x}\frac{d}{dx}\big(\rho u_xS^{(s)}\big)dx = \rho^{(u)}u^{(u)}\big(S^{(s)} - S_0^{(u)}\big), \tag{97}$$

with the use of Eq. (73a), where $S_0^{(u)}$ is the upstream equilibrium entropy per mass. Therefore, the local entropy is obtained by using either Eq. (82) or Eq. (96),

$$S^{(s)} - S_0^{(u)} = \frac{1}{\rho^{(u)}u^{(u)}}\left(-\frac{Q_x}{T} + \int_{-\infty}^{x}\sigma^{(s)}dx\right), \tag{98a}$$

$$S^{(s)} - S_0^{(u)} = \frac{\mathcal{E}}{T} + \frac{3}{2}\frac{k_B}{m}\ln\frac{T}{T^{(u)}} - \frac{k_B}{m}\ln\frac{\rho}{\rho^{(u)}}. \tag{98b}$$

The entropy production in Eq. (88) gives

$$\frac{m}{k_B}\frac{\lambda^{(u)}}{\rho^{(u)}u^{(u)}}\int_{-\infty}^{x}\sigma^{(s)}dx$$
$$= \int_{-\infty}^{x}\frac{4}{\widetilde{u}}\frac{1+5p_0+\widetilde{u}^2}{(1+5p_0-\widetilde{u}^2)^2}(\widetilde{u}-1)\big(\widetilde{u}-\widetilde{u}^{(d)}\big)\frac{d\widetilde{u}}{d\widetilde{x}}dx. \tag{99}$$

Since $4(\widetilde{u}-\widetilde{u}^{(d)}) = 4\widetilde{u}-1-5p_0$, the indefinite integration of the integral of the RHS of Eq. (99) is carried out,

$$\int\left[\frac{\widetilde{u}-1}{\widetilde{u}}\frac{(1+5p_0+\widetilde{u}^2)(4\widetilde{u}-1-5p_0)}{(1+5p_0-\widetilde{u}^2)^2}\right]d\widetilde{u}$$
$$= \ln\left[\widetilde{u}\big(1+5p_0-\widetilde{u}^2\big)^{\frac{3}{2}}\right] + \frac{5[1+5p_0-(1+p_0)\widetilde{u}]}{1+5p_0-\widetilde{u}^2}. \tag{100}$$

Applying upper and lower limits of integration and using the relation in Eq. (79),

$$\frac{m}{k_B}\frac{1}{\rho^{(u)}u^{(u)}}\int_{-\infty}^{x}\sigma^{(s)}dx$$
$$= \ln\big(\widetilde{u}\widetilde{T}^{\frac{3}{2}}\big) + \frac{4}{5p_0\widetilde{T}}(\widetilde{u}-1)\big(\widetilde{u}-\widetilde{u}^{(d)}\big). \tag{101}$$

Therefore, Eq. (98a) gives

$$\frac{m}{k_B}\big(S^{(s)} - S_0^{(u)}\big)$$
$$= \ln\big(\widetilde{u}\widetilde{T}^{\frac{3}{2}}\big) + \frac{4}{5p_0\widetilde{T}}(\widetilde{u}-1)\big(\widetilde{u}-\widetilde{u}^{(d)}\big) - \frac{\widetilde{Q}}{p_0\widetilde{T}}, \tag{102}$$

where

$$\widetilde{Q} \equiv \frac{Q_x}{\rho^{(u)}\big(u^{(u)}\big)^3}. \tag{103}$$

It is immediate to rewrite Eq. (98b) in dimensionless form,

$$\frac{m}{k_B}\big(S^{(s)} - S_0^{(u)}\big) = \frac{\widetilde{\mathcal{E}}}{p_0\widetilde{T}} + \frac{3}{2}\ln\widetilde{T} - \ln\widetilde{\rho}, \tag{104}$$

where

$$\widetilde{\mathcal{E}} \equiv \frac{\mathcal{E}}{\big(u^{(u)}\big)^2}. \tag{105}$$

Both expressions, Eqs. (102) and (104), are equivalent, as shown in the next section.

VI. ANALYSES OF DSMC DATA

Because the present formulation is more or less fundamental than modeling a particular phenomenon, the purpose of this section is to demonstrate the validity of the theory by analyzing the DSMC data on 1D normal shock wave. The data are generated for hard spheres using the DSMC1S.FOR program written by Professor Graeme Bird [3]. The literature data on DSMC given by Nanbu and Watanabe [30] for Maxwell molecules are also used. The coordinate origin is defined at the location of half-density, and the distance from the origin is scaled by the upstream mean free path. Details of the program run and data manipulations are given in Appendix B.

It is convenient to introduce dimensionless quantities,

$$\widetilde{\mathcal{P}} \equiv \mathcal{P}/p^*, \quad \widetilde{\Pi} \equiv \Pi_{xx}/p^*, \quad \widetilde{\mathbb{P}} \equiv \mathbb{P}_{xx}/p^*,$$
$$\widetilde{p} \equiv p/p^*, \quad p^* \equiv \rho^{(u)}\big(u^{(u)}\big)^2,$$
$$\widetilde{\eta} \equiv \eta/\eta^*, \quad \widetilde{\zeta} \equiv \zeta/\eta^*, \quad \eta^* \equiv \lambda^{(u)}\rho^{(u)}u^{(u)}, \tag{106}$$
$$\widetilde{\kappa} \equiv \frac{\kappa T^{(u)}}{\lambda^{(u)}u^{(u)}p^*} = \frac{mp_0}{k_B}\kappa/\eta^*,$$

where p_0 is defined in Eq. (77), and also, $\widetilde{Q}$, $\widetilde{\mathcal{E}}$, $\widetilde{\rho}$, $\widetilde{u}$, and $\widetilde{T}$ have already been defined. The mean free path of upstream molecules is taken in parallel to the hard-sphere value [3], defining

$$\lambda^{(u)} = \frac{8}{5}\frac{\eta^{(u)}}{\rho^{(u)}}\sqrt{\frac{2m}{\pi k_BT^{(u)}}}, \tag{107}$$

in which $\eta^{(u)}$ is the shear viscosity of the upstream gas.

A. Shock wave structure

Equations (73) are rewritten in terms of dimensionless quantities:

$$\tilde{\rho}\tilde{u} = 1, \tag{108a}$$

$$\tilde{\Pi} + \tilde{\mathcal{P}} + \tilde{p} + \tilde{\rho}\tilde{u}^2 = p_0 + 1, \tag{108b}$$

$$5\tilde{u}\tilde{p} + \tilde{\rho}\tilde{u}^3 = 5p_0 + 1, \tag{108c}$$

$$5\tilde{u}\tilde{\mathcal{P}} + 2\tilde{Q} + 2\tilde{u}\tilde{\Pi} = 0. \tag{108d}$$

Equations (108a) and (108c) give the relations among $\tilde{\rho}$, $\tilde{u}$, and $\tilde{p}$. Taking $\tilde{u}$ as independent, others are expressed in terms of $\tilde{u}$:

$$\tilde{\rho} = \frac{1}{\tilde{u}}, \tag{109a}$$

$$\tilde{p} = \frac{1}{5\tilde{u}}(1 + 5p_0 - \tilde{u}^2). \tag{109b}$$

It is noteworthy that these relations are independent of particular force models of molecules and degrees of approximation to the distribution function. There are four unknowns, $\tilde{u}$, $\tilde{\Pi}$, $\tilde{\mathcal{P}}$, and $\tilde{Q}$, in the remaining two equations, (108b) and (108d). It is useful to rearrange them,

$$\tilde{u}\tilde{\Pi} + \tilde{Q} = -\frac{5}{2}\tilde{u}\tilde{\mathcal{P}}, \tag{110a}$$

$$3\tilde{u}\tilde{\Pi} - 2\tilde{Q} = X, \tag{110b}$$

where

$$\begin{aligned} X &= (1 - \tilde{u})(4\tilde{u} - 1 - 5p_0) \\ &= -4\big(\tilde{u} - \tilde{u}^{(u)}\big)\big(\tilde{u} - \tilde{u}^{(d)}\big). \end{aligned} \tag{111}$$

For illustrative purposes, the agreements between theoretical balance equations and DSMC results are demonstrated by applying the simulated data for $\tilde{u}$, $\tilde{\Pi}$, and $\tilde{Q}$ to Eq. (110b). Bird's program DSMC1S.FOR provides an option to select molecular models from the hard sphere to the Maxwell molecule. The results of examination of Eq. (110b) by changing the molecular parameter and the Mach number show that the simulated data satisfy the equation within 1%. For illustration, the LHS and the RHS of Eq. (110b) inputting the DSMC data are shown in Fig. 1 for hard spheres and in Fig. 2 for Maxwell molecules at different Mach numbers, $M = 3$ and 10. In Fig. 2, the literature data for Maxwell molecules, given by Nanbu and Watanabe [30], are used.

The shock wave equation, (80), can be rewritten in terms of dimensionless variables. By using Eqs. (56) and (57),

$$\tilde{\Pi} = -\frac{4}{3}\tilde{\eta}\frac{d\tilde{u}}{d\tilde{x}}, \tag{112a}$$

$$\tilde{Q} = -\tilde{\kappa}\frac{d\tilde{T}}{d\tilde{x}}, \tag{112b}$$

$$\frac{d\tilde{T}}{d\tilde{x}} = -\frac{2\tilde{u}}{5p_0}\frac{d\tilde{u}}{d\tilde{x}}, \tag{112c}$$

Eq. (110b) gives

$$\frac{d\tilde{u}}{d\tilde{x}} = -\frac{5p_0}{4\tilde{u}}\frac{X}{\tilde{\kappa} + 5p_0\tilde{\eta}}. \tag{113}$$

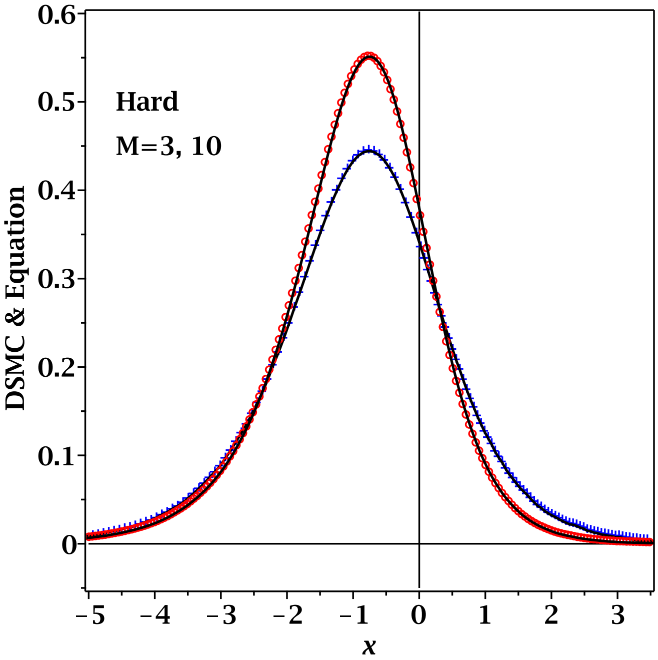

FIG. 1. Agreements between DSMC data and predictions of the balance equation, (110b), for hard spheres at $M = 3$ (lower curve; crosses) and $M = 10$ (upper curve; circles). The symbols are LHS values of the equation, and the lines are RHS values.

Shock profiles can be obtain by solving (113) for known $\tilde{\kappa}$ and $\tilde{\eta}$. The main task in the shock wave problem, therefore, is the modeling of $\tilde{\kappa}$ and $\tilde{\eta}$ for particular molecules.

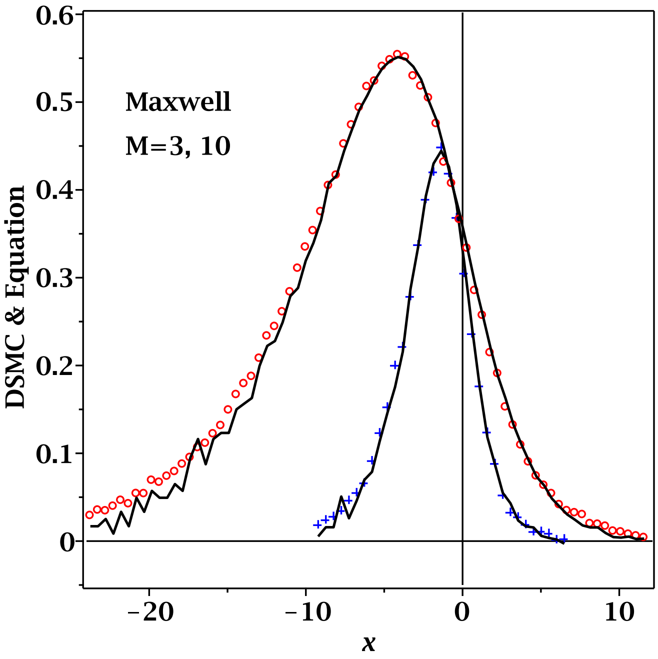

FIG. 2. Agreements between DSMC data and predictions of the balance equation, (110b), for a Maxwell molecular gas at $M = 3$ (lower curve; crosses) and $M = 10$ (upper curve; circles). The symbols are LHS values of the equation, and the lines are RHS values.

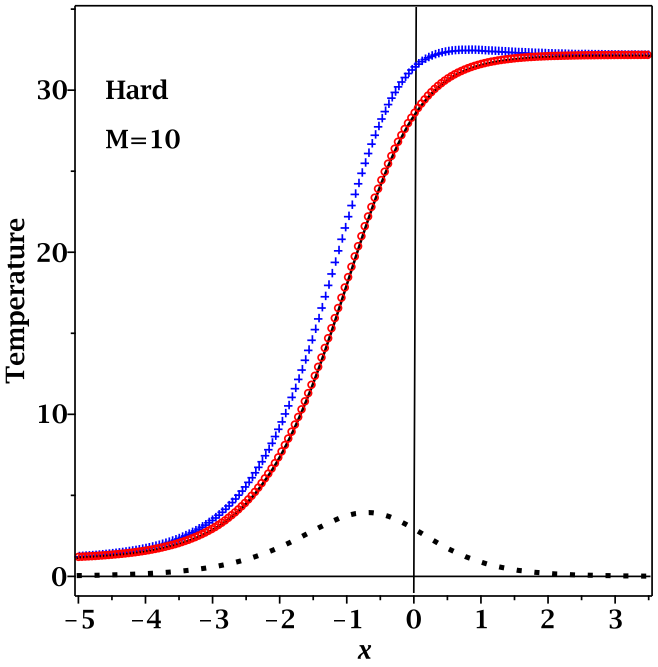

FIG. 3. Temperature and exopressure profiles vs $\widetilde{x}$, by the DSMC simulation for hard spheres at $M = 10$. The $\widetilde{T}$ values are plotted by the solid line using the DSMC $\widetilde{u}$ and Eq. (79) and by circles using Eq. (115). The overshooting $\widetilde{T}_k$ values are represented by crosses, and the dotted curve shows the contribution of $(\widetilde{u}/p_0)\widetilde{\mathcal{P}}$ in Eq. (115).

B. Nonequilibrium temperature

The DSMC programs employ the definition in Eq. (1) to produce the temperature. However, it is actually the internal energy in Eq. (20), evaluated in temperature units. Let us define the kinetic temperature T_k,

$$\frac{3}{2}k_B T_k = \frac{1}{n}\int \frac{1}{2}mC^2 f\,d\mathbf{v}. \tag{114}$$

The DSMC temperature should be read as T_k, and it is related to T by the relations in Eqs. (20)–(24),

$$\widetilde{T} = \widetilde{T}_k - \frac{\widetilde{u}}{p_0}\widetilde{\mathcal{P}}, \tag{115}$$

in dimensionless quantities, where $\widetilde{T}_k = T_k/T^{(u)}$. The simulated data for $\widetilde{\Pi}$ and $\widetilde{Q}$ produce $\widetilde{\mathcal{P}}$ by using Eq. (110a), which gives $\widetilde{T}$ by Eq. (115) using the simulated $\widetilde{T}_k$ data. The monotonic profiles of $\widetilde{T}$ thus obtained are shown in Fig. 3 for hard spheres and in Fig. 4 for Maxwell molecules [30], at $M = 10$. The overshooting $\widetilde{T}_k$ curve, which has been known until now as the temperature profile, and the contribution of exopressure, which has been ignored in conventional theories, are shown in the same figures. The overshooting occurs when the Mach number is increased over a certain value, e.g., $M > 3.3$ for Maxwell molecules [9]. Figures 5 and 6 are drawn for the same quantities as Figs. 3 and 4, at $M = 3$.

C. Nonequilibrium entropy

In Eq. (92), the local entropy creation per molecule during the mean free time, i.e., the mean time between successive collisions of upstream molecules, is given in entropy units.

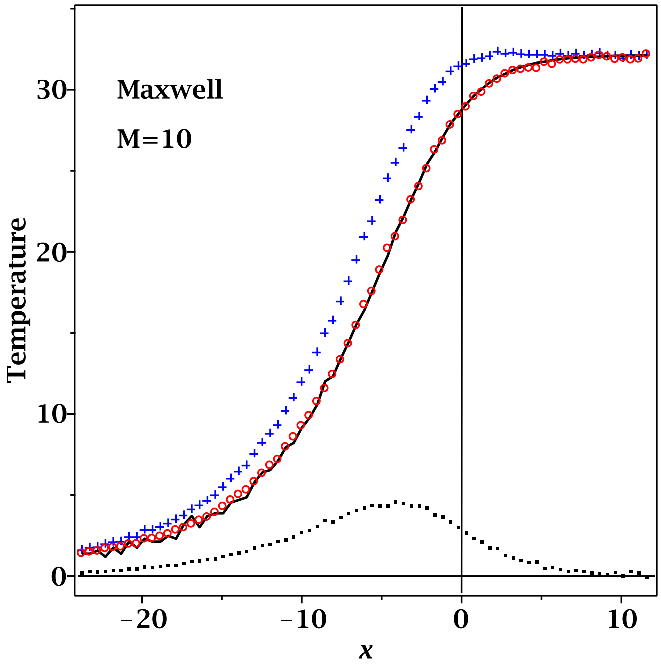

FIG. 4. Temperature and exopressure profiles vs $\widetilde{x}$, by the DSMC simulation for Maxwell molecules with $M = 10$. The $\widetilde{T}$ values are plotted by the solid line using the DSMC $\widetilde{u}$ and Eq. (79) and by circles using Eq. (115). The overshooting $\widetilde{T}_k$ values are represented by crosses, and the dotted curve shows the contribution of $(\widetilde{u}/p_0)\widetilde{\mathcal{P}}$ in Eq. (115).

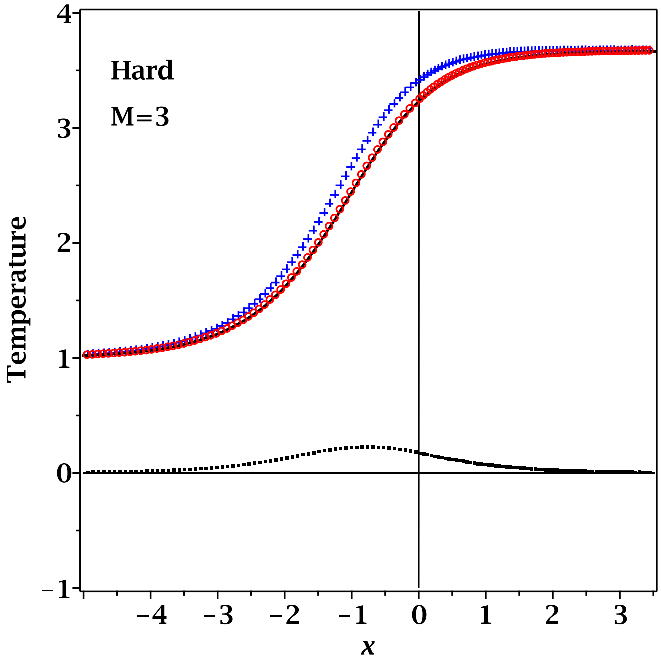

FIG. 5. Temperature and exopressure profiles vs $\widetilde{x}$, by the DSMC simulation for hard spheres with $M = 3$. The $\widetilde{T}$ values are plotted by the solid line using the DSMC $\widetilde{u}$ and Eq. (79) and by circles using Eq. (115). The $\widetilde{T}_k$ values are represented by crosses, and the dotted curve shows the contribution of $(\widetilde{u}/p_0)\widetilde{\mathcal{P}}$ in Eq. (115).

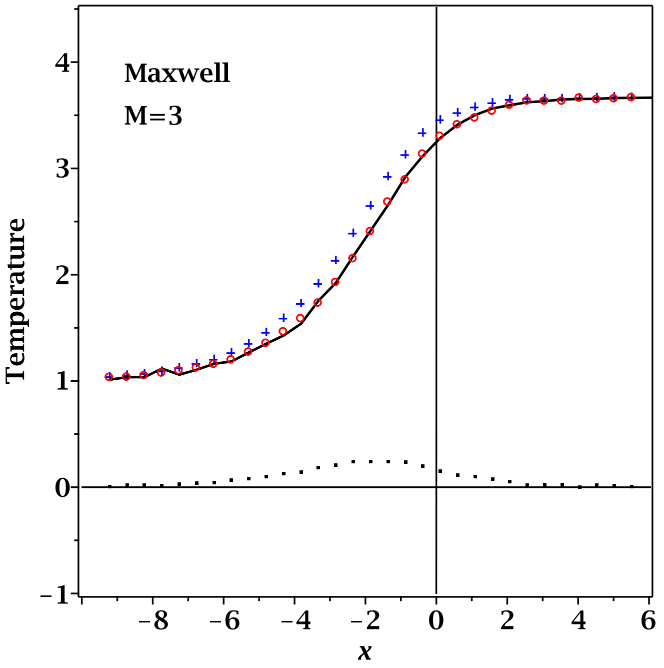

FIG. 6. Temperature and exopressure profiles vs $\tilde{x}$, by the DSMC simulation for Maxwell molecules with $M = 3$. The $\tilde{T}$ values are plotted by the solid line using the DSMC $\tilde{u}$ and Eq. (79) and by circles using Eq. (115). The $\tilde{T}_k$ values are represented by crosses, and the dotted curve shows the contribution of $(\tilde{u}/p_0)\tilde{\mathcal{P}}$ in Eq. (115).

It is straightforward to evaluate the distribution of entropy production along the streamline of the shock wave, using the value of $d\tilde{u}/d\tilde{x}$ obtainable by numerical differentiation of DSMC $\tilde{u}$ data. For local entropy, $S^{(s)}(x)$, there are two expressions, Eqs. (102) and (104), which should be equivalent in order for the theory to be self-consistent. Substituting the $\tilde{Q}$ obtained from Eq. (110a) into Eq. (102),

$$\frac{m}{k_B}\left(S^{(s)} - S_0^{(u)}\right) = \frac{4}{5p_0\tilde{T}}(\tilde{u}-1)(\tilde{u}-\tilde{u}^{(d)}) + \frac{\tilde{u}}{p_0\tilde{T}}\left(\frac{5}{2}\tilde{\mathcal{P}} + \tilde{\Pi}\right) + \ln(\tilde{u}\tilde{T}^{\frac{3}{2}}). \tag{116}$$

By using the $\tilde{\Pi}$ from Eq. (108b) and $\tilde{p}$ from Eq. (109b), it is obtained that

$$\frac{5}{2}\tilde{\mathcal{P}} + \tilde{\Pi} = \frac{3}{2}\tilde{\mathcal{P}} - \frac{4}{5\tilde{u}}(\tilde{u}-1)(\tilde{u}-\tilde{u}^{(d)}), \tag{117}$$

in which the values in Eqs. (76) and $\tilde{\rho}\tilde{u} = 1$ have been applied. Therefore, Eq. (116) becomes

$$\frac{m}{k_B}\left(S^{(s)} - S_0^{(u)}\right) = \ln\left(\tilde{u}\tilde{T}^{\frac{3}{2}}\right) + \frac{3}{2}\frac{\tilde{u}\tilde{\mathcal{P}}}{p_0\tilde{T}}, \tag{118}$$

which is equivalent to Eq. (104) for $\tilde{\mathcal{P}} = \frac{2}{3}\tilde{\rho}\tilde{\mathcal{E}}$ and $\tilde{\rho}\tilde{u} = 1$.

In the literature, there have been two different approaches to evaluating the entropy of 1D shock waves. One of them [28,31] is the efforts to apply the phenomenological entropy equation derived by De Groot and Mazur (DGM) [13]; the other [32] is an application of the Boltzmann H theorem, with the use of the approximate velocity distribution function, to shock waves. The results of the two are quite different. The former gives a maximum entropy behavior within the shock layer, while the latter does not.

The basic assumption of the DGM theory is that the Gibbs relation of equilibrium thermodynamics can be applied to nonequilibrium processes if the thermodynamic variables are regarded as local quantities, i.e., quantities which are functions of $(\mathbf{r}, t)$. It has been well known that the assumption holds in the state of near-equilibrium. In this theory, the temperature should be read as T_k as defined in Eq. (114), and $\mathcal{E} = 0$, because the theory is founded on the temperature defined in Eq. (1). By using the continuity equation, (27a), and the internal energy equation, (31), the Gibbs relation gives the entropy balance equation,

$$\rho\frac{DS}{Dt} = \frac{\rho}{T_k}\frac{DU}{Dt} - \frac{p}{T_k\rho}\frac{D\rho}{Dt} \tag{119a}$$

$$= -\frac{1}{T_k}\nabla_r Q_r - \frac{1}{T_k}\Pi_{rs}\nabla_s u_r, \tag{119b}$$

in which care should be taken not to confuse the subscript k in T_k with the tensor components r and s. By introducing the entropy flux vector, $\mathbf{Q}/T_k$, and the entropy production per unit volume, $\sigma^{(D)}$, it is written as

$$\rho\frac{DS^{(D)}}{Dt} = -\nabla_r\left(\frac{Q_r}{T_k}\right) + \sigma^{(D)}, \tag{120}$$

where the superscript (D) is used to emphasize the DGM theory, and

$$\sigma^{(D)} = -\frac{Q_r}{T_k^2}\nabla_r T_k - \frac{\Pi_{rs}}{T_k}\nabla_r u_s. \tag{121}$$

In the practical calculation of entropy, either Eq. (119a) or Eq. (119b) can be used, and they should give equivalent results, however, there is a lack of consistency because the DGM theory employs the dissipative energy equation rather than the isentropic equation in order to derive the entropy balance equation, whereas the Gibbs relation is the law of virtual local equilibrium.

The entropy balance equation in Eq. (120) takes the form at steady state

$$\rho u_x\frac{dS^{(D)}}{dx} = -\frac{d}{dx}\left(\frac{Q_x}{T_k}\right) + \sigma^{(D)}, \tag{122}$$

where

$$\sigma^{(D)} = -\frac{Q_x}{T_k^2}\frac{dT_k}{dx} - \frac{\Pi_{xx}}{T_k}\frac{du_x}{dx}. \tag{123}$$

In dimensionless form,

$$\frac{m}{k_B}\frac{\lambda^{(u)}\sigma^{(D)}}{\rho^{(u)}u^{(u)}} = -\frac{1}{p_0}\left(\frac{\tilde{Q}}{\tilde{T}_k^2}\frac{d\tilde{T}_k}{d\tilde{x}} + \frac{\tilde{\Pi}}{\tilde{T}_k}\frac{d\tilde{u}}{d\tilde{x}}\right), \tag{124}$$

and

$$\Sigma^{(D)} \equiv \frac{\tau\sigma^{(D)}}{k_B}\frac{m}{\rho^{(u)}} = -p_0^{-\frac{3}{2}}\left(\frac{\tilde{Q}}{\tilde{T}_k^2}\frac{d\tilde{T}_k}{d\tilde{x}} + \frac{\tilde{\Pi}}{\tilde{T}_k}\frac{d\tilde{u}}{d\tilde{x}}\right). \tag{125}$$

The local entropy is evaluated by the integration,

$$\int_{-\infty}^{x}\rho u_x\frac{dS^{(D)}}{dx}dx = -\frac{Q_x}{T_k} + \int_{-\infty}^{x}\sigma^{(D)}dx. \tag{126}$$

Rewriting it in dimensionless form,

$$\frac{m}{k_B}\left(S^{(D)} - S_0^{(u)}\right) = -\frac{\widetilde{Q}}{p_0\widetilde{T}_k} - \frac{1}{p_0}\int_{-\infty}^{\widetilde{x}}\left(\frac{\widetilde{Q}}{\widetilde{T}_k^2}\frac{d\widetilde{T}_k}{d\widetilde{x}} + \frac{\widetilde{\Pi}}{\widetilde{T}_k}\frac{d\widetilde{u}}{d\widetilde{x}}\right)d\widetilde{x}. \tag{127}$$

The local entropy can also be evaluated by using the Gibbs relation. Since the hydrostatic pressure takes the form $p = \rho k_B T_k/m$, and the internal energy, $U = \frac{3}{2}k_B T_k/m$, in the DGM theory, the Gibbs relation in Eq. (119a) is rewritten as

$$\frac{DS^{(D)}}{Dt} = \frac{k_B}{m}\left(\frac{3}{2}\frac{D}{Dt}\ln T_k - \frac{D}{Dt}\ln\rho\right). \tag{128}$$

For 1D stationary shock waves, it takes the form,

$$\frac{m}{k_B}\frac{dS^{(D)}}{dx} = \frac{3}{2}\frac{d}{dx}\ln T_k - \frac{d}{dx}\ln\rho. \tag{129}$$

Integration from $-\infty$ to a certain x gives

$$\frac{m}{k_B}\left(S^{(D)} - S_0^{(u)}\right) = \frac{3}{2}\ln\widetilde{T}_k - \ln\widetilde{\rho} \tag{130}$$

in dimensionless form. Equations (127) and (130) are not ensured to be consistent.

In order to compare the present theory and the DGM theory, the same DSMC data are used. For $d\widetilde{T}_k/d\widetilde{x}$ in Eqs. (125) and (127), numerical differentiation of DSMC $\widetilde{T}_k$ data has been carried out. For the local entropy of DGM, the integral in Eq. (127) has been calculated by numerical integration. Figure 7 shows the local entropy thus obtained and the results from Eqs. (118) and (130) for hard spheres at $M = 3$ and 10. Also, the entropy production values in Eqs. (92) and (125) are shown in Fig. 8.

The present work supports the results given by Morduchow and Libby [28] and Velasco and Uribe [31]. The maximum peak of local entropy is regarded as the incoming entropy flux due to the internal heat flow within the shock layer being maximum at the peak. The sole contribution of the entropy production to the local entropy should be a monotonic increase, like Margolin's results [32], because the integration in Eq. (98a) gives a monotonic increasing curve.

VII. DISCUSSION

A. Limiting properties

1. Shock wave structure

It is worthwhile to examine the shock wave structure near the upstream and downstream limits. Since $\widetilde{u}^{(u)} = 1$, substituting $\widetilde{u} = 1 + \widetilde{u}_1^{(u)}$ and $\widetilde{u} = \widetilde{u}^{(d)} + \widetilde{u}_1^{(d)}$ into Eq. (113) and keeping the first-order terms,

$$\frac{d\widetilde{u}_1^{(u)}}{d\widetilde{x}} = \frac{5p_0}{4}\frac{(3-5p_0)\widetilde{u}_1^{(u)}}{\widetilde{\kappa}^{(u)} + 5p_0\widetilde{\eta}^{(u)}}, \tag{131a}$$

$$\frac{d\widetilde{u}_1^{(d)}}{d\widetilde{x}} = -\frac{5p_0}{1+5p_0}\frac{(3-5p_0)\widetilde{u}_1^{(d)}}{\widetilde{\kappa}^{(d)} + 5p_0\widetilde{\eta}^{(d)}}. \tag{131b}$$

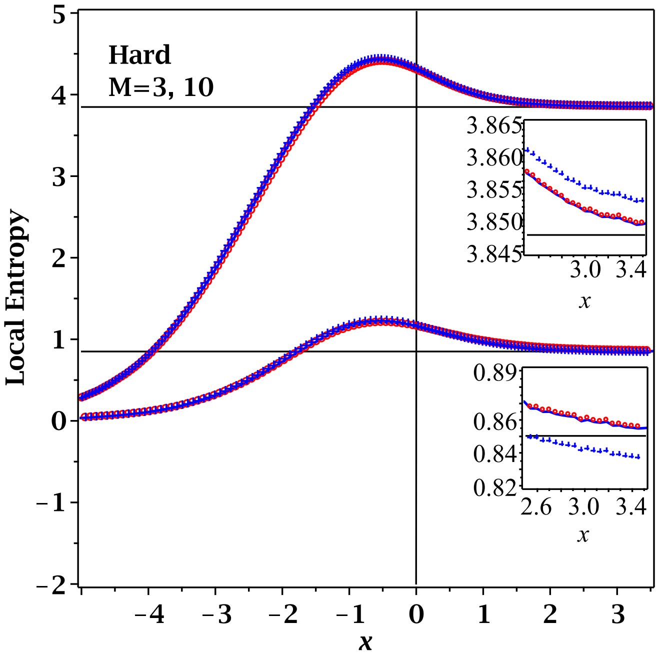

FIG. 7. Local entropy distribution along the streamline of a shock wave of hard spheres at $M = 3$ (lower curve and symbols) and $M = 10$ (upper curve and symbols). Solid lines represent the present work in Eq. (118), circles the local equilibrium values in Eq. (130), and crosses the values of numerical integration of Eq. (127). Insets: The lack of consistency in the local entropy of the De Groot and Mazur theory; horizontal lines represent the downstream equilibrium entropy at $M = 3$ and $M = 10$.

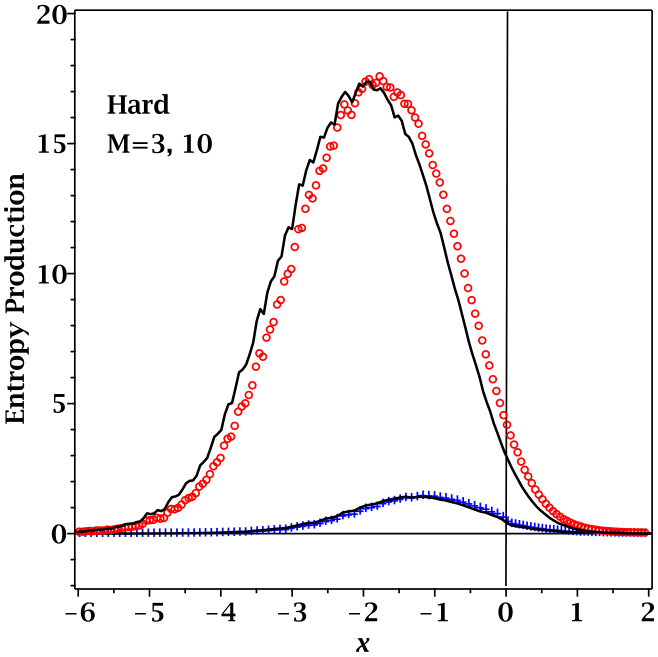

FIG. 8. Entropy generation per molecule during the mean free time of upstream molecules in entropy units for hard spheres at $M = 3$ (lower curve and crosses) and $M = 10$ (upper curve and circles). Solid lines represent results of the present work in Eq. (92), and symbols the De Groot and Mazur theory in Eq. (125).

The solutions are

$$\widetilde{u}_1^{(u)} = \widetilde{u}_1^{(u)}\big(\widetilde{x}_0^{(u)}\big)\exp\left[\frac{5p_0}{4}\frac{(3-5p_0)\big(\widetilde{x}-\widetilde{x}_0^{(u)}\big)}{\widetilde{\kappa}^{(u)}+5p_0\widetilde{\eta}^{(u)}}\right], \tag{132a}$$

$$\widetilde{u}_1^{(d)} = \widetilde{u}_1^{(d)}\big(\widetilde{x}_0^{(d)}\big)\exp\left[-\frac{5p_0}{1+5p_0}\frac{(3-5p_0)\big(\widetilde{x}-\widetilde{x}_0^{(d)}\big)}{\widetilde{\kappa}^{(d)}+5p_0\widetilde{\eta}^{(d)}}\right], \tag{132b}$$

where $\widetilde{x}_0^{(u)}$ and $\widetilde{x}_0^{(d)}$ are certain locations at the limits of the upstream equilibrium and the downstream equilibrium, respectively. The boundary conditions,

$$\lim_{\widetilde{x}\to-\infty}\widetilde{u}_1^{(u)} = 0, \quad \lim_{\widetilde{x}\to\infty}\widetilde{u}_1^{(d)} = 0, \tag{133}$$

impose $3-5p_0>0$. Since $p_0=\frac{3}{5}M^{-2}$, this gives the shock condition, $M>1$, that the upstream should be supersonic. The downstream subsonic condition can be derived from the upstream condition. Let us consider

$$\begin{aligned}\big(u^{(d)}\big)^2 - \frac{5k_BT^{(d)}}{3m} &= \big(u^{(u)}\widetilde{u}^{(d)}\big)^2 - \frac{5k_BT^{(u)}}{3m}\widetilde{T}^{(d)}\\ &= \big(u^{(u)}\big)^2\left[\big(\widetilde{u}^{(d)}\big)^2 - \frac{5}{3}p_0\widetilde{T}^{(d)}\right]\\ &= \frac{\big(u^{(u)}\big)^2}{12}(1+5p_0)(5p_0-3).\end{aligned} \tag{134}$$

Since $p_0<\frac{3}{5}$ for $M>1$, it should be that

$$u^{(d)} < \sqrt{\frac{5k_BT^{(d)}}{3m}}, \tag{135}$$

where $\sqrt{5k_BT^{(d)}/(3m)}$ is the sound speed of the downstream equilibrium gas.

2. *Entropy production*

The limiting values of entropy generation per molecule during the mean free time of the upstream, $\Sigma^{(u)}$, and the downstream, $\Sigma^{(d)}$, can be estimated by using Eq. (92). Using Eqs. (111) and (113),

$$\Sigma^{(s)} = \frac{20p_0^{\frac{1}{2}}(1+5p_0+\widetilde{u}^2)}{[\widetilde{u}(1+5p_0-\widetilde{u}^2)]^2}\frac{(\widetilde{u}-1)^2(\widetilde{u}-\widetilde{u}^{(d)})^2}{\widetilde{\kappa}+5p_0\widetilde{\eta}}. \tag{136}$$

Therefore, the limiting values take the forms

$$\Sigma^{(u)} = \frac{4}{5}p_0^{-\frac{3}{2}}(2+5p_0)\frac{\big(1-\widetilde{u}^{(d)}\big)^2\big(\widetilde{u}_1^{(u)}\big)^2}{\widetilde{\kappa}^{(u)}+5p_0\widetilde{\eta}^{(u)}}, \tag{137}$$

$$\Sigma^{(d)} = \frac{20p_0^{\frac{1}{2}}\big[1+5p_0+\big(\widetilde{u}^{(d)}\big)^2\big]}{\big(\widetilde{u}^{(d)}\big)^2\big[1+5p_0-\big(\widetilde{u}^{(d)}\big)^2\big]^2}\frac{\big(\widetilde{u}^{(d)}-1\big)^2\big(\widetilde{u}_1^{(d)}\big)^2}{\widetilde{\kappa}^{(d)}+5p_0\widetilde{\eta}^{(d)}}. \tag{138}$$

Substituting,

$$1-\widetilde{u}^{(d)} = \frac{1}{4}(3-5p_0), \tag{139a}$$

$$1+5p_0+\big(\widetilde{u}^{(d)}\big)^2 = \frac{1}{16}(1+5p_0)(17+5p_0), \tag{139b}$$

$$1+5p_0-\big(\widetilde{u}^{(d)}\big)^2 = \frac{5}{16}(1+5p_0)(3-p_0), \tag{139c}$$

it is obtained that

$$\Sigma^{(u)} = \frac{p_0^{-\frac{3}{2}}(2+5p_0)(3-5p_0)^2\big(\widetilde{u}_1^{(u)}\big)^2}{20\big(\widetilde{\kappa}^{(u)}+5p_0\widetilde{\eta}^{(u)}\big)}, \tag{140a}$$

$$\Sigma^{(d)} = \frac{64p_0^{\frac{1}{2}}(17+5p_0)(3-5p_0)^2\big(\widetilde{u}_1^{(d)}\big)^2}{5(1+5p_0)^3(3-p_0)^2\big(\widetilde{\kappa}^{(d)}+5p_0\widetilde{\eta}^{(d)}\big)}. \tag{140b}$$

Considering $p_0=\frac{3}{5}M^{-2}$, it is evident that the limiting values of the entropy production approach zeros for weak shock, $M\to1$, at the rate

$$(3-5p_0)^2 = 9\left(1-\frac{1}{M^2}\right)^2 \sim (M^2-1)^2. \tag{141}$$

For the behavior for strong shock, it is necessary to rewrite the $\widetilde{\eta}$ and $\widetilde{\kappa}$, because they comprise $u^{(u)}$. Using Eqs. (147), it is obtained that

$$\widetilde{\kappa}+5p_0\widetilde{\eta} = \frac{5}{8}\sqrt{\frac{\pi}{2}}p_0^{\frac{3}{2}}\left(\frac{m}{k_B}\frac{\kappa}{\eta^{(u)}}+5\frac{\eta}{\eta^{(u)}}\right). \tag{142}$$

Therefore,

$$\Sigma^{(u)} = \frac{2}{25p_0^3}\sqrt{\frac{2}{\pi}}(2+5p_0)(3-5p_0)^2K^{(u)}\big(\widetilde{u}_1^{(u)}\big)^2, \tag{143a}$$

$$\Sigma^{(d)} = \frac{512}{25p_0}\sqrt{\frac{2}{\pi}}\frac{(17+5p_0)(3-5p_0)^2}{(1+5p_0)^3(3-p_0)^2}K^{(d)}\big(\widetilde{u}_1^{(d)}\big)^2, \tag{143b}$$

where

$$K^{(i)} = \left(\frac{m}{k_B}\frac{\kappa^{(i)}}{\eta^{(u)}}+5\frac{\eta^{(i)}}{\eta^{(u)}}\right)^{-1}, \tag{144}$$

in which the superscript (i)'s mean that $i=u$ for upstream and $i=\ d$ for downstream. The entropy generations during the mean free time become infinity at the boundary limits when $M\to\infty$ at the rates

$$\Sigma^{(u)} \sim p_0^{-3} \sim M^6, \tag{145a}$$

$$\Sigma^{(d)} \sim p_0^{-1} \sim M^2. \tag{145b}$$

It is interesting to note that the entropy production goes to infinity on the upstream side more quickly than on the downstream side. Since the entropy production is related to the heat generation converting the kinetic energy of molecules into thermal energy, the limiting properties in Eqs. (145) imply that the heat is produced mainly on the upstream side of the shock layer (Fig. 8), then the generated heat causes an increase in the downstream temperature. At steady state, the heat flows from the higher temperature downstream to the lower temperature upstream according to the thermodynamic law, giving rise to the maximum peak of local entropy due to the increased entropy flux. Because the higher temperature gives less entropy flux according to Eq. (69), the local entropy is lessened on the downstream side, giving the maximum peak on the upstream side (Fig. 7). It is worthwhile to consider that the downstream temperature given in Eq. (76) goes to infinity when $M\to\infty$, while the upstream temperature is finite.

B. Becker theory (BT)

The bulk viscosity ζ is related to the shear viscosity and the heat conductivity; rewriting Eq. (60),

$$\zeta = \frac{2}{5}\eta^{(u)}\left(\frac{1}{\mathrm{Pr}}\frac{\kappa}{\kappa^{(u)}} - \frac{4}{3}\frac{\eta}{\eta^{(u)}}\right), \tag{146}$$

where Pr is the Prandtl number of the upstream equilibrium gas. Since $u^{(u)}$ takes the form of Eq. (89) and $\lambda^{(u)}$ is defined in Eq. (107), it is immediate to write

$$\widetilde{\kappa} = \frac{mp_0}{k_B}\frac{\kappa}{\lambda^{(u)}\rho^{(u)}u^{(u)}} = \frac{5}{8}\sqrt{\frac{\pi}{2}}p_0^{\frac{3}{2}}\frac{m\kappa}{k_B\eta^{(u)}}, \tag{147a}$$

$$\widetilde{\eta} = \frac{\eta}{\lambda^{(u)}\rho^{(u)}u^{(u)}} = \frac{5}{8}\sqrt{\frac{\pi}{2}}p_0^{\frac{1}{2}}\frac{\eta}{\eta^{(u)}}, \tag{147b}$$

which give

$$\frac{\kappa}{\kappa^{(u)}} = \frac{16}{25}\mathrm{Pr}\sqrt{\frac{2}{\pi}}p_0^{-\frac{3}{2}}\widetilde{\kappa}, \tag{148a}$$

$$\frac{\eta}{\eta^{(u)}} = \frac{8}{5}\sqrt{\frac{2}{\pi}}p_0^{-\frac{1}{2}}\widetilde{\eta}. \tag{148b}$$

Therefore,

$$\frac{\zeta}{\eta^{(u)}} = \frac{32}{25}\sqrt{\frac{2}{\pi p_0}}\left(\frac{\widetilde{\kappa}}{5p_0} - \frac{2\widetilde{\eta}}{3}\right). \tag{149}$$

It is apparent that $\zeta = 0$ when $\frac{1}{5}\widetilde{\kappa}/p_0 = \frac{2}{3}\widetilde{\eta}$, regardless of the Pr value. Since

$$\widetilde{\kappa} = -\widetilde{Q}\left(\frac{d\widetilde{T}}{d\widetilde{x}}\right)^{-1} = \frac{5p_0}{2\widetilde{u}}\widetilde{Q}\left(\frac{d\widetilde{u}}{d\widetilde{x}}\right)^{-1}, \tag{150a}$$

$$\widetilde{\eta} = -\frac{3}{4}\widetilde{\Pi}\left(\frac{d\widetilde{u}}{d\widetilde{x}}\right)^{-1}, \tag{150b}$$

it becomes

$$\frac{\widetilde{\kappa}}{5p_0} - \frac{2\widetilde{\eta}}{3} = \frac{1}{2}\left[\frac{1}{\widetilde{u}}\widetilde{Q} + \widetilde{\Pi}\right]\left(\frac{d\widetilde{u}}{d\widetilde{x}}\right)^{-1}. \tag{151}$$

The bulk viscosity should be 0 for any Pr values when

$$\widetilde{Q} + \widetilde{u}\widetilde{\Pi} = 0, \tag{152}$$

which is the case for $\widetilde{\mathcal{P}} = 0$ in Eq. (110a), the case for the physical local equilibrium, and also the case for the Becker theory [23]. The condition in Eq. (152) is more inclusive than the original Becker's condition, $\mathrm{Pr} = \frac{3}{4}$.

The BT is essentially a local equilibrium theory based on the Gibbs relation in Eq. (119a). The governing equations for the virtual local equilibrium should be the continuity, the Euler, and the isentropic equations. However, the BT takes the viscous momentum balance equation rather than the Euler equation for the equation of motion. This is regarded as a physical approximation of the BT. The condition in Eq. (152) derives the entropy equation, as well as the relation between the temperature and the flow velocity. Conversely, it is possible to derive the condition from the entropy equation.

The entropy equation at steady state takes the form

$$\rho\frac{D^{(s)}S}{Dt} = \frac{k_B}{m}\rho u_x\frac{d}{dx}\ln\frac{T_k^{\frac{3}{2}}}{\rho}, \tag{153}$$

in which T_k is used rather than T, because the BT disregards the exoenergy. The momentum balance equation in Eq. (51b) is rewritten as

$$\frac{d\Pi_{xx}}{dx} + \frac{k_B}{m}\frac{d}{dx}(\rho T_k) + \frac{d}{dx}(\rho u_x^2) = 0. \tag{154}$$

The Gibbs relation gives the entropy equation in the form

$$\rho\frac{D^{(s)}S}{Dt} = -\frac{1}{T_k}\frac{dQ_x}{dx} - \frac{1}{T_k}\Pi_{xx}\frac{du_x}{dx}. \tag{155}$$

Considering Eqs. (153) and (155),

$$\frac{3}{2}\frac{k_B}{m}\frac{\rho u_x}{T_k}\frac{dT_k}{dx} + \frac{1}{T_k}\frac{dQ_x}{dx} - \frac{k_B}{m}u_x\frac{d\rho}{dx} + \frac{1}{T_k}\Pi_{xx}\frac{du_x}{dx} = 0. \tag{156}$$

Since

$$\Pi_{xx}\frac{du_x}{dx} = \frac{d}{dx}(u_x\Pi_{xx}) - u_x\frac{d\Pi_{xx}}{dx}, \tag{157}$$

applying Eq. (154) to (156) and using $d(\rho u_x)/dx = 0$, the continuity equation, it is obtained that

$$\frac{1}{T_k}\frac{d}{dx}(Q_x + u_x\Pi_{xx}) + \frac{1}{2}\rho\frac{d}{dx}\left(5\frac{k_BT_k}{m} + u_x^2\right) = 0. \tag{158}$$

Let us consider the energy equation, (31), for this problem:

$$\frac{3}{2}\frac{k_B}{m}\rho u_x\frac{dT_k}{dx} = -\frac{dQ_x}{dx} - \mathsf{P}_{xx}\frac{du_x}{dx}. \tag{159}$$

Since $\mathsf{P}_{xx} = \Pi_{xx} + \rho k_B T_k/m$, applying Eqs. (154) to (159) in the same way, it is obtained that

$$\frac{d}{dx}(Q_x + u_x\Pi_{xx}) + \frac{1}{2}\rho u_x\frac{d}{dx}\left(5\frac{k_BT_k}{m} + u_x^2\right) = 0. \tag{160}$$

In order for Eqs. (158) and (160) to hold simultaneously, it should be that

$$\frac{d}{dx}(Q_x + u_x\Pi_{xx}) = 0 \tag{161a}$$

and

$$\frac{d}{dx}\left(5\frac{k_BT_k}{m} + u_x^2\right) = 0. \tag{161b}$$

The equilibrium boundary condition gives

$$Q_x + u_x\Pi_{xx} = 0, \tag{162a}$$

$$5\frac{k_BT_k}{m} + u_x^2 = 5\frac{k_BT^{(u)}}{m} + (u^{(u)})^2. \tag{162b}$$

The entropy equation of the BT gives a consistent local entropy with the value of the Gibbs relation, in contrast to the DGM theory. However, the inconsistency comes from the entropy production. The nonzero heat flux and stress tensor in the BT give rise to a finite entropy production. According to Eq. (119b), the entropy equation of the BT is written as

$$\rho\frac{DS}{Dt} = -\frac{1}{T_k}\frac{dQ_x}{dx} - \frac{1}{T_k}\Pi_{xx}\frac{du_x}{dx}$$
$$= \frac{d}{dx}\left(\frac{u_x}{T_k}\Pi_{xx}\right) + \frac{1}{T_k}\Pi_{xx}\left(\frac{u_x}{T_k}\frac{dT_k}{dx} - \frac{du_x}{dx}\right), \quad (163)$$

which gives the entropy production,

$$\sigma^{(B)} = \frac{1}{T_k}\Pi_{xx}\left(\frac{u_x}{T_k}\frac{dT_k}{dx} - \frac{du_x}{dx}\right)$$
$$= -\frac{1}{T_k}\left(\frac{2}{5}\frac{mu_x^2}{k_BT_k} + 1\right)\Pi_{xx}\frac{du_x}{dx}, \quad (164)$$

in which the superscript (B) indicates the BT. It is noted that Eq. (164) is in exactly the same form as Eq. (84) in the present work, except that T and $\mathbb{P}_{xx}$ are replaced by T_k and Π_{xx} for $\mathcal{P} = 0$. Because the relation between T_k and u_x in Eq. (162b) is also in the same form as Eq. (78) in the present work, with T replaced by T_k, the BT may be regarded as an approximation of the present work putting $\mathcal{P} = 0$, or the present work may be regarded as a generalization of the BT for $\mathcal{P} \neq 0$. In any case, it should be emphasized that the present theory was motivated to resolve the temperature anomaly of 1D shock waves and to try to do this by introducing $\mathcal{P} \neq 0$. In the present formulation, the state $\mathcal{P} = 0$ is a physical local equilibrium, the equations for which have not yet branched.

VIII. CONCLUDING REMARKS

Let us consider an equation,

$$A + B = 0, \quad (\mathrm{I})$$

and its solution or solutions, termed SOL-I. Let us also consider a set of equations,

$$A + Y = 0, \quad B - Y = 0, \quad (\mathrm{II})$$

and their solution(s), SOL-II. It is evident that SOL-II are sufficiently solutions of Eq. (I), however, SOL-I do not necessarily satisfy Eq. (II), which means that SOL-II is a subset of SOL-I. Of the SOL-I, there can be other solutions than the SOL-II.

The motivation for the present work is to resolve the abnormal overshooting temperature profile of 1D normal shock waves. Since the overshoot gives a negative heat conductivity by the sign change of the temperature gradient, there should be a proper explanation of it.

In the present work, a new physical quantity, the exoenergy (or the exopressure), has been introduced, and the nonequilibrium temperature redefined. Because the exoenergy is defined as a part of the internal energy, it has been attempted to split the energy equation into two parts. One of them is taken as the equation for the exoenergy, and the other part as the equation for the redefined temperature. The solutions of the equations thus obtained should be regarded as a subset of the solutions of the original energy equation. In order to rationalize the equation splitting, the nonequilibrium thermodynamics has been reconsidered and applied to 1D normal shock waves. The derived equations are self-consistent and well analyze the DSMC data on shock waves. The important results are the finite bulk viscosity of monatomic dilute gases and its relation to the shear viscosity and heat conductivity, together with the general form of the shock wave equation.

APPENDIX A: PHYSICAL LOCAL EQUILIBRIUM

The characteristic function of the velocity distribution function is defined by

$$\Psi(\xi, \mathbf{r}, t) = \frac{1}{n}\int e^{-i\xi\cdot(\mathbf{v}-\mathbf{u})} f(\mathbf{v}, \mathbf{r}, t)d\mathbf{v}. \quad (\mathrm{A1})$$

For the Maxwell-Boltzmann distribution function,

$$\Psi_0 = \exp\left(-\frac{\theta}{2}\xi^2\right), \quad (\mathrm{A2})$$

where $\theta = k_BT/m$. The Boltzmann equation for Ψ_0 is

$$\frac{D\Psi_0}{Dt} + \frac{1}{n}\left(\frac{Dn}{Dt} + n\nabla_r u_r\right)\Psi_0 + i\nabla_r\frac{\partial\Psi_0}{\partial\xi_r} - i\frac{Du_r}{Dt}\xi_r\Psi_0$$
$$+ i\frac{1}{n}(\nabla_r n)\frac{\partial\Psi_0}{\partial\xi_r} + (\nabla_s u_r)\xi_r\frac{\partial\Psi_0}{\partial\xi_s} = 0. \quad (\mathrm{A3})$$

Using

$$\frac{D\Psi_0}{Dt} = -\frac{1}{2}\xi^2\Psi_0\frac{D\theta}{Dt}, \quad (\mathrm{A4a})$$
$$\frac{\partial\Psi_0}{\partial\xi_r} = -\xi_r\Psi_0\theta, \quad (\mathrm{A4b})$$

it is obtained that

$$\frac{1}{n}\left(\frac{Dn}{Dt} + n\nabla_r u_r\right)\Psi_0 - \frac{i}{n}\left[n\frac{Du_r}{Dt} + \nabla_r(\theta n)\right]\xi_r\Psi_0$$
$$-\left(\frac{1}{2}\frac{D\theta}{Dt} + \frac{1}{3}\theta\nabla_r u_r\right)\xi^2\Psi_0 - \left(\xi_s\xi_r - \frac{1}{3}\delta_{sr}\xi^2\right)\Psi_0\theta\nabla_s u_r$$
$$+\frac{i}{2}\xi^2\xi_r\Psi_0\theta\nabla_r\theta = 0. \quad (\mathrm{A5})$$

Since Eq. (A5) should be true for any ξ_i,

$$\frac{Dn}{Dt} + n\nabla_r u_r = 0, \quad (\mathrm{A6a})$$
$$n\frac{Du_i}{Dt} + \nabla_i(\theta n) = 0, \quad (\mathrm{A6b})$$
$$\frac{3}{2}\frac{D\theta}{Dt} + \theta\nabla_r u_r = 0, \quad (\mathrm{A6c})$$

and

$$\frac{1}{2}(\nabla_i u_j + \nabla_j u_i) - \frac{1}{3}\delta_{ij}\nabla_r u_r = 0, \quad (\mathrm{A6d})$$
$$\nabla_i\theta = 0, \quad (\mathrm{A6e})$$

in which the property

$$\left(\xi_i\xi_j - \frac{1}{3}\delta_{ij}\xi^2\right)\nabla_i u_j = \xi_i\xi_j\left(\nabla_i u_j - \frac{1}{3}\delta_{ij}\nabla_r u_r\right)$$
$$= \xi_i\xi_j\left[\frac{1}{2}(\nabla_i u_j + \nabla_j u_i) - \frac{1}{3}\delta_{ij}\nabla_r u_r\right] \quad (\mathrm{A7})$$

has been used.

Equations (A6) describe the behavior of the physical local equilibrium, which furcate into branches at the onset of nonequilibrium caused by external forces.

APPENDIX B: DSMC RUN

DSMC1S.FOR can be downloaded from Professor Bird's site http://www.gab.com.au/legacy.html. Before compiling the program, two bugs should be corrected as reported at the site:

(1) On line 965 the statement `"SUU=0."` should be added.

(2) The variables `NCU` and `NCD` should be added to those in the restart file.

Also, the `PARAMETER` value `MNM=20000` must be increased to `MNM=100000` for accuracy and speed.

To reproduce Fig. 1, the following lines should be inserted at the proper location in the `SUBROUTINE OUT1S` and used to calculate Eq. (110b).

(1) `txx=(denn*(suu-sm*uu-1/3*(smcc-sm*uu))/sn)/udn/fvel/fvel` for $\widetilde{\Pi}$.

(2) `hx=(denn*(0.5*(sccu-vel(1)*smcc)-suu*vel(1)+sm*uu*vel(1))/sn)/udn/fvel**3` for $\widetilde{Q}$.

(3) `Xval=-4.*(vel(1)-fvel)*(vel(1)-dvel)/fvel/fvel` for X.

The default data are for argon at $M = 1.4$. The time step value `DTM` and the boundary locations `SXB` and `DXB` should be adjusted properly to different Mach numbers. The coordinate origin is defined at the location of half-density,

$$\rho(0) = \tfrac{1}{2}(\rho^{(u)} + \rho^{(d)}).$$

The molecular parameters are `SP(4,1)=0.5` and `SP(5,1)=0` for hard spheres.

In order to use the Nanbu data, the following must be considered.

(1) The location of origin is defined at the half-velocity of upstream and downstream, but the Bird data at the half-density,

$$u_x(0) = \tfrac{1}{2}(u^{(u)} + u^{(d)}),$$

and the mean free path is defined by a different formula, $\lambda^{(u)} = 1.0186\lambda^{(u)}_{\mathrm{NANBU}}$. The location of origin and the length scale have been adjusted to fit Bird's definition for drawing the figures.

(2) The stress tensor and heat flux are in dimensionless values but defined differently, $\widetilde{\Pi} = -2p_0\widetilde{\Pi}_{\mathrm{NANBU}}$ and $\widetilde{Q} = (2p_0)^{\frac{3}{2}}\widetilde{Q}_{\mathrm{NANBU}}$.

[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, London, 1970).

[2] S. G. Brush, *Kinetic Theory* (Pergamon Press, New York, 1972).

[3] G. A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows* (Clarendon Press, New York, 1994).

[4] J. G. Kirkwood, The statistical mechanical theory of transport processes, J. Chem. Phys. **14**, 180 (1946).

[5] L. E. Reichl, *A Modern Course in Statistical Physics*, 2nd ed. (Wiley, New York, 1998).

[6] M. N. Kogan, *Rarefied Gas Dynamics* (Plenum Press, New York, 1969).

[7] S. M. Yen and W. Ng, Shock-wave structure and intermolecular collision laws, J. Fluid Mech. **65**, 127 (1974).

[8] O. Kum, Wm. G. Hoover, and C. G. Hoover, Temperature maxima in stable two-dimensional shock waves, Phys. Rev. E **56**, 462 (1997).

[9] Y. G. Ohr, Improvement of the grad 13 moment method for strong shock waves, Phys. Fluids **13**, 2105 (2001).

[10] S. Taniguchi, T. Arima, T. Ruggeri, and M. Sugiyama, Overshoot of the non-equilibrium temperature in the shock wave structure of a rarefied polyatomic gas subject to the dynamic pressure, Int. J. Non-Lin. Mech. **72**, 66 (2016).

[11] Y. G. Ohr, Study on the non-equilibrium temperature behavior of normal shock waves and the bulk viscosity, Phys. Fluids **32**, 061707 (2020).

[12] C. S. Wang Chang, G. E. Uhlenbeck, and J. De Boer, The heat conductivity and viscosity of polyatomic gases, in *Studies in Statistical Mechanics*, Vol. II, edited by J. De Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1964), pp. 243–268.

[13] S. R. De Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1969).

[14] R. S. Chatwell and J. Vrabec, Bulk viscosity of liquid noble gases, J. Chem. Phys. **152**, 094503 (2020).

[15] J. Casas-Vázquez and D. Jou, Nonequilibrium temperature versus local-equilibrium temperature, Phys. Rev. E **49**, 1040 (1994).

[16] J. D. Anderson Jr., *Fundamentals of Aerodynamics*, 5th ed. (McGraw–Hill, New York, 2010).

[17] B. C. Eu, *Kinetic Theory of Nonequilibrium Ensemble, Irreversible Thermodynamics, and Generalized Hydrodynamics* (Springer, Cham, Switzerland, 2016).

[18] R. Marsland III, H. R. Brown, and G. Valente, Time and irreversibility in axiomatic thermodynamics, Am. J. Phys. **83**, 628 (2015).

[19] M. Campisi and P. Hänggi, Fluctuation, dissipation and the arrow of time, Entropy **13**, 2024 (2011).

[20] H. R. Brown and J. Uffink, The origin of time-asymmetry in thermodynamics: The minus first law, Stud. Hist. Philos. Mod. Phys. **32**, 525 (2001).

[21] H. B. Callen, Thermodynamics as a science of symmetry, Found. Phys. **4**, 423 (1974).

[22] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 3rd ed. (John Wiley and Sons, New York, 1985).

[23] R. Becker, Stoßwelle und Detonation, Z. Phys. **VIII**, 321 (1922). Translation: *Technical Memorandums, National Advisory Committee for Aeronautics. NACA-TM-505* (part 1), *NACA-TM-506* (part 2) (NACA, Washington, DC, 1929).

[24] F. J. Uribe and R. M. Velasco, Exact solutions for shock waves in dilute gases, Phys. Rev. E **100**, 023118 (2019).

[25] R. S. Myong, Analytical solutions of shock structure thickness and asymmetry in Navier-Stokes/Fourier framework, AIAA J. **52**, 1075 (2014).

[26] B. M. Johnson, Closed-form of shock solutions, J. Fluid Mech. **745**, R1 (2014).

[27] L. H. Thomas, Note on Becker's theory of the shock front, J. Chem. Phys. **12**, 449 (1949).

[28] M. Morduchow and P. A. Libby, On a complete solution of the one-dimensional equations of a viscous, heat-conducting, compressible gas, J. Aeronaut. Sci. **16**, 674 (1949).

[29] C. S. Wang Chang and G. E. Uhlenbeck, On the theory of the thickness of weak shock waves, in *Studies in Statistical Mechanics*, Vol. V, edited by J. De Boer and G. E. Uhlenbeck (North-Holland, Amsterdam, 1970), Chap. III.

[30] K. Nanbu and Y. Watanabe, *Report of the Institute of High Speed Mechanics*, Report Volume 48 (Institute of High Speed Mechanics, Tohoku University, Sendai, Japan, 1984).

[31] R. M. Velasco and F. J. Uribe, Shock-wave structure according to a linear irreversible thermodynamic model, Phys. Rev. E **99**, 023114 (2019).

[32] L. G. Margolin, Nonequilibrium entropy in a shock, Entropy **19**, 368 (2017).