PHYSICAL REVIEW FLUIDS **2**, 013401 (2017)

Duality principle from rarefied to dense gas and extended thermodynamics with six fields

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(Received 23 July 2016; published 19 January 2017)

We present an extended thermodynamics (ET) theory of dissipative dense gases. In particular, we study the ET theory with six fields, where we neglect shear viscosity and heat conductivity. We postulate a simple principle of duality between rarefied and dense gases. This principle is based on the microscopic analysis of the energy exchange between different modes of the molecular motion. The basic system of equations satisfies all principles of ET, that is, Galilean invariance, entropy principle, and thermodynamic stability (entropy convexity), and, as in the ET theory of rarefied gases, the constitutive equations are completely determined by the thermal and caloric equations of state. The system is simplest after the Euler system, but, in contrast to the Euler system, we may have a global smooth solution due to the fact that the system is dissipative symmetric hyperbolic and satisfies the so-called K condition. There emerge two nonequilibrium temperatures; one is due to the translational modes, and the other is due to the internal modes such as rotation and vibration of a molecule. This viewpoint allows us to understand the origin of the dynamic pressure in a more clear way. Furthermore we evaluate the characteristic velocities associated with the hyperbolic system and address the fluctuation-dissipation relation of the bulk viscosity. As a typical example, we analyze van der Waals fluids based on the present theory.

DOI: 10.1103/PhysRevFluids.2.013401

I. INTRODUCTION

The main objective of extended thermodynamics (ET) [1,2] is to study highly nonequilibrium phenomena that are out of range of thermodynamics of irreversible processes (TIPs) based on the local equilibrium assumption [3]. The ET theory of gases adopts dissipative fluxes such as viscous stress and heat flux as independent variables in addition to the usual hydrodynamic ones. Then a closed system of balance equations with local-type constitutive equations is established so as to satisfy strictly the universal physical principles: (1) the Galilean invariance and the objectivity principle, (2) the entropy principle, and (3) the causality and thermodynamic stability (i.e., convexity of the entropy). In particular, the classical Navier-Stokes-Fourier (NSF) theory, which is a typical theory of TIP, is deduced from the ET theory as a limiting case of small relaxation times.

For rarefied monatomic gases, in the ET theory [1], the same hierarchy structure of the balance equations is adopted as in the moment theory based on the Boltzmann equation such as Grad's moment theory [4] although the phenomenological independent variables are not the moments of

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the distribution function. The features of the system of balance equations are that (1) the tensorial rank of the equations increases one by one starting from the mass balance equation and (2) the flux in one equation becomes the density in the next equation. The prototype of the phenomenological ET theory is the 13-field theory that adopts the mass density, velocity, internal energy, shear stress, and heat flux as independent fields [5]. The ET theory in the relativistic framework also has been proposed in Ref. [6]. Moreover, in order to describe highly nonequilibrium phenomena such as ultrasonic waves and shock waves with large Mach numbers, the so-called molecular ET theory, which describes a state of a gas by the moments of a distribution function, has been proposed [7]. The closure of molecular ET is achieved by using the maximum entropy principle [7,8], which was proved to be equivalent to the entropy principle [9].

A recent complementary approach of molecular ET is Ref. [10] in which it is proved that the infinite hierarchy of moments possesses a Hamiltonian structure.

Recently, the ET theory of rarefied polyatomic gases and moderately dense gases has been proposed [2,11–13]. This theory adopts the balance equations with a binary hierarchy structure where the existence of the dynamic pressure (nonequilibrium pressure) is properly taken into account. The number of independent fields is now 14: the mass density, velocity, internal energy, dynamic pressure, shear stress, and heat flux. One of the hierarchies consists of the balance equations for mass density, momentum density, and momentum flux, and the other one consists of the balance equations for energy density and energy flux. Each hierarchy of the balance equations has also the features (1) and (2) above.

This binary hierarchy was introduced in previous simple model [14], in kinetic approach [15], and, for the first time, in the phenomenological 14-field theory [11]. This hierarchy has a mesoscopic motivation [16] in the generalized kinetic theory where the distribution function depends on an extra variable that takes into account the internal degrees of freedom of a molecule such as rotation and vibration [17,18]. The molecular ET theory of rarefied polyatomic gases with any number of fields has been established in Refs. [19,20], and the convergence to the singular limit of monatomic gas when the degrees of freedom $D \to 3$ was proved [21].

The validity of the 14-field theory of rarefied polyatomic gases has been successfully confirmed by comparing the theoretical predictions to the experimental data of linear waves [22], shock waves [23], and light scattering [24] in the region where the NSF theory fails.

For dense gases, however, the present status of the ET theory is not quite satisfactory because the theory is valid only for moderately dense gases. It was shown that the convexity region of the entropy density in the ET theory of dense gases covers only the limited stable region in the state space. For example, the theory cannot be applied to the hard-sphere system with large mass density [2,11–13]. It was discovered that this difficulty comes from the convexity condition relating to the dynamic pressure. Therefore one of the big challenges in the study of ET is to construct an ET theory of dense gases that is valid in a wider region in the state space.

The role of the dynamic pressure has been studied by the ET theory with six fields (ET_6): mass density, velocity, specific internal energy, and dynamic pressure [25–27]. This theory is the simplest extension of the Euler theory and is compatible with the Meixner theory with one internal variable [28,29]. The correspondence relation between ET_6 and the Meixner theory was shown explicitly in Ref. [25]. Recently the ET_6 theory with a nonlinear constitutive equation was proposed and developed [30–33]. It is also noteworthy that the ET_6 theory of rarefied gases is perfectly consistent with the kinetic theory [34,35]. By using the ET_6 theory, it has been shown that the effect of the dynamic pressure becomes enormously large in some gases, e.g., hydrogen gases. This fact is remarkable because the dynamic pressure is usually related to the bulk viscosity under the assumption of the Newtonian fluid, and sometimes it is assumed to be zero (Stokes' assumption).

A first tentative move to go beyond the previous ET_6 theory was made in Ref. [36], where the binary hierarchy of balance equations no longer has feature (2). The authors adopted the following type of binary hierarchy:

$$\begin{aligned}
&\frac{\partial F}{\partial t}+\frac{\partial F_k}{\partial x_k}=0,\\
&\frac{\partial F_i}{\partial t}+\frac{\partial F_{ik}}{\partial x_k}=0,\\
&\frac{\partial \bar{F}_{ii}}{\partial t}+\frac{\partial F_{iik}}{\partial x_k}=P_{ii},\qquad \frac{\partial G_{ii}}{\partial t}+\frac{\partial G_{iik}}{\partial x_k}=0.
\end{aligned}\tag{1}$$

Note that, in general in (1), $\bar{F}_{ii}\neq F_{ii}$. Here, since the balance equations of the densities F, F_i, and G_{ii} represent, respectively, the conservation laws of mass, momentum, and energy without shear stress and heat flux [25–27], we have the following expressions of the densities and fluxes in terms of the commonly used macroscopic variables:

$$\begin{aligned}
&F=\rho,\qquad F_i=\rho v_i,\qquad F_{ij}=(p+\Pi)\delta_{ij}+\rho v_i v_j,\\
&G_{ii}=2\rho\varepsilon+\rho v^2,\qquad G_{iik}=2(\rho\varepsilon+p+\Pi)v_k+\rho v^2 v_k,
\end{aligned}$$

where $\rho, v_i, p, \varepsilon$, and Π are the mass density, the velocity, the pressure, the specific internal energy density, and the dynamic pressure, respectively. The problem remaining is the determination of the quantities: density $\bar{F}_{ii}$, flux F_{iik}, and production P_{ii}. According to the Galilean invariance, it was proved [36] that the previous system can be rewritten in the following form:

$$\begin{aligned}
&\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x_i}(\rho v_i)=0,\qquad \frac{\partial\rho v_j}{\partial t}+\frac{\partial}{\partial x_i}\{\rho v_i v_j+(p+\Pi)\delta_{ij}\}=0,\\
&\frac{\partial}{\partial t}(2\rho\varepsilon+\rho v^2)+\frac{\partial}{\partial x_i}\{[2\rho\varepsilon+\rho v^2+2(p+\Pi)]v_i\}=0,\\
&\frac{\partial}{\partial t}\{3(\bar{p}+\bar{\Pi})+\rho v^2\}+\frac{\partial}{\partial x_i}\{[\rho v^2+3(\bar{p}+\bar{\Pi})+2(p+\Pi)]v_i\}=\hat{P}_{ll},
\end{aligned}\tag{2}$$

where $\hat{P}_{ll}$ is the velocity-independent production. We have now two undetermined quantities, $\bar{p}$ and $\bar{\Pi}$, which, in the case of rarefied-gas limit, approach p and Π, respectively. Unfortunately it was proved [36] that the entropy principle is not able to specify the new functions.

In the study of rarefied gases [21,37], it is shown that $G_{ii}-\bar{F}_{ii}$ is a characteristic variable for polyatomic gases that vanishes in the monatomic limit. Therefore it is better to substitute the difference between the third and fourth equations of (2) for the last equation of (2):

$$\begin{aligned}
&\frac{\partial\rho}{\partial t}+\frac{\partial}{\partial x_i}(\rho v_i)=0,\qquad \frac{\partial\rho v_j}{\partial t}+\frac{\partial}{\partial x_i}\{\rho v_i v_j+(p+\Pi)\delta_{ij}\}=0,\\
&\frac{\partial}{\partial t}(2\rho\varepsilon+\rho v^2)+\frac{\partial}{\partial x_i}\{[2\rho\varepsilon+\rho v^2+2(p+\Pi)]v_i\}=0,\\
&\frac{\partial}{\partial t}(2\rho\varepsilon-3\bar{p}-3\bar{\Pi})+\frac{\partial}{\partial x_i}\{(2\rho\varepsilon-3\bar{p}-3\bar{\Pi})v_i\}=-\hat{P}_{ll}.
\end{aligned}\tag{3}$$

The purpose of the present paper is to construct an ET$_6$ theory of dense gases that is free from the difficulties mentioned above by adopting a simple principle that bridges the gap between rarefied and dense gases. As a theory of dense gases, the Meixner theory [28,29] has been used to study various phenomena such as shock waves. However, this theory introduces several quantities that are quite difficult to be identified explicitly.

We will see that, in dense gases as well, the system can be closed if the caloric and thermal equations of the state are given. We will clarify the convexity condition of the entropy. The system of balance equations is symmetric hyperbolic with well-posedness of the Cauchy problem, and the existence of global smooth solutions for small initial data is guaranteed. The characteristic velocities and dispersion relation of a ultrasonic wave will be analyzed. The nonequilibrium temperatures of the translational modes and of internal modes of molecules will play an important role in the ET theory of dense gases. We will also address the following points: the origin of the dynamic pressure, the characteristic velocities associated with the hyperbolic system, the K condition for the existence of global smooth solutions, and the fluctuation-dissipation relation of the bulk viscosity. As a typical example, a van der Waals (vdW) fluid will be studied by using the present theory. We will find that a nonequilibrium spinodal curve is similar to the one of Euler system but the temperature and pressure are nonequilibrium ones. We will also prove that the so-called locus of the vanishing *critical derivative* (locally exceptional region) is always in the unstable region in contrast with the Euler fluid. Therefore no rarefaction shocks are admissible in the present model.

II. EQUATIONS OF STATE

In this section, as a preliminary step, we prescribe the equations of state of a gas explicitly.

A. Rarefied gas

From a microscopic point of view, the Hamiltonian of a rarefied polyatomic gas is given in the form

$$H = H^K + H^I,$$

where H^K is the *kinetic energy* of molecular translational motion and H^I is the *energy of the internal motion* of molecules such as molecular rotation and vibration.

We study nonpolytropic gases within a temperature range where the classical (i.e., nondegenerate) equations of state are valid. Therefore the pressure p and the specific internal energy density ε are expressed by the mass density ρ and the temperature T as follows:

$$p = p(\rho,T) \equiv \frac{k_B}{m}\rho T, \quad \varepsilon = \varepsilon(T),$$

where k_B and m are the Boltzmann constant and the mass of a molecule, respectively. Note that ε has, in general, nonlinear dependence on T.

The pressure p can be divided into two parts [38]: the pressure p^K due to H^K and the pressure p^I due to H^I. However, as $p^I = 0$, we have

$$p = p^K; \quad p^K = \frac{k_B}{m}\rho T.$$

Similarly we have

$$\varepsilon = \varepsilon^K + \varepsilon^I; \quad \varepsilon^K = \frac{3}{2}\frac{k_B}{m}T, \quad \varepsilon^I = \varepsilon^I(T).$$

The expression of ε^K comes from the equipartition law of energy for a classical gas. However, we take into account the quantum effects of molecular rotation and vibration in the expression of ε^I (nonpolytropic gas) [38].

B. Dense gas

The Hamiltonian of a dense polyatomic gas is given in the form

$$H = H^{K+U} + H^I,$$

where H^{K+U} is composed of the kinetic energy of molecular translational motion and the *potential energy* among molecules, and H^I is the energy of the internal motion of molecules. The thermal and caloric equations of state in terms of ρ and T are expressed as

$$p = p(\rho,T), \quad \varepsilon = \varepsilon(\rho,T).$$

Note that ε depends also on ρ due to the potential energy.

As before, the pressure p can be divided into two parts: the pressure p^{K+U} due to H^{K+U} and the pressure p^I due to H^I. However, as $p^I = 0$ also in a dense gas, we have

$$p = p^{K+U}; \quad p^{K+U} = p^{K+U}(\rho,T).$$

Similarly we have

$$\varepsilon = \varepsilon^{K+U} + \varepsilon^I; \quad \varepsilon^{K+U} = \varepsilon^{K+U}(\rho,T), \quad \varepsilon^I = \varepsilon^I(T).$$

Note that ε^I depends only on T [38].

III. NONEQUILIBRIUM TEMPERATURES AND DUALITY PRINCIPLE

In the following, we will study a polyatomic gas excluding the case of monatomic gas, and therefore $\varepsilon^I(T) \neq 0$. Then we may define two *positive* parameters Θ and ϑ through the corresponding quantities Π and $\bar{\Pi}$:

$$\Pi = p(\rho,\vartheta) - p(\rho,T), \tag{4}$$

$$\bar{\Pi} = \tfrac{2}{3}\rho[\varepsilon^I(T) - \varepsilon^I(\Theta)]. \tag{5}$$

As will be discussed below, Θ and ϑ have the physical meaning of nonequilibrium temperatures.

A. Rarefied gas

In the case of rarefied gases, we know that $\bar{p} = p$ and $\bar{\Pi} = \Pi$ [36]. Therefore, from (4) and (5), we have the following relation between the two parameters:

$$\varepsilon^I(T) - \varepsilon^I(\Theta) = \varepsilon^K(\vartheta) - \varepsilon^K(T) \tag{6}$$

and

$$p = p^K(\rho,T), \quad \bar{p} = \tfrac{2}{3}\rho\varepsilon^K(T). \tag{7}$$

Moreover we know that the nonequilibrium specific entropy density k is given by [31,35]

$$k = \eta - s = \int_T^{\vartheta} \frac{c_v^K(T')}{T'}\,dT' + \int_T^{\Theta} \frac{c_v^I(T')}{T'}\,dT' = \frac{3}{2}\frac{k_B}{m}\log\left(\frac{\vartheta}{T}\right) + \int_T^{\Theta} \frac{c_v^I(T')}{T'}\,dT',$$

where η is the nonequilibrium specific entropy density, s is the equilibrium specific entropy density that satisfies the Gibbs relation $Tds = d\varepsilon - \frac{p}{\rho^2}\,d\rho$, and $c_v^K \equiv \frac{d\varepsilon^K}{dT} = \frac{3}{2}\frac{k_B}{m}$ and $c_v^I \equiv \frac{d\varepsilon^I}{dT}$ are the specific heats due to, respectively, H^K and H^I. It is easily proved that η is expressed as

$$\eta = s^K(\rho,\vartheta) + s^I(\Theta), \tag{8}$$

where

$$s = s^K(\rho,T) + s^I(T), \quad s^K(\rho,T) = \frac{k_B}{m}\left(\log\frac{T^{3/2}}{\rho}\right) + s_0^K, \quad s^I(T) = \int_{T_0}^{T} \frac{c_v^I(T')}{T'}\,dT' + s_0^I$$

with constants s_0^K, s_0^I, and T_0 at a reference state.

Remark 1. From (6), we can interpret the dynamical pressure as the one caused by the energy exchange:

$$\Delta = \varepsilon^I(\Theta) - \varepsilon^I(T),$$

which put the internal modes into the nonequilibrium state with a nonequilibrium temperature Θ from the state with the local equilibrium temperature T. For this reason we may say that Θ is the temperature of the internal modes of a molecule, while ϑ is the nonequilibrium temperature of the translational modes of molecules induced by $-\Delta$. In the following, we will see that such nonequilibrium temperatures play important roles to describe the elementary process in a concise and clear way. Last it is worth noting that, in the context of the kinetic theory for rarefied gases [15,39,40], the dynamic pressure is related to the nonequilibrium energy exchange among several kinds of motions of a molecule.

Remark 2: We observe that $\bar{p}$ and $\bar{\Pi}$ appear in the last equation of (3). Therefore we can regard this equation as the equation that describes the time evolution of the energy exchange Δ. Then $\bar{p}$ and $\bar{\Pi}$ are regarded as the quantities that are closely related to energy more than pressure, while p and Π appear in the momentum flux, and therefore these are necessarily related to pressure. This justifies the expressions (4), (5), and (7), where we have introduced, respectively, pressure, and energy in accordance with this rule.

B. Dense gas

In order to construct an ET$_6$ model of *dense* gases, we need to find out a suitable bridge between rarefied and dense gases. For this purpose, it seems natural to adopt the following duality principle (see also Remark 3 below for its physical implications):

Duality Principle: The differential system of a dense gas can be obtained from the system of a rarefied gas by the following substitution:

$$(p^K, \varepsilon^K) \quad \to \quad (p^{K+U}, \varepsilon^{K+U}).$$

According to this principle we have, from (7),

$$p = p^{K+U}(\rho, T), \quad \bar{p} = \tfrac{2}{3}\rho\varepsilon^{K+U}(\rho, T),$$

while ϑ and Θ are now related through, instead of (6), the following relation due to the duality principle:

$$\varepsilon^I(\Theta) - \varepsilon^I(T) = \varepsilon^{K+U}(\rho, T) - \varepsilon^{K+U}(\rho, \vartheta). \tag{9}$$

Then the expressions (4) and (5) are explicitly expressed, also for dense gases, in terms of the nonequilibrium temperatures. The remarkable point is that $\bar{\Pi} \neq \Pi$ and $\bar{p} \neq p$ as we expect for dense gases.

Remark 3: What we have done in the above based on the duality principle is, physically speaking, that we have assumed that the dynamic pressure Π is caused by the energy exchange Δ between H^{K+U} and H^I. In polyatomic gases, it seems that this nonequilibrium process is the most dominant mechanism for the emergence of the dynamic pressure Π. In reality, however, there exist several mechanisms. As we may conceive of different kinds of energy exchange, the above one is probably one of them. In fact, in the monatomic-gas limit, the present mechanism predicts that the dynamic pressure Π disappears not only in a rarefied gas case but also in a dense gas case, and then the bulk viscosity is always zero. It is evident that we need to introduce other mechanisms in order to explain the dynamic pressure in a *dense* monatomic gas. For example, in Ref. [41], Hirai and Eyring pointed out the two possible mechanisms. The first one is essentially the same as the present one. The second one is due to the so-called structural relaxation mechanism: the change from a structure to other one takes time, and the lag is the cause of the dynamic pressure. The hierarchy structure of the system of field equations, therefore, will be changed. The monatomic gas case is not the simplest case despite its first impression. Also in the rarefied limit the monatomic gas that seems apparently the most simple case of polyatomic gas is in reality a singular limit of polyatomic gas. In fact, the number of differential equations is different in the limit between polyatomic to monatomic gas, and it is not so simple to prove the convergence of the solution of polyatomic gas to the monatomic one when the degrees of freedom $D \to 3$ (see Refs. [21,37]).

Therefore, although the applicability range of the present model seems to be rather wide, it is fair to say that the model is appropriate only for a gas where the mechanism adopted here is overwhelming and other mechanisms can be safely neglected.

IV. ET$_6$ OF DENSE POLYATOMIC GASES

The main results of the present paper are shown in this section.

A. System of field equations

If we choose $(\rho,\mathbf{v},T,\Theta)$ as independent variables, according to the above discussions, we may propose the differential system for dense gases as follows:

$$\begin{aligned}
&\frac{\partial \rho}{\partial t}+\frac{\partial}{\partial x_i}(\rho v_i)=0, \quad \frac{\partial \rho v_j}{\partial t}+\frac{\partial}{\partial x_i}\{\rho v_i v_j+(p+\Pi)\delta_{ij}\}=0,\\
&\frac{\partial}{\partial t}(2\rho\varepsilon+\rho v^2)+\frac{\partial}{\partial x_i}\{[2\rho\varepsilon+\rho v^2+2(p+\Pi)]v_i\}=0,\\
&\frac{\partial}{\partial t}[2\rho\varepsilon^I(\Theta)]+\frac{\partial}{\partial x_i}[2\rho\varepsilon^I(\Theta)v_i]=-\hat{P}_{ll},
\end{aligned} \tag{10}$$

where Π is expressed in terms of Θ in the parametric form with the parameter ϑ [see (4) and (9)] and p and ε are specified by the thermal and caloric equations of state as functions of (ρ,T).

If we prefer to use the material derivative, the system can be rewritten as follows:

$$\begin{aligned}
&\dot{\rho}+\rho\frac{\partial v_k}{\partial x_k}=0, \quad \rho\dot{v}_i+\frac{\partial}{\partial x_i}(p+\Pi)=0,\\
&\rho c_v(T)\dot{T}+(p-\rho^2\varepsilon_\rho+\Pi)\frac{\partial v_k}{\partial x_k}=0, \quad \dot{\varepsilon}^I(\Theta)=-\frac{P_{ll}}{2\rho},
\end{aligned} \tag{11}$$

where $c_v \equiv \frac{\partial \varepsilon}{\partial T}$ is the specific heat.

B. Galilean invariance and the entropy principle

The system (10) is a particular case of the following balance law system of N equations:

$$\frac{\partial \mathbf{F}}{\partial t}+\frac{\partial \mathbf{F}^i}{\partial x^i}=\mathbf{f}, \tag{12}$$

where $\mathbf{F}$, $\mathbf{F}^i$, and $\mathbf{f}$ are, respectively, the density, the flux, and the production. It is convenient to split the flux vector into the convective and nonconvective ones:

$$\mathbf{F}^i=\mathbf{F}v^i+\mathbf{\Phi}^i.$$

The Galilean invariance of the balance equations requires the following velocity dependences of the densities, nonconvective flux, and production. There exists an exponential $(N\times N)$ matrix $\mathbf{X}(\mathbf{v})$,

$$\mathbf{X}(\mathbf{v})=\exp(\mathbf{A}^r v_r), \tag{13}$$

with constant $(N\times N)$ matrices $\mathbf{A}^r$ $(r=1,2,3)$ that satisfy the commutativity conditions $\mathbf{A}^r\mathbf{A}^s=\mathbf{A}^s\mathbf{A}^r$. Then we have the relations [42]

$$\mathbf{F}=\mathbf{X}(\mathbf{v})\hat{\mathbf{F}}, \quad \mathbf{\Phi}^i=\mathbf{X}(\mathbf{v})\hat{\mathbf{\Phi}}^i, \quad \mathbf{f}=\mathbf{X}(\mathbf{v})\hat{\mathbf{f}}, \tag{14}$$

where the symbol hat indicates the velocity-independent part of a quantity. When, as in ET, there exists a natural order in the equations, $\mathbf{X}(\mathbf{v})$ is a triangular matrix and $\mathbf{A}^r$ are nilpotent matrices of order n. This implies that the matrix $\mathbf{X}(\mathbf{v})$ is a polynomial matrix of degree n, which is the maximum tensorial order of the densities.

The entropy principle requires the following inequality [1,2] with h $(=\rho\eta)$ being the entropy density, h^i the entropy flux, and Σ the entropy production:

$$\frac{\partial h}{\partial t}+\frac{\partial h^i}{\partial x_i}=\Sigma\geqslant 0 \tag{15}$$

for any solution $\mathbf{u}(x_i,t)$ of the system, which we call the *thermodynamic process*.

In the case of local constitutive equations typical of ET,

$$\mathbf{F}^0 \equiv \mathbf{F}^0(\mathbf{u}), \quad \mathbf{F}^i \equiv \mathbf{F}^i(\mathbf{u}), \quad \mathbf{f} \equiv \mathbf{f}(\mathbf{u}), \tag{16}$$

the entropy principle dictates the existence of a privileged field (*main field*) $\mathbf{u}'$ such that

$$\mathbf{u}' \cdot d\mathbf{F} = dh, \quad \mathbf{u}' \cdot d\mathbf{F}^i = dh^i, \quad \mathbf{u}' \cdot \mathbf{f}(\mathbf{u}) = \Sigma(\mathbf{u}) \geqslant 0. \tag{17}$$

The Galilean invariance of the entropy inequality (15) implies the velocity dependence of the main field $\mathbf{u}'$ as follows:

$$\mathbf{u}' = \hat{\mathbf{u}}'\mathbf{X}^{-1}(\mathbf{v}) = \hat{\mathbf{u}}'\mathbf{X}(-\mathbf{v}). \tag{18}$$

From (14) and (18), the conditions (17) are equivalent to

$$\hat{\mathbf{u}}' \cdot d\hat{\mathbf{F}} = d\hat{h}, \quad \hat{\mathbf{u}}' \cdot d\hat{\mathbf{\Phi}}^i = d\hat{h}^i, \quad \hat{\mathbf{u}}' \cdot \hat{\mathbf{f}} = \Sigma \geqslant 0, \tag{19}$$

$$\hat{\mathbf{u}}' \cdot \mathbf{A}^r \hat{\mathbf{F}} = 0, \quad (h - \hat{\mathbf{u}}' \cdot \hat{\mathbf{F}})\delta^{rj} = \hat{\mathbf{u}}' \cdot \mathbf{A}^r \hat{\mathbf{\Phi}}^j. \tag{20}$$

In the present case, $N = 6$ and

$$\begin{aligned} \mathbf{F} &\equiv (\rho, \rho v^j, 2\rho\varepsilon + \rho v^2, 2\rho\varepsilon^I(\Theta))^T, \\ \mathbf{\Phi}^i &\equiv (0, (p + \Pi)\delta_{ij}, 2(p + \Pi)v_i, 0)^T, \\ \mathbf{f} &\equiv (0, 0_j, 0, -P_{ll})^T, \end{aligned} \tag{21}$$

where 0_i denotes the zero raw R^3 vector. Taking into account (21) we have

$$\mathbf{X}(\mathbf{v}) = \begin{pmatrix} 1 & 0_k & 0 & 0 \\ v^k & \delta_k^j & 0 & 0 \\ v^2 & 2v_k & 1 & 0 \\ 0 & 0_k & 0 & 1 \end{pmatrix},$$

while from (13) the matrices $\mathbf{A}^r$ are given by

$$\mathbf{A}^r = \left.\frac{\partial \mathbf{X}}{\partial v_r}\right|_{\mathbf{v}=0} = \begin{pmatrix} 0 & 0_k & 0 & 0 \\ \delta^{kr} & 0_k^j & 0 & 0 \\ 0 & 2\delta_k^r & 0 & 0 \\ 0 & 0_k & 0 & 0 \end{pmatrix},$$

where 0_k^j denotes the null 3×3 matrix.

Let us express $\mathbf{u}'$ in the component form:

$$\mathbf{u}' \equiv (\lambda, \lambda_i, \mu, \zeta), \tag{22}$$

then we have, from the first equation of (20), $\hat{\lambda}_i = 0$, and, from the first equation of (19), we have

$$\hat{\lambda} = \eta + \rho\eta_\rho - \frac{1}{c_v(\rho, T)}(\varepsilon + \rho\varepsilon_\rho)\eta_T - \frac{\varepsilon^I(\Theta)}{c_v^I(\Theta)}\eta_\Theta, \quad \hat{\mu} = \frac{1}{2c_v(\rho, T)}\eta_T, \quad \hat{\zeta} = \frac{1}{2c_v^I(\Theta)}\eta_\Theta, \tag{23}$$

where a subscript attached to η or ε indicates a partial derivative. The second equation of (19) is automatically satisfied and gives

$$\hat{h}^i = 0, \quad \rightarrow \quad h^i = hv^i. \tag{24}$$

While, inserting (23) into the second equation of (20), we obtain the following partial differential equation for η:

$$\eta_\rho + \frac{1}{c_v}\left(\frac{p+\Pi}{\rho^2} - \varepsilon_\rho\right)\eta_T = 0. \tag{25}$$

The solution η is expressed compactly by using the nonequilibrium temperatures ϑ and Θ, if we divide the equilibrium-specific entropy density s into two parts: s^{K+U} due to H^{K+U} and s^I due to H^I. Then we can prove, according with the duality principle [see (8)], that a solution of (25) is given by

$$\eta = s^{K+U}(\rho,\vartheta) + s^I(\Theta) \tag{26}$$

for a given temperature T. We now prove that (26) satisfies (25). From the Gibbs relation due to H^{K+U} (the $(K+U)$ part) [43] we have

$$\vartheta ds^{K+U} = d\varepsilon^{K+U} - \frac{p^{K+U}}{\rho^2}d\rho, \tag{27}$$

then

$$\begin{aligned}\vartheta ds^{K+U} &= c_v^{K+U}(\rho,\vartheta)\,d\vartheta + \left[\frac{\partial\varepsilon^{K+U}(\rho,\vartheta)}{\partial\rho} - \frac{p^{K+U}(\rho,\vartheta)}{\rho^2}\right]d\rho\\ &= c_v^{K+U}(\rho,\vartheta)\vartheta_\rho\,d\rho + c_v^{K+U}(\rho,\vartheta)\vartheta_T\,dT + c_v^{K+U}(\rho,\vartheta)\vartheta_\Theta\,d\Theta\\ &\quad + \left[\frac{\partial\varepsilon^{K+U}(\rho,\vartheta)}{\partial\rho} - \frac{p^{K+U}(\rho,\vartheta)}{\rho^2}\right]d\rho,\end{aligned} \tag{28}$$

where $c_v^{K+U}(\rho,\vartheta) \equiv \frac{\partial\varepsilon^{K+U}(\rho,\vartheta)}{\partial\vartheta}$ is the specific heat of the $(K+U)$ part. By using the following relations derived from (9):

$$\begin{gathered}c_v^{K+U}(\rho,\vartheta)\vartheta_\rho = \frac{\partial}{\partial\rho}[\varepsilon^{K+U}(\rho,T) - \varepsilon^{K+U}(\rho,\vartheta)],\\ c_v^{K+U}(\rho,\vartheta)\vartheta_T = c_v(\rho,T), \quad c_v^{K+U}(\rho,\vartheta)\vartheta_\Theta = -c_v^I(\Theta),\end{gathered}$$

the relation (28) is rewritten as

$$\vartheta\, ds^{K+U} = \left[\frac{\partial\varepsilon^{K+U}(\rho,T)}{\partial\rho} - \frac{p^{K+U}(\rho,\vartheta)}{\rho^2}\right]d\rho + c_v(\rho,T)\,dT - c_v^I(\Theta)\,d\Theta.$$

On the other hand, the Gibbs equation due to H^I (I part) is given by

$$\Theta\, ds^I = d\varepsilon^I(\Theta) = c_v^I(\Theta)\,d\Theta. \tag{29}$$

From (26), (28), and (29), we have the nonequilibrium Gibbs relation:

$$d\eta = \frac{1}{\vartheta}\left\{\left[\frac{\partial\varepsilon(\rho,T)}{\partial\rho} - \frac{p(\rho,\vartheta)}{\rho^2}\right]d\rho + c_v(\rho,T)dT\right\} + \left(\frac{1}{\Theta} - \frac{1}{\vartheta}\right)c_v^I(\Theta)\,d\Theta. \tag{30}$$

Therefore we have the following expressions of the derivatives of η:

$$\eta_\rho = \frac{1}{\vartheta}\left[\frac{\partial\varepsilon(\rho,T)}{\partial\rho} - \frac{p(\rho,\vartheta)}{\rho^2}\right], \quad \eta_T = \frac{1}{\vartheta}c_v(\rho,T), \quad \eta_\Theta = \left(\frac{1}{\Theta} - \frac{1}{\vartheta}\right)c_v^I(\Theta). \tag{31}$$

Inserting these derivatives into (25) and noting the relation (4), we can easily check that η given by (26) certainly satisfies (25). Finally, we check on the fact that the solution (26) has evidently an equilibrium entropy at an equilibrium state with $\Theta = \vartheta = T$:

$$\eta|_E = s^{K+U}(\rho,T) + s^I(T) = s(\rho,T).$$

By using (31), we can rewrite the components of $\hat{\mathbf{u}}'$ in (23) as follows:

$$\hat{\lambda} = -\frac{g^{K+U}(\rho,\vartheta)}{\vartheta} - \frac{g^{I}(\Theta)}{\Theta}, \quad \hat{\mu} = \frac{1}{2\vartheta}, \quad \hat{\zeta} = \frac{1}{2}\left(\frac{1}{\Theta} - \frac{1}{\vartheta}\right), \tag{32}$$

where we have defined the chemical potentials of the $(K+U)$ part and I part:

$$g^{K+U}(\rho,\vartheta) = \varepsilon^{K+U}(\rho,\vartheta) + \frac{p^{K+U}(\rho,\vartheta)}{\rho} - \vartheta s^{K+U}(\rho,\vartheta), \quad g^{I}(\Theta) = \varepsilon^{I}(\Theta) - \Theta s^{I}(\Theta).$$

From (22), (32), and (18), we deduce the main field components:

$$\lambda = -\frac{g^{K+U}(\rho,\vartheta)}{\vartheta} - \frac{g^{I}(\Theta)}{\Theta} + \frac{v^2}{2\vartheta}, \quad \lambda_i = \frac{v_i}{\vartheta}, \quad \mu = \frac{1}{2\vartheta}, \quad \zeta = \frac{1}{2}\left(\frac{1}{\Theta} - \frac{1}{\vartheta}\right). \tag{33}$$

The residual inequality of the entropy principle [the third equation of (17)] is expressed as

$$\Sigma = \frac{1}{3}\eta_\Theta \hat{P}_{ll} \geqslant 0. \tag{34}$$

From this inequality, we have

$$\hat{P}_{ll} = \alpha\eta_\Theta, \quad \alpha \geqslant 0.$$

In the simplest case, we can assume that α is an equilibrium quantity, i.e., it is independent of Θ: $\alpha \equiv \alpha(\rho,T)$.

C. Convexity principle

The thermodynamic stability condition requires that the entropy must be convex with respect to the densities:

$$\frac{\partial^2 h}{\partial\mathbf{F}\partial\mathbf{F}} \quad \text{is negative definite.}$$

From the first equation of (17), this condition corresponds to the following negative quadratic form:

$$Q = \delta\mathbf{u}' \cdot \delta\mathbf{F} < 0.$$

Taking into account the first equation of (14) and (18), we have [42]

$$Q = \bar{Q} - 2\hat{\mathbf{u}}'\mathbf{A}^r\delta\mathbf{F}\delta v_r - g^{rs}\delta v_r\delta v_s, \tag{35}$$

where

$$\bar{Q} = \delta\hat{\mathbf{u}}' \cdot \delta\hat{\mathbf{F}}, \quad g^{rs} = \hat{\mathbf{u}}'\mathbf{A}^r\mathbf{A}^s\hat{\mathbf{F}}.$$

In the present case, as the second term in the right-hand side of (35) vanishes and $g^{rs} = (\rho/\vartheta)\delta_{rs}$, we have

$$Q = \bar{Q} - \frac{\rho}{\vartheta}||\delta\mathbf{v}||^2 \quad \text{with} \quad \bar{Q} = \delta\rho\delta\hat{\lambda} + 2\delta(\rho\varepsilon)\delta\hat{\mu} + 2\delta[\rho\varepsilon^{I}(\Theta)]\delta\hat{\zeta}$$
$$= -\frac{p_\rho(\rho,\vartheta)}{\rho\vartheta}(\delta\rho)^2 - \frac{\rho c_v^{K+U}(\rho,\vartheta)}{\vartheta^2}(\delta\vartheta)^2 - \frac{\rho c_v^{I}(\Theta)}{\Theta^2}(\delta\Theta)^2 < 0.$$

Then the state (ρ,T,Θ) is stable if and only if the following inequalities are satisfied:

$$\left(\frac{\partial p}{\partial\rho}\right)_\vartheta(\rho,\vartheta(\rho,T,\Theta)) > 0, \quad \left(\frac{\partial\varepsilon^{K+U}}{\partial\vartheta}\right)_\rho(\rho,\vartheta(\rho,T,\Theta)) > 0, \quad \frac{d\varepsilon^{I}}{d\Theta}(\Theta) > 0. \tag{36}$$

Therefore under these conditions, the system of the present theory can be put in a symmetric form [44,45] by choosing the main field given in (33) as independent fields.

In particular, an equilibrium state (ρ,T,T) is stable if

$$\left(\frac{\partial p}{\partial \rho}\right)_T(\rho,T) > 0, \quad \left(\frac{\partial \varepsilon^{K+U}}{\partial T}\right)_\rho(\rho,T) > 0, \quad \frac{d\varepsilon^I}{dT}(T) > 0.$$

We remark that the usual thermodynamic stability implies a weaker condition requiring only that the total specific heat must positive:

$$\left(\frac{\partial p}{\partial \rho}\right)_T(\rho,T) > 0, \quad \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho(\rho,T) > 0. \tag{37}$$

It is worth noticing that the symmetrization of the Euler system requires the usual thermodynamic stability (37).

D. Upper and lower bounds for the nonequilibrium temperatures

Differentiating (9) with respect to ϑ keeping ρ and T fixed, we easily obtain the relation

$$\frac{d\Theta}{d\vartheta} = -\frac{c_v^{K+U}(\rho,\vartheta)}{c_v^I(\Theta)} < 0. \tag{38}$$

If ϑ increases (decreases), then Θ decreases (increases), and, as both Θ and ϑ are equal to T in equilibrium, if $\vartheta \gtrless T$ then $\Theta \lessgtr T$.

Moreover, in the definition of the nonequilibrium temperatures, we have assumed that these are positive quantities. This is also consistent with the fact that the entropy must be an increasing function of the energy [see (27) and (29)]. Therefore all solutions must satisfy the condition $\vartheta > 0, \Theta > 0$. Taking into account (38) and (9), we obtain immediately the upper bound for these quantities:

$$\begin{aligned} &0 < \Theta < \Theta_{\max} \quad \text{with} \quad \varepsilon^I(\Theta_{\max}) = \varepsilon(\rho,T) - \varepsilon^{K+U}(\rho,0),\\ &0 < \vartheta < \vartheta_{\max} \quad \text{with} \quad \varepsilon^{K+U}(\vartheta_{\max}) = \varepsilon(\rho,T) - \varepsilon^I(0). \end{aligned} \tag{39}$$

E. Characteristic velocity, subcharacteristic conditions, and local exceptionality

It is well known that the characteristic velocities V associated with a hyperbolic system of type (12) and (16) can be obtained from the system by the operator chain rule (see Ref. [2]):

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

where n_i denotes the i component of the unit normal to the wave front, and δ is a differential operator [2]. In the present case, if we choose $\{\rho,\eta,\Theta\}$ as independent variables instead of $\{\rho,T,\Theta\}$, and adopt the entropy law (15) and (24):

$$\rho\dot{\eta} = \Sigma$$

instead of the energy equation in the third equation of (11), we obtain the following linear algebraic system:

$$-U\delta\rho + \rho\delta v_n = 0, \quad -\rho U\delta v_i + n_i\delta p(\rho,\vartheta) = 0, \quad -\rho c_v^I(\Theta)U\delta\Theta = 0, \quad -\rho U\delta\eta = 0, \tag{40}$$

where $U = V - v_n$ and $v_n = v_j n_j$. The solution of (40) gives

$$\textit{Contact waves}: \quad V = v_n = 0, \tag{41}$$

(multiplicity 4)

$$\textit{Sound waves}: \quad V = v_n \pm \sqrt{\left[\frac{\partial p(\rho,\vartheta(\rho,\eta,\Theta))}{\partial \rho}\right]_{\eta,\Theta}}$$

(each of multiplicity 1). (42)

Taking into account the Gibbs equations (29), we can rewrite the velocity of the sound wave as follows:

$$\begin{aligned} U^2 &= p_\rho(\rho,\vartheta) + \frac{p_\vartheta(\rho,\vartheta)}{c_v^{K+U}(\rho,\vartheta)}\left\{\frac{p^{K+U}(\rho,\vartheta)}{\rho^2} - \varepsilon_\rho^{K+U}(\rho,\vartheta)\right\} \\ &= p_\rho(\rho,\vartheta) + \frac{\vartheta p_\vartheta^2(\rho,\vartheta)}{\rho^2 c_v^{K+U}(\rho,\vartheta)}. \end{aligned} \tag{43}$$

In particular, in an equilibrium case, we have

$$U_E^2 = p_\rho(\rho,T) + \frac{T p_T^2(\rho,T)}{\rho^2 c_v^{K+U}(\rho,T)}, \tag{44}$$

while, for Eulerian fluids, we have

$$U_{\text{Euler}}^2 = p_\rho(\rho,T) + \frac{T p_T^2(\rho,T)}{\rho^2 c_v(\rho,T)}. \tag{45}$$

As the system of ET$_6$ includes the Euler system as the subsystem [46], we have the following *subcharacteristic condition*:

$${U_E}^2 - U_{\text{Euler}}^2 = \frac{T p_T^2(\rho,T)}{\rho^2}\frac{c_v^I(T)}{c_v(\rho,T)c_v^{K+U}(\rho,T)} > 0. \tag{46}$$

It is well known that a characteristic velocity associated with a wave is classified as (see, e.g., Ref. [2]):

(1) *Genuinely nonlinear* if

$$\delta V = \nabla_{\mathbf{u}} V \cdot \delta\mathbf{u} \;\propto\; \nabla_{\mathbf{u}} V \cdot \mathbf{r} \neq 0, \;\; \forall \mathbf{u}.$$

(2) *Linearly degenerate or exceptional* if

$$\delta V \equiv 0, \;\; \forall \mathbf{u}.$$

(3) *Locally linearly degenerate or locally exceptional* if

$$\delta V = 0, \;\; \text{for some} \quad \mathbf{u}, \tag{47}$$

where $\mathbf{r}$ is the corresponding right eigenvector associated to the system (12) and (16). The contact waves (41) are exceptional, while the sound waves (42) can be locally exceptional if (47) is satisfied. Simple algebra similar to the one in Ref. [47] gives that, if the hyper-surface of local exceptionality exists, the following relation is satisfied on it:

$$\frac{\partial}{\partial\rho}\left\{\rho^2\left[\frac{\partial p(\rho,\vartheta)}{\partial\rho}\right]_{\eta,\Theta}\right\}_{\eta,\Theta} = \frac{\partial}{\partial\rho}\{\rho^2 U^2\}_{\eta,\Theta} = 0. \tag{48}$$

F. K condition

As is well known, the Euler fluid cannot have global smooth solutions for all time because there appears shock formation or blowup. However, our system with the dynamical pressure belongs to the group of dissipative hyperbolic systems due to the presence of the production term in the last equation in (10). In this case, global smooth solutions can exist due to the interrelationship between the conservation laws and the remaining dissipative one. In fact, for generic hyperbolic systems composed of conservation laws and balance laws, endowed with a convex entropy law, the so-called Kawashima-Shizuta condition (K condition) [48] becomes a sufficient condition for the existence of global smooth solutions, provided that the initial data are sufficiently small [49–52]. It was proved in Ref. [53] (see also Ref. [2]) that the K condition corresponds to

$$\delta\mathbf{f}|_E \neq 0.$$

In the present case, from (10), the above condition is expressed as

$$\delta \hat{P}_{ll}|_E \neq 0. \tag{49}$$

Taking into account that $\hat{P}_{ll}|_E = 0$ and that only the linear part of the nonequilibrium quantities enters into the expression (49), we have from (34)

$$\hat{P}_{ll} = \alpha \eta_\Theta = \alpha[\eta_{\Theta\Theta}|_E(\Theta - T) + O(2)],$$

where $O(2)$ indicates terms of second order or more with respect to the nonequilibrium quantity $\Theta - T$. Therefore we have

$$\delta \hat{P}_{ll}|_E = \alpha[\eta_{\Theta\Theta}(\delta\Theta - \delta T)]|_E. \tag{50}$$

But, for sonic waves, from (40), we have $\delta\Theta = \delta\eta = 0$, and from (30) we obtain

$$\delta T|_E = \frac{1}{c_v(\rho,T)}\left[\frac{\partial \varepsilon(\rho,T)}{\partial \rho} - \frac{p(\rho,T)}{\rho^2}\right]\delta\rho = \frac{T p_T}{\rho^2 c_v}\delta\rho.$$

Inserting the last expression into (50) we obtain

$$\delta \hat{P}_{ll}|_E = -\alpha\left(\eta_{\Theta\Theta}|_E \frac{T p_T}{\rho^2 c_v}\right)\delta\rho.$$

If $p_T \neq 0$ as usual, the term in the right-hand side is always different from zero due to the convexity argument of η. Also, for contact waves, we can prove that the K condition holds. Therefore, in contrast with the Euler system, our system that expresses the simplest dissipative system after the Euler system has a global smooth solution for sufficiently small initial data. This is an interesting result that reinforces the physical meaning of the present model.

G. Comparison with the Meixner theory

Since the balance equations (10) have the same mathematical structure as those of rarefied polyatomic gases, the correspondence relations between the present theory and the Meixner theory with one internal variable are the same as those in the case of rarefied polyatomic gases [25,30]. Therefore $\varepsilon^I(\Theta)$ plays the role of the internal variable, and the temperature ϑ is identified as the Meixner temperature.

H. Alternative representation of the system of balance equations

When the initial and boundary conditions are given in terms of the nonequilibrium temperatures Θ and ϑ and/or when we want to explicitly trace the evolution of these temperatures, it is more convenient to adopt the independent fields $\{\rho, v_i, \Theta, \vartheta\}$ instead of $\{\rho, v_i, T, \Theta\}$. Therefore, for completeness, we write the system of balance equations of the fields $\{\rho, v_i, \Theta, \vartheta\}$:

$$\begin{aligned}
&\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i}(\rho v_i) = 0, \quad \frac{\partial \rho v_j}{\partial t} + \frac{\partial}{\partial x_i}\{p^{K+U}(\rho,\vartheta)\delta_{ij} + \rho v_i v_j\} = 0,\\
&\frac{\partial}{\partial t}[2\rho\varepsilon^I(\Theta)] + \frac{\partial}{\partial x_i}[2\rho\varepsilon^I(\Theta)v_i] = -\hat{P}_{ll},\\
&\frac{\partial}{\partial t}(2\rho\varepsilon^{K+U}(\rho,\vartheta) + \rho v^2) + \frac{\partial}{\partial x_i}\{[2p^{K+U}(\rho,\vartheta) + 2\rho\varepsilon^{K+U}(\rho,\vartheta) + \rho v^2]v_i\} = \hat{P}_{ll}.
\end{aligned}$$

V. NEAR-EQUILIBRIUM CASE AND THE BULK VISCOSITY

The simplest way to obtain the linear approximation of the system around an equilibrium state (ρ, T) is to expand the system with respect to the energy exchange Δ up to the first order. The other quantities are expressed in terms of Δ. In fact, we have, from (9),

$$\Theta - T = \frac{\Delta}{c_v^I(T)}, \qquad \vartheta - T = -\frac{\Delta}{c_v^{K+U}(\rho,T)},$$

and, from (4),

$$\Pi = p_T(\rho,T)(\vartheta - T) = -\frac{p_T(\rho,T)}{c_v^{K+U}(\rho,T)}\Delta. \tag{51}$$

The production term is given by

$$\hat{P}_{ll} = \frac{2\rho}{\tau_\Delta}\Delta,$$

where $\tau_\Delta(\rho,T)$ is the relaxation time for Δ, which is positive by the entropy principle. In particular, from (10), the linear equation of Δ is obtained as

$$\dot{\Delta} - \frac{p_T c_v^I}{\rho c_v}\left(T - \frac{\Delta}{c_v^{K+U}}\right)\frac{\partial v_k}{\partial x_k} = -\frac{1}{\tau_\Delta}\Delta. \tag{52}$$

A. Maxwellian iteration

Let us derive the relationship between the relaxation time τ_Δ and the bulk viscosity. When the relaxation time is small, we can apply the Maxwellian iteration [54] to (52). The first iterate of Δ is obtained by putting $\Delta = 0$ in the left-hand side of (52):

$$\Delta^{(1)} = \frac{p_T c_v^I}{\rho c_v} T \tau_\Delta \frac{\partial v_k}{\partial x_k}. \tag{53}$$

Inserting (53) into (51), we have the relation between Π and $\partial v_k/\partial x_k$. Then taking into account the definition of the bulk viscosity ν:

$$\Pi = -\nu \frac{\partial v_k}{\partial x_k},$$

we obtain the relationship between τ_Δ and ν:

$$\nu = \frac{T p_T^2 c_v^I}{\rho c_v c_v^{K+U}} \tau_\Delta. \tag{54}$$

In the rarefied-gas limit, this expression is consistent with the previous results obtained by different approaches [39,40]. If the experimental data on the bulk viscosity are available, the relaxation time τ_Δ can be estimated by using this relationship.

B. Dispersion relation

Let us study a linear plane harmonic wave that is expressed, without loss of generality, in the following form:

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

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

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

where $\boldsymbol{w}$ is the amplitude, ω is the frequency, and k is the complex wave number. From the linearized system of field equations with respect to $\bar{\boldsymbol{u}}$, we can easily obtain the dispersion relation

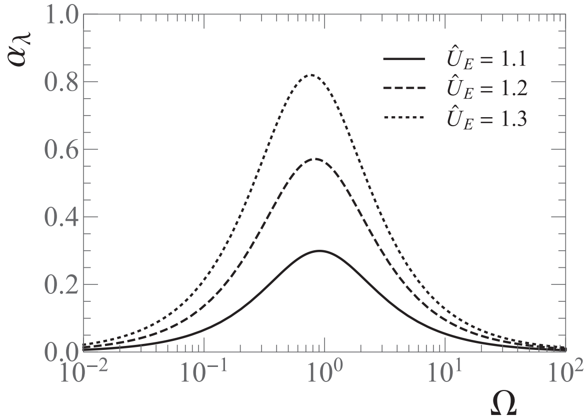

FIG. 1. Dependence of attenuation per wavelength on dimensionless frequency with $\hat{U}_E = 1.1, 1.2, 1.3$.

$\omega = \omega(k)$ [1] as the function of the dimensionless frequency $\Omega = \tau_\Delta \omega$ and the dimensionless characteristic velocity $\hat{U}_E = U_E/U_{\mathrm{Euler}} (> 1)$ as follows:

$$\frac{k}{\omega} = \frac{1}{U_{\mathrm{Euler}}}\sqrt{\frac{1+\mathrm{i}\Omega}{1+\mathrm{i}\hat{U}_E^2\Omega}} = \frac{1}{U_{\mathrm{Euler}}}\sqrt{w_2 + \frac{\mathrm{i}}{\Omega}(w_1 - w_2)}, \tag{55}$$

where

$$w_1 = \frac{1+\Omega^2}{1+\hat{U}_E^4\Omega^2}, \quad w_2 = \frac{1+\hat{U}_E^2\Omega^2}{1+\hat{U}_E^4\Omega^2}.$$

It is interesting that the dispersion relation (55) is essentially determined by the ratio of the characteristic velocity of ET_6 to the one of Euler system.

From the dispersion relation, the phase velocity v_{ph} and the attenuation factor α are obtained as follows:

$$v_{\mathrm{ph}} = \frac{\omega}{\Re(k)} = \pm U_{\mathrm{Euler}} \frac{\sqrt{2}}{\sqrt{\sqrt{w_1} + w_2}}, \quad \alpha = -\Im(k) = \pm \frac{\Omega}{\sqrt{2} U_{\mathrm{Euler}} \tau_\Delta}\sqrt{\sqrt{w_1} - w_2}. \tag{56}$$

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

$$\lim_{\Omega\to\infty} v_{\mathrm{ph}} = \pm U_E,$$

$$\lim_{\Omega\to\infty} \alpha = \pm \frac{1}{2U_{\mathrm{Euler}}\tau_\Delta}\frac{\hat{U}_E^2 - 1}{\hat{U}_E^3}.$$

In the literature of the experimental studies of sound waves, the attenuation per wavelength α_λ defined by

$$\alpha_\lambda = \frac{2\pi v_{\mathrm{ph}} \alpha}{\omega},$$

and the peak value of α_λ are measured. The dependence of α_λ on Ω is shown in Fig. 1 in the cases of $\hat{U}_E = 1.1, 1.2, 1.3$. From (56) we notice that α_λ has the maximum value:

$$\alpha_\lambda^{\max} = 2\pi \frac{\hat{U}_E - 1}{\hat{U}_E + 1} \quad \text{at} \quad \Omega = \frac{1}{\hat{U}_E}.$$

From the experimental data on $\alpha_\lambda^{\max}$, we can estimate the bulk viscosity as was done by the previous theory of ultrasonic waves [55]. Usually, $\alpha_\lambda^{\max}$ has been measured in a fluid in which the internal rotational and/or vibrational modes of a molecule play dominant role. As ET$_6$ is a simplified model, it is expected that the theory based on this model can predict the experimental data on the sound absorption caused by the relaxation of the internal rotational mode, which was clearly observed, for example, in hydrogen gases. The description of the simultaneous relaxations of the internal rotational and vibrational modes may be out of the applicable range of the theory. Because of the lack of suitable experimental data with which the present ET theory can be compared, we have summarized only theoretical predictions above. Moreover, one point worthy of careful consideration is that the measured value of $\alpha_\lambda^{\max}$ includes the contribution from the shear viscosity and heat conductivity. Although such an effect is usually eliminated by the classical theory [56,57], the accurate estimation should be done by the ET theory with 14 fields with the shear stress and heat flux.

C. Fluctuation-dissipation relation

The entropy density η is also expanded with respect to Δ around an equilibrium state up to the second order:

$$\eta = s(\rho,T) - \frac{1}{2\Psi}\Delta^2, \quad \Psi = \left[\frac{1}{T^2}\left(\frac{1}{c_v^{K+U}} + \frac{1}{c_v^I}\right)\right]^{-1} = T^2\frac{c_v^{K+U}c_v^I}{c_v}. \tag{57}$$

Since $c_v^{K+U} > 0$ and $c_v^I > 0$, the convexity condition is always satisfied. Moreover, in the case of rarefied gases, the result (57) is equivalent to the one obtained in the previous works [25,26].

We can estimate the fluctuation of the energy exchange Δ, which obeys the Gaussian distribution functional $f(\Delta(\boldsymbol{x}))$. Except for the normalization factor, the distribution functional is given by

$$f[\Delta(\boldsymbol{x})] \sim \exp\left(\int_{\mathcal{V}} \frac{\rho\eta}{k_B}\, d\boldsymbol{x}\right)$$

with η being given by (57). Here the integration is taken over the whole system $\mathcal{V}$. Therefore we have the estimation given as a simultaneous spatial correlation:

$$\langle\Delta(\boldsymbol{x})\Delta(\boldsymbol{x}')\rangle = \frac{k_B T^2}{\rho}\frac{c_v^{K+U}c_v^I}{c_v}\delta(\boldsymbol{x}-\boldsymbol{x}'),$$

where $\langle\ \rangle$ indicates the thermal average at an equilibrium state. From (51), the fluctuation of the dynamic pressure Π is also estimated as

$$\langle\Pi(\boldsymbol{x})\Pi(\boldsymbol{x}')\rangle = \frac{k_B T^2 p_T^2 c_v^I}{\rho c_v c_v^{K+U}}\delta(\boldsymbol{x}-\boldsymbol{x}').$$

Then the bulk viscosity (54) is rewritten as follows:

$$\nu = \frac{\tau_\Delta}{k_B T|\mathcal{V}|}\iint_{\mathcal{V}}\langle\Pi(\boldsymbol{x})\Pi(\boldsymbol{x}')\rangle d\boldsymbol{x}\, d\boldsymbol{x}',$$

where $|\mathcal{V}|$ is the volume of the system. This is a fluctuation-dissipation relation. From (46), it is also interesting to notice the following relation:

$$\nu = \rho\tau_\Delta\left(U_E^2 - U_{\text{Euler}}^2\right).$$

VI. AN EXAMPLE: THE ET$_6$ THEORY OF VAN DER WAALS FLUIDS

A. Equations of state, nonequilibrium temperatures, and dynamic pressure

Let us study, as a typical example, a polytropic vdW fluid of which thermal and caloric equations of state are given by

$$p = \frac{k_B}{m}\frac{T\rho}{1-b\rho} - a\rho^2, \quad \varepsilon = \frac{D}{2}\frac{k_B}{m}T - a\rho, \tag{58}$$

where D is related to the degrees of freedom of a molecule and the material-dependent constants a and b represent, respectively, a measure of the strength of the attraction between constituent molecules and the effective volume (or exclusion volume) of a molecule. In this case, we have

$$\varepsilon^{K+U}(\rho,T) = \frac{3}{2}\frac{k_B}{m}T - a\rho, \quad \varepsilon^{I}(T) = \frac{D-3}{2}\frac{k_B}{m}T,$$

and, from (4), (5), and (9), we have

$$\Pi = \frac{k_B}{m}\frac{\rho}{1-b\rho}(\vartheta - T), \quad \bar{\Pi} = \frac{k_B}{m}\rho(\vartheta - T), \quad \frac{\Theta - T}{\vartheta - T} = -\frac{3}{D-3}.$$

Moreover the relation between the bulk viscosity and the relaxation time (54) is explicitly obtained as follows:

$$\nu = \frac{k_B}{m}\frac{2(D-3)}{3D}\frac{T\rho}{(1-b\rho)}\tau_\Delta.$$

B. Nonequilibrium entropy and bounded domain of Θ in a vdW fluid

From equilibrium thermodynamics, the equilibrium entropy density s is given by

$$s = s^{K+U} + s^{I}, \quad s^{K+U} = \frac{k_B}{m}\log\left(T^{\frac{3}{2}}\frac{1-b\rho}{\rho}\right) + s_0^{K+U}, \quad s^{I} = \frac{k_B}{m}\log T^{\frac{D-3}{2}} + s_0^{I},$$

where s_0^{K+U} and s_0^{I} are constants at a reference state. From (26) the nonequilibrium entropy density η is obtained as follows:

$$\begin{aligned}\eta &= s^{K+U}(\rho,\vartheta) + s^{I}(\Theta)\\ &= \frac{k_B}{m}\left\{\log\left(\vartheta^{\frac{3}{2}}\frac{1-b\rho}{\rho}\right) + \log\Theta^{\frac{D-3}{2}}\right\} + s_0,\end{aligned} \tag{59}$$

where $s_0 = s_0^{K+U} + s_0^{I}$.

From (39), we have the condition for the nonequilibrium temperature ϑ:

$$0 < \vartheta < \frac{D}{3}T. \tag{60}$$

This condition corresponds to the condition of Θ:

$$0 < \Theta < \frac{D}{D-3}T.$$

C. Convexity for a vdW fluid

As the conditions in the second and third equations of (36) are identically satisfied, the convexity condition of $h = \rho\eta$ with η given by (59) comes only from the first equation of (36) and is expressed as

$$\hat{p}(\hat{\rho},\hat{\vartheta}) > (3 - 2\hat{\rho})\hat{\rho}^2, \tag{61}$$

where we have introduced the following dimensionless variables:

$$\hat{p} = \frac{p}{p_{cr}}, \quad \hat{\rho} = \frac{\rho}{\rho_{cr}}, \quad \hat{T} = \frac{T}{T_{cr}}, \quad \hat{\vartheta} = \frac{\vartheta}{T_{cr}}, \tag{62}$$

with $p_{cr} = a/(27b^2)$, $\rho_{cr} = 1/(3b)$, and $T_{cr} = 8a/(27\frac{k_B}{m}b)$, which are the quantities at the critical point. We notice that the boundary (spinodal curve) is independent of $\hat{\vartheta}$, similarly to the case of the

Euler system in which the spinodal curve for equilibrium pressure is independent of the temperature. From (60), $\hat{\vartheta}$ is bounded as follows:

$$0 < \hat{\vartheta} < \frac{D}{3}\hat{T}.$$

The critical point is the point on the spinodal curve with the condition that the second derivative also vanishes:

$$\left[\frac{\partial^2 p(\rho,\vartheta)}{\partial \rho^2}\right]_{\vartheta} = 0.$$

With (61), we have, as the Euler system,

$$\hat{\rho} = 1, \quad \hat{\vartheta} = 1, \quad \hat{p}(\hat{\rho},\hat{\vartheta}) = 1.$$

It should be noted that, in the space (ρ, p, Θ), we can observe now a spinodal surface instead of the spinodal curve and a critical line instead of the critical point. Using the present ET model, we can develop critical dynamics [58,59], which is the subject for subsequent works.

D. Characteristic velocity in a vdW fluid

From (43), (44), and (45) and the equations of state (58), the velocities U, U_E, and U_{Euler} are obtained as follows:

$$\begin{aligned} U^2 &= \frac{5}{3}\frac{k_B}{m}\frac{\vartheta}{(1-b\rho)^2} - 2a\rho \\ &= \frac{5}{3}\frac{k_B}{m}\frac{T}{(1-b\rho)^2} - 2a\rho + \frac{5(D-3)}{9}\frac{k_B}{m}\frac{T-\Theta}{(1-b\rho)^2}. \end{aligned} \tag{63}$$

In an equilibrium case with $\Theta = T$, we have

$$U_E^2 = \frac{5}{3}\frac{k_B}{m}\frac{T}{(1-b\rho)^2} - 2a\rho.$$

It is remarkable that if $\Theta \lesseqgtr T$ then $U \gtreqless U_E$. For Eulerian fluids, we have

$$U_{\text{Euler}}^2 = \frac{D+2}{D}\frac{k_B}{m}\frac{T}{(1-b\rho)^2} - 2a\rho < U_E^2$$

for any $D > 3$. This inequality is the subcharacteristic condition. Last, the dimensionless characteristic velocity which determines the dispersion relation is obtained as follows:

$$\hat{U}_E = \sqrt{\frac{\frac{20}{3}\hat{T} - (\hat{\rho}-3)^2\hat{\rho}}{4\frac{D+2}{D}\hat{T} - (\hat{\rho}-3)^2\hat{\rho}}}. \tag{64}$$

From (64) with (61), we can prove $\hat{U}_E > \hat{U}_E^{\text{rarefied}}$ where $\hat{U}_E^{\text{rarefied}} = \lim_{\hat{\rho}\to 0}\hat{U}_E = \sqrt{\frac{5}{3}\frac{D}{D+2}}$ is the dimensionless characteristic velocity in rarefied gases. Moreover, we notice that $\hat{U}_E$ has an extremum at $\hat{\rho} = 1,3$ and $\lim_{\hat{\rho}\to 3}\hat{U}_E = \hat{U}_E^{\text{rarefied}}$. The dependence of $\hat{U}_E$ on $\hat{\rho}$ is shown in Fig. 2 for $\hat{T} = 1.0,\ 1.5,\ 2.0$ with $D = 5$.

E. Critical derivative in a vdW fluid

Solving $p = p(\rho,\vartheta)$ given by (58) with respect to ϑ and substituting it into (63), we obtain immediately the result that, from (48), the locus of the local exceptionality is expressed as, in the

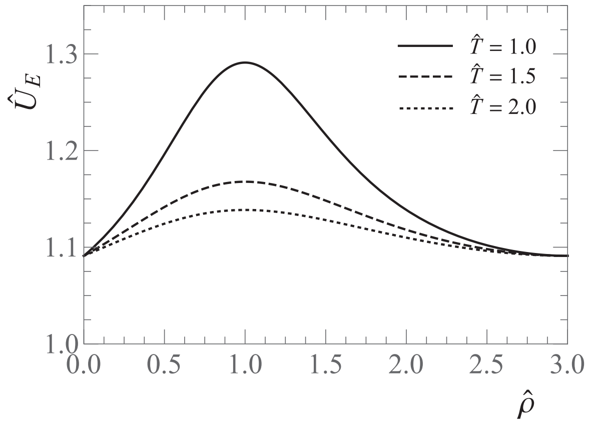

FIG. 2. Dependence of $\hat{U}_E$ on dimensionless mass density for $\hat{T} = 1.0$, 1.5, 2.0 with $D = 5$.

dimensionless form with (62),

$$\hat{p}(\hat{\rho},\hat{\vartheta}) = \hat{\rho}^2\left\{\frac{9}{20}(3-\hat{\rho})^2 - 3\right\}. \tag{65}$$

It is interesting to observe that the locus is independent of the nonequilibrium variables and coincides with the curve for a monatomic Euler fluid. As is well known among fluid dynamics researchers, this curve has been called the critical derivative curve (for details and references see Ref. [47]). Comparing this curve with the spinodal curve (61), we notice that the curve of local exceptionality always resides in the unstable region. Therefore, as far as the van der Waals equation of state is concerned, the rarefaction shock does not appear in the present ET theory in contrast to the Euler system [47]. It is needed to clarify the admissibility of the rarefaction shock by the more realistic ET theory with shear viscosity and heat conductivity. On the other hand, from an experimental point of view, it is well known that the existence of the rarefaction shock is still controversial. We hope that

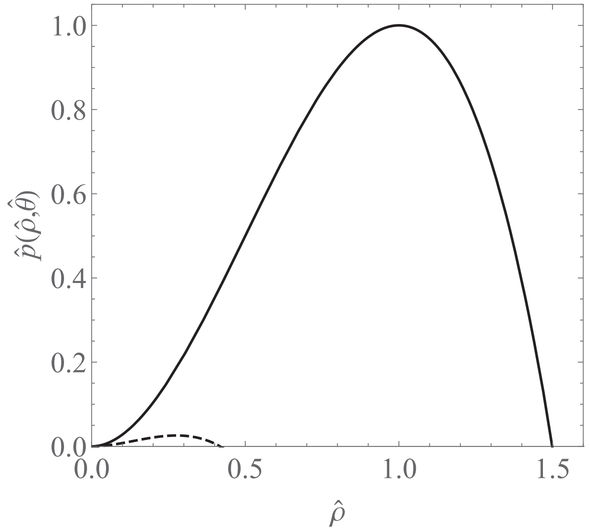

FIG. 3. Spinodal curve, that is, the boundary of (61) (solid line) and locus of the local exceptionality (65) (dashed line) in the $(\hat{\rho}, \hat{p}(\hat{\rho},\hat{\theta}))$ plane.

our theoretical prediction may give an insight into this longstanding problem. In Fig. 3, the locus of the local exceptionality is depicted with the spinodal curve in the $(\hat{\rho}, \hat{p}(\hat{\rho},\hat{\theta}))$ plane.

VII. CONCLUDING REMARKS

An ET theory of dense polyatomic gases has been proposed, and some of its characteristic features are elucidated. As this theory is applicable also to liquid phase, we may say that we have established an *ET theory of fluids* including both gas and liquid. As an example, a van der Waals *fluid* is studied on the basis of the present theory.

Our concluding remarks are given as follows:

(1) We have shown that we can extract interesting information about nonequilibrium processes and fluctuations in molecules from the equations of state by dividing them into a $(K + U)$ part and I part. Specifically, we successfully accomplished the theoretical extension from rarefied polyatomic gases to dense polyatomic gases by using the duality principle. We obtained the nonequilibrium and nonlinear entropy density explicitly. Then we derived a new thermodynamic inequality and the distribution function near equilibrium from which the fluctuation-dissipation relation for the bulk viscosity comes out. If necessary, we may divide the equations of state into several parts and analyze the nonequilibrium phenomena in fluids in a similar but finer way. In particular, in higher temperatures, internal rotational modes and internal vibrational modes in a molecule should be treated separately to obtain more reliable model. We can adopt the same method presented in this paper to obtain such a model.

(2) Fluctuating hydrodynamics based on the ET theory was studied in Refs. [60,61]. It seems to be a promising next step to study this subject by using the present model. Such a study will give us, for example, a more detailed and sophisticated analytical result of the fluctuation-dissipation relation than that presented above.

(3) The ET$_6$ theory is an essential but a simplified model. In order to study the nonequilibrium phenomena for viscous heat-conducting dense fluids beyond the applicability range of the Navier-Stokes Fourier theory, an ET theory with 14 fields (ET$_{14}$) that takes into account heat flux and shear stress is necessary. It can also be developed in a similar way by adopting the duality principle, and its details will soon be reported. Various applications of the ET$_{14}$ theory are expected, for example, applications to shock waves, dynamics of gas-liquid phase transition, in particular dynamics near the critical point, nonequilibrium hydrodynamic fluctuation, and so on.

(4) In the present paper, the construction of an ET theory of dense *monatomic* gases remains as future work. In its construction it will be necessary for us to identify the most appropriate elementary process that is responsible for the emergence of the dynamic pressure.

ACKNOWLEDGMENTS

This work was partially supported by JSPS KAKENHI Grant Numbers 15K21452 (T.A.) and 25390150 (M.S.), by the National Group of Mathematical Physics GNFM-INdAM, and by the University of Bologna, FARB 2012 Project “Extended Thermodynamics of Non-Equilibrium Processes from Macro- to Nano-Scale” (T.R.).

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