

CHARACTERISTIC FEATURES OF EXTENDED THERMODYNAMICS OF DENSE GASES

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ABSTRACT. A recently-developed theory of extended thermodynamics of dense gases is reviewed and its characteristic features are discussed. The discussion is made in the following four cases separately: (i) Rarefied monatomic gases, (ii) rarefied polyatomic gases, (iii) dense monatomic gases, and (iv) dense polyatomic gases. In particular, for rarefied polyatomic gases, we exemplify the validity of the theory through comparing the dispersion relation for sound with experimental data.

*Dedicated to Prof. Giuseppe Grioli
on the occasion of his 100th birthday.*

1. Introduction

In an endeavor to understand ubiquitous nonequilibrium phenomena, a number of thermodynamic theories have been proposed and developed. Among others, thermodynamics of irreversible processes (TIP), which adopts the assumption of local equilibrium as one of the essential theoretical ingredients, is well-known owing to its systematic and comprehensive theoretical structure [1]. The Navier-Stokes Fourier (NSF) theory for fluids [1, 2] is a typical one. TIP has repeatedly demonstrated its practical usefulness in various situations. From a theoretical point of view, however, it involves a serious problem, that is, the problem of infinite speed of disturbances, which is sometimes called symbolically the paradox of heat conduction, due to the parabolic character of the basic equations with spatially non-local constitutive equations [3]. To avoid this difficulty, extended thermodynamics (ET) [4, 5] basing on a hyperbolic system of field equations was conceived. ET is applicable to highly nonequilibrium phenomena with steep gradients in space and rapid changes in time out of local equilibrium by adopting dissipative fluxes as independent fields and the spatio-temporally local constitutive equations. Such constitutive equations are severely restricted by imposing the universal physical principles; *Entropy principle*, *Causality*, and *Objectivity*, details of which will be explained below.

In the early stage of ET, a theory for rarefied monatomic gases was developed [6]. For example, the ET theory of rarefied monatomic gases with 13 fields is a theory of 13 independent fields; mass density, momentum density, momentum flux, and energy flux [4, 6]. By the use of the proper constitutive equations compatible with the universal physical principles, a closed system of field equations is obtained. A remarkable point is that the

constitutive equations can be explicitly determined from the equilibrium caloric and thermal equations of state. It is shown that the NSF theory comes out as a limiting case of ET through carrying out the Maxwellian iteration [7]. The closed system of field equations is totally consistent with the counterpart system of the moments in the kinetic theory [8].

After the establishment of ET of rarefied monatomic gases, there appeared many studies of ET for rarefied polyatomic gases [9, 10, 11] and also for dense gases [12, 13, 14, 15, 16]. In contrast to ET of rarefied monatomic gases, in these theories, there exists a fatal difficulty that the constitutive equations can not be determined in a fully explicit way from the caloric and thermal equations of state. There remain many phenomenological constants in the constitutive equations that are impossible to be evaluated experimentally or theoretically. Finally, in 2011, an ET theory of dense gases that successfully overcomes the difficulty is developed [17]. Needless to say, the theory is applicable also to rarefied monatomic and polyatomic gases because these gases can be regarded as the special ones of dense gases.

The purpose of the present paper is to review this new theory briefly (section 2) and to discuss its characteristic features (section 3). The discussion will be made in the following four cases separately: (i) Rarefied monatomic gases, (ii) rarefied polyatomic gases, (iii) dense monatomic gases, and (iv) dense polyatomic gases.

For convenience we here summarize some notations used throughout the paper:

(a) A dot on a generic quantity ψ represents the material time derivative:

$$\dot{\psi} \equiv \frac{\partial \psi}{\partial t} + v_i \frac{\partial \psi}{\partial x_i},$$

where t is the time, x_i is the position, and v_i is the velocity.

(b) Parentheses around a set of N indices represent the symmetrization, that is, the sum over all $N!$ permutations of the indices divided by $N!$. For example,

$$a_{(ij}b_{j)} = \frac{1}{2!}(a_ib_j + a_jb_i).$$

(c) Angular brackets denote the symmetric traceless part (deviatoric part). For example,

$$a_{\langle ij \rangle} = a_{(ij)} - \frac{1}{3}a_{kk}\delta_{ij}.$$

2. Extended Thermodynamics of Dense Gases

In this section, we show the essence of the ET theory of dense gases [17].

2.1. Independent fields and balance equations. The theory of ET of dense gases adopts the 14 independent fields:

$$\begin{aligned} \text{mass density:} & \quad F (= \rho), \\ \text{momentum density:} & \quad F_i (= \rho v_i), \\ \text{energy density:} & \quad G_{ii}, \\ \text{momentum flux:} & \quad F_{ij}, \\ \text{energy flux:} & \quad G_{ppi}. \end{aligned} \tag{1}$$

Time evolution of the fields is governed by the following balance equations:

$$\begin{aligned}
 \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\
 \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\
 \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{ij}, \quad \frac{\partial G_{ii}}{\partial t} + \frac{\partial G_{iik}}{\partial x_k} = 0, \\
 \frac{\partial G_{ppi}}{\partial t} + \frac{\partial G_{ppik}}{\partial x_k} &= Q_{ppi},
 \end{aligned} \tag{2}$$

where F_{ijk} and G_{ppik} are the fluxes of F_{ij} and G_{ppi} , respectively, and P_{ij} and Q_{ppi} are the productions with respect to F_{ij} and G_{ppi} , respectively. The balance equations of F , F_i and G_{ii} are, respectively, the conservation laws of mass, momentum and energy, therefore their productions vanish. It is noteworthy that there are two parallel series in the balance equations; the one starts from the balance equation with the mass density (F -series) and the other from the balance equation with the energy density (G -series). In each series, the flux in one equation becomes the density in the next equation. In the case of rarefied polyatomic gases, this structure of the balance equations emerges naturally for the moments defined in the kinetic theory [18, 19].

We need the constitutive equations in order to set up the closed system of field equations. We assume that the constitutive quantities at one point and time depend on the independent fields at that point and time. The restrictions we impose upon the constitutive equations come from the following universal physical principles [4]:

Entropy principle: All solutions of the system of field equations must satisfy the entropy balance with a non-negative entropy production Σ :

$$\frac{\partial h}{\partial t} + \frac{\partial h_i}{\partial x_i} = \Sigma \geq 0, \tag{3}$$

where h is the entropy density and h_i is the entropy flux, both of which are constitutive quantities.

Causality: This requires the concavity of the entropy density and guarantees the hyperbolicity of the system of field equations.¹ This also ensures the well-posedness (local in time) of a Cauchy problem and the finiteness of the propagation speeds of disturbances.

Objectivity: The proper constitutive equations are independent of an observer. The material frame indifference principle together with the requirement of the Galilean invariance of balance laws constitute the so-called objectivity principle (the principle of relativity).

Let us make clear the velocity dependence of the fields by the Galilean invariance. We firstly decompose the fluxes into the convective and non-convective parts such that

$$\begin{aligned}
 F_{i_1 \dots i_n k} &= F_{i_1 \dots i_n} v_k + H_{i_1 \dots i_n k}, \\
 G_{i_1 \dots i_n k} &= G_{i_1 \dots i_n} v_k + J_{i_1 \dots i_n k}, \\
 h_i &= h v_i + \varphi_i.
 \end{aligned}$$

¹The entropy density used in the mathematical community has usually opposite sign to the present entropy density. As a consequence, they speak about convexity instead of concavity.

In particular, the quantities F_{ijk} and G_{ppik} are decomposed such that $F_{ijk} = F_{ij}v_k + H_{ijk}$ and $G_{ppik} = G_{ppi}v_k + J_{ppik}$. Then we have the following assertion: As the entropy inequality (3) should be invariant under the Galilean transformation [20], h and φ_i do not depend on the velocity. Similarly, because of the Galilean invariance of the balance equations (2), the velocity dependence of the quantities is expressed as

$$\begin{aligned} G_{ii} &= \rho v_i v_i + m_{ii}, \\ F_{ij} &= \rho v_i v_j + M_{ij}, \\ G_{ppi} &= \rho v_p v_p v_i + m_{pp} v_i + 2M_{pi} v_p + m_{ppi}, \\ H_{ijk} &= 2v_{(i} M_{j)k} + M_{ijk}, \\ J_{ppik} &= 3v_{(p} v_p M_{i)k} + 2v_p M_{pik} + v_i m_{ppk} + m_{ppik}, \\ Q_{ppi} &= Q_i + 2v_p P_{pi}, \end{aligned} \quad (4)$$

where m_{ii} , M_{ij} , m_{ppi} , M_{ijk} and m_{ppik} do not depend on the velocity, and the productions P_{ij} and Q_i are also independent of the velocity.

From the conservation laws in (2), we can relate M_{ij} , m_{ii} and m_{ppi} to the following conventional quantities:

$$\text{stress:} \quad t_{ij} = -M_{ij} (= -(p + \Pi) \delta_{ij} + S_{(ij)}), \quad (5)$$

$$\text{specific internal energy:} \quad \varepsilon = \frac{1}{2\rho} m_{ii}, \quad (6)$$

$$\text{heat flux:} \quad q_i = \frac{1}{2} m_{ppi}, \quad (7)$$

where the pressure p depends only on ρ and m_{ii} , S_{ij} is the viscous stress, and $\Pi (\equiv -S_{ii}/3)$ is the dynamic pressure.

2.2. Constitutive equations. Through the well-established procedures in ET called the constitutive theory [4], we obtain explicitly the constitutive equations. The linear constitutive equations, in particular, are summarized as follows:

$$\begin{aligned} M_{iik} &= 3Lq_k, \\ M_{(ij)k} &= Kq_{(i}\delta_{j)k}, \\ m_{ppik} &= \left\{ \beta_1 + \left[\frac{h_4}{2h_2} \left(L - \frac{1}{\rho} \left(\frac{\partial p}{\partial T} \right)_\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho^{-1} \right) + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right] \Pi \right\} \delta_{ik} \\ &\quad - \left(\frac{h_4}{2h_3} K + 2 \left(\varepsilon + \frac{p}{\rho} \right) \right) S_{(ik)}, \end{aligned} \quad (8)$$

where T is the temperature. The coefficients h_2, h_3, h_4, L and K are the functions of ρ and T given by

$$\begin{aligned} h_2 &= -\frac{5}{6}Tp + \frac{\rho T}{2} \left(\frac{\partial p}{\partial \rho}\right)_T + \frac{T^2}{2\rho} \left(\frac{\partial p}{\partial T}\right)_\rho^2 \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}, \\ h_3 &= -Tp, \quad h_4 = 2T^2 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho - T^2 \left(\frac{\partial \beta_1}{\partial T}\right)_\rho, \\ L &= \frac{1}{h_4} \left[\beta_2 - 4h_2 \left(\varepsilon + \frac{p}{\rho}\right)\right], \quad K = \frac{1}{h_4} \left[\beta_3 - 4h_3 \left(\varepsilon + \frac{p}{\rho}\right)\right]. \end{aligned} \tag{9}$$

And the quantities β_1, β_2 and β_3 satisfy the following relations:

$$\begin{aligned} \left(\frac{\partial \beta_1}{\partial \rho}\right)_T &= 2 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{\partial p}{\partial \rho}\right)_T, \\ \left(\frac{\partial \beta_2}{\partial \rho}\right)_T &= \frac{5}{6} \left(\frac{\partial \beta_3}{\partial \rho}\right)_T + \frac{\partial}{\partial \rho} \left(4 \left(\varepsilon + \frac{p}{\rho}\right) \left(h_2 - \frac{5}{6}h_3\right)\right), \\ \left(\frac{\partial \beta_3}{\partial \rho}\right)_T &= -4T \left(\varepsilon + 2\frac{p}{\rho}\right) \left(\frac{\partial p}{\partial \rho}\right)_T, \\ \left(\frac{\partial \beta_2}{\partial T}\right)_\rho &= \frac{2}{3T}\beta_2 + \frac{10}{9T}\beta_3 + \frac{5}{3T}h_4 - \frac{\rho}{T} \left(\frac{\partial h_4}{\partial \rho}\right)_T - h_2 \left[\frac{8}{3T} \left(\varepsilon + \frac{p}{\rho}\right) - \frac{4}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho\right] \\ &\quad + 4 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{10}{9}p + \left(\frac{\partial h_2}{\partial T}\right)_\rho\right), \\ \left(\frac{\partial \beta_3}{\partial T}\right)_\rho &= \frac{2}{T}\beta_2 + \frac{1}{3T}\beta_3 + \frac{2}{T}h_4 - 8 \left(\varepsilon + \frac{p}{\rho}\right) \left(\frac{p}{3} + \frac{h_2}{T}\right) - 4T \left(\varepsilon + 2\frac{p}{\rho}\right) \left(\frac{\partial p}{\partial T}\right)_\rho. \end{aligned} \tag{10}$$

Then β_1, β_2 and β_3 are determined explicitly by the integration of Eq. (10), where we assume that the integration constants vanish. This assumption is consistent with the result from the kinetic theory. Then we have the relation $L = \frac{5}{6}K$. By using the equilibrium thermal and caloric equations of state ($p = \hat{p}(\rho, T)$, $\varepsilon = \hat{\varepsilon}(\rho, T)$), we can derive uniquely the explicit expressions of these coefficients.

The linear constitutive equations of the productions may be expressed as

$$P_{\langle ij \rangle} = -\frac{\sigma}{2h_3} S_{\langle ij \rangle}, \quad P_{ii} = \frac{3\zeta}{2h_2} \Pi, \quad Q_i = \frac{\tau}{h_4} q_i, \tag{11}$$

where σ, ζ and τ are positive, and are the functions of ρ and T .

2.3. Concavity of the entropy density and causality. With the linear constitutive equations (8), the entropy density and the entropy flux are expressed as

$$h = h^E + \frac{1}{4h_2} \Pi^2 + \frac{1}{4h_3} S_{\langle ij \rangle} S_{\langle ij \rangle} + \frac{1}{h_4} q_i q_i, \tag{12}$$

$$\varphi_k = \frac{1}{T} q_k + \frac{1}{2h_2} \left(L - \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1} \right) \Pi q_k - \frac{K}{2h_3} q_i S_{\langle ik \rangle}, \tag{13}$$

where h^E is the entropy density at a reference equilibrium state.

The system (2) must be symmetric hyperbolic so as to ensure the causality. Near equilibrium this requirement corresponds to the condition of the concavity of the entropy density [4, 21]. As the second derivative of the entropy density h near equilibrium is given by

$$d^2h = d^2h^E + \frac{1}{4h_2}(d\Pi)^2 + \frac{1}{4h_3}dS_{\langle ij \rangle}dS_{\langle ij \rangle} + \frac{1}{h_4}dq_i dq_i, \quad (14)$$

the concavity condition is expressed by the following set of inequalities:

$$p > 0, \quad \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho > 0, \quad \left(\frac{\partial p}{\partial \rho} \right)_T > 0, \quad h_2 < 0, \quad h_4 < 0. \quad (15)$$

2.4. Closed system of field equations. By substituting the constitutive equations (8) into (2) with (4), the closed system of field equations is given by

$$\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} - \frac{\partial S_{\langle ij \rangle}}{\partial x_j} &= 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} - \frac{\partial v_i}{\partial x_k} S_{\langle ik \rangle} + \frac{\partial q_k}{\partial x_k} &= 0, \\ \dot{S}_{\langle ij \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + S_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + 2 \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle j \rangle k} \\ + C_{S1} \frac{\partial \rho}{\partial x_k} q_{\langle i} \delta_{j \rangle k} + C_{S2} \frac{\partial T}{\partial x_k} q_{\langle i} \delta_{j \rangle k} + C_{S3} \frac{\partial q_{\langle i}}{\partial x_{j \rangle}} &= -\frac{1}{\tau_S} S_{\langle ij \rangle}, \\ \dot{\Pi} + (C_{\Pi 1} + C_{\Pi 2} \Pi) \frac{\partial v_k}{\partial x_k} + C_{\Pi 3} \frac{\partial v_{\langle i}}{\partial x_k} S_{\langle ik \rangle} + C_{\Pi 4} q_k \frac{\partial \rho}{\partial x_k} \\ + C_{\Pi 5} q_k \frac{\partial T}{\partial x_k} + C_{\Pi 6} \frac{\partial q_k}{\partial x_k} &= -\frac{1}{\tau_\Pi} \Pi, \\ \dot{q}_i + C_{q1} q_i \frac{\partial v_k}{\partial x_k} + C_{q2} q_k \frac{\partial v_k}{\partial x_i} + C_{q3} q_k \frac{\partial v_i}{\partial x_k} + C_{q4} \frac{\partial T}{\partial x_i} + C_{q5} \frac{\partial \Pi}{\partial x_i} + C_{q6} \frac{\partial S_{\langle ik \rangle}}{\partial x_k} \\ + \Pi \left[C_{q7} \frac{\partial \rho}{\partial x_i} + C_{q8} \frac{\partial T}{\partial x_i} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_i} + \frac{1}{\rho} \frac{\partial S_{\langle ik \rangle}}{\partial x_k} \right] \\ - S_{\langle ik \rangle} \left[C_{q9} \frac{\partial \rho}{\partial x_k} + C_{q10} \frac{\partial T}{\partial x_k} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_k} + \frac{1}{\rho} \frac{\partial S_{\langle jk \rangle}}{\partial x_j} \right] &= -\frac{1}{\tau_q} q_i, \end{aligned} \quad (16)$$

where the coefficients C_{Sa} ($a = 1, 2, 3$), $C_{\Pi b}$ ($b = 1, \dots, 6$) and C_{qc} ($c = 1, \dots, 10$), and the relaxation times τ_S, τ_q, τ_Π are the functions of ρ and T . With h_2, h_3, h_4, L and K ,

these are expressed as

$$\begin{aligned}
 C_{S1} &= -\left(\frac{\partial K}{\partial \rho}\right)_T, \quad C_{S2} = -\left(\frac{\partial K}{\partial T}\right)_\rho, \quad C_{S3} = -K, \\
 C_{\Pi 1} &= -\frac{2h_2}{T}, \quad C_{\Pi 2} = \frac{5}{3} - \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}, \quad C_{\Pi 3} = -\frac{2}{3} + \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}, \\
 C_{\Pi 4} &= \frac{5}{6} \left(\frac{\partial K}{\partial \rho}\right)_T, \quad C_{\Pi 5} = \frac{5}{6} \left(\frac{\partial K}{\partial T}\right)_\rho, \quad C_{\Pi 6} = \frac{5}{6}K - \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}, \\
 C_{q1} &= 1 + \frac{K}{2}, \quad C_{q2} = \frac{K}{2}, \quad C_{q3} = 1 + \frac{K}{2}, \quad C_{q4} = -\frac{h_4}{2T^2}, \\
 C_{q5} &= \frac{h_4}{4h_2} \left(\frac{5}{6}K - \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_\rho \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho^{-1}\right), \quad C_{q6} = -\frac{h_4}{4h_3}K, \\
 C_{q7} &= \left(\frac{\partial \varepsilon}{\partial \rho}\right)_T - \frac{p}{\rho^2} + \left(\frac{\partial C_{q5}}{\partial \rho}\right)_T, \quad C_{q8} = \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho + \left(\frac{\partial C_{q5}}{\partial T}\right)_\rho, \\
 C_{q9} &= \left(\frac{\partial \varepsilon}{\partial \rho}\right)_T - \frac{p}{\rho^2} - \left(\frac{\partial C_{q6}}{\partial \rho}\right)_T, \quad C_{q10} = \left(\frac{\partial \varepsilon}{\partial T}\right)_\rho - \left(\frac{\partial C_{q6}}{\partial T}\right)_\rho.
 \end{aligned} \tag{17}$$

And, for the relaxation times, we have

$$\tau_S = -\frac{2h_3}{\sigma}, \quad \tau_{\Pi} = -\frac{2h_2}{\zeta}, \quad \tau_q = -\frac{2h_4}{\tau}.$$

By carrying out the Maxwellian iteration [4, 7], these are related to the shear viscosity μ , bulk viscosity ν , and heat conductivity κ as follows:

$$\mu = p\tau_S, \quad \nu = -\frac{2h_2}{T}\tau_{\Pi}, \quad \kappa = -\frac{h_4}{2T^2}\tau_q. \tag{18}$$

To sum up, we have indeed obtained explicitly the closed system of field equations with the knowledge of the thermal and caloric equations of state, and also the shear viscosity, bulk viscosity and heat conductivity.

3. Characteristic Features of the Theory

As shown above, the thermal and caloric equations of state play a crucial role in the ET theory of dense gases. In general, the equations of state can be expressed as

$$p = p_{ideal}(\rho, T) + p_\phi(\rho, T), \quad \varepsilon = \varepsilon_{ideal}(T) + \varepsilon_\phi(\rho, T), \tag{19}$$

where p_{ideal} and ε_{ideal} are, respectively, the pressure and the specific internal energy in a rarefied gas limit. In a dense gas, as the average distance between the constituent molecules is finite, the interaction between the molecules also contributes to both the pressure and the specific internal energy, which are denoted by p_ϕ and ε_ϕ . Furthermore, ε_{ideal} can be divided into two parts:

$$\varepsilon_{ideal} = \varepsilon_{trans}(T) + \varepsilon_{int}(T),$$

where ε_{trans} and ε_{int} are the specific internal energies due to, respectively, the molecular translational modes and the internal modes of a molecule such as rotational and vibrational modes. Between p and ε , there is a relation, so-called Gibbs relation:

$$\left(\frac{\partial \varepsilon}{\partial \rho}\right)_T = \frac{1}{\rho^2} \left(p - T \left(\frac{\partial p}{\partial T} \right)_\rho \right). \quad (20)$$

Owing to the general character of the equations of state mentioned above, we have the following four disjoint CASEs 1-4:

CASE 1: Rarefied monatomic gases ($p_\phi = 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi = 0$),

CASE 2: Rarefied polyatomic gases ($p_\phi = 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi = 0$),

CASE 3: Dense monatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi \neq 0$),

CASE 4: Dense polyatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi \neq 0$).

Any gas belongs to one of the cases. See also Fig.1.

An advantage of this classification is that the effect of the internal modes of a molecule on nonequilibrium phenomena in a gas can be analyzed clearly by comparing the results of CASE 1 and CASE 2 (or of CASE 3 and CASE 4). In a similar way, the effect of the inter-molecular potential, for example, can be analyzed by comparing the results of CASE 1 and CASE 3 (or of CASE 2 and CASE 4). CASE 1 has already been fully developed [4], while CASEs 2-4 are those to be explored by the present ET theory of dense gases.

	$p_\phi = 0, \varepsilon_\phi = 0$	$p_\phi \neq 0, \varepsilon_\phi \neq 0$
$\varepsilon_{int} = 0$	Rarefied monatomic (CASE 1)	Dense monatomic (CASE 3)
$\varepsilon_{int} \neq 0$	Rarefied polyatomic (CASE 2)	Dense polyatomic (CASE 4)

Figure 1. Any gas belongs to one of the CASEs 1-4. The darker part is an unexplored territory and is expected to be studied by the present ET theory of dense gases.

In this section, we discuss the characteristic features of the present theory in CASEs 1-4 separately.

3.1. CASE 1: Rarefied monatomic gases. The equations of state are given by

$$p = p_{ideal}(\rho, T), \quad \varepsilon = \varepsilon_{trans}(T), \quad (21)$$

and there is a relationship between p and ε :

$$3p = 2\rho\varepsilon.$$

For classical gases, in particular, we have

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T,$$

where k_B and m are, respectively, the Boltzmann constant and the mass of a molecule. We may utilize these equations of state to obtain the system of field equations in CASE 1.

Let us discuss a subtle point in the system thus obtained. Equation (16)₅ is now reduced to $\Pi = 0$ as is expected for rarefied monatomic gases, and it plays no more role. The theory, therefore, becomes singular because of the change of the system itself, that is, the change from 14 equations to 13 equations. Furthermore, as G_{ii} is congruent with F_{ii} in this case, the G -series merges with F -series. As a result we have the following system of field equations:

$$\begin{aligned} \frac{\partial F}{\partial t} + \frac{\partial F_k}{\partial x_k} &= 0, \\ \frac{\partial F_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= 0, \\ \frac{\partial F_{ij}}{\partial t} + \frac{\partial F_{ijk}}{\partial x_k} &= P_{\langle ij \rangle}, \\ \frac{\partial F_{ppi}}{\partial t} + \frac{\partial F_{ppik}}{\partial x_k} &= P_{ppi}, \end{aligned} \tag{22}$$

where F_{ppik} and P_{ppi} are the flux and production of F_{ppi} , respectively. This is exactly the same as that of ET of rarefied monatomic gases [4]. In conclusion, the system of field equations (16) for dense gases contains the system of 13 field equations for rarefied monatomic gases as a special case in a singular way.

3.2. CASE 2: Rarefied polyatomic gases. The equations of state, when the temperature is not extremely low, are expressed as

$$p = \frac{k_B}{m} \rho T, \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T + \varepsilon_{int}(T).$$

It may be useful to introduce the specific heat $c_v = d\varepsilon/dT$, which, in general, depends on the temperature. Then we obtain the system of field equations for non-polytropic gases.

It can be proved that the system of field equations in CASE 2 is fully consistent with the system derived from a kinetic model for diatomic gases [22] and from the kinetic theory with the maximum entropy principle [23, 24, 25, 26] for polyatomic gases. This consistency is, of course, vitally important for the validity test of the theory of dense gases itself as a necessary condition. The detailed study of such an interrelationship between ET and the kinetic theory must be a promising new direction in the future research.

In what follows in this subsection, we discuss an experimental verification of the present theory [28].

3.2.1. A test of the ET theory for rarefied polyatomic gases : Dispersion relation for sound. In order to obtain the dispersion relation for weak sound, we decompose the independent variable $\mathbf{u} = (\rho, v_i, T, S_{\langle ij \rangle}, \Pi, q_i)^T$ into the equilibrium state vector at a reference equilibrium, $\mathbf{u}_0 = (\rho_0, 0, T_0, 0, 0, 0)^T$, and the deviation from the equilibrium state,

$\bar{\mathbf{u}} = (\bar{\rho}, \bar{v}_i, \bar{T}, \bar{S}_{\langle ij \rangle}, \bar{\Pi}, \bar{q}_i)^T$, as follows:

$$\mathbf{u} = \mathbf{u}_0 + \bar{\mathbf{u}}. \quad (23)$$

We study a plane longitudinal wave propagating in the x -direction with the frequency ω and the complex wave number $k = k_r + ik_i$ ($k_r = \Re(k)$, $k_i = \Im(k)$) such that

$$\bar{\mathbf{u}} = \mathbf{w}e^{i(\omega t - kx)} \quad (24)$$

with \mathbf{w} being a constant amplitude vector. Then \bar{v}_i , $\bar{S}_{\langle ij \rangle}$ and \bar{q}_i are expressed as

$$\bar{v}_i \equiv \begin{pmatrix} \bar{v} \\ 0 \\ 0 \end{pmatrix}, \quad \bar{S}_{\langle ij \rangle} \equiv \begin{pmatrix} \bar{S} & 0 & 0 \\ 0 & -\frac{1}{2}\bar{S} & 0 \\ 0 & 0 & -\frac{1}{2}\bar{S} \end{pmatrix}, \quad \bar{q}_i \equiv \begin{pmatrix} \bar{q} \\ 0 \\ 0 \end{pmatrix}. \quad (25)$$

The dispersion relation is explicitly given by

$$\begin{aligned} & \frac{c_v^*(c_0 z)^4}{3\Omega^2(1+c_v^*)^2} \left(-3\frac{1+c_v^*}{\tau_{ps}} - i\Omega \left(5c_v^* + \frac{3+7c_v^*}{\tau_{ps}} \right) + 9\Omega^2 c_v^* \right) \\ & + \frac{(c_0 z)^2}{3\Omega^3(1+c_v^*)^2} \left[-3i\frac{(1+c_v^*)^2}{\tau_{qs}\tau_{ps}} + \Omega(1+c_v^*) \left(\frac{5c_v^*}{\tau_{qs}} + 6\frac{1+c_v^*}{\tau_{ps}} + \frac{3+7c_v^*}{\tau_{qs}\tau_{ps}} \right) \right. \\ & \quad \left. + i\Omega^2 \left(c_v^*(13+8c_v^*) + 9c_v^*\frac{1+c_v^*}{\tau_{qs}} + \frac{6+20c_v^*+10c_v^{*2}}{\tau_{ps}} \right) - 3\Omega^3 c_v^*(7+4c_v^*) \right] \\ & + \frac{(\Omega-i)(\tau_{ps}\Omega-i)(\tau_{qs}\Omega-i)}{\Omega^3\tau_{ps}\tau_{qs}} = 0, \end{aligned} \quad (26)$$

where

$$\begin{aligned} z &= \frac{k}{\omega}, \quad c_v^* = \frac{(c_v)_0}{k_B/m}, \quad \Omega = (\tau_S)_0\omega, \\ \tau_{qs} &= \left(\frac{\tau_q}{\tau_S} \right)_0 = (1+c_v^*)^{-1} \frac{\kappa}{\mu k_B/m}, \quad \tau_{ps} = \left(\frac{\tau_{\Pi}}{\tau_S} \right)_0 = \left(\frac{2}{3} - \frac{1}{c_v^*} \right)^{-1} \frac{\nu}{\mu}, \end{aligned} \quad (27)$$

and c_0 is the sound speed:

$$c_0 = \sqrt{\left(\frac{\partial p}{\partial \rho} \right)_0 + \frac{T_0}{\rho_0^2} \left(\frac{\partial p}{\partial T} \right)_0^2} = \sqrt{aT_0 \left(1 + \frac{1}{c_v^*} \right)}. \quad (28)$$

Here the suffix 0 indicates the values at the reference equilibrium state. Therefore, for given c_v^* , τ_{qs} and τ_{ps} , the quantity $c_0 z (= c_0 k/\omega)$ is calculated from Eq. (26) as the function of $\Omega (= (\tau_S)_0\omega)$. The phase velocity v_{ph} and the attenuation factor α are derived from the relations:

$$v_{ph}(\omega) = \frac{\omega}{\Re(k)} = \frac{1}{\Re(z)}, \quad \alpha(\omega) = -\Im(k) = -\omega\Im(z). \quad (29)$$

From Eq. (27), with the help of the experimental data on μ , κ and ν , we can estimate the values of τ_{qs} and τ_{ps} . However, at present, as we have reliable data only on μ and κ [30],

we adopt, in the analysis below, an adjustable parameter:

$$\varphi = \frac{\nu}{\mu}. \quad (30)$$

In Fig. 2, we show the phase velocity and the attenuation factor for normal hydrogen (n-H₂) gases derived from the ET theory and the NSF theory at $T_0 = 293\text{K}$, and also the experimental data on the phase velocity at $T_0 = 273.5, 296.8\text{K}$ by Rhodes [29] and on the attenuation factor at $T_0 = 293\text{K}$ by Sluijter et al. [30]. Here we estimated the values of c_v^* with the help of statistical mechanics [31, 32]. The values of μ and κ are adopted from experimental data [30]. At $T_0 = 293\text{K}$, the adopted values are as follows: $c_v^* = 2.45$, $c_0 = 1300$ [m/s], $\mu = 8.82$ [$\mu\text{Pa}\cdot\text{s}$], $\kappa = 182$ [mW/(m $\cdot\text{K}$)] and $\tau_{qs} = 1.46$.

In the region with small Ω the predictions by ET and NSF coincide with each other and φ is selected to be 37 to fit these results with the experimental data. Therefore $\nu = 326$ [$\mu\text{Pa}\cdot\text{s}$] and $\tau_{ps} = 144$. When Ω becomes large the prediction by the ET theory is evidently superior to that by the NSF theory. The difference between the two theories emerges around $\Omega = \omega(\tau_S)_0 = 10^{-3}$. The ET theory exhibits its good fitting with experimental data up until $\Omega = 10^{-1}$.

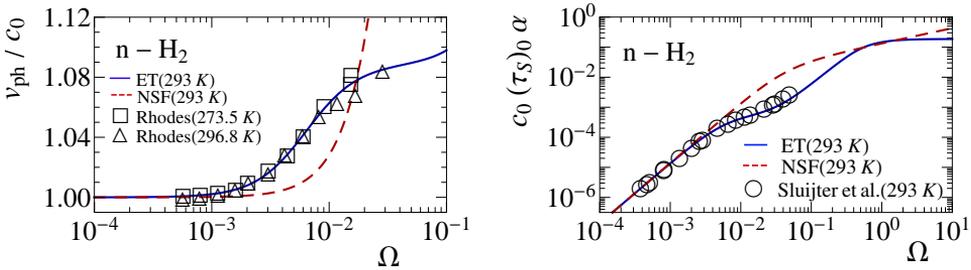


Figure 2. Dependence of the dimensionless phase velocity v_{ph}/c_0 (left) and the attenuation factor $c_0(\tau_S)_0\alpha$ (right) on the dimensionless frequency Ω for n-H₂ gases. The squares and triangles in the left figure are the experimental data at $T_0 = 273.5$ and 296.8K , respectively, by Rhodes [29], and the circles in the right figure are those at $T_0 = 293\text{K}$ by Sluijter et al. [30]. The solid and dashed lines are predictions at 293K by the ET and NSF theories, respectively. We adopt $\varphi = 37$.

In Fig. 3, we show a similar comparison for para hydrogen (p-H₂) gases. The experimental data on the phase velocity at $T_0 = 273.8, 298.4\text{K}$ are measured by Rhodes [29] and the attenuation factor at $T_0 = 293\text{K}$ by Sluijter et al. [30]. At $T_0 = 293\text{K}$, the adopted values are as follows: $c_v^* = 2.61$, $c_0 = 1290$ [m/s], $\mu = 8.82$ [$\mu\text{Pa}\cdot\text{s}$], $\kappa = 192$ [mW/(m $\cdot\text{K}$)] and $\tau_{qs} = 1.46$. The selected value of the parameter φ is 31. Then, $\nu = 273$ [$\mu\text{Pa}\cdot\text{s}$] and $\tau_{ps} = 109$.

From these figures, we see clearly that the present theory of ET is consistent with the experimental data even in the high frequency range where the local equilibrium assumption is no more valid. Although the comparisons with the experimental data have been made

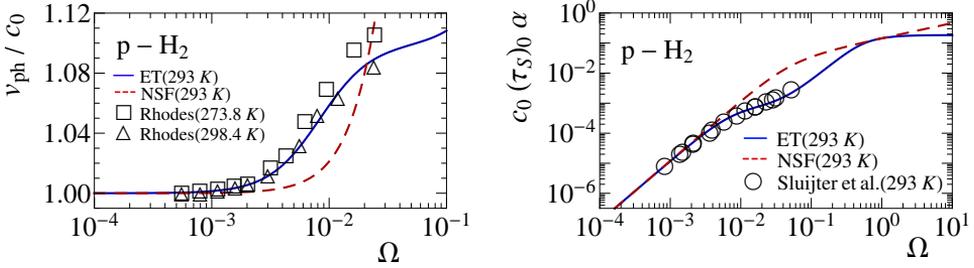


Figure 3. Dependence of the dimensionless phase velocity v_{ph}/c_0 (left) and the attenuation factor $c_0(\tau_S)_0\alpha$ (right) on the dimensionless frequency Ω for p-H₂ gases. The squares and triangles in the left figure are the experimental data at $T_0 = 273.8$ and 298.4 K, respectively, by Rhodes [29], and the circles in the right figure are those at $T_0 = 293$ K by Sluijter et al. [30]. The solid and dashed lines are predictions at 293 K by the ET and NSF theories, respectively. We adopt $\varphi = 31$.

only for the rarefied diatomic gases, the consistency gives us a strong confidence that the ET theory for dense gases deserves further studies.

3.3. CASE 3: Dense monatomic gases. The CASE 3 has been little explored by ET up to now, but is the case that is highly expected to be studied by the present ET theory. Such a study must be challenging not only theoretically but also practically.

The equations of state are expressed as

$$p = \frac{k_B}{m}\rho T + p_\phi(\rho, T), \quad \varepsilon = \frac{3}{2}\frac{k_B}{m}T + \varepsilon_\phi(\rho, T). \quad (31)$$

The explicit forms of p_ϕ and ε_ϕ may be given in the virial expansion form. Up to the first correction with respect to ρ , with the help of the Gibbs relation (20), we have the following expression:

$$p_\phi = \frac{k_B}{m}TB_2(T)\rho^2 + O(\rho^3), \quad \varepsilon_\phi = -\frac{k_B}{m}T^2B_2'(T)\rho + O(\rho^2), \quad (32)$$

where the second virial coefficient B_2 is the function of the temperature T , and a prime means a derivative with respect to T .

Substituting the equations of state (31) with (32) into (9) and (10), we obtain the first correction of h_2, h_3, h_4 and K with respect to ρ :

$$\begin{aligned} h_2 &= \frac{k_B}{m} T^2 \rho \left(\frac{15B_2 + 20TB_2' + 4T^2 B_2''}{18} \rho + O(\rho^2) \right), \\ h_3 &= -\frac{k_B}{m} T^2 \rho (1 + B_2 \rho + O(\rho^2)), \\ h_4 &= -\left(\frac{k_B}{m} \right)^2 T^3 \rho (5 + (5B_2 - T^2 B_2'') \rho + O(\rho^2)), \\ K &= \frac{4}{5} + \frac{10TB_2' + 4T^2 B_2''}{25} \rho + O(\rho^2). \end{aligned} \quad (33)$$

We here make only one remark. When we analyze the concavity condition (15), we find that there is a subtle point such that the condition is not always satisfied. The hard-sphere system with constant B_2 is probably the most extreme case in the sense that the condition is not satisfied for any ρ as far as we adopt the equations of state above. This fact is intimately related to the singularity of the system of field equations mentioned in CASE 1 where the dynamic pressure Π vanishes. Detailed study of such a delicate point will soon be reported elsewhere.

3.4. CASE 4: Dense polyatomic gases. The equations of state are expressed as

$$p = \frac{k_B}{m} \rho T + p_\phi(\rho, T), \quad \varepsilon = \frac{3}{2} \frac{k_B}{m} T + \varepsilon_{int}(T) + \varepsilon_\phi(\rho, T). \quad (34)$$

For later convenience, we introduce

$$c_{v_{ideal}}^*(T) = \frac{d\varepsilon_{ideal}(T)}{dT} \Big/ \frac{k_B}{m} = \frac{3}{2} + \frac{d\varepsilon_{int}(T)}{dT} \Big/ \frac{k_B}{m}. \quad (35)$$

Then, with the virial expansion form (32), we have the first correction of h_2, h_3, h_4 and K with respect to ρ :

$$\begin{aligned} h_2 &= \frac{k_B}{m} T^2 \rho \left[\frac{3 - 2c_{v_{ideal}}^*}{6c_{v_{ideal}}^*} \right. \\ &\quad \left. + \frac{(c_{v_{ideal}}^*)^2 + 6c_{v_{ideal}}^*}{6c_{v_{ideal}}^*{}^2} B_2 + \frac{6(1 + c_{v_{ideal}}^*)TB_2' + 3T^2 B_2''}{6c_{v_{ideal}}^*{}^2} \rho + O(\rho^2) \right], \\ h_3 &= -\frac{k_B}{m} T^2 \rho (1 + B_2 \rho + O(\rho^2)), \\ h_4 &= -2 \left(\frac{k_B}{m} \right)^2 T^3 \rho \left[1 + c_{v_{ideal}}^* + \left((1 + c_{v_{ideal}}^*) B_2 - \frac{1}{2} T^2 B_2'' \right) \rho + O(\rho^2) \right], \\ K &= \frac{2}{c_{v_{ideal}}^* + 1} + \frac{(c_{v_{ideal}}^* + 1)TB_2' + T^2 B_2''}{(c_{v_{ideal}}^* + 1)^2} \rho + O(\rho^2). \end{aligned} \quad (36)$$

The CASE 4 has been totally unexplored by ET until now. This case is also highly expected to be studied by the present ET theory.

4. Summary

A recently-developed theory of ET of dense gases has been reviewed and its characteristic features have been discussed. The discussion has been made in the CASEs 1-4 separately. We have emphasized that the last three cases are still being not fully explored and that they can be analyzed by this new theory. This means that there are potentially many research fields where this theory may play a crucial role. The analysis of wave propagation phenomena in dense gases, for example, seems to be interesting as a next study. The subtle point with respect to the concavity condition in the case of monatomic gases should be also studied.

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