Extended thermodynamics of real gases with dynamic pressure: An extension of the Meixner's theory

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Abstract

Basing on the recent theory of extended thermodynamics of dense gases, we study a thermodynamic theory of gases with the energy transfer from molecular translational mode to internal modes as an extension of the Meixner's theory. We focus our attention on the simplest case with only one dissipative process due to the dynamic pressure. The dispersion relation for sound derived from the present theory is compared with that from the Meixner's theory. Kinetic theoretical basis of the present approach is also discussed.

Keywords: Extended thermodynamics, Dynamic pressure, Dispersion relation for sound, Meixner's theory, Kinetic theory

1. Introduction

Energy transfer from molecular translational mode to internal modes, such as rotational and vibrational modes, affects the propagation speed and attenuation of a sound in a gas composed of polyatomic molecules. Especially when the frequency ω of the sound is in the same order of magnitude as the inverse of the relaxation time of the energy transfer, $1/\tau$, the effect on the sound is prominent. Such nonequilibrium phenomena are usually observed in the ultrasonic frequency range.

The thermodynamic theory with nonequilibrium parameters governed by the relaxation equations [1, 2, 3] has been utilized to describe the phenomena for many years. In order to grasp the essence of the theory, let us consider the simplest case where only one relaxation equation for a nonequilibrium parameter ξ is present in addition to the system of Euler equations for a gas that expresses the mass, momentum and energy conservation laws. That is, we neglect all dissipative processes but the relaxation process. The relaxation equation is introduced in such a way that

$$\dot{\xi} = -\beta A, \tag{1}$$

where a dot on ξ represents the material time derivative, β is a positive coefficient, and A is the affinity of the relaxation process of the energy transfer that depends not only on ξ but also on other thermodynamic quantities, say, the mass density and the entropy density. When $\omega\tau \ll 1$, it was proved that the relaxation process may be interpreted in terms of the dynamic pressure Π, which is related to the gas velocity $\boldsymbol{v}$ as

$$\Pi = -\nu^{\mathrm{eff}} \mathrm{div}\, \boldsymbol{v}$$

with ν^{eff} being the effective bulk viscosity.

Although the Meixner's theory mentioned above seems to be natural, there remain some problems that should be overcome: (i) In the Meixner's theory, the relaxation equation (1) is not fully congruous with the Euler equations. It has not been introduced on the same ground of the Euler equations as one of the general thermodynamic basic field equations. In fact, in a rarefied gas limit, the relaxation equation is not consistent with its counterpart of the moment equations derived from the kinetic theory of gases [4]. See also section 4.2 below. (ii) The Meixner's theory is formulated within the framework of thermodynamics of irreversible processes [3]. The local equilibrium assumption is premised from the beginning. However, in such phenomena as ultrasonic wave propagation where temporal and spatial changes are rapid and steep, this assumption is not well-satisfied [5].

In this paper, we propose a fully-consistent thermodynamic theory of the sound propagation in a gas with the energy transfer where the local equilibrium assumption is not necessarily valid, and thereby try to extend the Meixner's theory. We adopt the theory of extended thermodynamics (ET) [6] of dense gases [7]. As before, the essence of our theory can be most clearly shown by studying the simplest case where only one dissipative process due to the dynamic pressure exists. In section 2, we derive the closed system of field equations for gases. In section 3, we study the dispersion relation for sound and compare it with that derived from the Meixner's theory. The last section is devoted to concluding remarks with the discussions of subsystems and the kinetic theoretical basis of the present theory.

2. Extended thermodynamics of real gases with 6 fields

First of all, let us recall that, for a rarefied monatomic gas, it is simple to costruct a rational theory of extended thermodynamics as a hyperbolic counterpart of the Navier-Stokes-

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Fourier theory becasue the hierarchy of the basic system of differential equations is properly dictated by the kinetic theory [6]. While, for rarefied polyatomic gases and for dense gases, a satisfactory theory was not established [8, 9, 10, 11, 12, 13] until the appropriate binary hierarchy of the differential equations for dense gases with 14 fields has been proposed by the present authors [7]. In fact, using only general principles such as the Galilean invariance and the entropy principle, we proved that the system of field equations can be closed with respect to the independent field variables and the constitutive functions are determined explicitly by the equilibrium thermal and caloric equations of state.

2.1. Binary hierarchy of the differential equations

As mentioned above, we restrict our study within the simplest case of 6 independent field variables, that is,

mass density:	$F\ (=\rho)$,
momentum density:	$F_i\ (=\rho v_i)$,
energy density:	G_{ii}
trace part of momentum flux:	F_{ii}.

We adopt the following binary hierarchy (F-series and G-series, see also section 4.2.) of the balance equations [7]:

$$\begin{aligned}
&\frac{\partial F}{\partial t}+\frac{\partial F_k}{\partial x_k}=0,\\
&\frac{\partial F_i}{\partial t}+\frac{\partial F_{ik}}{\partial x_k}=0,\\
&\qquad\qquad\qquad\qquad \frac{\partial G_{ii}}{\partial t}+\frac{\partial G_{iik}}{\partial x_k}=0,\\
&\frac{\partial F_{ii}}{\partial t}+\frac{\partial F_{iik}}{\partial x_k}=P_{ii}
\end{aligned} \tag{2}$$

where F_{ik} is the momentum flux, F_{iik} is the flux of F_{ii}, G_{iik} is the energy flux, and P_{ii} is the production with respect to F_{ii}. The equations with no production term represent the mass, momentum and energy conservation laws.

As the balance equations (2) should be invariant under the *Galilean transformation*, the dependence of the quantities on the velocity can be expressed as follows [14]:

$$\begin{aligned}
&F_{ij}=\rho v_i v_j+M_{ij},\\
&G_{ii}=\rho v_i v_i+m_{ii},\\
&F_{iik}=\rho v_i v_i v_k+3M_{(ik}v_{i)}+M_{iik},\\
&G_{iik}=\rho v_i v_i v_k+m_{ii}v_k+2M_{ik}v_i+m_{iik},
\end{aligned} \tag{3}$$

where M_{ij}, m_{ii}, M_{iik} and m_{iik} do not depend on the velocity. Parentheses around a set of indices represent the symmetrization with respect to the indices. The production P_{ii} is also independent of the velocity.

With Eq. (3), the balance equations (2) can be rewritten as

$$\begin{aligned}
&\dot\rho+\rho\frac{\partial v_k}{\partial x_k}=0,\\
&\rho\dot v_i+\frac{\partial M_{ij}}{\partial x_j}=0,\\
&\dot m_{ii}+m_{ii}\frac{\partial v_k}{\partial x_k}+\frac{\partial m_{iik}}{\partial x_k}+2\frac{\partial v_i}{\partial x_k}M_{ik}=0,\\
&\dot M_{ii}+M_{ii}\frac{\partial v_k}{\partial x_k}+\frac{\partial M_{iik}}{\partial x_k}+2\frac{\partial v_i}{\partial x_k}M_{ik}=P_{ii}.
\end{aligned} \tag{4}$$

We notice that the quantities M_{ij}, m_{ii} and m_{ppi} have the following conventional meanings:

stress:	$t_{ij}=-M_{ij}\ (=-(p+\Pi)\,\delta_{ij}+M_{\langle ij\rangle})$,
specific internal energy:	$\varepsilon=\dfrac{1}{2\rho}m_{ii}$,
heat flux:	$q_i=\dfrac{1}{2}m_{ppi}$,

where the pressure p depends only on ρ and m_{ii}, Π is the dynamic pressure, and angular brackets denote the symmetric traceless part.

We may now adopt $\{\rho,\ v_i,\ m_{ii},\ \Pi\}$ as a set of independent variables instead of $\{F,\ F_i,\ G_{ii},\ F_{ii}\}$. The balance equation of M_{ii} (Eq. $(4)_4$) is then rewritten as

$$\begin{aligned}
&\dot\Pi+\left(\frac{5}{3}p-\rho\left(\frac{\partial p}{\partial\rho}\right)_{m_{ii}}-(m_{rr}+2p)\left(\frac{\partial p}{\partial m_{qq}}\right)_\rho\right)\frac{\partial v_k}{\partial x_k}\\
&+\left(\frac{5}{3}-2\left(\frac{\partial p}{\partial m_{qq}}\right)_\rho\right)\Pi\frac{\partial v_k}{\partial x_k}+2\left(\frac{1}{3}-\left(\frac{\partial p}{\partial m_{qq}}\right)_\rho\right)\frac{\partial v_r}{\partial x_k}M_{\langle rk\rangle}\\
&+\frac{1}{3}\frac{\partial M_{rrk}}{\partial x_k}-\left(\frac{\partial p}{\partial m_{qq}}\right)_\rho\frac{\partial m_{rrk}}{\partial x_k}=\frac{P_{rr}}{3}.
\end{aligned}$$

2.2. Constitutive equations

We need the constitutive equations in order to set up the closed system of field equations. We assume that the constitutive equations at one point and time depend on the independent fields at that point and time. Therefore the constitutive quantities $\{M_{\langle ij\rangle},\ M_{iik},\ m_{iik},\ P_{ii}\}$ are expressed as functions of

$$(\rho,\ m_{ii},\ \Pi).$$

We apply the constitutive theory of ET [6] where the following universal physical principles (A)-(C) are imposed on the constitutive equations: (A) *Material frame indifference principle*: This requires that constitutive equations are independent of an observer. This principle and the Galilean invariance for the balance laws constitute the objectivity principle (the principle of relativity). (B) *Entropy principle*: All solutions of the system of field equations must satisfy the entropy balance law:

$$\frac{\partial h}{\partial t}+\frac{\partial(hv_k+\varphi_k)}{\partial x_k}=\Sigma\geqq 0\Leftrightarrow\dot h+h\frac{\partial v_k}{\partial x_k}+\frac{\partial\varphi_k}{\partial x_k}=\Sigma\geqq 0$$

where h is the entropy density, h_k is the entropy flux ($h_k = hv_k + \varphi_k$: φ_k is the non-convective entropy flux), and Σ is the entropy production. Here h and φ_k are constitutive quantities:

$$h \equiv \hat{h}(\rho,\, m_{ii},\, \Pi), \quad \varphi_k \equiv \hat{\varphi}_k(\rho,\, m_{ii},\, \Pi).$$

(C) *Causality*: This requires the concavity of the entropy density and guarantees the hyperbolicity of the system of field equations. This also ensures the well-posedness (local in time) of a Cauchy problem and the finiteness of the propagation speeds of disturbances.

As the result of the universal principles, in the neighborhood of equilibrium, we obtain the constitutive equations:

$$M_{\langle ij\rangle} = 0, \quad M_{iik} = 0, \quad m_{iik} = 0, \quad P_{ii} = -\frac{3\zeta}{Ta_1}\Pi, \tag{5}$$

where ζ is a positive function of the density ρ and the temperature T, and a_1 is given by [7]

$$a_1 = \frac{5}{3}p - \rho\left(\frac{\partial p}{\partial \rho}\right)_T - \frac{T}{\rho}\left(\frac{\partial p}{\partial T}\right)_\rho^2 \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}.$$

The entropy density and entropy flux are given by

$$h = h^E - \frac{1}{2Ta_1}\Pi^2, \quad \varphi_k = 0, \tag{6}$$

where h^E is the entropy density in equilibrium. From (6), we obtain the concavity conditions at an equilibrium state:

$$\left(\frac{\partial \varepsilon}{\partial T}\right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho}\right)_T > 0, \quad a_1 > 0.$$

2.3. Field equations

The closed system of field equations is obtained by substituting the constitutive equations (5) into the system (4):

$$\begin{aligned}
&\dot{\rho} + \rho\frac{\partial v_k}{\partial x_k} = 0,\\
&\rho\dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} = 0,\\
&\rho\left(\frac{\partial \varepsilon}{\partial T}\right)_\rho \dot{T} + \left[p + \Pi - \rho^2\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T\right]\frac{\partial v_k}{\partial x_k} = 0,\\
&\dot{\Pi} + (a_1 + a_2\Pi)\frac{\partial v_k}{\partial x_k} = -\frac{1}{\tau_\Pi}\Pi,
\end{aligned} \tag{7}$$

where the relaxation time τ_Π and a_2 are given by

$$\tau_\Pi = \frac{Ta_1}{\zeta}, \qquad a_2 = \frac{5}{3} - \frac{1}{\rho}\left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}.$$

The evolution equation $(7)_4$ for Π is now obtained consistently, which may be seen as the counterpart of the relaxation equation in the Meixner's theory.

If we apply the Maxwellian iteration [6, 15] to the system (7), the first iterate $\Pi^{(1)}$ is obtained by the substitution of the 0th iterate $\Pi^{(0)} = 0$ into the left hand side of $(7)_4$:

$$\Pi^{(1)} = -a_1\tau_\Pi\frac{\partial v_k}{\partial x_k},$$

from which the bulk viscosity ν is given by

$$\nu = a_1\tau_\Pi = \frac{Ta_1^2}{\zeta}.$$

Therefore we can calculate ζ from the experimental data of ν.

3. Dispersion relation for sound: comparison with the Meixner's theory

In this section, we study a linear plane harmonic wave and obtain its dispersion relation. The result obtained is compared with that from the Meixner's theory.

Without loss of generality, we may study the wave in the following form:

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

where $\boldsymbol{u} = (\rho, v, T, \Pi)^T$ is a state vector with v being the x-component of the velocity $\boldsymbol{v}$, $\boldsymbol{u}_0 = (\rho_0, 0, T_0, 0)^T$ is a state vector at a reference equilibrium state, and $\bar{\boldsymbol{u}} = (\bar{\rho}, \bar{v}, \bar{T}, \bar{\Pi})^T$ is the deviation from $\boldsymbol{u}_0$ expressed as

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

Here $\boldsymbol{w}$ is the amplitude, ω is the frequency, and k is the complex wave number such that $k = k_r + \mathrm{i}k_i$ ($k_r = \Re(k)$, $k_i = \Im(k)$).

From the linearized system of field equations, which is obtained by linearizing (7) with respect to $\bar{\boldsymbol{u}}$, we can easily obtain the dispersion relation [6]:

$$\det\left(\boldsymbol{I} - z\boldsymbol{A}_0 + \frac{\mathrm{i}}{\omega}\boldsymbol{B}_0\right) = 0, \tag{8}$$

where $z = k/\omega$, $\boldsymbol{I}$ is the unit matrix, and

$$\boldsymbol{A}_0 = \begin{pmatrix} 0 & \rho & 0 & 0 \\ \dfrac{1}{\rho}\left(\dfrac{\partial p}{\partial \rho}\right)_T & 0 & \dfrac{1}{\rho}\left(\dfrac{\partial p}{\partial T}\right)_\rho & \dfrac{1}{\rho} \\ 0 & \dfrac{p - \rho^2\left(\dfrac{\partial \varepsilon}{\partial \rho}\right)_T}{\rho\left(\dfrac{\partial \varepsilon}{\partial T}\right)_\rho} & 0 & 0 \\ 0 & a_1 & 0 & 0 \end{pmatrix}_0,$$

$$\boldsymbol{B}_0 = \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\dfrac{1}{\tau_\Pi} \end{pmatrix}_0.$$

The index 0 indicates the values at the reference state.

From the dispersion relation, the phase velocity v_{ph} and the attenuation factor α are obtined as the functions of ω:

$$v_{\mathrm{ph}} = \frac{\omega}{\Re(k)} = \frac{1}{\Re(z)}, \qquad \alpha = -\Im(k) = -\omega\Im(z).$$

By the requirement of the linear stability, α must be positive (negative) for the waves traveling to the x-positive (negative) direction.

The high-frequency limits of $v_{\rm ph}$ and α are given by [6, 16] :

$$\lim_{\omega\to\infty} v_{\rm ph}(\omega) = \lambda_0 = \sqrt{\frac{5p_0}{3\rho_0}}, \quad \lim_{\omega\to\infty} \alpha(\omega)\lambda_0 = -\boldsymbol{l}_0 \cdot \boldsymbol{B}_0 \cdot \boldsymbol{d}_0, \tag{9}$$

where the characteristic velocity λ_0 is the non-zero eigenvalue of $\boldsymbol{A}_0$, and $\boldsymbol{l}_0$ and $\boldsymbol{d}_0$ are the left and right eigenvectors of $\boldsymbol{A}_0$, respectively. It is remarkable that, even for polyatomic gases, the high frequency limit $v_{\rm ph}(\infty)$ does not depend on the internal degrees of freedom in a rarefied gas limit. The attenuation factor is given by

$$\alpha(\infty) = \pm\frac{1}{2\tau_\Pi}\sqrt{\frac{3\rho_0}{5p_0}}\left(1 - \frac{3}{5}c_0^2\frac{\rho_0}{p_0}\right),$$

where c_0 is the sound velocity in the reference state:

$$c_0^2 = \left(\left(\frac{\partial p}{\partial \rho}\right)_T + \frac{\left(\frac{\partial p}{\partial T}\right)_\rho^2 T}{\left(\frac{\partial \varepsilon}{\partial T}\right)_\rho \rho^2}\right)_0.$$

Finally let us compare the dispersion relation (8) with that of the Meixner's theory. The relation (8) can be rewritten as

$$(c_0 z)^2\left(-\frac{5p_0}{3c_0^2\rho_0} + \frac{\rm i}{\tau_\Pi\omega}\right) + 1 - \frac{\rm i}{\tau_\Pi\omega} = 0.$$

While the dispersion relation derived from the Meixner's theory is given by [3]

$$(c_0 z)^2\left(-\frac{v_{\rm ph}(\infty)^2}{c_0^2} + \frac{\rm i}{\tau\omega}\right) + 1 - \frac{\rm i}{\tau\omega} = 0.$$

By taking the relation $(9)_1$ into account, it is easy to show that, if $\tau_\Pi = \tau$, both dispersion relations coincide with each other.

4. Subsystems and kinetic theory

We have shown in the above that, through studying the simplest case, a fully-consistent thermodynamic theory of sounds in a gas with the energy transfer can be established on the basis of ET. This is valid even in the region beyond the local equilibrium assumption. The relationship between the present theory with 6 independent variables and the Meixner's theory is also shown. It is found that, as far as the dispersion relation for a weak sound propagating in an equilibrium state is concerned, both theories predict the same expression of the relation.

Lastly we make four concluding remarks 4.1-4.4:

4.1. ET of 14 fields and the concept of subsystems

The extended thermodynamic theory of dense gases that takes into account not only the dynamic pressure but also the shear stress and heat flux has already been proposed by the present authors [7]. This is the theory of real gases with 14 field variables. In this respect, it is important to recognize that the theory with 6 variables presented above is a *principal subsystem* of the 14-variable theory according to the definiton due to Boillat and Ruggeri [17]. We may, therefore, assert that the 6-variable theory is the simplest variant among dissipative systems from the non-dissipative Euler system. In contrast to the well-known Navier-Stokes-Fourier model that is of parabolic type, the present variant is of hyperbolic type. To sum up, the present 6-variable system is the simplest non-trivial hyperbolic one next to the system of Euler equations.

4.2. Consistency with the kinetic theory of polyatomic gases

Let us study the system (7) in the rarefied gas limit, and adopt the thermal and caloric equations of state:

$$p = \frac{k_{\rm B}}{m}\rho T, \quad \varepsilon = \frac{D}{2}\frac{k_{\rm B}}{m}T, \tag{10}$$

where $k_{\rm B}$ and m are the Boltzmann constant and the mass of a molecule, and the constant D is the degrees of freedom of a molecule, i.e., $D = 3 + f$ where 3 corresponds to the translational motion and f is the internal degrees of freedom. The system of field equations are expressed as

$$\begin{aligned}
&\dot\rho + \rho\frac{\partial v_k}{\partial x_k} = 0,\\
&\rho\dot v_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} = 0,\\
&\dot T + \frac{2}{D\frac{k_B}{m}\rho}(p+\Pi)\frac{\partial v_k}{\partial x_k} = 0,\\
&\dot\Pi + \frac{2(D-3)}{3D}p\frac{\partial v_k}{\partial x_k} + \frac{5D-6}{3D}\Pi\frac{\partial v_k}{\partial x_k} = -\frac{1}{\tau_\Pi}\Pi.
\end{aligned} \tag{11}$$

The relaxation time τ_Π and the bulk viscosity ν are given by

$$\tau_\Pi = \frac{2(D-3)pT}{3D\zeta}, \quad \nu = \frac{2(D-3)}{3D}p\tau_\Pi.$$

For monatomic gases ($D = 3$), as is expected, τ_Π and ν vanish and the evolution equation $(11)_4$ for Π has now no role.

In this subsection, we show that above results are fully consistent with the kinetic theory. That is, the balance equations for rarefied polyatomic gases (11) can be obtained via the kinetic theory [18] in which the internal energy of a molecule I is taken into account. Physical quantities are expressed as the moments of a one-body distribution function $f(x_i, c_i, t, I)$ with c_i being the velocity of a molecule. The mass density ρ and the momentum density ρv_i are expressed as

$$\begin{aligned}
\rho &= \int m f(x_i, c_i, t, I)\varphi(I){\rm d}I{\rm d}c_1{\rm d}c_2{\rm d}c_3,\\
\rho v_i &= \int m c_i f(x_i, c_i, t, I)\varphi(I){\rm d}I{\rm d}c_1{\rm d}c_2{\rm d}c_3,
\end{aligned} \tag{12}$$

where $\varphi(I){\rm d}I$ is a nonnegative measure. We adopt $\varphi(I) = I^\sigma$ [18], where σ will be related to the degrees of freedom D below. The integration range is taken as $[0, \infty)$ for I and $(-\infty, \infty)$ for c_1, c_2 and c_3. By using the peculiar velocity C_i defined by

$$C_i \equiv c_i - v_i,$$

the internal energy ε, and the sum of the pressure p and the dynamic pressure Π are expressed as

$$\begin{aligned} 2\rho\varepsilon &= \int (mC^2 + 2I) f(x_i, c_i, t, I)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3, \\ 3(p+\Pi) &= \int mC^2 f(x_i, c_i, t, I)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3, \end{aligned} \tag{13}$$

where $C^2 = C_iC_i$. It is noticeable that there exist two kinds of second order moments: the energy density and the momentum flux, which appear in the binary structure introduced in section 2. Therefore, as proposed in [19], the moments of the F-series and G-series can be obtained at the kinetic level:

$$\begin{aligned} F_{i_1 i_2 \cdots i_n} &= \int mc_{i_1}c_{i_2}\cdots c_{i_n} f(x_i, c_i, t, I)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3, \\ G_{i_1 i_2 \cdots i_n ll} &= \int (mc^2 + 2I)c_{i_1}c_{i_2}\cdots c_{i_n} f(x_i, c_i, t, I)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3, \end{aligned}$$

where $c^2 = c_ic_i$.

We adopt the Bhatnagar-Gross-Krook (BGK) equation [20] as the basic equation in the kinetic approach:

$$\frac{\partial f}{\partial t} + c_i\frac{\partial f}{\partial x_i} = -\frac{f - f_\mathrm{E}}{\tau'},$$

where τ' is the relaxation time and f_E is the local equilibrium distribution function given by [18]

$$f_\mathrm{E} = \frac{n}{q(T)}\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2} \mathrm{e}^{-\frac{1}{k_\mathrm{B}T}\left(\frac{m}{2}C^2 + I\right)} \tag{14}$$

with n being the number density ($n = \rho/m$) and $q(T)$ the normalization function defined by

$$q(T) = \int \varphi(I)\mathrm{e}^{-\frac{I}{k_\mathrm{B}T}}\mathrm{d}I.$$

Inserting (14) into (13), we have the relation $\sigma = (D-5)/2$ due to the consistency between (13) and (10).

Multiplying the BGK equation by $m\mathbf{\Phi}(c_i, I) \equiv m\left(1, c_i, (c^2 + 2I/m), c^2\right)$ and integrating over the whole space, we have the balance equations of 6 moments $\mathbf{u} \equiv (F, F_i, G_{ii}, F_{ii})$, which are certainly the same as (2) with the collision term: $P_{ii} = -(1/\tau')\int mc^2\left(f - f_\mathrm{E}\right)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3$.

Concerning the closure at the kinetic level, we adopt the maximum entropy principle (MEP) proposed for rarefied monatomic gases in [21, 6] and for polyatomic ones in [19]. Under MEP, the distribution function is calculated by maximizing the enrtopy, which is a functional of f, under the constraints of fixed values for the moments. In the neighborhood of equilibrium the distribution function is given by [22, 23]

$$f = f_\mathrm{E}\left(1 - \frac{m}{k_\mathrm{B}}\mathbf{\Lambda}\cdot\mathbf{\Phi}(c_i, I)\right), \tag{15}$$

where $\mathbf{\Lambda}$ is the non equilibrium Lagrange multiplier. The nonequilibrium part of $\mathbf{u}$ is thus given by

$$\mathbf{u} - \mathbf{u}_\mathrm{E} = -\frac{m^2}{k_\mathrm{B}}\int f_\mathrm{E}\ \mathbf{\Lambda}\cdot\mathbf{\Phi}(c_i, I)\ \mathbf{\Phi}(c_i, I)\varphi(I)\mathrm{d}I\mathrm{d}c_1\mathrm{d}c_2\mathrm{d}c_3,$$

where $\mathbf{u}_\mathrm{E}$ is the equilibrium part. On the other hand, from the definitions of (12) and (13), we know that $\mathbf{u} - \mathbf{u}_\mathrm{E} \equiv (0, 0, 0, 3\Pi)$. Therefore we obtain $\mathbf{\Lambda}$ in terms of the independent variables. By using the distribution function (15) with this $\mathbf{\Lambda}$, all moments are expressed in closed forms. These are the same, if $\tau' = \tau_\Pi$, as the constitutive equations used in (11).

In this way, we have confirmed in the case of rarefied polyatomic gases that our macroscopic thermodynamic theory is perfectly in agreement with the kinetic theory and also in this case the entropy principle gives the same results of the MEP as in the case of monatomic gases [22]. The compatibility between two different approaches supports the validity of the present macroscopic ET theory for any real gases given by the general system (7).

Finally we recall that the basic system of differential equations can be written in a symmetric form by using the main field $\mathbf{u}'$ that, in the case of rarefied polyatomic gases, coincides with the Lagrange multiplier vector $\mathbf{\Lambda} + \boldsymbol{\lambda}_\mathrm{E}$ (see [22] and references therein):

$$\begin{aligned} \boldsymbol{\lambda}_\mathrm{E} &\equiv \frac{1}{T}\left(-g + \frac{v^2}{2},\ -v_i,\ \frac{1}{2},\ 0\right) \\ \mathbf{\Lambda} &\equiv \frac{m}{k_\mathrm{B}\rho T^2}\Pi\left(-\frac{v^2}{2},\ v_i,\ \frac{3}{2(D-3)},\ -\frac{D}{2(D-3)}\right) \end{aligned} \tag{16}$$

with g being the chemical potential.

4.3. Characteristic velocities and hyperbolic region

In a general nonequilibrium state, the characteristic velocities are given by

$$\lambda = v_n \ \text{(multiplicity 4)}, \quad \lambda = v_n \pm \sqrt{\frac{5}{3}\frac{p+\Pi}{\rho}}$$

where $v_n = \mathbf{v}\cdot\mathbf{n}$ with $\mathbf{n}$ being the unit normal of the wave front. The condition of hyperbolicity is then expressed by $\Pi > -p$.

4.4. Possible applications of ET of dense gases

Obviously, the consistent thermodynamic theory of dense gases that is valid beyond the local equilibrium assumption is crucially important, for example, in acoustics [24] and gas dynamics [25], and in their various applications in the fields of engineering, biology and so on. Study of nonlinear waves such as acceleration waves and shock waves in dense gases based on the theory of ET is also quite promising.

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[1] J. Meixner, Ann. Physik 43 (1943) 470.
[2] J. Meixner, Acoustica 2 (1952) 101.
[3] S. R. de Groot, P. Mazur, Non-Equilibirum Thermodynamics, Dover, New York (1984).
[4] G. M. Kremer, Continuum Mech. Thermodyn. 1 (1989) 21.
[5] T. Arima, S. Taniguchi, T. Ruggeri, M. Sugiyama, Dispersion Relation for Sound in Rarefied Polyatomic Gases Based on Extended Thermodynamics, to be submitted.
[6] I. Müller, T. Ruggeri, Rational Extended Thermodynamics, Second Edition, Springer, New York (1998).

[7] T. Arima, S. Taniguchi, T. Ruggeri, M. Sugiyama, Continuum Mech. Thermodyn. (2012) DOI: 10.1007/s00161-011-0213-x.
[8] I.-S. Liu, Arch. Rational Mech. Anal. 88 (1985) 1.
[9] G. M. Kremer, Physica 144 (1987) 156.
[10] I.-S. Liu, G. M. Kremer, Mat. Aplic. Comp. 9 (1990) 123.
[11] I.-S. Liu, J. A. Salvador, Continuum Mech. Thermodyn. 2 (1990) 179.
[12] G. Kremer, Taylor and Francis, New York (1992) 140.
[13] M. C. Carrisi, M. A. Mele, S. Pennisi, Proc. R. Soc. A 466 (2010) 1645.
[14] T. Ruggeri, Continuum Mech. Thermodyn. 1 (1989) 3.
[15] E. Ikenberry, C. Truesdell, J. Rational Mech. Anal. 5 (1956) 1.
[16] T. Ruggeri, A. Muracchini, L. Seccia. Wave Motion 15 (1992) 143.
[17] G. Boillat, T. Ruggeri, Arch. Rational Mech. Anal. 137 (1997) 305.
[18] L. Desvillettes, R. Monaco and F. Salvarani, Euro. J. Mech. B/ Fluids 24 (2005) 219.
[19] M. Pavic, T. Ruggeri and S. Simic, Maximum Entropy Principle for Polyatomic Gases, to be submitted.
[20] P. L. Bhatnagar, E. P. Gross and M. Krook, Phys. Rev. 94 (1954) 511.
[21] W. Dreyer, J. Phys. A 20 (1987) 6505.
[22] G. Boillat and T. Ruggeri, Continuum Mech. Thermodyn. 9 (1997) 205.
[23] F. Brini and T. Ruggeri, Continuum Mech. Thermodyn. 14 (2002) 165.
[24] W. P. Mason (ed.), Physical Acoustics, Principles and Methods, Volume II - Part A, Academic Press, New York, London (1965).
[25] W. G. Vincenti, C. H. Kruger Jr., Introduction to Physical Gas Dynamics, John Wiley and Sons., New York, London, Sydney (1965).