Rational extended thermodynamics of a rarefied polyatomic gas with molecular relaxation processes

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We present a more refined version of rational extended thermodynamics of rarefied polyatomic gases in which molecular rotational and vibrational relaxation processes are treated individually. In this case, we need a triple hierarchy of the moment system and the system of balance equations is closed via the maximum entropy principle. Three different types of the production terms in the system, which are suggested by a generalized BGK-type collision term in the Boltzmann equation, are adopted. In particular, the rational extended thermodynamic theory with seven independent fields (ET_7) is analyzed in detail. Finally, the dispersion relation of ultrasonic wave derived from the ET_7 theory is confirmed by the experimental data for CO_2, Cl_2, and Br_2 gases.

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I. INTRODUCTION

Nonequilibrium phenomena observed in polyatomic gases, where energy exchanges among the translational, rotational, and vibrational modes of a molecule play a key role [1], have attracted longstanding interest in various fields, such as physics, chemistry, and engineering. To describe such phenomena, the thermodynamic theory of relaxation processes of internal variables [2–4], which can be set within the framework of thermodynamics of irreversible processes (TIP) [5], has been adopted. Absorption and dispersion of ultrasonic waves [6,7] and shock waves [8], in particular, have been studied by using the theory.

TIP relies essentially on the assumption of local equilibrium [5]. A theory of viscous heat-conducting fluids based on TIP is the well-known Navier-Stokes Fourier theory of the Newtonian fluids. Nowadays, however, there exist increasing demands for deeper understanding of strong nonequilibrium phenomena in polyatomic gases, that is, the phenomena out of local equilibrium in nanotechnology, space science, molecular biology, and so on [9–15].

Rational extended thermodynamics (hereafter referred to as ET for simplicity instead of RET) [9–11] has been developed as a thermodynamic theory being applicable to nonequilibrium phenomena with steep gradients and rapid changes in space-time, which are out of local equilibrium. ET of rarefied monatomic gases is summarized in Refs. [9,10], while ET of rarefied polyatomic gases with one relaxation process is presented in Ref. [11]. In ET, two different closure methods of a system of field equations have been proposed and extensively applied to various problems:

(1) Phenomenological ET. The closure is obtained by using the universal principles of continuum thermomechanics—objectivity, entropy, and causality principles—to select admissible constitutive equations (see Refs. [9,10,16] for monatomic gases and Refs. [11,17] for polyatomic ones);

(2) Molecular ET. The fields are moments of a distribution function and the closure is obtained by using the maximum entropy principle (MEP) [9,18]. In molecular ET, it was proved that the closure by the MEP is equivalent to imposition of the entropy principle on the truncated moment equations both for monatomic gases [19] and for polyatomic gases [20].

It was verified that the two closure methods are equivalent to each other and also equivalent to the Grad kinetic closure based on the perturbation around the Maxwellian via Hermite polynomials [21] (see Refs. [9,10,18] for monatomic gases with 13 fields and Refs. [11,22,23] for polyatomic gases with 14 fields).

For later reference, we briefly explain ET of rarefied polyatomic gases with one relaxation process [11]. In polyatomic gases, the molecular internal degrees of freedom, which are not present in monatomic gases, come into play [24]. In particular, the internal specific energy is no longer related to the pressure in a simple way.

After the ET theory of monatomic gases with 13 fields has been established [16], Kremer [25] tried to construct the ET theory with 14 fields using a single hierarchy of balance laws to incorporate the dynamic (nonequilibrium) pressure into the theory. The same author also presented an ET theory with 17 fields [26,27] to take into account the effect of molecular internal motion although the dynamic pressure was introduced indirectly. About two decades later, Arima, Taniguchi, Ruggeri, and Sugiyama [17] have realized the necessity of the binary hierarchy of balance laws for the 14 independent fields: mass density, velocity, specific internal energy, shear stress, dynamic pressure, and heat flux. This theory is called ET_{14}. The Navier-Stokes Fourier theory is included in ET_{14} as a limiting case, and the ET theory of monatomic gases with 13 fields can be derived from ET_{14} as a singular limit [28].

Concerning the kinetic counterpart of ET_{14}, a crucial step toward the development of the theory of rarefied polyatomic gases was made by an idea of Borgnakke and Larsen [29]. The distribution function is assumed to depend on an additional continuous variable representing the energy of the internal degrees of a molecule to take into account the exchange of energy (other than translational one) in binary collisions. This model was initially used for Monte Carlo simulations of polyatomic gases, and later it was applied to the derivation of

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the generalized Boltzmann equation by Bourgat, Desvillettes, Le Tallec, and Perthame [30] and was applied also to chemically reacting mixtures [31].

In this model, a nonnegative energy of the internal degrees of a molecule, I, is introduced. The velocity distribution function depends on this additional parameter, i.e., $f \equiv f(\mathbf{x},\mathbf{c},t,I)$, where $f(\mathbf{x},\mathbf{c},t,I)\,d\mathbf{x}\,d\mathbf{c}$ is the number density of molecules with the energy I at time t and in the volume element $d\mathbf{x}\,d\mathbf{c}$ of the phase space (6D position-velocity space) centered at $(\mathbf{x},\mathbf{c}) \in \mathbb{R}^3 \times \mathbb{R}^3$. The Boltzmann equation is formally the same as the one of monatomic gases:

$$\partial_t f + c_i\,\partial_i f = Q(f), \tag{1}$$

but, for the collision term $Q(f)$, we take into account the influence of internal degrees of freedom through the collision cross-section [29,30]. Here, $\partial_t \equiv \partial/\partial t$ and $\partial_i \equiv \partial/\partial x_i$. Then, from the Boltzmann Eq. (1), we have a binary hierarchy of the field equations [11,20,22]:

$$\begin{aligned}
&\partial_t F + \partial_i F_i = 0,\\
&\partial_t F_{i_1} + \partial_i F_{ii_1} = 0,\\
&\partial_t F_{i_1 i_2} + \partial_i F_{ii_1 i_2} = P_{i_1 i_2}, \qquad \partial_t G_{ll} + \partial_t G_{lli} = 0,\\
&\partial_t F_{i_1 i_2 i_3} + \partial_i F_{ii_1 i_2 i_3} = P_{i_1 i_2 i_3}, \quad \partial_t G_{lli_1} + \partial_t G_{llii_1} = Q_{lli_1},\\
&\quad\vdots \qquad\qquad\qquad\qquad \vdots,
\end{aligned} \tag{2}$$

involving the *momentum-like* moments F and the *energy-like* moments G:

$$\begin{aligned}
F &= \int_{\mathbb{R}^3}\int_0^\infty m f \phi(I)\,dI d\mathbf{c},\\
F_{i_1\ldots i_j} &= \int_{\mathbb{R}^3}\int_0^\infty m c_{i_1}\cdots c_{i_j} f \phi(I)\,dI d\mathbf{c},\\
G_{ll} &= \int_{\mathbb{R}^3}\int_0^\infty m\left(c^2 + \frac{2I}{m}\right) f \phi(I)\,dI d\mathbf{c},\\
G_{lli_1\ldots i_k} &= \int_{\mathbb{R}^3}\int_0^\infty m\left(c^2 + \frac{2I}{m}\right) c_{i_1}\cdots c_{i_k} f \phi(I)\,dI d\mathbf{c},
\end{aligned}$$

where m is the mass of a molecule, $\phi(I)$ is the state density of the internal mode, that is, $\phi(I)dI$ represents the number of the internal states of a molecule having the internal energy between I and $I + dI$, and $j,k = 1,2,\ldots$. The first five moments are conserved quantities: the mass density $F(=\rho)$, the momentum density $F_i(=\rho v_i)$, and twice the energy density $G_{ll}(= 2\rho\varepsilon + \rho v^2 = 2\rho(\varepsilon^K + \varepsilon^I) + \rho v^2)$, where v_i is the mean velocity (and $v^2 = v_i v_i$), and ε is the specific internal energy composed of the kinetic part ε^K and the internal part ε^I. The quantities P's and Q's in the right-hand side of Eq. (2) are the production terms derived from the collision term:

$$\begin{aligned}
P_{i_1\ldots i_j} &= \int_{\mathbb{R}^3}\int_0^\infty m c_{i_1}\cdots c_{i_j} Q(f)\phi(I)\,dI d\mathbf{c},\\
Q_{lli_1\ldots i_k} &= \int_{\mathbb{R}^3}\int_0^\infty m\left(c^2 + \frac{2I}{m}\right) c_{i_1}\cdots c_{i_k} Q(f)\phi(I)\,dI d\mathbf{c},
\end{aligned}$$

where $j = 2,3,\ldots$ and $k = 1,2,\ldots$.

Using the molecular approach and the MEP, Pavić, Ruggeri, and Simić [22] (see also Ref. [11]) deduced the equilibrium distribution function that maximizes the entropy:

$$\bar{f}_E = \frac{\rho}{mA(T)}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left\{-\frac{1}{k_B T}\left(\frac{1}{2}mC^2 + I\right)\right\}, \tag{3}$$

which is the generalized Maxwellian in the case of polyatomic gases. $A(T)$ is the normalization factor:

$$A(T) = \int_0^\infty \phi(I) e^{-\beta_E I}\,dI,$$

where $\beta_E \equiv 1/(k_B T)$, k_B is the Boltzmann constant, T is the absolute temperature related with the kinetic energy in equilibrium:

$$\varepsilon_E^K = \frac{3}{2}\frac{k_B}{m}T,$$

and $C^2 = C_i C_i$ with $C_i \equiv c_i - v_i$ being the peculiar velocity. Then the same authors derived the system of ET_{14} using the MEP and obtained the same closure as the one in the phenomenological approach [17].

The validity of ET_{14} has been confirmed by comparing the theoretical predictions to the experimental data of linear waves [32], shock waves [33,34], and light scattering [35], in particular, in the region where the Navier-Stokes Fourier theory fails.

If all the dissipative fluxes except for the dynamic pressure are negligible, ET_{14} reduces to a simpler ET theory with six independent fields (ET_6): mass density, velocity, specific internal energy, and dynamic pressure [36,37]. This theory is the simplest extension of the Euler theory of perfect fluids and is compatible with the Meixner theory with one internal variable [3,4]. The correspondence relation between ET_6 and the Meixner theory was shown explicitly in Ref. [36]. The distinct shock wave structure observed in polyatomic gases such as CO_2 gas is explained satisfactorily also by the ET_6 theory [38].

Furthermore, the ET_6 theory with a nonlinear constitutive equation was studied in detail [39–42]. It is noteworthy that the nonlinear ET_6 theory is perfectly consistent with the molecular approach of the kinetic theory in polytropic gases [43] and also in nonpolytropic ones [44]. In particular, in Ref. [44], comparison was also made between the present method via the continuous energy parameter I in the distribution function and the mixture-like approach based on a discrete internal energy given by Groppi and Spiga [45].

The ET theory with any number of independent fields has also been constructed [20,46], and the convergence to the singular limit of monatomic gas when the degrees of freedom of a molecule $D \to 3$ was proved [47].

It is evident, however, that the ET theory of polyatomic gases with the binary hierarchy has the limitation of its applicability, although the theory has been successfully utilized to analyze various nonequilibrium phenomena as explained above. In fact, we have many experimental data showing that the relaxation times of the rotational mode and of the vibrational mode are quite different to each other. In such a case, more than one molecular relaxation processes should be taken into account to make the ET theory more precise. Our aim of the present paper is to establish such an ET theory with much wider applicability range for rarefied polyatomic gases and to show its usefulness by studying ultrasonic wave propagation.

The present paper is organized as follows: In Sec. II, we explain the kinetic model for a polyatomic gas with two internal relaxation processes by using two parameters expressing the rotational and vibrational energies of a molecule. The equilibrium distribution function, the expressions of the thermal and caloric equations of state, and the entropy density in equilibrium are also shown. In Sec. III, we make a general discussion on the system of balance equations in ET of polyatomic gases. Defining three kinds of moments, we derive a triple hierarchy of moment equations from the Boltzmann equation. And we study the truncated system of balance equations and its closure via MEP. In Sec. IV, we introduce a simple collision term with three relaxation times, which is a generalization of the BGK model. In Sec. V, we establish the ET_7 theory with seven independent fields: mass density, momentum density, translational energy density, rotational energy density, and vibrational energy density. We derive the nonequilibrium distribution function and the closed system of field equations. In Sec. VI, we summarize some features of the ET_7 theory. In Sec. VII, we study the dispersion relation of a plane harmonic wave. Theoretical prediction of the attenuation is compared with the experimental data for CO_2, Cl_2, and Br_2 gases. Final section is devoted to the concluding remarks and the discussion on some future problems.

II. DISTRIBUTION FUNCTION WITH TWO ENERGIES OF INTERNAL MODES

We adopt the closure of molecular ET in this paper; therefore, we first explain the kinetic model for a polyatomic gas with two internal relaxation processes and then derive its equilibrium distribution function. The thermal and caloric equations of state and the expression of the entropy density in equilibrium are also shown.

To describe the relaxation processes of rotational and vibrational modes separately, we decompose the energy of internal modes I as the sum of the energy of rotational mode I^R and the energy of vibrational mode I^V:

$$I = I^R + I^V. \tag{4}$$

Generalizing the Borgnakke-Larsen idea [29], we assume the same form of the Boltzmann Eq. (1) with a velocity distribution function that depends on these additional parameters, i.e., $f \equiv f(\mathbf{x},\mathbf{c},t,I^R,I^V)$. And we also take into account the effect of the parameters I^R and I^V on the collision term $Q(f)$.

Remark 1. As a state near the dissociation temperature, in which the molecular vibration is highly anharmonic, is out of the scope of the present study, the relation Eq. (4) can be safely assumed.

Remark 2. In a harmonic approximation of the molecular vibration, we may further divide I^V into the energies of several harmonic modes. However, in this paper, as we focus our study on the contribution from the rotational or vibrational mode as a whole, we do not enter into such details although the generalization in this direction is straightforward.

A. Equilibrium distribution function

We derive the equilibrium distribution function f_E by means of MEP. We remark that the collision invariants of the present model are m, mc_i, and $mc^2 + 2I^R + 2I^V$. These quantities correspond to the hydrodynamics variables, i.e., the mass density $F(=\rho)$, the momentum density $F_i(=\rho v_i)$ and twice the energy density $G_{ll}(=2\rho\varepsilon + \rho v^2)$ through the following relations:

$$\begin{aligned}
F &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mf\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
F_i &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc_i f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
G_{ll} &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty (mc^2 + 2I^R + 2I^V)\\
&\quad\times f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}.
\end{aligned} \tag{5}$$

Here $\varphi(I^R)$ and $\psi(I^V)$ are the state densities corresponding to I^R and I^V. And it is easy to see from Eq. $(5)_3$, that the specific internal energy ε is composed of the kinetic part ε^K and the parts of rotational mode ε^R and of vibrational mode ε^V, i.e.,

$$\varepsilon = \varepsilon^K + \varepsilon^R + \varepsilon^V.$$

The entropy density h is defined by

$$h = -k_B\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty f\log f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}, \tag{6}$$

where k_B is the Boltzmann constant.

Statement 1. The equilibrium distribution function f_E, which maximizes the entropy density Eq. (6) under the constraints Eq. (5), is given by

$$\begin{aligned}
f_E &= \frac{\rho}{mA^R(T)A^V(T)}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\\
&\quad\times\exp\left\{-\frac{1}{k_B T}\left(\frac{1}{2}mC^2 + I^R + I^V\right)\right\},
\end{aligned} \tag{7}$$

where $A^R(T)$ and $A^V(T)$ are normalization factors:

$$\begin{aligned}
A^R(T) &= \int_0^\infty \varphi(I^R)e^{-\beta_E I^R}dI^R,\\
A^V(T) &= \int_0^\infty \psi(I^V)e^{-\beta_E I^V}dI^V.
\end{aligned} \tag{8}$$

The proof is omitted here, for simplicity, because it is essentially the same as the one shown in [11,22,43]. In fact, replacing $I, \phi(I)$, and $A(T)$ in Eq. (3) by $I^R + I^V$, $\varphi(I^R)\psi(I^V)$, and $A^R(T)A^V(T)$, respectively, we can obtain Eq. (7).

The equilibrium distribution function can be expressed by the product of the equilibrium distribution functions of the three modes:

$$f_E = f_E^{(K)} f_E^{(R)} f_E^{(V)},$$

where

$$\begin{aligned}
f_E^{(K)} &= \frac{\rho}{m}\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{mC^2}{2k_B T}\right),\\
f_E^{(R)} &= \frac{1}{A^R(T)}\exp\left(-\frac{I^R}{k_B T}\right),\\
f_E^{(V)} &= \frac{1}{A^V(T)}\exp\left(-\frac{I^V}{k_B T}\right).
\end{aligned}$$

B. Thermal and caloric equations of state

By using the equilibrium distribution function f_E, we obtain the thermal and caloric equations of state. The pressure p is expressed by

$$p = p^K(\rho,T) \equiv \frac{k_B}{m}\rho T. \tag{9}$$

The caloric equation of state is given by

$$\varepsilon = \varepsilon_E(T) = \varepsilon_E^K(T) + \varepsilon_E^R(T) + \varepsilon_E^V(T), \tag{10}$$

and, proceeding in similar way as shown in Ref. [44], we have

$$\begin{aligned}
\varepsilon_E^K(T) &\equiv \frac{3}{2}\frac{k_B}{m}T,\\
\varepsilon_E^R(T) &\equiv \frac{k_B}{m}T^2\frac{d\log A^R(T)}{dT},\\
\varepsilon_E^V(T) &\equiv \frac{k_B}{m}T^2\frac{d\log A^V(T)}{dT}.
\end{aligned} \tag{11}$$

Therefore, if we know the normalization factors $A^R(T)$ and $A^V(T)$, similar to the partition function in statistical mechanics, we can derive the equilibrium energies of rotational and vibrational modes from Eq. (11). Vice versa if we know, at the macroscopic phenomenological level, the constitutive equations $\varepsilon_E^R(T)$ and $\varepsilon_E^V(T)$, we can obtain by integration of Eqs. $(11)_{2,3}$

$$\begin{aligned}
A^R(T) &= A_0^R \exp\left(\frac{m}{k_B}\int_{T_0}^{T}\frac{\varepsilon_E^R(T')}{T'^2}dT'\right),\\
A^V(T) &= A_0^V \exp\left(\frac{m}{k_B}\int_{T_0}^{T}\frac{\varepsilon_E^V(T')}{T'^2}dT'\right),
\end{aligned}$$

where A_0^R, A_0^V, and T_0 are inessential constants. As is observed in Refs. [41,44], the functions A^R and A^V are, according to Eq. (8), the Laplace transforms of φ and ψ, respectively:

$$\begin{aligned}
&A^R(T) = L_u[\varphi(I^R)](s), \quad A^V(T) = L_u[\psi(I^V)](s),\\
&s = \frac{1}{k_B T},
\end{aligned}$$

and then we obtain the state functions $\varphi(I^R)$ and $\psi(I^V)$ as the inverse Laplace transforms of $A^R(T)$ and $A^V(T)$, respectively:

$$\begin{aligned}
&\varphi(I^R) = L_u^{-1}[A^R(T)](I^R), \quad \psi(I^V) = L_u^{-1}[A^V(T)](I^V),\\
&T = \frac{1}{k_B s}.
\end{aligned}$$

We also notice the relation

$$p^K(\rho,T) = \tfrac{2}{3}\rho\varepsilon_E^K(T), \tag{12}$$

and the specific entropy density $s = h_E/\rho$ in equilibrium is given by

$$s = s_E(\rho,T) = s_E^K(\rho,T) + s_E^R(T) + s_E^V(T),$$

where

$$\begin{aligned}
s_E^K(\rho,T) &\equiv -\frac{k_B}{\rho}\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty f_E\log f_E^{(K)}\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
&= \frac{k_B}{m}\log\left(\frac{T^{3/2}}{\rho}\right) + \frac{\varepsilon_E^K(T)}{T} - \frac{k_B}{m}\log\left[\frac{1}{m}\left(\frac{m}{2\pi k_B}\right)^{3/2}\right],\\
s_E^R(T) &\equiv -\frac{k_B}{\rho}\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty f_E\log f_E^{(R)}\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
&= \frac{k_B}{m}\log A^R(T) + \frac{\varepsilon_E^R(T)}{T},\\
s_E^V(T) &\equiv -\frac{k_B}{\rho}\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty f_E\log f_E^{(V)}\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
&= \frac{k_B}{m}\log A^V(T) + \frac{\varepsilon_E^V(T)}{T}.
\end{aligned} \tag{13}$$

The Gibbs relations of the three modes are given by

$$Tds_E^K(\rho,T) = d\varepsilon_E^K(T) - \frac{p(\rho,T)}{\rho^2}d\rho, \quad Tds_E^R(T) = d\varepsilon_E^R(T), \quad Tds_E^V(T) = d\varepsilon_E^V(T). \tag{14}$$

III. NONEQUILIBRIUM TRIPLE HIERARCHY OF MOMENT EQUATIONS

Before going into a specific ET theory, we briefly make a general discussion on the system of balance equations in ET of polyatomic gases.

Let us introduce three kinds of moments F, H^R, and H^V as follows:

$$F_{i_1\dots i_j} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc_{i_1}\cdots c_{i_j} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$
$$H^R_{lli_1\dots i_k} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^R c_{i_1}\cdots c_{i_k} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$
$$H^V_{lli_1\dots i_l} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^V c_{i_1}\cdots c_{i_l} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$

where $j,k,l = 1,2,\cdots$. From the Boltzmann Eq. (1), we obtain three hierarchies (a triple hierarchy) of balance equations, i.e., F, H^R, and H^V hierarchies in the following form:

$$\begin{aligned}
&\partial_t F + \partial_i F_i = 0,\\
&\partial_t F_{i_1} + \partial_i F_{ii_1} = 0,\\
&\partial_t F_{i_1i_2} + \partial_i F_{ii_1i_2} = P^K_{i_1i_2}, && \partial_t H^R_{ll} + \partial_i H^R_{lli} = P^R_{ll}, && \partial_t H^V_{ll} + \partial_i H^V_{lli} = P^V_{ll},\\
&\partial_t F_{i_1i_2i_3} + \partial_i F_{ii_1i_2i_3} = P^K_{i_1i_2i_3}, && \partial_t H^R_{lli_1} + \partial_i H^R_{llii_1} = P^R_{lli_1}, && \partial_t H^V_{lli_1} + \partial_i H^V_{llii_1} = P^V_{lli_1},\\
&\quad\vdots && \quad\vdots && \quad\vdots,
\end{aligned}$$

where the production terms are related to the collision term as follows:

$$P^K_{i_1\dots i_j} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc_{i_1}\cdots c_{i_j} Q(f)\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$
$$P^R_{lli_1\dots i_k} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^R c_{i_1}\cdots c_{i_k} Q(f)\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$
$$P^V_{lli_1\dots i_l} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^V c_{i_1}\cdots c_{i_l} Q(f)\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}.$$

We notice that the first and second equations of the F-hierarchy represent the conservation laws of mass and momentum, while the sum of the balance equations of F_{ll}, H^R_{ll}, and H^R_{ll} represents the conservation law of energy with

$$Q_{ll} = P^K_{ll} + P^R_{ll} + P^V_{ll} = 0. \tag{15}$$

In each of the three hierarchies, the flux in one equation appears as the density in the next equation.

Remark 3. Equivalently, instead of the one of the three hierarchies, we may adopt the hierarchy of the total energy (G-hierarchy):

$$\begin{aligned}
&\partial_t G_{ll} + \partial_i G_{lli} = 0,\\
&\partial_t G_{lli_1\cdots i_m} + \partial_i G_{llii_1\cdots i_m} = Q_{lli_1\cdots i_m}, \quad m = 1,2,\cdots,
\end{aligned}$$

where G_{ll} is given by Eq. $(5)_3$ and

$$G_{lli_1\cdots i_m} = \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty (mc^2 + 2I^R + 2I^V) \times c_{i_1}\cdots c_{i_m} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},$$

and

$$Q_{lli_1\cdots i_m} = P^K_{lli_1\cdots i_m} + P^R_{lli_1\cdots i_m} + P^V_{lli_1\cdots i_m} \quad m = 1,2,\cdots.$$

The G hierarchy has been introduced in the theory with the binary hierarchy of balance equations [see Eq. (2)].

Truncated system of balance equations and its closure

To have a finite system of balance equations, we truncate the F, H^R, and H^V hierarchies at the orders of N, M, and L, respectively. For conciseness, it is convenient to introduce a multi-index A:

$$c_A = \begin{cases} 1 & \text{for } A = 0\\ c_{i_1}\cdots c_{i_A} & \text{for } A \geqslant 1 \end{cases}.$$

The multi-index is also introduced for other quantities in a similar way (see for more details Ref. [11]). Then, we can express the densities as follows:

$$\begin{aligned}
F_A &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc_A f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
H^R_{llA'} &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^R c_{A'} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c},\\
H^V_{llA''} &= \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^V c_{A''} f\,\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}.
\end{aligned} \tag{16}$$

The fluxes F_{iA}, $H^R_{lliA'}$, $H^V_{lliA''}$ and the productions P^K_A, $P^R_{llA'}$, $P^V_{llA''}$ are also expressed in a similar way.

Then a triple hierarchy of moments truncated at the orders $N, M,$ and L [(N,M,L) *system*] is compactly

expressed as

$$\partial_t F_A + \partial_i F_{iA} = P^K_A, \quad (0 \leqslant A \leqslant N) \qquad \partial_t H^R_{llA'} + \partial_i H^R_{lliA'} = P^R_{llA'}, \quad (0 \leqslant A' \leqslant M) \qquad \partial_t H^V_{llA''} + \partial_i H^V_{lliA''} = P^V_{llA''}, \quad (0 \leqslant A'' \leqslant L) \tag{17}$$

with $P^K = 0$ and $P^K_1 = 0$ and with the condition Eq. (15) representing the conservation laws of mass, momentum, and energy.

1. Galilean invariance

Since the velocity-independent variables are the moments in terms of the peculiar velocity C_i instead of c_i, it is possible to express the velocity dependence of the densities $\mathbf{F} = (F_A, H^R_{llA'}, H^V_{llA''})^T$, the nonconvective fluxes $\mathbf{\Phi} = (F_{iA} - F_A v_i, H^R_{lliA'} - H^R_{llA'} v_i, H^V_{lliA''} - H^V_{llA''} v_i)^T$, and the production terms $\mathbf{P} = (P^K_A, P^R_{llA'}, P^V_{llA''})$ as follows [48]:

$$\mathbf{F} = \mathbf{X}(\mathbf{v})\hat{\mathbf{F}}, \quad \mathbf{\Phi} = \mathbf{X}(\mathbf{v})\hat{\mathbf{\Phi}}, \quad \mathbf{P} = \mathbf{X}(\mathbf{v})\hat{\mathbf{P}},$$

where a hat on a quantity indicates the velocity-independent part of the quantity.

We assume that the constitutive quantities $\hat{F}_{iN}$, $\hat{H}^R_{lliM}$, $\hat{H}^V_{lliL}$, $\hat{P}^K_A$, $\hat{P}^R_{A'}$, and $\hat{P}^V_{A''}$, which we express as $\hat{\Psi}$ generically, depend on the densities locally and instantaneously:

$$\hat{\Psi} = \hat{\Psi}(\hat{F}_A, \hat{H}^R_{llA'}, \hat{H}^V_{llA''}). \tag{18}$$

Remark 4. In principle, the truncated orders N, M, and L may be chosen independently. However, if we naturally impose the condition that the (N,M,L) system can make the G-hierarchy be Galilean invariant, the inequality; $\min(M,L) \leqslant N-1$ should be satisfied [20] because of the relation

$$G_{lla} = X_{ab}\left(\hat{F}_{llb} + \hat{H}^R_{llb} + \hat{H}^V_{llb} + 2v_l \hat{F}_{lb} + v^2 \hat{F}_b\right) \quad [0 \leqslant a,b \leqslant \min(M,L)].$$

2. MEP and the closure of the system

To obtain the constitutive Eqs. (18) explicitly, we utilize the MEP. That is, the most suitable distribution function $f_{(N,M,L)}$ is the one that maximizes the functional defined by (we omit the symbol of summation for the repeated indices: A from 0 to N, A' from 0 to M, and A'' from 0 to L)

$$\begin{aligned}\mathcal{L}_{(N,M,L)}(f) = &-k_B \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty f \log f\, \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c} + \lambda_A\left(F_A - \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty m c_A f \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c}\right)\\ &+ \mu^R_{A'}\left(H^R_{llA'} - \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^R c_{A'} f \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c}\right)\\ &+ \mu^V_{A''}\left(H^V_{llA''} - \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2I^V c_{A''} f \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c}\right),\end{aligned}$$

where λ_A, $\mu^R_{A'}$, and $\mu^V_{A''}$ are the Lagrange multipliers. As a consequence [49], we have

$$f_{(N,M,L)} = \exp\left(-1 - \frac{m}{k_B}\chi_{(N,M,L)}\right),$$
$$\chi_{(N,M,L)} = \lambda_A c_A + \frac{2I^R}{m}\mu^R_{A'} c_{A'} + \frac{2I^V}{m}\mu^V_{A''} c_{A''}.$$

Due to the Galilean invariance, the distribution function can be expressed in terms of the velocity-independent quantities:

$$\begin{aligned} f_{(N,M,L)} &= \exp\left(-1 - \frac{m}{k_B}\hat{\chi}_{(N,M,L)}\right),\\ \hat{\chi}_{(N,M,L)} &= \hat{\lambda}_A C_A + \frac{2I^R}{m}\hat{\mu}^R_{A'} C_{A'} + \frac{2I^V}{m}\hat{\mu}^V_{A''} C_{A''}.\end{aligned} \tag{19}$$

Therefore, we obtain the velocity dependence of the Lagrange multipliers $\boldsymbol{\lambda} \equiv (\lambda_A, \mu^R_{A'}, \mu^V_{A''})$ as follows [10,48]:

$$\boldsymbol{\lambda} = \hat{\boldsymbol{\lambda}}\mathbf{X}(-\mathbf{v}). \tag{20}$$

By inserting Eq. (19) into Eq. (16), the Lagrange multipliers λ_A, $\mu^R_{A'}$, and $\mu^V_{A''}$ are evaluated in terms of the densities F_A, $H^R_{llA'}$, and $H^V_{llA''}$. And, finally, by plugging Eq. (19) into the last fluxes and production terms, the system is closed. In this way, we obtain the ET theory for the (N,M,L) system.

Remark 5. An alternative approach to achieve the closure (phenomenological closure) of the system makes use of the entropy principle. In this case, it is required that all the solutions of Eq. (17) satisfy the entropy inequality:

$$\partial_t h + \partial_i h_i = \Sigma \geqslant 0,$$

where h is given by Eq. (6), and h_i and Σ are the entropy flux and the entropy production defined by

$$\begin{aligned} h_i &= -k_B \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty c_i f \log f\, \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c},\\ \Sigma &= -k_B \int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty Q(f) \log f\, \varphi(I^R)\psi(I^V)\, dI^R dI^V d\mathbf{c}.\end{aligned} \tag{21}$$

According with the general results given first in Ref. [19] the two closure methods give the same closed system of balance

equations. Moreover, we obtain the following relations:

$$\begin{aligned} dh &= \lambda_A dF_A + \mu^R_{A'} dH^R_{llA'} + \mu^V_{A''} dH^V_{llA''}, \\ dh_i &= \lambda_A dF_{iA} + \mu^R_{A'} dH^R_{lliA'} + \mu^V_{A''} dH^V_{lliA''}, \\ \Sigma &= \lambda_A P^K_A + \mu^R_{A'} P^R_{llA'} + \mu^V_{A''} P^V_{llA''} \geqslant 0. \end{aligned} \tag{22}$$

IV. GENERALIZED BGK MODEL

Concerning the collision term, Struchtrup [50] and Rahimi and Struchtrup [51] proposed a variant of the BGK model [52] to take into account a relaxation of the energy of the internal mode. In this section, we introduce a simple collision term with three relaxation times to describe a more refined model in which rotational and vibrational modes are treated individually.

A. Three relaxation times

In polyatomic gases, we may introduce three characteristic times corresponding to three relaxation processes caused by the molecular collision (see also Refs. [7,53–55]):

(i) Relaxation time τ_K: This characterizes the relaxation process within the translational mode (mode K) of molecules. The process shows the tendency to approach an equilibrium state of the mode K with the distribution function $f_{K:E}$ having the temperature θ^K, explicit expression of which is shown below. However, the rotational and vibrational modes are, in general, in nonequilibrium. This process is observable also in monatomic gases.

(ii) Relaxation time $\tau_{\mathfrak{bc}}$: There are energy exchanges among the three modes: mode K, rotational mode (mode R), and vibrational mode (mode V). The relaxation process occurs in such a way that two of the three modes [say $(\mathfrak{bc}) = (\mathrm{KR}), (\mathrm{KV}), (\mathrm{RV})$] approach, after the relaxation time $\tau_{\mathfrak{bc}}$, an equilibrium state characterized by the distribution function $f_{\mathfrak{bc}:E}$ with a common temperature $\theta^{\mathfrak{bc}}$, explicit expression of which is shown below. Because of the lack of experimental data, we have no reliable magnitude-relationship between τ_K and $\tau_{\mathfrak{bc}}$. However, it seems natural to adopt the relation: $O(\tau_{\mathfrak{bc}}) \gtrsim O(\tau_K)$, which we assume hereafter (see also Sec. VII). In Table I, three possible cases are summarized depending on the choice of $\mathfrak{b}$ and $\mathfrak{c}$.

(iii) Relaxation time τ of the last stage: After the relaxation process between $\mathfrak{b}$ and $\mathfrak{c}$, all modes, K, R, and V, eventually approach a local equilibrium state characterized by f_E with a common temperature T among K, R, and V modes, which is given by Eq. (7). Naturally, we have the relation: $\tau > \tau_{\mathfrak{bc}}$.

Diagrams of the possible relaxation processes are shown in Fig. 1.

TABLE I. Three possible relaxation processes in the second stage (ii).

$(\mathfrak{bc})$ Process	$(\mathfrak{a},\mathfrak{b},\mathfrak{c})$	Relaxation time	Collision term
(KR) process	(V,K,R)	τ_{KR}	$Q^{KR}(f)$
(KV) process	(R,K,V)	τ_{KV}	$Q^{KV}(f)$
(RV) process	(K,R,V)	τ_{RV}	$Q^{RV}(f)$

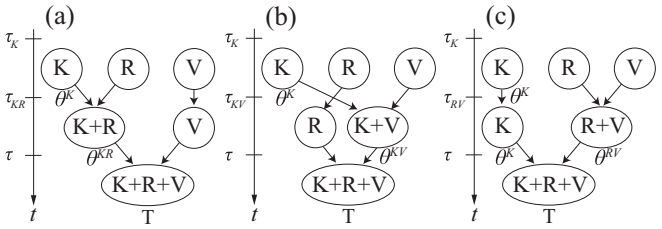

FIG. 1. Diagram of the three possible relaxation processes of the translational mode (K), rotational mode (R), and vibrational mode (V) for (a) (KR) process, (b) (KV) process, and (c) (RV) process. The symbols θ^K, $\theta^{\mathfrak{bc}}$ $[(\mathfrak{bc}) = (\mathrm{KR}), (\mathrm{KV}), (\mathrm{RV})]$ are partial equilibrium temperatures and T is the local equilibrium temperature. A mode without attaching a symbol of the temperature is not necessarily in partial equilibrium.

B. Generalized BGK collision term

The generalized BGK collision term for $(\mathfrak{bc})$ process $[(\mathfrak{bc}) = (\mathrm{KR}), (\mathrm{KV}), (\mathrm{RV})]$ is proposed as follows:

$$Q^{\mathfrak{bc}}(f) = -\frac{1}{\tau_K}(f - f_{K:E}) - \frac{1}{\tau_{\mathfrak{bc}}}(f - f_{\mathfrak{bc}:E}) - \frac{1}{\tau}(f - f_E), \tag{23}$$

where the distribution functions $f_{K:E}$ and $f_{\mathfrak{bc}:E}$ are given as follows:

(a) Distribution function $f_{K:E}$. This is given by

$$f_{K:E} = \frac{\rho^{RV}(I^R, I^V)}{m}\left(\frac{m}{2\pi k_B \theta^K}\right)^{3/2} \exp\left(-\frac{mC^2}{2k_B\theta^K}\right), \tag{24}$$

where

$$\rho^{RV}(I^R, I^V) = \int_{\mathbb{R}^3} m f d\mathbf{c}. \tag{25}$$

This is the equilibrium function with respect to the K mode with the temperature θ^K and with the "frozen" energies, I^R and I^V. In other words, $f_{K:E}$ is a Maxwellian with the mass density $\rho^{RV}(I^R, I^V)$ and temperature θ^K. Therefore, $f_{K:E}$ given in Eq. (24) is obtained by maximizing not the true entropy Eq. (6) but the entropy with the frozen energies:

$$h^{RV}(I^R, I^V) = -k_B \int_{\mathbb{R}^3} f \log f \, d\mathbf{c},$$

under the constraints

$$\begin{pmatrix} \rho^{RV}(I^R, I^V) \\ \rho^{RV}(I^R, I^V) v_i \\ 2\rho^{RV}(I^R, I^V)\varepsilon^K_E(\theta^K) \end{pmatrix} = \int_{\mathbb{R}^3} \begin{pmatrix} m \\ mc_i \\ mC^2 \end{pmatrix} f d\mathbf{c}.$$

Then we have the relation Eq. (25), and the relation

$$\varepsilon^K = \varepsilon^K_E(\theta^K),$$

from which we can determine the temperature θ^K.

(b) Distribution function $f_{KR:E}$. Let us study the process in which the K and R modes reach their common equilibrium with the temperature θ^{KR} and the vibrational energy I^V can be considered as frozen. In this case, we have the distribution

function:

$$f_{KR:E} = \frac{\rho^V(I^V)}{mA^R(\theta^{KR})}\left(\frac{m}{2\pi k_B\theta^{KR}}\right)^{3/2} \times \exp\left\{-\frac{1}{k_B\theta^{KR}}\left(\frac{mC^2}{2}+I^R\right)\right\},$$

where

$$\rho^V(I^V) = m\int_{\mathbb{R}^3}\int_0^\infty f\,\varphi(I^R)\,dI^R d\mathbf{c}. \tag{26}$$

Since the equilibrium state is described by the mass density $\rho^V(I^V)$ with the frozen vibrational energy I^V and the internal energy $\varepsilon_E^{K+R}(\theta^{KR}) \equiv \varepsilon^K(\theta^{KR}) + \varepsilon^R(\theta^{KR})$, we obtain $f_{KR:E}$ by using the MEP and searching the maximum of the entropy,

$$h^V(I^V) = -k_B\int_{\mathbb{R}^3}\int_0^\infty f\log f\,\varphi(I^R)dI^R\,d\mathbf{c},$$

under the constraints

$$\begin{pmatrix}\rho^V(I^V)\\ \rho^V(I^V)v_i\\ 2\rho^V(I^V)\varepsilon_E^{K+R}(\theta^{KR})\end{pmatrix} = \int_{\mathbb{R}^3}\int_0^\infty\begin{pmatrix}m\\ mc_i\\ mC^2+2I^R\end{pmatrix} f\varphi(I^R)dI^R\,d\mathbf{c}.$$

Therefore, we have the relation Eq. (26), and the relation

$$\varepsilon^{K+R} \equiv \varepsilon^K + \varepsilon^R = \varepsilon_E^K(\theta^{KR}) + \varepsilon_E^R(\theta^{KR}) \equiv \varepsilon_E^{K+R}(\theta^{KR}), \tag{27}$$

from which we can determine the temperature θ^{KR}.

(c) Distribution function $f_{KV:E}$. In a similar way, we have

$$f^{KV} = \frac{\rho^R(I^R)}{mA^V(\theta^{KV})}\left(\frac{m}{2\pi k_B\theta^{KV}}\right)^{3/2} \times \exp\left\{-\frac{1}{k_B\theta^{KV}}\left(\frac{mC^2}{2}+I^V\right)\right\},$$

where

$$\rho^R(I^R) = \int_{\mathbb{R}^3}\int_0^\infty mf\psi\left(I^V\right)d\mathbf{c}dI^V.$$

And we have the relation, from which we can determine the temperature θ^{KV}:

$$\varepsilon^{K+V} \equiv \varepsilon^K + \varepsilon^V = \varepsilon_E^K(\theta^{KV}) + \varepsilon_E^V(\theta^{KV}) \equiv \varepsilon_E^{K+V}(\theta^{KV}). \tag{28}$$

(d) Distribution function $f_{RV:E}$. In this case, the K mode is in equilibrium with the temperature θ^K, and R and V modes are also in equilibrium but with the different temperature θ^{RV}. Then we have the expression similar to Eq. (7):

$$f_{RV:E} = \frac{\rho}{mA^R(\theta^{RV})A^V(\theta^{RV})}\left(\frac{m}{2\pi k_B\theta^K}\right)^{3/2} \times \exp\left(-\frac{mC^2}{2k_B\theta^K} - \frac{I^R+I^V}{k_B\theta^{RV}}\right),$$

where the temperature θ^{RV} is determined by the relation:

$$\varepsilon^{R+V} \equiv \varepsilon^R + \varepsilon^V = \varepsilon_E^R(\theta^{RV}) + \varepsilon_E^V(\theta^{RV}) \equiv \varepsilon_E^{R+V}(\theta^{RV}). \tag{29}$$

(e) Distribution function f_E. This is the local equilibrium distribution function given by Eq. (7), in which the temperature T is given by the condition

$$\varepsilon = \varepsilon_E(T). \tag{30}$$

C. H-theorem

From the definition of the distribution functions $f_{K:E}$, $f_{KR:E}$, $f_{KV:E}$, $f_{RV:E}$, and f_E, it is easy to verify the following relations [$(\mathfrak{bc}) = (\mathrm{KR}), (\mathrm{KV}), (\mathrm{RV})$]:

$$\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty (f-f_{K:E})\log f_{K:E}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c} = 0,$$

$$\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty (f-f_{\mathfrak{bc}:E})\log f_{\mathfrak{bc}:E}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c} = 0,$$

$$\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty (f-f_E)\log f_E\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c} = 0.$$

Then the entropy production Eq. (21) can easily be shown to be positive:

$$\Sigma = k_B\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty\left\{\frac{f-f_{K:E}}{\tau^K}\log\frac{f}{f_{K:E}} + \frac{f-f_{\mathfrak{bc}:E}}{\tau_{\mathfrak{bc}}} \times \log\frac{f}{f_{\mathfrak{bc}:E}} + \frac{f-f_E}{\tau}\log\frac{f}{f_E}\right\} \times \varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c} \geqslant 0,$$

and the H-theorem holds.

V. ET THEORY WITH SEVEN INDEPENDENT FIELDS: ET$_7$

The simplest system of Eq. (17) next to the Euler system in the present approach is the system with seven independent fields (ET$_7$):

$$\begin{aligned}&\text{Mass density:} && F = \rho,\\ &\text{Momentum density:} && F_i = \rho v_i,\\ &\text{Translational energy density:} && F_{ll} = 2\rho\varepsilon^K + \rho v^2,\\ &\text{Rotational energy density:} && H_{ll}^R = 2\rho\varepsilon^R,\\ &\text{Vibrational energy density:} && H_{ll}^V = 2\rho\varepsilon^V.\end{aligned} \tag{31}$$

By neglecting the dissipation due to the shear stress and heat flux, the ET$_7$ theory focuses on the description of the internal relaxation processes in a molecule.

In this section, by means of the kinetic closure, we derive the nonequilibrium distribution function and the closed system of field equations following the general procedure adopted in Refs. [36,43,44]. We assume the generalized BGK model of the collision term introduced above.

A. System of balance equations

From Eq. (17), the system of balance equations is expressed as follows:

$$\begin{aligned}
&\frac{\partial F}{\partial t}+\frac{\partial F_i}{\partial x_i}=0,\\
&\frac{\partial F_j}{\partial t}+\frac{\partial F_{ij}}{\partial x_i}=0,\\
&\frac{\partial F_{ll}}{\partial t}+\frac{\partial F_{lli}}{\partial x_i}=P_{ll}^K,\\
&\frac{\partial H_{ll}^R}{\partial t}+\frac{\partial H_{lli}^R}{\partial x_i}=P_{ll}^R,\\
&\frac{\partial H_{ll}^V}{\partial t}+\frac{\partial H_{lli}^V}{\partial x_i}=P_{ll}^V,
\end{aligned} \tag{32}$$

where $(F_{lli}, H_{lli}^R, H_{lli}^V)$ and $(P_{ll}^K, P_{ll}^R, P_{ll}^V)$ are the fluxes and productions of the densities $(F_{ll}, H_{ll}^R, H_{ll}^V)$. It is easily verified that the production terms are velocity independent.

B. Nonequilibrium distribution function

First of all, we start with the following statement:

Statement 2. The nonequilibrium distribution function for the truncated system Eq. (32) obtained by using the MEP is expressed as

$$\begin{aligned}
f^{(7)}=&\frac{\rho}{mA^R(\theta^R)A^V(\theta^V)}\left(\frac{m}{2\pi k_B\theta^K}\right)^{3/2}\\
&\times\exp\left(-\frac{mC^2}{2k_B\theta^K}-\frac{I^R}{k_B\theta^R}-\frac{I^V}{k_B\theta^V}\right),
\end{aligned} \tag{33}$$

where $A^R(\theta^R)$ and $A^V(\theta^V)$ are normalization factors given by Eq. (8). Nonequilibrium temperatures θ^R and θ^V of R and V modes are determined through the relations

$$\varepsilon^R=\varepsilon_E^R(\theta^R),\quad \varepsilon^V=\varepsilon_E^V(\theta^V).$$

The proof of this statement is given in the Appendix. A similar result was obtained in Ref. [44] in the case of ET_6. In the present case, as shown also in the Appendix, the Lagrange multipliers are given as the functions of $(\rho,v_i,\theta^K,\theta^R,\theta^V)$:

$$\begin{aligned}
&\lambda=-\frac{g_E^K(\rho,\theta^K)}{\theta^K}-\frac{g_E^R(\theta^R)}{\theta^R}-\frac{g_E^V(\theta^V)}{\theta^V}+\frac{v^2}{2\theta^K},\\
&\lambda_i=-\frac{v_i}{\theta^K},\quad \mu^K=\frac{1}{2\theta^K},\quad \mu^R=\frac{1}{2\theta^R},\quad \mu^V=\frac{1}{2\theta^V},
\end{aligned} \tag{34}$$

where $g_E^K(\rho,\theta^K), g_E^R(\theta^R)$, and $g_E^V(\theta^V)$ are the nonequilibrium chemical potentials of the modes:

$$\begin{aligned}
g_E^K(\rho,\theta^K)&=\varepsilon_E^K(\theta^K)+\frac{p^K(\rho,\theta^K)}{\rho}-\theta^K s_E^K(\rho,\theta^K),\\
g_E^R(\theta^R)&=\varepsilon_E^R(\theta^R)-\theta^R s_E^R(\theta^R),\\
g_E^V(\theta^V)&=\varepsilon_E^V(\theta^V)-\theta^V s_E^V(\theta^V).
\end{aligned} \tag{35}$$

Remark 6. From Eq. (33), we notice that, within ET_7, any nonequilibrium state can be identified by assigning the nonequilibrium temperatures θ^K, θ^R, and θ^V together with ρ and v_i. In other words, ET_7 adopts the approximation that K, R, and V modes are always in equilibrium but, in general, with different temperatures from each other. Therefore, ET_7 does not take into account the relaxation (i) with the relaxation time τ_K. See also Fig. 1.

Remark 7. The nonequilibrium temperatures have been introduced in many studies although there still remain subtle conceptual problems [56]. In the context of ET, the nonequilibrium temperature is defined through the Lagrange multiplier corresponding to the conservation law of energy [11,57]. Indeed, the expression of the Lagrange multiplies of ET_7, Eq. (34), ensures the present definition of the nonequilibrium temperatures θ^K, θ^R, and θ^V.

C. Closed system of field equations

By using the distribution function Eq. (33), we obtain the constitutive equations for the fluxes as follows:

$$\begin{aligned}
F_{ij}&=\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc_ic_jf^{(7)}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}\\
&=p^K(\rho,\theta^K)\delta_{ij}+\rho v_iv_j,\\
F_{lli}&=\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty mc^2c_if^{(7)}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}\\
&=\left\{2\rho\varepsilon_E^K(\theta^K)+2p^K(\rho,\theta^K)+\rho v^2\right\}v_i,\\
H_{lli}^R&=\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2c_iI^Rf^{(7)}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}\\
&=2\rho\varepsilon_E^R(\theta^R)v_i,\\
H_{lli}^V&=\int_{\mathbb{R}^3}\int_0^\infty\int_0^\infty 2c_iI^Vf^{(7)}\varphi(I^R)\psi(I^V)\,dI^R dI^V d\mathbf{c}\\
&=2\rho\varepsilon_E^V(\theta^V)v_i.
\end{aligned} \tag{36}$$

We notice that the velocity-independent parts of F_{lli}, H_{lli}^R, and H_{lli}^V vanish.

The trace part of the momentum flux F_{ll} is related to the pressure p and the dynamic pressure Π in continuum mechanics as follows:

$$F_{ll}=3(p+\Pi)+\rho v^2.$$

Comparing this relation with Eq. $(36)_2$, we notice that Π is given by

$$\Pi=p^K(\rho,\theta^K)-p^K(\rho,T), \tag{37}$$

or, from Eq. (12), it is given by

$$\Pi = \tfrac{2}{3}\rho\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(T)\right].$$

Therefore, as was shown in Refs. [44,58], the dynamic pressure is related to the energy exchange.

Using the constitutive equations above, we obtain the closed system of field equations for the independent seven fields, $\rho, v_i, \theta^K, \theta^R, \theta^V$ [the equations of state are given by Eqs. (9) and (10)]:

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0, \quad \frac{\partial \rho v_j}{\partial t} + \frac{\partial}{\partial x_i}\{p^K(\rho,\theta^K)\delta_{ij} + \rho v_i v_j\} = 0,$$
$$\frac{\partial}{\partial t}\left\{2\rho\varepsilon_E^K(\theta^K) + \rho v^2\right\} + \frac{\partial}{\partial x_i}\left\{\left(2\rho\varepsilon_E^K(\theta^K) + \rho v^2 + 2p^K(\rho,\theta^K)\right)v_i\right\} = P_{ll}^K, \quad \frac{\partial}{\partial t}\left\{2\rho\varepsilon_E^R(\theta^R)\right\} + \frac{\partial}{\partial x_i}\left\{2\rho\varepsilon_E^R(\theta^R)v_i\right\} = P_{ll}^R,$$
$$\frac{\partial}{\partial t}\left\{2\rho\varepsilon_E^V(\theta^V)\right\} + \frac{\partial}{\partial x_i}\left\{2\rho\varepsilon_E^V(\theta^V)v_i\right\} = P_{ll}^V, \tag{38}$$

where expressions of the production terms are given in Sec. V E.

By using the material derivative, the system Eq. (38) is rewritten as follows:

$$\dot\rho + \rho\frac{\partial v_i}{\partial x_i} = 0, \quad \rho\dot v_i + \frac{\partial p^K(\rho,\theta^K)}{\partial x_i} = 0, \quad \dot\varepsilon_E^K(\theta^K) + \frac{p^K(\rho,\theta^K)}{\rho}\frac{\partial v_k}{\partial x_k} = \frac{P_{ll}^K}{2\rho}, \quad \dot\varepsilon_E^R(\theta^R) = \frac{P_{ll}^R}{2\rho}, \quad \dot\varepsilon_E^V(\theta^V) = \frac{P_{ll}^V}{2\rho}. \tag{39}$$

D. Entropy density and production

The nonequilibrium specific entropy density $\eta = h/\rho$ for the truncated system Eq. (32) is obtained from Eq. (6) as follows:

$$\eta = s^K(\rho,\theta^K) + s^R(\theta^R) + s^V(\theta^V), \tag{40}$$

where $s^K(\rho,\theta^K)$, $s^R(\theta^R)$, and $s^V(\theta^V)$ are calculated by Eq. (13). From Eq. (40) with Eq. (14), we obtain the extension of the Gibbs relation in nonequilibrium as follows:

$$d\eta = \frac{1}{\theta^K}\left(d\varepsilon^K - \frac{p^K(\rho,\theta^K)}{\rho^2\theta^K}d\rho\right) + \frac{1}{\theta^R}d\varepsilon^R + \frac{1}{\theta^V}d\varepsilon^V. \tag{41}$$

In the present case, the nonconvective part of the entropy flux is zero. Therefore, we have

$$h_i = hv_i.$$

Then the balance law of the entropy density is written as follows:

$$\rho\dot\eta = \Sigma, \tag{42}$$

where, from Eq. (22) with Eq. (34), we obtain the entropy production:

$$\Sigma = \frac{P_{ll}^K}{2\theta^K} + \frac{P_{ll}^R}{2\theta^R} + \frac{P_{ll}^V}{2\theta^V} \geqslant 0.$$

E. Production terms in the generalized BGK model

As we can prove that $f^{(7)} = f^{(7)}_{K:E}$, the relaxation time τ_K plays no role in the production term. This is natural from the *Remark 6* above. By using the collision term for the processes, Eq. (23), the production terms are given explicitly as follows:

Process (KR):

$$P_{ll}^K = -\frac{2\rho}{\tau_{KR}}\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(\theta^{KR})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(T)\right],$$
$$P_{ll}^R = -\frac{2\rho}{\tau_{KR}}\left[\varepsilon_E^R(\theta^R) - \varepsilon_E^R(\theta^{KR})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^R(\theta^R) - \varepsilon_E^R(T)\right],$$
$$P_{ll}^V = -\frac{2\rho}{\tau}\left[\varepsilon_E^V(\theta^V) - \varepsilon_E^V(T)\right], \tag{43}$$

where, from Eq. (27), θ^{KR} is determined by

$$\varepsilon_E^{K+R}(\theta^{KR}) = \varepsilon_E^K(\theta^K) + \varepsilon_E^R(\theta^R),$$

and, from Eq. (30), T is determined by

$$\varepsilon_E(T) = \varepsilon_E^K(\theta^K) + \varepsilon_E^R(\theta^R) + \varepsilon_E^V(\theta^V). \tag{44}$$

Process (KV):

$$P_{ll}^K = -\frac{2\rho}{\tau_{KV}}\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(\theta^{KV})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(T)\right],$$
$$P_{ll}^R = -\frac{2\rho}{\tau}\left[\varepsilon_E^R(\theta^R) - \varepsilon_E^R(T)\right],$$
$$P_{ll}^V = -\frac{2\rho}{\tau_{KV}}\left[\varepsilon_E^V(\theta^V) - \varepsilon_E^V(\theta^{KV})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^V(\theta^V) - \varepsilon_E^V(T)\right],$$

where, from Eq. (28), θ^{KV} is determined by

$$\varepsilon_E^{K+V}(\theta^{KV}) = \varepsilon_E^K(\theta^K) + \varepsilon_E^V(\theta^V),$$

and T is determined by Eq. (44).

Process (RV):

$$P_{ll}^K = -\frac{2\rho}{\tau}\left[\varepsilon_E^K(\theta^K) - \varepsilon_E^K(T)\right],$$
$$P_{ll}^R = -\frac{2\rho}{\tau_{RV}}\left[\varepsilon_E^R(\theta^R) - \varepsilon_E^R(\theta^{RV})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^R(\theta^R) - \varepsilon_E^R(T)\right],$$
$$P_{ll}^V = -\frac{2\rho}{\tau_{RV}}\left[\varepsilon_E^V(\theta^V) - \varepsilon_E^V(\theta^{RV})\right] - \frac{2\rho}{\tau}\left[\varepsilon_E^V(\theta^V) - \varepsilon_E^V(T)\right],$$

where, from Eq. (29), θ^{RV} is determined by

$$\varepsilon_E^{R+V}(\theta^{RV}) = \varepsilon_E^R(\theta^R) + \varepsilon_E^V(\theta^V),$$

and T is determined by Eq. (44).

VI. CHARACTERISTIC FEATURES OF ET_7

We summarize some features of the ET_7 theory.

A. Comparison with the Meixner theory

Thermodynamic theories with internal variables have been developed [5,59–62], the prototype of which is the Meixner theory [3–5]. The system of field equations of the Meixner theory with two internal variables, $\xi^{(1)}$ and $\xi^{(2)}$, is expressed as follows:

$$\begin{aligned} &\dot{\rho}+\rho\frac{\partial v_i}{\partial x_i}=0, \quad \rho\dot{v}_i+\frac{\partial \mathcal{P}}{\partial x_i}=0,\\ &\rho\dot{\mathcal{E}}+\mathcal{P}\frac{\partial v_k}{\partial x_k}=0, \quad \dot{\xi}^{(1)}=-\beta^{(1)}\mathcal{A}^{(1)},\\ &\dot{\xi}^{(2)}=-\beta^{(2)}\mathcal{A}^{(2)}, \end{aligned} \tag{45}$$

where $\mathcal{P}$, $\mathcal{E}$, and $\mathcal{A}^{(a)}(a=1,2)$ are, respectively, the pressure, the specific internal energy, and the affinities of the relaxation processes, and $\beta^{(a)}$ are positive phenomenological coefficients. The generalized Gibbs relation in the Meixner theory is assumed to be

$$\mathcal{T}d\mathcal{S}=d\mathcal{E}-\frac{\mathcal{P}}{\rho^2}d\rho-\sum_{a=1}^{2}\mathcal{A}^{(a)}d\xi^{(a)}, \tag{46}$$

where $\mathcal{T}$ is the temperature and $\mathcal{S}$ is the specific entropy. Note that the quantities $\mathcal{T}$, $\mathcal{S}$, $\mathcal{P}$, and $\mathcal{A}$ depend not only on the mass density ρ and the specific internal energy $\mathcal{E}$ but also on the internal variables $\xi^{(a)}$. From Eq. (46), with the use of Eq. (45), we obtain

$$\dot{\mathcal{S}}=\frac{1}{\mathcal{T}}\sum_{a=1}^{2}\beta^{(a)}\mathcal{A}^{(a)2}. \tag{47}$$

Comparing the system of the ET_7 theory Eqs. (39), (41), and (42) with the system of the Meixner theory Eqs. (45), (46), and (47), we have the following relationship between the Meixner theory and the ET_7 theory:

$$\begin{aligned} &\xi^{(1)}=\varepsilon_E^R(\theta^R), \quad \xi^{(2)}=\varepsilon_E^V(\theta^V), \quad \mathcal{P}=p^K(\rho,\theta^K),\\ &\mathcal{E}=\varepsilon_E(T), \quad \mathcal{S}=\eta(\rho,\theta^K,\theta^R,\theta^V),\\ &\mathcal{T}=\theta^K, \quad \mathcal{A}^{(1)}=-\theta^K\left(\frac{1}{\theta^R}-\frac{1}{\theta^K}\right),\\ &\mathcal{A}^{(2)}=-\theta^K\left(\frac{1}{\theta^V}-\frac{1}{\theta^K}\right),\\ &\beta^{(1)}=\frac{1}{2\rho\theta^K}\left(\frac{1}{\theta^R}-\frac{1}{\theta^K}\right)^{-1}P_{ll}^R,\\ &\beta^{(2)}=\frac{1}{2\rho\theta^K}\left(\frac{1}{\theta^V}-\frac{1}{\theta^K}\right)^{-1}P_{ll}^V. \end{aligned}$$

To sum up, we have identified the quantities in the Meixner theory in terms of the more understandable quantities of ET_7. In particular, the nonequilibrium temperature $\mathcal{T}$ is recognized as the temperature of the translational mode θ^K. This is reasonable because, from Eq. (46), $\mathcal{T}(=\theta^K)$ is the temperature of a state in equilibrium under a constraint that the system is kept at fixed values of $\xi^{(a)}[=\varepsilon_E^R(\theta^R),\varepsilon_E^V(\theta^V)]$.

B. Characteristic velocity, subcharacteristic conditions, and local exceptionality

It is well known that the characteristic velocity V associated with a hyperbolic system of equations can be obtained by using the operator chain rule (see Ref. [11]):

$$\frac{\partial}{\partial t}\to -V\delta, \quad \frac{\partial}{\partial x_i}\to n_i\delta, \quad \mathbf{f}\to 0,$$

where n_i denotes the i component of the unit normal to the wave front, $\mathbf{f}$ is the production terms, and δ is a differential operator [11]. In the present case, if we choose $\{\rho,v_i,\eta,\theta^R,\theta^V\}$ as independent variables instead of $\{\rho,v_i,\theta^K,\theta^R,\theta^V\}$, and adopt the entropy law Eq. (42) instead of the energy equation of the K mode in Eq. $(39)_3$, we obtain

$$\textbf{Contact Waves}: \quad V=v_n=0 \tag{48}$$

(multiplicity 5),

$$\textbf{Sound Waves}: \quad V=v_n\pm\sqrt{\left(\frac{\partial p(\rho,\theta^K(\rho,\eta,\theta^R,\theta^V))}{\partial\rho}\right)_{\eta,\theta^R,\theta^V}}$$

(each of multiplicity 1), (49)

where $v_n=v_jn_j$. Here and hereafter, p^K is denoted by p for simplicity. We can rewrite the velocity of the sound wave $U=V-v_n$ as follows:

$$U^2=p_\rho(\rho,\theta^K)+\frac{\theta^K p_{\theta^K}^2(\rho,\theta^K)}{\rho^2c_v^K(\theta^K)},$$

where a subscript attached to p indicates a partial derivative and c_v^K is the specific heat of the translational mode defined by $c_v^K(T)=d\varepsilon_E^K(T)/dT$. In an equilibrium case, we have

$$U_E^2=p_\rho(\rho,T)+\frac{Tp_T^2(\rho,T)}{\rho^2c_v^K(T)}.$$

The sound velocity of the Euler fluid is given by

$$U_{\text{Euler}}^2=p_\rho(\rho,T)+\frac{Tp_T^2(\rho,T)}{\rho^2c_v(T)},$$

where c_v is the specific heat defined by $c_v(T)=d\varepsilon_E(T)/dT$ and

$$c_v=c_v^K+c_v^R+c_v^V,$$

with the specific heat of the rotational mode c_v^R and the vibrational mode c_v^V: $c_v^R(T)=d\varepsilon_E^R(T)/dT$ and $c_v^V(T)=d\varepsilon_E^V(T)/dT$. Since the specific heats of the three modes are positive, we notice that the subcharacteristic condition [49] is satisfied:

$$U_E>U_{\text{Euler}}.$$

It is well known that a characteristic velocity associated with a wave is classified as (see, e.g., Ref. [11]): *genuinely nonlinear* if $\delta V=\nabla_{\mathbf{u}}V\cdot\delta\mathbf{u}\propto\nabla_{\mathbf{u}}V\cdot\mathbf{r}\neq 0$, $\forall\mathbf{u}$; *linearly degenerate or exceptional* if $\delta V\equiv 0$, $\forall\mathbf{u}$; *locally linearly degenerate or locally exceptional* if $\delta V=0$, for some $\mathbf{u}$, where $\mathbf{r}$ is the corresponding eigenvector associated to the system Eq. (32). The contact waves Eq. (48) are exceptional while the sound waves Eq. (49) can be locally exceptional if the condition is satisfied. Simple algebra similar to the one in

Ref. [63] gives that, if the hypersurface of local exceptionality exists, the following relation is satisfied on it:

$$\delta V = \frac{1}{2\rho^2 U}\left(\frac{\partial \rho^2 U^2}{\partial \rho}\right)_{\eta,\theta^R,\theta^V} = 0.$$

The results obtained here will be useful in the analysis of nonlinear waves such as shock waves.

C. ET_6 theories as the principal subsystems of the ET_7 theory

Let us consider the $(\mathfrak{bc})$ process $[(\mathfrak{bc}) = (KR), (KV), (RV)]$ defined in Eq. (23) again, and assume that the relaxation time τ is of several orders larger than the relaxation time $\tau_{\mathfrak{bc}}$. In such a case, the composite system of $\mathfrak{b}$ mode and $\mathfrak{c}$ mode quickly reaches a state with the common temperature $\theta^{\mathfrak{bc}}$. Therefore, except for the short period of $O(\tau_{\mathfrak{bc}})$ after the initial time, we have the relation

$$\theta^{\mathfrak{b}} = \theta^{\mathfrak{c}} = \theta^{\mathfrak{bc}}.$$

As the balance equation of the density $[\varepsilon_E^{\mathfrak{b}}(\theta^{\mathfrak{b}}) - \varepsilon_E^{\mathfrak{c}}(\theta^{\mathfrak{c}})]$ is identically satisfied in the present approximation, the remaining equations are given by

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0,$$

$$\frac{\partial \rho v_j}{\partial t} + \frac{\partial}{\partial x_i}\{(p+\Pi)\delta_{ij} + \rho v_i v_j\} = 0,$$

$$\frac{\partial}{\partial t}\{2\rho\varepsilon + \rho v^2\} + \frac{\partial}{\partial x_i}\{(2\rho\varepsilon + 2p + 2\Pi + \rho v^2)v_i\} = 0,$$

$$\frac{\partial (2\rho\mathcal{E})}{\partial t} + \frac{\partial (2\rho\mathcal{E}_i)}{\partial x_i} = P_{\mathcal{E}},$$

where $\mathcal{E}$ is the nonequilibrium energy density characterizing the relaxation process, and $\mathcal{E}_i$ and $P_{\mathcal{E}}$ are its flux and production. We may regard this system as the ET theory with six fields, which we call $ET_6^{\mathfrak{bc}}$. In Table II, three possible ET_6 theories corresponding the types of the relaxation process are summarized.

The above argument can be rigorously formulated by using the idea of the principal subsystem [10]. In the present case, ET_6 is the principal subsystem of ET_7. The crucial point is that all the universal principles of continuum thermomechanics—objectivity, entropy, and causality principles—are automatically preserved also in the subsystem.

The characteristic velocity of ET_6^{RV} is obtained as

$$U^{RV\,2} = p_\rho(\rho,\theta^K) + \frac{\theta^K p_{\theta^K}^2(\rho,\theta^K)}{\rho^2 c_v^K(\theta^K)},$$

which is the same as the characteristic velocity of ET_7: $U^{RV} = U$. On the other hand, for $ET_6^{\mathfrak{bc}}$ with $(\mathfrak{b},\mathfrak{c}) = (K,R)$ or (K,V), we obtain

$$U^{\mathfrak{bc}\,2} = p_\rho(\rho,\theta^{\mathfrak{bc}}) + \frac{\theta^{\mathfrak{bc}} p_{\theta^{\mathfrak{bc}}}^2(\rho,\theta^{\mathfrak{bc}})}{\rho^2 c_v^{\mathfrak{b}+\mathfrak{c}}(\theta^{\mathfrak{bc}})},$$

where $c_v^{\mathfrak{b}+\mathfrak{c}} = c_v^{\mathfrak{b}} + c_v^{\mathfrak{c}}$. Since $c_v > c_v^{\mathfrak{b}+\mathfrak{c}} > c_v^K$, we have the following relation in equilibrium:

$$U_E > U_E^{\mathfrak{bc}} > U_{\text{Euler}}.$$

Remark 8. The ET_6 theory studied in the previous papers [36–42] directly corresponds to the ET_6^{RV} theory in the present notation. However, it should be noted that the previous ET_6 theory may also correspond to the ET_7 theories with (KR) and (KV) processes as far as the V mode is kept in the ground state and has no role in the phenomena under study.

TABLE II. Three possible ET_6 theories.

	Process	$(\mathfrak{a},\mathfrak{b},\mathfrak{c})$	$p+\Pi$	$\mathcal{E}$	$\mathcal{E}_i$	$P_{\mathcal{E}}$
ET_6^{KR}	(KR)	(V,K,R)	$p(\rho,\theta^{KR})$	$\varepsilon_E^V(\theta^V)$	$\varepsilon_E^V(\theta^V)v_i$	P_{ll}^V
ET_6^{KV}	(KV)	(R,K,V)	$p(\rho,\theta^{KV})$	$\varepsilon_E^R(\theta^R)$	$\varepsilon_E^R(\theta^R)v_i$	P_{ll}^R
ET_6^{RV}	(RV)	(K,R,V)	$p(\rho,\theta^K)$	$\varepsilon_E^{RV}(\theta^{RV})$	$\varepsilon_E^{RV}(\theta^{RV})v_i$	$P_{ll}^R + P_{ll}^V$

D. Near-equilibrium case

In the $(\mathfrak{bc})$ process $[(\mathfrak{bc}) = (KR), (KV), (RV)]$, energy exchanges among $\mathfrak{a}$, $\mathfrak{b}$, and $\mathfrak{c}$ modes are characterized by the following quantities:

$$\delta \equiv \varepsilon_E^{\mathfrak{b}}(\theta^{\mathfrak{b}}) - \varepsilon_E^{\mathfrak{b}}(\theta^{\mathfrak{bc}}) = -\varepsilon_E^{\mathfrak{c}}(\theta^{\mathfrak{c}}) + \varepsilon_E^{\mathfrak{c}}(\theta^{\mathfrak{bc}}),$$

$$\Delta \equiv \varepsilon_E^{\mathfrak{a}}(\theta^{\mathfrak{a}}) - \varepsilon_E^{\mathfrak{a}}(T) = -\varepsilon_E^{\mathfrak{b}+\mathfrak{c}}(\theta^{\mathfrak{bc}}) + \varepsilon_E^{\mathfrak{b}+\mathfrak{c}}(T).$$

By expanding the nonequilibrium energies of the three modes with respect to the nonequilibrium temperatures around an equilibrium temperature T up to the first order, we obtain

$$\delta = c_v^{\mathfrak{b}}(\theta^{\mathfrak{b}} - \theta^{\mathfrak{bc}}) = -c_v^{\mathfrak{c}}(\theta^{\mathfrak{c}} - \theta^{\mathfrak{bc}}),$$

$$\Delta = c_v^{\mathfrak{a}}(\theta^{\mathfrak{a}} - T) = -c_v^{\mathfrak{b}+\mathfrak{c}}(\theta^{\mathfrak{bc}} - T).$$

Here and hereafter we use the notation $c_v^{\mathfrak{a}}$ instead of $c_v^{\mathfrak{a}}(T)$ and so on for simplicity. Inversely, the nonequilibrium temperatures are expressed as follows:

$$\theta^{\mathfrak{a}} - T = \frac{\Delta}{c_v^{\mathfrak{a}}}, \quad \theta^{\mathfrak{bc}} - T = -\frac{\Delta}{c_v^{\mathfrak{b}+\mathfrak{c}}},$$

$$\theta^{\mathfrak{b}} - T = \frac{\delta}{c_v^{\mathfrak{b}}} - \frac{\Delta}{c_v^{\mathfrak{b}+\mathfrak{c}}}, \quad \theta^{\mathfrak{c}} - T = -\frac{\delta}{c_v^{\mathfrak{c}}} - \frac{\Delta}{c_v^{\mathfrak{b}+\mathfrak{c}}}.$$

The production terms are now given by

$$P_{ll}^{\mathfrak{a}} = -2\rho\frac{\Delta}{\tau},$$

$$P_{ll}^{\mathfrak{b}} = -2\rho\frac{\delta}{\tau_\delta} + 2\rho\frac{c_v^{\mathfrak{b}}}{c_v^{\mathfrak{b}+\mathfrak{c}}}\frac{\Delta}{\tau},$$

$$P_{ll}^{\mathfrak{c}} = 2\rho\frac{\delta}{\tau_\delta} + 2\rho\frac{c_v^{\mathfrak{c}}}{c_v^{\mathfrak{b}+\mathfrak{c}}}\frac{\Delta}{\tau},$$

where τ_δ is defined as

$$\frac{1}{\tau_\delta} \equiv \frac{1}{\tau_{\mathfrak{bc}}} + \frac{1}{\tau}.$$

Then the entropy production is given by

$$\Sigma = \frac{\rho}{T^2}\frac{c_v^{\mathfrak{b}+\mathfrak{c}}}{c_v^{\mathfrak{b}} c_v^{\mathfrak{c}}}\frac{1}{\tau_\delta}\delta^2 + \frac{\rho}{T^2}\frac{c_v}{c_v^{\mathfrak{a}} c_v^{\mathfrak{b}+\mathfrak{c}}}\frac{1}{\tau}\Delta^2.$$

Since $c_v^K > 0$, $c_v^R > 0$ and $c_v^V > 0$, and $\tau_\delta > 0$, $\tau > 0$, the entropy production is nonnegative.

TABLE III. Explicit expression of A_1, A_2, and Π.

$(\mathfrak{bc})$	A_1	A_2	Π
(KR) or (KV)	$\frac{c_v^{\mathfrak{c}}}{c_v^{\mathfrak{b}+\mathfrak{c}}}$	0	$\frac{p_T}{c_v^{\mathfrak{b}}}\delta - \frac{p_T}{c_v^{\mathfrak{b}+\mathfrak{c}}}\Delta$
(RV)	0	c_v	$\frac{p_T}{c_v^K}\Delta$

The system of field Eqs. (39) is rewritten as follows:

$$\begin{aligned}
&\dot\rho + \rho\frac{\partial v_i}{\partial x_i} = 0,\\
&\rho\dot v_i + \frac{\partial}{\partial x_i}(p+\Pi) = 0,\\
&\rho c_v\dot T + (p+\Pi)\frac{\partial v_i}{\partial x_i} = 0,\\
&\dot\delta + \frac{p+\Pi}{\rho}\left\{A_1 + \frac{1}{c_v}\frac{d}{dT}\left(\frac{c_v^{\mathfrak{b}}}{c_v^{\mathfrak{b}+\mathfrak{c}}}\right)\Delta\right\}\frac{\partial v_i}{\partial x_i} = -\frac{\delta}{\tau_\delta},\\
&\dot\Delta + \frac{p+\Pi}{\rho}\frac{A_2 - c_v^{\mathfrak{a}}}{c_v}\frac{\partial v_i}{\partial x_i} = -\frac{\Delta}{\tau},
\end{aligned} \tag{50}$$

where $p = p(\rho,T)$, and A_1, A_2, and Π are given in Table III. In the limit $\tau_\delta \to 0$, this system reduces to the system of $\mathrm{ET}_6^{\mathfrak{bc}}$.

When we apply the Maxwellian iteration [64] on Eq. $(50)_{4,5}$ and retain the first-order terms with respect to the relaxation times τ_δ and τ, we obtain the following approximations for small relaxation times:

$$\delta = -\tau_\delta\frac{p}{\rho}A_1\frac{\partial v_i}{\partial x_i}, \quad \Delta = -\tau\frac{p}{\rho}\frac{A_2 - c_v^{\mathfrak{a}}}{c_v}\frac{\partial v_i}{\partial x_i}.$$

For $(\mathfrak{bc})$ process [$(\mathfrak{bc}) = $ (KR) or (KV)], from Eq. (37), we have

$$\begin{aligned}
&\Pi = \Pi^{\mathfrak{bc}} + \Pi^{\mathfrak{a}}, \quad \text{with}\\
&\Pi^{\mathfrak{bc}} = p(\rho,\theta^K) - p(\rho,\theta^{\mathfrak{bc}}) = -\tau_\delta p\frac{\hat c_v^{\mathfrak{c}}}{\hat c_v^{\mathfrak{b}}\hat c_v^{\mathfrak{b}+\mathfrak{c}}}\frac{\partial v_i}{\partial x_i},\\
&\Pi^{\mathfrak{a}} = p(\rho,\theta^{\mathfrak{bc}}) - p(\rho,T) = -\tau p\frac{\hat c_v^{\mathfrak{a}}}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}\hat c_v}\frac{\partial v_i}{\partial x_i},
\end{aligned}$$

where $\hat c_v = c_v/(k_B/m)$, $\hat c_v^K = c_v^K/(k_B/m)$, $\hat c_v^{K+R} = c_v^{K+R}/(k_B/m)$, and $\hat c_v^V = c_v^V/(k_B/m)$. Recalling the definition of the bulk viscosity ν,

$$\Pi = -\nu\frac{\partial v_i}{\partial x_i},$$

we have its expression as follows:

$$\nu = \tau_\delta p\frac{\hat c_v^{\mathfrak{c}}}{\hat c_v^{\mathfrak{b}}\hat c_v^{\mathfrak{b}+\mathfrak{c}}} + \tau p\frac{\hat c_v^{\mathfrak{a}}}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}\hat c_v}.$$

This expression is a generalization of the previous results [65,66]. If $\tau \gg \tau_\delta$ and $\hat c_v^{\mathfrak{a}}$ has a value of $O(1)$, the bulk viscosity is approximated by

$$\nu^{\mathfrak{a}} = \tau p\frac{\hat c_v^{\mathfrak{a}}}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}\hat c_v} = \left[\left(\tilde U_E^{\mathfrak{b}+\mathfrak{c}}\right)^2 - (\tilde U_{\mathrm{Euler}})^2\right]\tau p, \tag{51}$$

where $\tilde U_E^{\mathfrak{b}+\mathfrak{c}} = U_E^{\mathfrak{b}+\mathfrak{c}}/\sqrt{k_BT/m}$ and $\tilde U_{\mathrm{Euler}} = U_{\mathrm{Euler}}/\sqrt{k_BT/m}$. This expression can be derived also from $\mathrm{ET}_6^{\mathfrak{bc}}$.

For (RV) process, we have

$$\delta = 0, \quad \Pi = -\tau p\frac{\hat c_v^{R+V}}{\hat c_v^K\hat c_v}\frac{\partial v_i}{\partial x_i},$$

and the bulk viscosity is evaluated as

$$\nu = \tau p\frac{\hat c_v^{R+V}}{\hat c_v^K\hat c_v},$$

which is the same as the one derived from ET_6^{RV} [36,37].

E. Homogeneous solution and relaxation of nonequilibrium temperatures

To focus our attention on the behavior of the internal molecular relaxation processes, we study first a simple case: homogeneous solutions of the system Eq. (39), i.e., solutions in which the unknowns are independent of space coordinates and depend only on the time t. The system Eq. (39) reduces now to an ODE system:

$$\begin{aligned}
&\frac{d\rho}{dt} = 0, \quad \frac{d\mathbf{v}}{dt} = 0, \quad \frac{d\varepsilon_E^K(\theta^K)}{dt} = \frac{P_{ll}^K}{2\rho},\\
&\frac{d\varepsilon_E^R(\theta^R)}{dt} = \frac{P_{ll}^R}{2\rho}, \quad \frac{d\varepsilon_E^V(\theta^V)}{dt} = \frac{P_{ll}^V}{2\rho}.
\end{aligned} \tag{52}$$

The first two equations give that ρ and $\mathbf{v}$ are constant and for Galilean invariance we can assume without any loss of generality that $\mathbf{v} = 0$. Moreover, from Eq. (44), summing the last three equations of Eqs. (52), and taking into account that the sum of the productions is zero and that $\varepsilon_E(T)$ is monotonous function, we conclude that also T is constant. Therefore there remain only the last three equations of Eqs. (52) that govern the relaxation of the nonequilibrium temperatures.

For simplicity, we now assume a process near equilibrium and then consider a linearized version. Taking into account Eq. (43), we obtain the following linear ODE system:

$$\begin{aligned}
&\frac{d\bar\theta^{\mathfrak{a}}}{dt} = -\frac{1}{\tau}\bar\theta^{\mathfrak{a}},\\
&\frac{d\bar\theta^{\mathfrak{b}}}{dt} = -\frac{1}{\tau}\bar\theta^{\mathfrak{b}} - \frac{1}{\tau_{\mathfrak{bc}}}(\bar\theta^{\mathfrak{b}} - \bar\theta^{\mathfrak{bc}}),\\
&\frac{d\bar\theta^{\mathfrak{c}}}{dt} = -\frac{1}{\tau}\bar\theta^{\mathfrak{c}} - \frac{1}{\tau_{\mathfrak{bc}}}(\bar\theta^{\mathfrak{c}} - \bar\theta^{\mathfrak{bc}}),
\end{aligned} \tag{53}$$

where $\bar\theta^{\mathfrak{a}} \equiv \theta^{\mathfrak{a}} - T$, $\bar\theta^{\mathfrak{b}} \equiv \theta^{\mathfrak{b}} - T$, $\bar\theta^{\mathfrak{c}} \equiv \theta^{\mathfrak{c}} - T$, and

$$\bar\theta^{\mathfrak{bc}} \equiv \theta^{\mathfrak{bc}} - T = \frac{c_v^{\mathfrak{b}}\bar\theta^{\mathfrak{b}} + c_v^{\mathfrak{c}}\bar\theta^{\mathfrak{c}}}{c_v^{\mathfrak{b}+\mathfrak{c}}}. \tag{54}$$

The solution with the initial data $\bar\theta_0^{\mathfrak{a}} = \bar\theta^{\mathfrak{a}}|_{t=0}$, $\bar\theta_0^{\mathfrak{b}} = \bar\theta^{\mathfrak{b}}|_{t=0}$ and $\bar\theta_0^{\mathfrak{c}} = \bar\theta^{\mathfrak{c}}|_{t=0}$ is given by

$$\begin{aligned}
&\bar\theta^{\mathfrak{a}} = \bar\theta_0^{\mathfrak{a}}e^{-\hat t},\\
&\bar\theta^{\mathfrak{b}} = \frac{1}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}}\left(\hat c_v^{\mathfrak{b}}\bar\theta_0^{\mathfrak{b}} + \hat c_v^{\mathfrak{c}}\bar\theta_0^{\mathfrak{c}}\right)e^{-\hat t} + \frac{\hat c_v^{\mathfrak{c}}}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}}\left(\bar\theta_0^{\mathfrak{b}} - \bar\theta_0^{\mathfrak{c}}\right)e^{-\hat t/\hat\tau_\delta},\\
&\bar\theta^{\mathfrak{c}} = \frac{1}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}}\left(\hat c_v^{\mathfrak{b}}\bar\theta_0^{\mathfrak{b}} + \hat c_v^{\mathfrak{c}}\bar\theta_0^{\mathfrak{c}}\right)e^{-\hat t} - \frac{\hat c_v^{\mathfrak{b}}}{\hat c_v^{\mathfrak{b}+\mathfrak{c}}}\left(\bar\theta_0^{\mathfrak{b}} - \bar\theta_0^{\mathfrak{c}}\right)e^{-\hat t/\hat\tau_\delta},
\end{aligned} \tag{55}$$

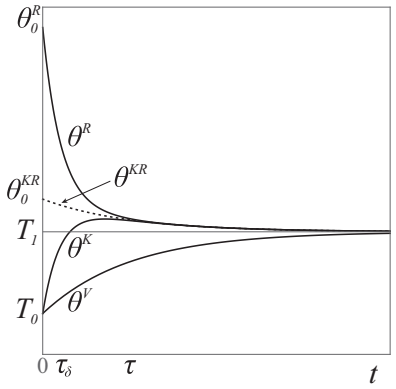

FIG. 2. Schematic time-evolution of the relaxation of the nonequilibrium temperatures $\theta^K, \theta^R, \theta^V$, and θ^{KR} in the (KR) process. The R mode is excited from T_0 to θ_0^R instantaneously at the initial time, while K and V modes are initially at the temperature T_0. Final equilibrium temperature is T_1. Relaxation times τ_δ and τ in this case are also indicated.

where

$$\hat{t} = \frac{t}{\tau}, \quad \hat{\tau}_\delta = \frac{\tau_\delta}{\tau} = \frac{\tau_{\mathfrak{bc}}/\tau}{1+\tau_{\mathfrak{bc}}/\tau}.$$

We have also the following relations:

$$\begin{aligned} \bar{\theta}^{\mathfrak{b}} - \bar{\theta}^{\mathfrak{bc}} &= \frac{\hat{c}_v^{\mathfrak{c}}}{\hat{c}_v^{\mathfrak{b}+\mathfrak{c}}}\left(\bar{\theta}_0^{\mathfrak{b}} - \bar{\theta}_0^{\mathfrak{c}}\right)e^{-\hat{t}/\hat{\tau}_\delta}, \\ \bar{\theta}^{\mathfrak{c}} - \bar{\theta}^{\mathfrak{bc}} &= -\frac{\hat{c}_v^{\mathfrak{b}}}{\hat{c}_v^{\mathfrak{b}+\mathfrak{c}}}\left(\bar{\theta}_0^{\mathfrak{b}} - \bar{\theta}_0^{\mathfrak{c}}\right)e^{-\hat{t}/\hat{\tau}_\delta}. \end{aligned} \tag{56}$$

As is expected, we can clearly see, from Eqs. (55), (56), and (54), that the temperatures $\theta^{\mathfrak{b}}$ and $\theta^{\mathfrak{c}}$ relax to the temperature $\theta^{\mathfrak{bc}}$ with the relaxation time τ_δ, while the temperatures $\theta^{\mathfrak{bc}}$ and $\theta^{\mathfrak{a}}$ relax to the equilibrium temperature T with the relaxation time τ.

From experimental data on polyatomic gases such as CO_2, Cl_2, Br_2 gases, the (KR) process is a suitable process [54,55] (see also the analysis in Sec. VII). Therefore, as a typical example, we particularly focus on this process and study the relaxation evolved from a nonequilibrium initial state: $\theta^K|_{t=0} = \theta^V|_{t=0} = T_0$, $\theta^R|_{t=0} = \theta_0^R$ ($> T_0$). This initial state may be generated experimentally as follows: we first prepare the equilibrium state with the temperature with T_0, then we excite only the R mode from the temperature T_0 to the temperature θ_0^R instantaneously at the initial time. The relaxation is analyzed by solving Eq. (53) under the initial condition, in which T should be replaced by T_1. From the condition Eq. (44), T_1 is given by

$$T_1 = T_0 + \frac{c_v^R\left(\theta_0^R - T_0\right)}{c_v}.$$

The time-evolution of the relaxation is shown schematically in Fig. 2, from which we understand the two-step relaxation, and the energy redistribution from the R mode to the K and V modes. We also notice that, after the elapse of a period of time of $O(\tau_\delta)$ from the initial time, the relation $\theta^K = \theta^R = \theta^{KR}$ is approximately satisfied. Therefore, the results derived from ET_6^{KR} and ET_7 with (KR) process are nearly the same with each other. This means that ET_7 can be safely replaced by the simpler theory, ET_6^{KR}.

VII. DISPERSION AND ATTENUATION OF ULTRASONIC WAVE: AN APPLICATION OF ET_7

We derive the dispersion relation of a plane harmonic wave in Sec. VII A, and discuss its general features in Sec. VII B. Theoretical prediction of the attenuation per wavelength α_λ is compared with the experimental data in the case of CO_2 [67], Cl_2, and Br_2 [68] gases in Sec. VII C.

A. Dispersion relation

Let us study a plane harmonic wave propagating along the x axis expressed by

$$\boldsymbol{u} = \boldsymbol{u}_0 + \bar{\boldsymbol{u}},$$

where $\boldsymbol{u} = (\rho, v, T, \delta, \Delta)$ is a state vector with v being the x component of the velocity v_i, and $\boldsymbol{u}_0 = (\rho_0, 0, T_0, 0, 0)$ is a state vector at a reference equilibrium state at rest. The deviation $\bar{\boldsymbol{u}} = (\bar{\rho}, \bar{v}, \bar{T}, \bar{\delta}, \bar{\Delta})$ from $\boldsymbol{u}_0$ is expressed by

$$\bar{\boldsymbol{u}} = \boldsymbol{w}e^{\mathrm{i}(\omega t - kx)},$$

where $\boldsymbol{w}$ is the amplitude vector, ω is the angular frequency, and k is the complex wave number: $k = \mathrm{Re}(k) + \mathrm{iIm}(k)$ being $\mathrm{Re}(k)$ and $\mathrm{Im}(k)$ the real and imaginary parts of k.

From the linearized system of field equations with respect to $\bar{\boldsymbol{u}}$, we obtain the dispersion relation, derivation method of which is given in Ref. [69]:

$$\frac{1}{(zU_{\mathrm{Euler}})^2} = \begin{cases} 1 + \left(\hat{U}_E^2 - \hat{U}_E^{\mathfrak{bc}^2}\right)\frac{\mathrm{i}\Omega\hat{\tau}_\delta}{1+\mathrm{i}\Omega\hat{\tau}_\delta} + \left(\hat{U}_E^{\mathfrak{bc}^2} - 1\right)\frac{\mathrm{i}\Omega}{1+\mathrm{i}\Omega} & \text{for } (\mathfrak{bc}) \text{ process } [(\mathfrak{bc}) = \text{(KR) or (KV)}], \\ 1 + \left(\hat{U}_E^2 - 1\right)\frac{\mathrm{i}\Omega}{1+\mathrm{i}\Omega} & \text{for (RV) process,} \end{cases}$$

where $z \equiv k/\omega$, $\Omega \equiv \omega\tau$, and the dimensionless characteristic velocities: $\hat{U}_E \equiv U_E/U_{\mathrm{Euler}}$ and $\hat{U}_E^{\mathfrak{bc}} \equiv U_E^{\mathfrak{bc}}/U_{\mathrm{Euler}}$ given by

$$\hat{U}_E^2 = \frac{\hat{c}_v}{\hat{c}_v^K}\frac{1+\hat{c}_v^K}{1+\hat{c}_v}, \quad \hat{U}_E^{\mathfrak{bc}^2} = \frac{\hat{c}_v}{\hat{c}_v^{\mathfrak{b}+\mathfrak{c}}}\frac{1+\hat{c}_v^{\mathfrak{b}+\mathfrak{c}}}{1+\hat{c}_v}.$$

For (RV) process, δ does not play any role in the dispersion relation as seen from the linearized equations of Eqs. (50).

From the dispersion relation, the phase velocity v_{ph}, the attenuation factor α, and the attenuation per wavelength α_λ are derived by using the relations:

$$v_{\mathrm{ph}} = \frac{\omega}{\mathrm{Re}(k)}, \quad \alpha = -\mathrm{Im}(k), \quad \alpha_\lambda = \frac{2\pi v_{\mathrm{ph}}\alpha}{\omega} = -2\pi\frac{\mathrm{Im}(k)}{\mathrm{Re}(k)}.$$

In the high-frequency limit $\Omega \to \infty$, we have

$$v_{\mathrm{ph},\infty} \equiv \lim_{\omega\to\infty} v_{\mathrm{ph}} = \pm U_E, \quad \alpha_\infty \equiv \lim_{\omega\to\infty} \alpha = \begin{cases} \pm \frac{1}{2U_{\mathrm{Euler}}\tau} \frac{\hat{U}_E^2 - \hat{U}_E^{\mathfrak{b}\mathfrak{c}^2} + \hat{\tau}_\delta(\hat{U}_E^{\mathfrak{b}\mathfrak{c}^2}-1)}{\hat{U}_E^3 \hat{\tau}_\delta} & \text{for } (\mathfrak{b}\mathfrak{c}) \text{ process } [(\mathfrak{b}\mathfrak{c}) = (\mathrm{KR}) \text{ or } (\mathrm{KV})], \\ \pm \frac{1}{2U_{\mathrm{Euler}}\tau} \frac{\hat{U}_E^2 - 1}{\hat{U}_E^3} & \text{for (RV) process.} \end{cases}$$

In a similar way, we can also derive the dispersion relations of the ET_6 theories explained in Sec. VI C, explicit expressions of which are omitted here for simplicity. A remarkable point is as follows: the dispersion relation of ET_6^{RV} [70] coincides with the dispersion relation of ET_7 with (RV) process. While the dispersion relation of $\mathrm{ET}_6^{\mathfrak{b}\mathfrak{c}}$ $[(\mathfrak{b}\mathfrak{c}) = (KR) \text{ or } (KV)]$ is obtained from the dispersion relation of ET_7 with $(\mathfrak{b}\mathfrak{c})$ process by taking the limit $\tau_\delta \to 0$.

B. Qualitative description of the dispersion relation

In this subsection, we discuss the general features of the dispersion relation by studying some typical cases so that we may address the following two questions: (i) For given experimental data, how can we determine the most suitable relaxation process among possible (KR), (KV), (RV) processes? (ii) What is the relationship between the applicability ranges of ET_7 and ET_6 theories?

In the above, we have noticed that the dispersion relation depends on the temperature through the specific heats. Therefore, before going into the main discussions, we remark here on the estimation method of the specific heats. As usual in thermodynamics, we may use the experimental data on the specific heats. However, for a simple gas like a homonuclear diatomic molecule gas, which we adopt in this subsection, the specific heats can be estimated by the statistical-mechanical considerations. That is, the specific heats c_v^R and c_v^V are evaluated by using the rotational and vibrational partition functions Z^R and Z^V as follows:

$$\begin{aligned} c_v^R(T) &= \frac{k_B}{m}\beta_E^2 \frac{\partial^2 Z^R}{\partial \beta_E^2}, \quad \text{with} \quad Z^R = Z_g^{\frac{s_n}{2s_n+1}} Z_u^{\frac{s_n+1}{2s_n+1}}, \\ Z_g &= \sum_{l=\mathrm{even}}^{\infty} (2l+1) e^{-k_B\Theta_R\beta_E l(l+1)}, \\ Z_u &= \sum_{l=\mathrm{odd}}^{\infty} (2l+1) e^{-k_B\Theta_R\beta_E l(l+1)}, \\ c_v^V(T) &= \frac{k_B}{m}\beta_E^2 \frac{\partial^2 Z^V}{\partial \beta_E^2}, \quad \text{with} \\ Z^V &= \prod_{i=1}^{N} \frac{e^{-k_B\Theta_{V_i}\beta_E/2}}{1 - e^{-k_B\Theta_{V_i}\beta_E}}, \end{aligned} \tag{57}$$

where s_n, Θ_R, and Θ_{V_i} are, respectively, the nuclear spin, the characteristic rotational temperature, and vibrational temperature of the ith harmonic mode. In the case of diatomic molecules with $s_n = 1/2$ and $N = 1$, a typical temperature dependence of the specific heats c_v, c_v^{K+R}, and c_v^{K+V} is shown in Fig. 3.

Let us study the temperature dependence of the phase velocity $v_{\mathrm{ph}}(\omega)$ and the attenuation per wavelength $\alpha_\lambda(\omega)$ in the five typical cases listed in Table IV. The temperature of the reference equilibrium state $\boldsymbol{u}_0$ increases from the case (A) to the case (E) as seen in Fig. 3.

As many experimental data [7] indicate that the ratio of the relaxation times $\hat{\tau}_\delta$ is $O(10^{-3})$ or more (see Sec. VII C for (KR) process), we assume here that $\hat{\tau}_\delta = 10^{-3}$ for all processes. Therefore, we can observe the slow and fast relaxation processes separately. In fact, we expect that the dispersion relation has a remarkable change at around $\Omega \sim O(1)$ $[\omega \sim O(\tau^{-1})]$ and $\Omega \sim O(10^3)$ $[\omega \sim O(\tau_\delta^{-1})]$. See also *Remark 9* below.

In Fig. 4, the dimensionless phase velocity $\hat{v}_{\mathrm{ph}} = v_{\mathrm{ph}}/U_{\mathrm{Euler}}$ and the attenuation per wavelength α_λ predicted by ET_7 with (KR), (KV), and (RV) processes in the five cases (A)–(E) are shown.

Noticeable points are summarized as follows:

(1) Among the three relaxation processes, i.e., (KR), (KV), and (RV) processes, the dependence of the curve $v_{\mathrm{ph}}(\omega)$ on the temperature is quite different from each other. In other words, each relaxation process has its own characteristic temperature dependence of the curve $v_{\mathrm{ph}}(\omega)$. Conversely, experimental data on such a temperature dependence can afford a suitable method to identify the relaxation process in a gas under study.

(2) The dependence of the curve $\alpha_\lambda(\omega)$ on the temperature is also quite different from each other among the three relaxation processes. Experimental data on such a temperature dependence can afford another suitable method to identify the relaxation process in a gas under study. To be more precise, let us focus on the temperature dependence of the value of α_λ at its peak in the low frequency region, i.e., the left peak in Fig. 4. The peak value $\alpha_\lambda^{\mathrm{peak}}$ attained at $\Omega = \Omega^{\mathrm{peak}}$ is explicitly

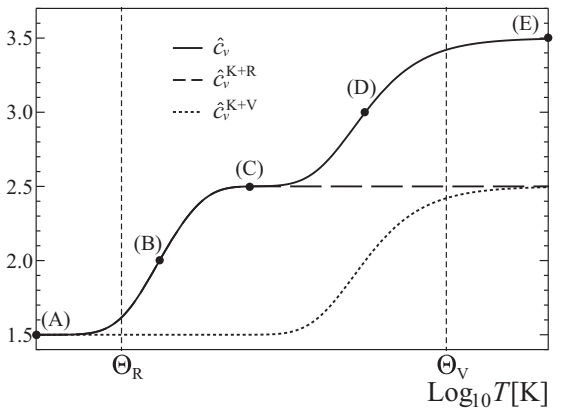

FIG. 3. Typical temperature dependence of the dimensionless specific heats; $\hat{c}_v$, $\hat{c}_v^{K+R}$, and $\hat{c}_v^{K+V}$. The five cases (A)–(E) listed in Table IV are also indicted.

TABLE IV. Five typical cases. Translational mode is fully excited in all cases.

Case	Specific heats	Rotational mode	Vibrational mode
(A)	$\hat{c}_v^K = 3/2, \hat{c}_v^R = 0, \hat{c}_v^V = 0$	Ground state	Ground state
(B)	$\hat{c}_v^K = 3/2, \hat{c}_v^R = 1/2, \hat{c}_v^V = 0$	Partly excited	Ground state
(C)	$\hat{c}_v^K = 3/2, \hat{c}_v^R = 1, \hat{c}_v^V = 0$	Fully excited	Ground state
(D)	$\hat{c}_v^K = 3/2, \hat{c}_v^R = 1, \hat{c}_v^V = 1/2$	Fully excited	Partly excited
(E)	$\hat{c}_v^K = 3/2, \hat{c}_v^R = 1, \hat{c}_v^V = 1$	Fully excited	Fully excited

given by

$$\alpha_\lambda^{\text{peak}} = 2\pi \frac{\hat{U}_E^{\mathfrak{bc}} - 1}{\hat{U}_E^{\mathfrak{bc}} + 1} \left(\Omega^{\text{peak}} = \frac{1}{\hat{U}_E^{\mathfrak{bc}}} \right)$$
$$[(\mathfrak{bc}) = (KR),(KV),(RV)],$$

and its temperature dependence is shown in Fig. 5.

(3) From the remark about the dispersion relation of ET_6 in Sec. VII A and the curves of ET_7 shown in Fig. 4, we conclude that the ET_6 theories are reliable in the frequency region $\Omega < O(10^1)$, where ET_6 theories are quite good approximation

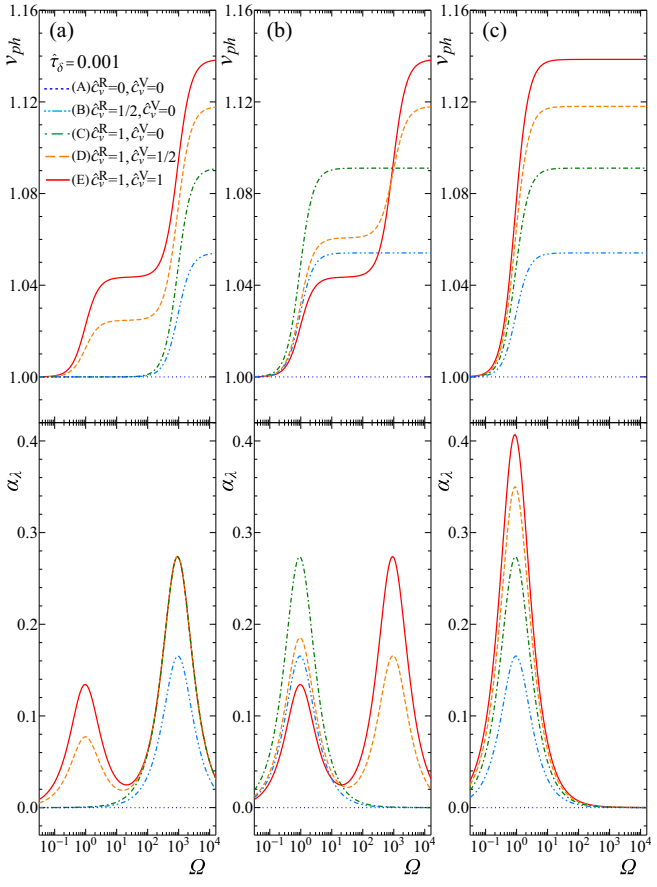

FIG. 4. Dimensionless phase velocity $\hat{v}_{\text{ph}} = v_{\text{ph}}/U_{\text{Euler}}$ and the attenuation per wavelength α_λ for (a) (KR) process, (b) (KV) process, and (c) (RV) process in the five cases (A)–(E) listed in Table IV. The ratio of the relaxation time $\hat{\tau}_\delta$ is 10^{-3}.

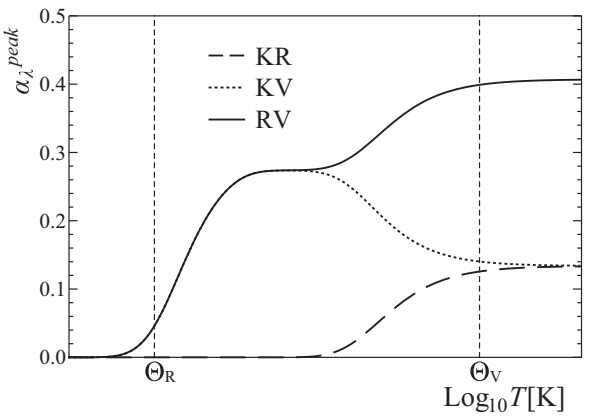

FIG. 5. Temperature dependence of $\alpha_\lambda^{\text{peak}}$ for (KR), (KV), and (RV) processes. The characteristic rotational and vibrational temperatures are denoted as Θ_R and Θ_V.

of the ET_7 theory. It should be emphasized that even in this frequency region we should pick up a suitable ET_6 theory among the three theories by using the methods mentioned above. When we go into higher frequency region $\Omega > O(10^1)$, we should adopt the the ET_7 theory instead of the ET_6 theory. This is true especially for (KR) and (KV) processes.

To sum up, we have proposed the selection methods for the most suitable relaxation process and made clear the applicability ranges of ET_6 and ET_7 theories. Finally, we point out that the general features of the dispersion relation discussed above can be found not only diatomic gases but also in polyatomic gases because such features come mainly from the global dependence of the specific heats on the temperature.

Remark 9. In Fig. 6, we show the dependence of α_λ on the ratio of the relaxation times $\hat{\tau}_\delta$ in the case of the (KR) process for an example. We notice from the figure that, when the ratio increases, two peaks gradually coalesce into a big one. In such a case the prediction of ET_6^{KR} is no longer valid even in the frequency region $\Omega < O(10^1)$, and ET_7 should be used.

Remark 10. As explained in Sec. V, the ET_7 theory neglects the so-called classical absorption, that is, the attenuation due to the shear viscosity and the heat conduction. For gases in which these effect emerges in the higher frequency region $\Omega \gg O(10^1)$ such as H_2 and CO_2 [32,33], there is a possibility

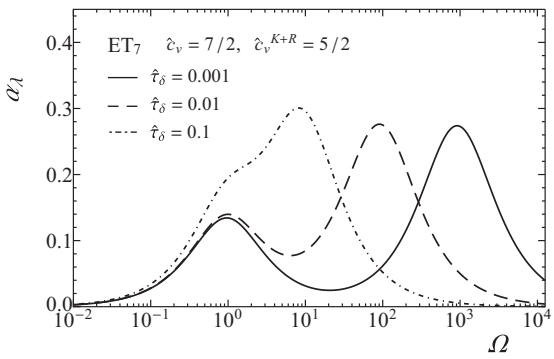

FIG. 6. Dependence of α_λ for (KR) process on Ω with $\hat{c}_v = 7/2$ and $\hat{c}_v^{K+R} = 5/2$. The solid, dashed, and dotted lines indicate, respectively, the cases with $\hat{\tau}_\delta = 0.001, 0.01$, and 0.1.

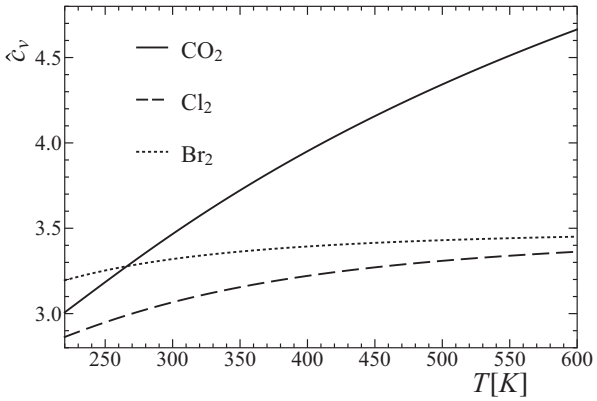

FIG. 7. Dependence of $\hat{c}_v$ on T.

that two peaks from this and from the rapid relaxation studied above, i.e., the right peak in Fig. 4 coalesce into one. Because of this, in the above, we have focused on the temperature dependence of the peak value of α_λ in the low frequency region. On the other hand, there is another possibility: for gases in which the effects of shear viscosity and heat conduction emerge around $\Omega \sim O(1)$, the peaks from this and from the left peak in Fig. 4 coalesce into one. Moreover, if $\hat{\tau}_\delta \sim O(1)$, all three peaks coalesce into one. In the next paper, we will study such combined effects in detail.

C. Comparison with experimental data

We compare the theoretical prediction of α_λ by ET_7 with the experimental data of CO_2 [67], Cl_2, and Br_2 gases [68].

As a preliminary step, we evaluate the specific heats of CO_2, Cl_2, and Br_2 gases by the statistical-mechanical method. In these gases, the characteristic rotational temperature Θ_R is very low. In fact, from the data on the rotational constant at the ground state [71], it is estimated as 0.56K for CO_2, 0.35K for Cl_2, and 0.12K for Br_2. Therefore, in the temperature range higher than the room temperature, the rotational degrees of freedom of these gases are in a fully excited state with $\hat{c}_v^{K+R} = 5/2$. While the temperature dependence of the vibrational specific heat is approximately calculated by Eq. (57). For CO_2 molecule with $N = 4$, the characteristic vibrational temperatures are given by $\Theta_{V_1} = \Theta_{V_2} = 960$ K, $\Theta_{V_3} = 1997$ K, and $\Theta_{V_4} = 3380$ K [71]. For Cl_2 and Br_2 molecules with $N = 1$, the characteristic vibrational temperatures are, respectively, $\Theta_V = 805$ K and $\Theta_V = 468$ K [71]. The temperature dependence of $\hat{c}_v$ is shown in Fig. 7.

Applying the selection method mentioned above to the experimental data on α_λ [67,68], we conclude that these gases have the (KR) process and the relaxation time τ is several orders larger than the relaxation time τ_δ. Therefore, as the present comparison is made only in the low frequency region, we may safely assume $\hat{\tau}_\delta = 10^{-3}$.

As the experimental data are summarized as the relationship between α_λ and f/p [Hz/Pa] ($f = \omega/2\pi$) [67,68], we use the quantity ω/p instead of Ω. Recalling that $\Omega = (\tau p)(\omega/p)$, we adopt the quantity τp as a fitting parameter determined by the least square method.

The comparison is made in Fig. 8. These figures show the excellent agreement between the theoretical prediction of ET_7

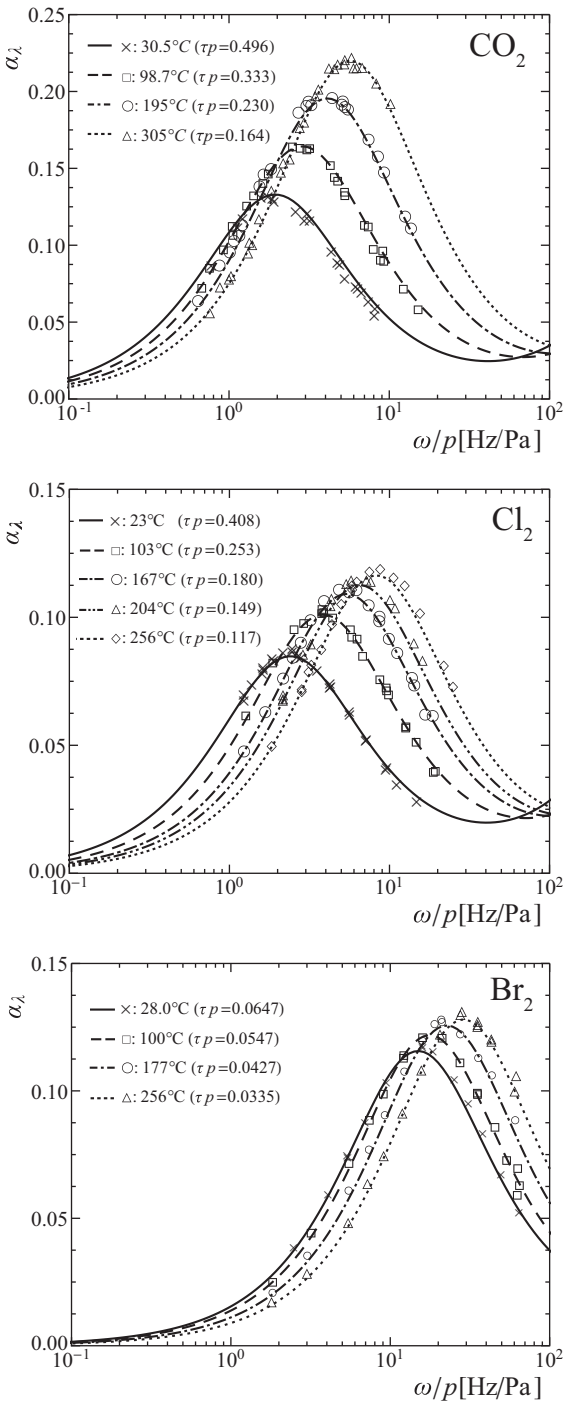

FIG. 8. Dependence of α_λ on ω/p [Hz/Pa] for several temperatures with $\hat{c}_v^{K+R} = 5/2$, $\hat{\tau}_\delta = 10^{-3}$ in rarefied CO_2, Cl_2, and Br_2 gases [67,68]. A parameter $p\tau$ is chosen to fit the experimental data by the least-square method.

and the experimental data. The selected parameter τp and the bulk viscosity ν^V estimated by using Eq. (51) are summarized in Table V. We also emphasize the importance of the dynamic pressure in the wave propagation phenomena. This is because the bulk viscosity coefficients of CO_2, Cl_2, and Br_2 gases are much larger than the shear viscosity coefficients that are estimated as 1.49×10^{-5}[Pa · s] for CO_2, 1.363×10^{-5} [Pa·s]

TABLE V. The parameter τp and the bulk viscosity.

Gas	T [°C]	τp [Pa · s]	ν^V [Pa · s]
CO_2	30.5	4.96×10^{-1}	5.61×10^{-2}
	98.7	3.33×10^{-1}	4.62×10^{-2}
	195	2.30×10^{-1}	3.75×10^{-2}
	305	1.64×10^{-1}	2.99×10^{-2}
Cl_2	23	4.08×10^{-1}	2.98×10^{-2}
	103	2.53×10^{-1}	2.19×10^{-2}
	167	1.80×10^{-1}	1.68×10^{-2}
	204	1.49×10^{-1}	1.43×10^{-2}
	256	1.17×10^{-1}	1.16×10^{-2}
Br_2	28.0	6.47×10^{-2}	6.40×10^{-3}
	100	5.47×10^{-2}	5.69×10^{-3}
	177	4.27×10^{-2}	4.57×10^{-3}
	256	3.35×10^{-2}	3.65×10^{-3}

for Cl_2, and 9.42×10^{-4}[Pa · s] for Br_2 at $T = 298$ K and $p = 1$ atm [72].

Remark 11. Many studies of the dispersion relation of sound in polyatomic gases have been made basing on nonequilibrium thermodynamics and/or the kinetic theory [1,73,74]. Except for different definitions of the relaxation times, these theories equally describe well the absorption of sound due to the energy exchange among the degrees of freedom of a molecule up to some limited frequency [7,53] (see also Ref. [75] for the classification of the previous studies). In particular, the Meixner theory with the relaxation processes of the molecular internal energies [3,4] has been used to describe the attenuation of sound phenomenologically. As shown in the present paper, by using the correspondence relationship between the Meixner theory and the ET_7 theory discussed in Sec. VI A, the Meixner theory seems to be valid also for phenomena out of local equilibrium to which ET_7 is applicable. However, as remarked above, in the high-frequency region where shear viscosity and heat conduction play roles, the ET theory with more independent variables becomes indispensable because there exists no such correspondence relationship.

VIII. SUMMARY AND OUTLOOK

The ET theory of rarefied polyatomic gases with two molecular relaxation processes for the rotational and vibrational modes has been constructed. We have introduced the generalized BGK model for the collision term. After discussing the general structure of the ET theory with the triple hierarchy, we have established, in particular, the ET_7 theory. This theory includes three six-field theories as special cases depending on the molecular collisional process. Finally, as an application of the ET_7 theory, the dispersion relation of ultrasonic wave has been derived, and excellent agreement between its theoretical prediction and the experimental data of CO_2, Cl_2, and Br_2 gases has been confirmed.

In our plan, the present paper is the first one in a series of papers. We will report the following studies: (i) As mentioned above, by using the triple hierarchy, more sophisticated ET theory including also the shear stress and heat flux as independent variables will soon be reported. (ii) In linear waves, the excitations of the translational, rotational, and vibrational modes from a reference state are small. However, the ET theory can be also applied to the phenomena in which large excitations take place. In this respect, shock wave phenomena is worth studying. In Ref. [38], peculiar shock wave structure in a polyatomic gas was studied by the ET_6 theory. When we analyze the shock wave phenomena by the present ET_7 theory, we can find a more detailed shock wave structure, in particular, in the relaxation region after the subshock. (iii) The ET theory of dense polyatomic gases with two molecular relaxation processes will also be constructed by using the duality principle developed in Ref. [58].

ACKNOWLEDGMENTS

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APPENDIX: PROOF OF STATEMENT 2

Let us introduce the Lagrange multipliers $\{\lambda, \lambda_i, \mu^K(\equiv \lambda_{ll}/3), \mu^R, \mu^V\}$ that correspond to the densities $\{F, F_i, F_{ll}, H^R_{ll}, H^V_{ll}\}$. The velocity dependence of the Lagrange multipliers Eq. (20) is explicitly expressed as follows:

$$\lambda = \hat{\lambda} - \hat{\lambda}_i v_i + \hat{\mu}^K v^2, \quad \lambda_i = \hat{\lambda}_i - 2\hat{\mu}^K v_i,$$
$$\mu^K = \hat{\mu}^K, \quad \mu^R = \hat{\mu}^R, \quad \mu^V = \hat{\mu}^V.$$

From Eq. (19), it is possible to express the distribution function of the truncated system Eq. (32) as follows:

$$f^{(7)} = \Omega e^{-\eta_i C_i} e^{-\beta^K \frac{mC^2}{2}} e^{-\beta^R I^R} e^{-\beta^V I^V}, \tag{A1}$$

where

$$\Omega = \exp\left(-1 - \frac{m}{k_B}\hat{\lambda}\right), \quad \eta_i = \frac{m}{k_B}\hat{\lambda}_i,$$
$$\beta^K = \frac{2}{k_B}\hat{\mu}^K, \quad \beta^R = \frac{2}{k_B}\hat{\mu}^R, \quad \beta^V = \frac{2}{k_B}\hat{\mu}^V.$$

In addition, we introduce the following three parameters θ^K, θ^R, and θ^V through β^K, β^R, and β^V as follows:

$$\theta^K = \frac{1}{k_B\beta^K}, \quad \theta^R = \frac{1}{k_B\beta^R}, \quad \theta^V = \frac{1}{k_B\beta^V}.$$

Recalling Eq. (8) and substituting Eq. (A1) into Eq. (31) evaluated at zero velocity, we obtain $\eta_i = 0$ and

$$\rho = m\left(\frac{2\pi k_B\theta^K}{m}\right)^{3/2} A^R(\theta^R)A^V(\theta^V)\Omega,$$
$$\varepsilon^K(\theta^K) = \frac{3}{2}\frac{k_B}{m}\theta^K,$$
$$\varepsilon^R(\theta^R) = \frac{k_B}{m}\theta^{R2}\frac{d\log A^R(\theta^R)}{d\theta^R},$$
$$\varepsilon^V(\theta^V) = \frac{k_B}{m}\theta^{V2}\frac{d\log A^V(\theta^V)}{d\theta^V}.$$

These indicate that θ^K, θ^R, and θ^V are the nonequilibrium temperatures of K, R, and V modes, respectively. Then Ω, β^K, β^R, and β^V are expressed in terms of ρ, θ^K, θ^R,

and θ^V as follows:

$$\Omega = \frac{\rho}{mA^R(\theta^R)A^V(\theta^V)}\left(\frac{m}{2\pi k_B\theta^K}\right)^{3/2}, \quad \beta^K = \frac{1}{k_B\theta^K}, \quad \beta^R = \frac{1}{k_B\theta^R}, \quad \beta^V = \frac{1}{k_B\theta^V},$$

and we finally obtain the nonequilibrium distribution function Eq. (33).

The Lagrange multipliers are expressed in terms of the independent fields as follows:

$$\hat{\lambda} = -\frac{k_B}{m}(1+\log\Omega), \quad \hat{\mu}^K = \frac{1}{2\theta^K}, \quad \hat{\mu}^R = \frac{1}{2\theta^R}, \quad \hat{\mu}^V = \frac{1}{2\theta^V}.$$

Recalling Eq. (13) with Eq. (35), we obtain the following relations:

$$\frac{k_B}{m}\log\left[\frac{m}{\rho}\left(\frac{2\pi k_B\theta^K}{m}\right)^{3/2}\right] = s_E^K(\rho,\theta^K) - \frac{\varepsilon_E^K(\theta^K)}{\theta^K} = -\frac{g_E^K(\rho,\theta^K)}{\theta^K},$$

$$\frac{k_B}{m}\log A^R(\theta^R) = s_E^R(\theta^R) - \frac{\varepsilon_E^R(\theta^R)}{\theta^R} = -\frac{g_E^R(\theta^R)}{\theta^R},$$

$$\frac{k_B}{m}\log A^V(\theta^V) = s_E^R(\theta^V) - \frac{\varepsilon_E^V(\theta^V)}{\theta^V} = -\frac{g_E^V(\theta^V)}{\theta^V},$$

and the relations Eq. (34) have been derived.

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