Acta Appl Math (2014) 132:527–548
DOI 10.1007/s10440-014-9923-y

Recent Developments in Extended Thermodynamics of Dense and Rarefied Polyatomic Gases

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Received: 27 November 2013 / Accepted: 8 February 2014 / Published online: 21 May 2014

Abstract We summarize the recent results and current open problems in extended thermodynamics (ET) of both dense and rarefied polyatomic gases. (i) We review, in particular, extended thermodynamics with 14 independent fields (ET14), that is, the mass density, the velocity, the temperature, the shear stress, the dynamic pressure, and the heat flux. (ii) We explain that, in the case of rarefied polyatomic gases, molecular extended thermodynamics with 14 independent fields (MET14) basing on the kinetic moment theory with the maximum entropy principle can be developed. ET14 and MET14 are fully consistent with each other. (iii) We show that the ET13 theory of rarefied monatomic gases is derived from the ET14 theory as a singular limit. (iv) We discuss briefly some typical applications of the ET14 theory. (v) We study the simple case of ET theory with 6 independent fields (ET6). (vi) The METn theories ($n > 14$) are presented briefly. We analyze, in particular, the dependence of the characteristic velocities for increasing number of moments.

Keywords Extended thermodynamics · Dense gas · Polyatomic gas · Kinetic theory · Singular limit · Symmetric hyperbolic systems · Characteristic velocity

1 Introduction

Non-equilibrium thermodynamics affords us the general theory for understanding nonequilibrium phenomena observed ubiquitously in macroscopic physical systems. The theory called thermodynamics of irreversible processes (TIP), in particular, is well known owing to its systematic and comprehensive theoretical structure [1]. It is based on the local equilibrium assumption. The Navier-Stokes Fourier (NSF) theory for fluids [1, 2] is a typical theory

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of TIP. Its practical usefulness has been demonstrated repeatedly in various situations. From a theoretical point of view, however, it has 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 its basic equations with spatially non-local constitutive equations [3].

To avoid the paradox, extended thermodynamics (ET) [4] basing on a hyperbolic system of field equations was proposed. ET is applicable to highly nonequilibrium phenomena with steep gradients in space and rapid changes in time being 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 shown in the next section.

In the early stage of ET, a theory for rarefied *monatomic* gases was developed in classical and quantal frameworks [5] and in relativistic framework [6]. For example, the ET13 theory of rarefied monatomic gases in non-relativistic context is a theory with 13 independent fields; the mass density, the momentum density, the momentum flux, and the energy flux [4, 5]. By the use of the proper constitutive equations compatible with the universal physical principles, a closed system of field equations is obtained. The constitutive equations can be explicitly determined by the equilibrium caloric and thermal equations of state. The NSF theory comes out as a limiting case of ET [4] through carrying out the Maxwellian iteration [7]. The closed system of field equations is perfectly consistent with the counterpart system of the moments in the kinetic theory [8].

For more details, consult the reference by Müller and Ruggeri [4]. And an interesting review of irreversible thermodynamics, elucidating different pathways to macroscopic equations, has recently been published by Müller and Weiss [9].

In the next stage, there appeared many studies of ET for rarefied *polyatomic* gases [10–12] and also for *dense* gases [13–18] postulating a hierarchy structure—similar to the structure of monatomic gases but with 14 densities, in which a fourth-rank tensorial density appeared. However, in this hierarchy of governing equations, the flux in one equation did not appear as a density in the next equation and, as a consequence of this generalization, the constitutive equations could not be fully determined from the knowledge of the equilibrium properties of gases. Moreover, when the Maxwellian iteration procedure is applied (i.e. in the limit case in which the relaxation times are assumed to be negligible [7]), we naturally expect to obtain the Navier-Stokes Fourier constitutive equations. However, as the fourth-rank tensorial density has no straightforward counterpart in the Navier-Stokes Fourier limit, the density and also the theory using it seem to be not well justified.

Recently an ET theory of dense gases that successfully overcomes the difficulty mentioned above has been developed [19]. Rarefied gases are regarded as a special case of dense gases. This is an extended thermodynamic theory with 14 independent fields (ET14), that is, the mass density, the velocity, the temperature, the shear stress, the dynamic pressure, and the heat flux.

Furthermore, in the case of rarefied polyatomic gases, molecular extended thermodynamics with 14 independent fields (MET14) basing on the kinetic moment theory with the maximum entropy principle has been developed [20]. ET14 and MET14 are proved to be fully consistent with each other.

The purpose of the present paper is to show the present status of art in extended thermodynamics of dense and rarefied polyatomic gases by reviewing the recent results obtained. Open problems remained are also pointed out.

For convenience we 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. Summation on repeated indices is assumed everywhere.

(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,

$$a_{(i}b_{j)} = \frac{1}{2!}(a_i b_j + a_j b_i).$$

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

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

where a_{kk} is the trace of a_{ij}.

2 Extended Thermodynamics with 14 Independent Fields

We present now the macroscopic approach of ET14 theory of dense gases [19].

2.1 Independent Fields and Balance Equations

The ET14 theory of dense gases adopts the following 14 independent fields:

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

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

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

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. There are two parallel series in the balance equations; the one starts from the balance equation with the mass density (F-hierarchy) and the other from the balance equation with the energy density (G-hierarchy). 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 [20–22].

We need the constitutive equations in order to obtain 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 imposed upon the constitutive equations come from the 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:

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

  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 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

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

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 [23], 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

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

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

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:

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

$$\text{specific internal energy:} \qquad \varepsilon = \frac{1}{2\rho} m_{ii}, \tag{6}$$

$$\text{heat flux:} \qquad q_i = \frac{1}{2} m_{ppi}, \tag{7}$$

where p is the pressure, $S_{ij} = -\Pi\delta_{ij} + S_{\langle ij\rangle}$ is the viscous stress, and $\Pi = -S_{ii}/3$ is the dynamic pressure.

2.2 Constitutive Equations

Through the well-established closure procedures in ET [4], the linear constitutive equations with respect to non-equilibrium variables are given by [19]

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

where T is the temperature.[2] The coefficients h_2, h_3, h_4, L and K are the functions of ρ and T given by

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

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

$$\begin{aligned}
\left(\frac{\partial \beta_1}{\partial \rho}\right)_T &= 2\left(\varepsilon + \frac{p}{\rho}\right)\left(\frac{\partial p}{\partial \rho}\right)_T,\\
\left(\frac{\partial \beta_2}{\partial \rho}\right)_T &= \frac{5}{6}\left(\frac{\partial \beta_3}{\partial \rho}\right)_T + \frac{\partial}{\partial \rho}\left(4\left(\varepsilon + \frac{p}{\rho}\right)\left(h_2 - \frac{5}{6}h_3\right)\right),\\
\left(\frac{\partial \beta_3}{\partial \rho}\right)_T &= -4T\left(\varepsilon + 2\frac{p}{\rho}\right)\left(\frac{\partial p}{\partial \rho}\right)_T,
\end{aligned}$$

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[2] For the definition of the temperature T in nonequilibrium, see the reference [19].

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

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. We have the relation $L=\frac{5}{6}K$. By using the equilibrium thermal and caloric equations of state ($p=\hat{p}(\rho,T)$ and $\varepsilon=\hat{\varepsilon}(\rho,T)$), we can derive uniquely the explicit expressions of these coefficients.

The linear constitutive equations of the productions may be expressed as

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

where σ, ζ and τ are positive 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

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

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

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. This requirement corresponds to the condition of the concavity of the entropy density [4, 24]. As the second differential of the entropy density h near equilibrium is given by

$$\mathrm{d}^2h=\mathrm{d}^2h^E+\frac{1}{4h_2}(\mathrm{d}\Pi)^2+\frac{1}{4h_3}\mathrm{d}S_{\langle ij\rangle}\mathrm{d}S_{\langle ij\rangle}+\frac{1}{h_4}\mathrm{d}q_i\mathrm{d}q_i,\tag{14}$$

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

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

2.4 Closed System of Field Equations

By substituting the constitutive equations (8) into (2) with (4), the closed system of field equations in terms of the material time derivative is given by [19]

$$
\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 \rangle} \\
&\qquad + 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 \rangle}} S_{\langle ik \rangle} + C_{\Pi 4} q_k \frac{\partial \rho}{\partial x_k} \\
&\qquad + 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} \\
&\qquad + \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] \\
&\qquad - 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}
\tag{16}
$$

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

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

And, for the relaxation times, we have

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

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

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

2.5 Classification of the ET Theory

As shown above, the thermal and caloric equations of state play an important role in the ET theory. In general, the equations of state are expressed as

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

where p_{ideal} and ε_{ideal} are, respectively, the pressure and the specific internal energy in a rarefied gas limit. In a dense gas, 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 the Gibbs relation:

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

We have the following four disjoint cases (i)–(iv) [25]:

Case (i) Rarefied monatomic gases ($p_\phi = 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi = 0$),
Case (ii) Rarefied polyatomic gases ($p_\phi = 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi = 0$),
Case (iii) Dense monatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} = 0$, $\varepsilon_\phi \neq 0$),
Case (iv) Dense polyatomic gases ($p_\phi \neq 0$, $\varepsilon_{int} \neq 0$, $\varepsilon_\phi \neq 0$).

Any gas belongs to one of the cases.

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 cases (i) and (ii) (or of cases (iii) and (iv)). In a similar way, the effect of the inter-molecular potential, for example, can be analyzed by comparing the results of cases (i) and (iii) (or of cases (ii) and (iv)). Case (i) has already been extensively studied [4], while cases (ii)–(iv) are expected to be explored by the present ET theory of dense gases. There are many open problems in these cases.

3 Rarefied Polyatomic Gases

The ET14 theory of dense gases is applicable to, as a particular case, rarefied polyatomic gases with the thermal and caloric equations of state:

$$p = \frac{k_B}{m}\rho T \quad \text{and} \quad \varepsilon = \frac{D}{2}\frac{k_B}{m}T \quad (D = 3 + f) \tag{21}$$

where k_B and m are the Boltzmann constant and the mass of a molecule, respectively. Here D is related to the degrees of freedom of a molecule given by the sum of the space dimension 3 for the translational motion and the contribution from the internal degrees of freedom $f(\geq 0)$. For monatomic gases, $D = 3$.

The closed system of balance equations for rarefied polyatomic gases with the equations of state (21) is explicitly expressed as follows, where, for simplicity, D is assumed to be constant:

$$
\begin{aligned}
&\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} = 0,\\
&\rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} - \frac{\partial S_{\langle ij\rangle}}{\partial x_j} = 0,\\
&\frac{D}{2}\frac{k_B}{m}\rho \dot{T} + \frac{\partial q_k}{\partial x_k} + \big((p+\Pi)\delta_{ik} - S_{\langle ik\rangle}\big)\frac{\partial v_i}{\partial x_k} = 0,\\
&\dot{S}_{\langle ij\rangle} - 2p\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} + S_{\langle ij\rangle}\frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_{j\rangle}}\\
&\quad + 2\frac{\partial v_{\langle i}}{\partial x_k} S_{\langle j\rangle k\rangle} - \frac{4}{D+2}\frac{\partial q_{\langle i}}{\partial x_{j\rangle}} = -\frac{1}{\tau_S} S_{\langle ij\rangle},\\
&\dot{\Pi} + \frac{2(D-3)}{3D} p \frac{\partial v_k}{\partial x_k} + \frac{5D-6}{3D}\Pi \frac{\partial v_k}{\partial x_k}\\
&\quad - \frac{2(D-3)}{3D}\frac{\partial v_{\langle i}}{\partial x_{k\rangle}} S_{\langle ik\rangle} + \frac{4(D-3)}{3D(D+2)}\frac{\partial q_k}{\partial x_k} = -\frac{1}{\tau_\Pi}\Pi,\\
&\dot{q}_i + \frac{D+4}{D+2} q_i \frac{\partial v_k}{\partial x_k} + \frac{2}{D+2} q_k \frac{\partial v_k}{\partial x_i} + \frac{D+4}{D+2} q_k \frac{\partial v_i}{\partial x_k}\\
&\quad - \frac{k_B}{m}\frac{T}{\rho}\big(\Pi \delta_{ki} - S_{\langle ki\rangle}\big)\frac{\partial \rho}{\partial x_k} + \frac{D+2}{2}\frac{k_B}{m}\big((p+\Pi)\delta_{ki} - S_{\langle ki\rangle}\big)\frac{\partial T}{\partial x_k}\\
&\quad + \frac{1}{\rho}\big((p-\Pi)\delta_{ki} + S_{\langle ki\rangle}\big)\left(\frac{\partial \Pi}{\partial x_k} - \frac{\partial S_{\langle kl\rangle}}{\partial x_l}\right) = -\frac{1}{\tau_q} q_i.
\end{aligned}
\tag{22}
$$

4 Molecular Extended Thermodynamics for Rarefied Polyatomic Gases

In the case of monatomic rarefied gases with 13 moments, the most important result is the proof of the assertion that the same closure is obtained by using three different methods: the Grad procedure, the extended thermodynamics based on the entropy principle, and the closure obtained by the so-called *Maximum Entropy Principle* (MEP) that consists of the determination of an approximated distribution function with the maximum entropy density under the constraints of some prescribed moments.

Motivated by the similarity between ET and the moment equations derived from the Boltzmann equation on one hand, and by Kogan's observation that Grad's distribution function maximizes the entropy [26] on the other, a maximum entropy principle was established first by Dreyer [27]. In the first edition of the book of ET by Müller and Ruggeri [28], this procedure was extended for any number of moments. Successively, a similar result was given by Levermore [29]. The complete equivalence between the entropy principle and MEP was proved subsequently by Boillat and Ruggeri [30].

The closure can be done also for a state far from equilibrium but, in general, some mathematical problems arise, that is, the problems concerning the convergence of the integrals and the difficulty to give inversion between the Lagrange multipliers and the fields of the density [30]. Therefore usually the closure is given in the neighborhood of an equilibrium state. For the expansion up to higher order terms with respect to an equilibrium state, consult the paper by Brini and Ruggeri [31].

As far as the kinetic counterpart of polyatomic gases is concerned, a crucial step towards the development of a theory of rarefied polyatomic gases was made in the work by Borgnakke and Larsen [32] in which the distribution function is assumed to depend on an additional continuous variable I representing the internal energy of a molecule, thus allowing to take into account the exchange of energy (other than translational) in binary collisions. This model was initially used for Monte Carlo simulations of polyatomic gases, and later it has been applied to the derivation of appropriate Boltzmann equation by Bourgat, Desvillettes, Le Tallec and Perthame [33].

Recently Pavić, Ruggeri and Simić have proven [20], using the MEP, that the kinetic model for rarefied polyatomic gases presented in [32] and [33] yields appropriate macroscopic balance laws in agreement with the ET14 theory, and presents a natural generalization to polyatomic gases of the classical procedure of MEP for monatomic ones. In fact, the two hierarchies of moment equations obtained with the distribution function presented in [20] are consistent with the hierarchies presented in [19]. In particular, it has been shown that the *momentum-like* hierarchy (or F-hierarchy) is related to the classical moments of the distribution function, and the *energy-like* hierarchy (G-hierarchy) is related to the moments with an additional continuous variable representing the internal energy of a molecule.

As a consequence of the introduction of one additional parameter, velocity distribution function $f(t, \mathbf{x}, \boldsymbol{\xi}, I)$ is defined on the extended domain $[0, \infty) \times \mathbb{R}^3 \times \mathbb{R}^3 \times [0, \infty)$. Its rate of change is determined by the Boltzmann equation which has the same form as the one of monatomic gases:

$$\frac{\partial f}{\partial t} + \xi_i \frac{\partial f}{\partial x_i} = Q,$$

but the collision integral $Q(f)$ takes into account the influence of internal degrees of freedom through the collisional cross section. Collision invariants for this model form a 5-vector:

$$\boldsymbol{\psi}(\boldsymbol{\xi}, I) = m\left(1, \xi_i, |\boldsymbol{\xi}|^2 + 2\frac{I}{m}\right)^T, \tag{23}$$

which leads to hydrodynamic variables in the form:

$$\begin{pmatrix} \rho \\ \rho v_i \\ \rho v^2 + 2\rho\varepsilon \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty \boldsymbol{\psi}(\boldsymbol{\xi}, I) f(t, \mathbf{x}, \boldsymbol{\xi}, I) \varphi(I)\, dI\, d\boldsymbol{\xi}. \tag{24}$$

The structure of the weighting function $\varphi(I)$ is determined such that it is possible to recover the caloric equation of state for polyatomic gases. It can be shown that $\varphi(I) = I^\alpha$ leads to an appropriate caloric equation in equilibrium (21) provided that

$$\alpha = \frac{D-5}{2}. \tag{25}$$

The entropy is defined by the following relation:

$$h = -k \int_{\mathbb{R}^3} \int_0^\infty f \log f \, \varphi(I) \, dI \, d\boldsymbol{\xi}. \tag{26}$$

Pavić, Ruggeri and Simić [20] firstly considered the Euler fluid with 5 moments and they considered the maximum entropy principle expressed in terms of the following variational problem: determine the velocity distribution function $f(t, \mathbf{x}, \xi, I)$ such that $h \to \max$, being subjected to the constraints (24). In this way they were able to determine the following equilibrium distribution function which maximizes the entropy (26) with the constraints (24):

$$f_E = \frac{\rho}{mq(T)} \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left\{ -\frac{1}{kT} \left(\frac{1}{2} m|\mathbf{C}|^2 + I \right) \right\}, \tag{27}$$

where $\mathbf{C} = \boldsymbol{\xi} - \mathbf{v}$ is the peculiar velocity and

$$q(T) = \int_0^\infty \exp\left(-\frac{I}{kT} \right) \varphi(I) \, dI, \tag{28}$$

that, in the case $\varphi(I) = I^\alpha$, becomes

$$q(T) = (kT)^{1+\alpha} \Gamma(1+\alpha)$$

where Γ is the gamma function.

The distribution (27) is the generalization of the classical Maxwellian equilibrium distribution in the case of polyatomic gases. It was derived in [32] and [34] by means of the H-theorem.

Pavić, Ruggeri and Simić [20] secondly considered the case of 14 moments. This case is completely in agreement with the binary hierarchy (2) with the moments:

$$\begin{gathered} \begin{pmatrix} F \\ F_{i_1} \\ F_{i_1 i_2} \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty m \begin{pmatrix} 1 \\ \xi_{i_1} \\ \xi_{i_1} \xi_{i_2} \end{pmatrix} f(t, \mathbf{x}, \boldsymbol{\xi}, I) \, \varphi(I) \, dI \, d\boldsymbol{\xi}, \\ \begin{pmatrix} G_{pp} \\ G_{ppk_1} \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty m \begin{pmatrix} |\boldsymbol{\xi}|^2 + 2\frac{I}{m} \\ (|\boldsymbol{\xi}|^2 + 2\frac{I}{m}) \xi_{k_1} \end{pmatrix} f(t, \mathbf{x}, \boldsymbol{\xi}, I) \, \varphi(I) \, dI \, d\boldsymbol{\xi}. \end{gathered} \tag{29}$$

For the entropy defined by (26), the following variational problem, expressing the maximum entropy principle, can be formulated: determine the velocity distribution function $f(t, \mathbf{x}, \mathbf{C}, I)$ such that $h \to \max$, being subjected to the constraints (29). The solution of the problem is as follows.

Near the equilibrium state the velocity distribution function, which maximizes the entropy (26) with the constraints (29) and the weighting function $\varphi(I) = I^\alpha$, has the form:

$$\begin{aligned} f = f_E \Bigg\{ & 1 - \frac{\rho}{p^2} q_i C_i + \frac{\rho}{p^2} \left[-S_{\langle ij \rangle} + \left(\frac{5}{2} + \alpha \right) (1+\alpha)^{-1} \Pi \delta_{ij} \right] C_i C_j \\ & - \frac{3}{2(1+\alpha)} \frac{\rho}{p^2} \Pi \left(\frac{1}{2} |\mathbf{C}|^2 + \frac{I}{m} \right) + \left(\frac{7}{2} + \alpha \right)^{-1} \frac{\rho^2}{p^3} q_i \left(\frac{1}{2} |\mathbf{C}|^2 + \frac{I}{m} \right) C_i \Bigg\}, \end{aligned} \tag{30}$$

where f_E is the equilibrium distribution (27) and $q(T)$ is the auxiliary function (28).

The non-equilibrium distribution (30) reduces to the velocity distribution obtained by Mallinger [36] for gases composed of diatomic molecules ($\alpha = 0$), and, for any $\alpha > -1$, the closure gives exactly the same equations (22) obtained before by using the entropy principle.

Therefore also in the case of rarefied polyatomic gases the 3 different procedures: Entropy Principle, Maximum Entropy Principle and Kinetic Grad method give, as in the monatomic gases, the same field equations! Of course the Molecular Extended Thermodynamics in principle has the advantage that if we know the collisional operator $Q(f)$ we can have explicit expressions for the relaxation times that appear in the production terms in (22): a simple example is presented in [20]. On this subject see also [35].

5 ET13 of Rarefied Monatomic Gases as the Singular Limit of ET14 of Rarefied Polyatomic Gases

We show that rarefied monatomic gases, where there no dynamic pressure exists, can be identified as a singular limit of rarefied polyatomic gases. We confine our discussion within the singular limit from ET14 of rarefied polyatomic gases to ET13 of rarefied monatomic gases [37]. General analysis with arbitrary number of independent fields will soon be reported elsewhere.

Let us discuss the limiting process in the system (22) from polyatomic to monatomic rarefied gases when we let D approach 3 from above, where D is assumed to be a continuous variable. The limit is singular in the sense that the system for rarefied polyatomic gases with 14 independent fields need to converge to the system with only 13 independent fields for rarefied monatomic gases.

The singularity can be seen also by the inequalities required for the symmetric hyperbolicity in equilibrium (15). This requirement is always satisfied in the ET13 theory of monatomic gases, while, in the present ET14 theory, it is expressed by the inequality $D > 3$. The condition is obviously satisfied only for polyatomic gases with $D > 3$, and the case of monatomic gases with $D = 3$ is not admissible. Therefore only the limit of D toward 3 from above is meaningful.

In the present case, by using the Maxwellian iteration [4, 7], the relaxation times τ_S, τ_Π and τ_q are, respectively, related to the shear viscosity μ, the bulk viscosity ν and the heat conductivity κ:

$$\mu = p\tau_S, \qquad \nu = \frac{2(D-3)}{3D} p\tau_\Pi, \qquad \kappa = \frac{D+2}{2}\frac{p^2}{\rho T}\tau_q. \tag{31}$$

We observe that the bulk viscosity vanishes when $D \to 3$ as is consistent in monatomic gases.

Let us take the limit $D \to 3$ of the system (22), that is, the limit from polyatomic to monatomic rarefied gases. Then we immediately notice that the limit of the system exists, but it still has 14 equations. However, we also notice the following three points (I)–(III):

(I) The limit of the equation for Π, $(22)_5$, is given by

$$\dot{\Pi} = -\left(\frac{1}{\tau_\Pi} + \frac{\partial v_k}{\partial x_k}\right)\Pi, \quad \longleftrightarrow \quad \left(\frac{\Pi}{\rho}\right)^{\bullet} = -\frac{1}{\tau_\Pi}\frac{\Pi}{\rho}. \tag{32}$$

This is the first-order quasi-linear partial differential equation with respect to the dynamic pressure Π.

As the limit case is the case of monatomic gases, the initial condition for (32) must be compatible with monatomic gases. We therefore should impose the following initial condition:

$$\Pi(0, \boldsymbol{x}) = 0. \tag{33}$$

Then, by assuming the uniqueness of the solution, the only possible solution of Eq. (32) under the initial condition (33) is given by

$$\Pi(t, \boldsymbol{x}) = 0 \quad \forall t > 0. \tag{34}$$

Therefore the dynamic pressure in monatomic gases vanishes identically for any time once we impose the initial condition (33).

(II) If we insert the solution (34) into the remaining equations in (22) with $D \to 3$, we confirm that the resulting equations are the same as the ones of ET13 for rarefied monatomic gases. This means that the solution of the limiting system with 14 equations is essentially equivalent to the solution of ET13 of monatomic gases.

(III) The violation of the symmetric hyperbolicity condition ($D > 3$) disappears because this inequality comes out from the non-vanishing dynamic pressure. Therefore the condition for the symmetric hyperbolicity is the same as the one in the ET13 theory, which is always satisfied in equilibrium.

To sum up, we may conclude that the ET14 theory is applicable also to rarefied monatomic gases if we impose the initial or boundary condition of zero dynamic pressure. In the reference [37], two illustrative numerical results in the process of the singular limit, that is, the linear waves and the shock waves are shown in order to grasp the asymptotic behavior of the physical quantities, in particular, of the dynamic pressure.

6 Applications of the ET14 Theory

Applications of the ET14 theory to specific problems have been made. In this section we review briefly some of them.

6.1 Stationary Heat Conduction in a Polyatomic Gas at Rest

The study of heat conduction in a gas has been important to clarify the features of extended thermodynamics. For example, stationary heat conduction in a monatomic gas at rest confined in a cylinder and a sphere was studied [38]. It was shown that the singularities of the temperature on the axis of the cylinder and at the center of the sphere predicted by the classical NSF theory, which are, of course, unphysical, can be removed by using the ET13 theory.

Recently stationary heat conduction in both rarefied and dense polyatomic gases at rest confined between two infinite parallel plates, two coaxial cylinders, and two concentric spheres has been studied by using the ET14 theory. The analytical results obtained were compared with those derived from the NSF theory with particular attention to the role of the dynamical pressure. The non-NSF behaviors in the temperature profile have been observed. And the polyatomic effects on the heat conduction have been elucidated. For these details, see the reference [39, 40].

6.2 Dispersion Relation for Sound in Rarefied Diatomic Gases

The dispersion relation for sound in rarefied diatomic gases; hydrogen, deuterium and hydrogen deuteride gases basing on the ET14 theory was recently studied in detail [41]. The relation was compared with those obtained in experiments and by the NSF theory. As is expected, the applicable frequency-range of the ET theory was shown to be much wider than that of the NSF theory. The values of the bulk viscosity and the relaxation times involved in nonequilibrium processes were evaluated. It was found that the relaxation time related to the dynamic pressure has a possibility to become much larger than the other relaxation times related to the shear stress and the heat flux. The isotope effects on sound propagation were also clarified. For details of these results, see the references [41, 42].

The analysis was made in the temperature range where the rotational modes in a molecule play an important role. The ET theory can be applied to many other rarefied polyatomic gases in a wider temperature range where the rotational and/or vibrational modes in a molecule play a role. Comprehensive study of this subject must be a promising future work.

The study was confined within the sound in some rarefied diatomic gases because suitable experimental data are scarce and are mainly restricted to rarefied gases. The study of the dispersion relation for sound in dense gases with and without internal degrees of freedom is, therefore, remained as another future work to be made.

6.3 Analysis of Light Scattering

Experiments of light scattering in a gas afford us with precise information about the irreversible process in a gas out of local equilibrium. The analyses of light scattering in monatomic gases on the basis of the ET theory were already made in detail [4, 43]. It was shown that the ET theory can describe the experimental data on light scattering very well if the number of the independent fields is appropriately large.

The analysis of the light scattering in polyatomic gases by using the ET theory is, however, quite primitive. At present the study by the ET14 theory has just begun. The preliminary results obtained until now indicate that the ET theory is quite promising [44]. We hope we will soon report its details elsewhere.

6.4 Shock Wave Structure in a Rarefied Polyatomic Gas

The shock wave structure in a rarefied polyatomic gas is, under some conditions, quite different from the shock wave structure in a rarefied monatomic gas due to the presence of the microscopic internal modes in a polyatomic molecule such as the rotational and vibrational modes [45, 46]. For examples: (1) The shock wave thickness in a rarefied monatomic gas is of the order of the mean free path. On the other hand, owing to the slow relaxation process involving the internal modes, the thickness of a shock wave in a rarefied polyatomic gas is several orders larger than the mean free path. (2) As the Mach number increases from unity, the profile of the shock wave structure in a polyatomic rarefied gas changes from the nearly symmetric profile (Type A) to the asymmetric profile (Type B), and then changes further to the profile composed of thin and thick layers (Type C) [47–52]. Schematic profiles of the mass density are shown in Fig. 1. Such change of the shock wave profile with the Mach number cannot be observed in a monatomic gas.

In order to explain the shock wave structure in a rarefied polyatomic gas, there have been two well-known approaches. One was proposed by Bethe and Teller [53] and the other is proposed by Gilbarg and Paolucci [54]. Although the Bethe-Teller theory can describe

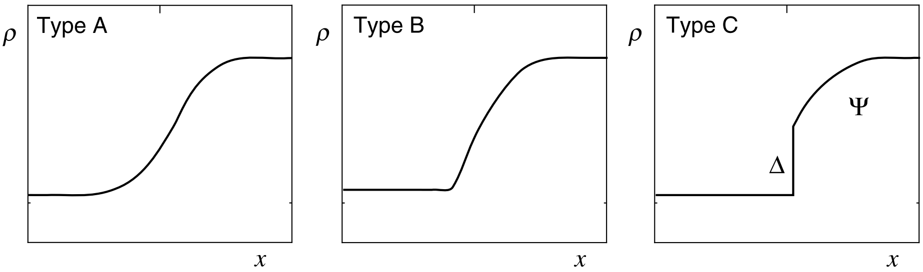

Fig. 1 Schematic representation of three types of the shock wave structure in a rarefied polyatomic gas, where ρ and x are the mass density and the position, respectively. As the Mach number increases from unity, the profile of the shock wave structure changes from Type A to Type B, and then to Type C that consists of the thin layer Δ and the thick layer Ψ

qualitatively the shock wave structure of Type C, its theoretical basis is not clear enough. The Gilbarg-Paolucci theory, on the other hand, cannot explain asymmetric shock wave structure (Type B) nor thin layer (Type C).

Recently it was shown that the ET14 theory can describe the shock wave structure of all Types A to C in a rarefied polyatomic gas [55, 56]. In other words the ET14 theory has overcome the difficulties encountered in the previous two approaches. This new approach indicates clearly the usefulness of the ET theory for the analysis of shock wave phenomena. For details of the recent results, see the references cited just above.

6.5 Fluctuating Hydrodynamics

The theory of fluctuating hydrodynamics based on extended thermodynamics has also been developed recently [57, 58]. The celebrated Landau-Lifshitz theory of hydrodynamic fluctuations [2, 59] is included in this theory as a special case.

Nowadays the Landau-Lifshitz theory attracts much attention, especially, as the basic theory for microflows and nanoflows, which may play an important role, for example, in the fields of nano-technology and molecular biology. As mentioned above the applicability range of the ET theory of fluctuating hydrodynamics is wider than that of the Landau-Lifshitz theory, it is highly expected that the ET theory will play an important role in the fields of nano-technology, molecular biology, and so on.

7 ET6—The Particular Simple Case of ET of Dense Gases

As seen in the preceding sections, a typical theory in ET of dense gases is the ET14 theory. This theory is particularly important because it is a natural extension of the Navier-Stokes Fourier (NSF) theory. In the ET14 theory, there exist 3 relaxation times τ_S, τ_Π, and τ_q that characterize the relaxation of the shear stress, the dynamic pressure, and the heat flux, respectively. The relaxation times depend on the mass density and the temperature, and their values are usually comparable with each other.

It was shown, however, by studying the dispersion relation of linear harmonic waves [41] and the shock wave structure [55, 60] that, in an appropriate temperature range of some polyatomic gases such as a hydrogen gas or a carbon dioxide gas, the relaxation time τ_Π is several orders larger than the other two relaxation times τ_S and τ_q. In such a situation, the dynamic pressure relaxes very slowly compared with the relaxation of the shear stress and the heat flux. And the effect of the shear stress and the heat flux on the relaxation process is negligibly small.

In order to focus our attention on such slow relaxation phenomena, a simplified version of the ET14 theory, that is, an ET theory with 6 independent fields of the mass density, the velocity, the temperature, and the dynamic pressure (ET6) has been proposed [21, 61]. The system of field equations is given by

$$\begin{aligned}
&\dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} = 0, \\
&\rho \dot{v}_i + \frac{\partial (p + \Pi)}{\partial x_i} = 0, \\
&\rho \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho \dot{T} + \left[p + \Pi - \rho^2 \left(\frac{\partial \varepsilon}{\partial \rho} \right)_T \right] \frac{\partial v_k}{\partial x_k} = 0, \\
&\dot{\Pi} + (a_1 + a_2 \Pi) \frac{\partial v_k}{\partial x_k} = -\frac{1}{\tau_\Pi} \Pi.
\end{aligned} \tag{35}$$

The coefficients a_1 and a_2 are given by

$$a_1 = \rho \left[\frac{5}{3} \frac{p}{\rho} - \left(\frac{\partial p}{\partial \rho} \right)_s \right], \qquad a_2 = \frac{5}{3} - \frac{1}{\rho T} \left(\frac{\partial p}{\partial s} \right)_\rho,$$

where s is the specific entropy in equilibrium.

The entropy balance law holds with the entropy density h and the entropy flux h_k being given by

$$h = \rho s - \frac{1}{2 T a_1} \Pi^2, \qquad h_k = h v_k, \tag{36}$$

where ρs is the entropy density in equilibrium. From Eq. $(36)_1$, the concavity condition of the entropy density (or symmetric hyperbolic condition [4]) at an equilibrium state is given by

$$c_v = \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho > 0, \qquad 0 < \left(\frac{\partial p}{\partial \rho} \right)_s < \frac{5}{3} \frac{p}{\rho},$$

where c_v is the specific heat at constant volume.

It was shown [21] that the ET6 theory can be regarded as an extension of the well-known Meixner theory of relaxation phenomena [62, 63]. The ET6 theory can also describe the shock wave structure in a rarefied polyatomic gases [60]. Indeed, it is the ET6 theory that can be regarded as a consistent and unified extension of the Bethe-Teller theory for the shock wave structure. ET6 is the principal sub-system of ET14 in the sense of Boillat and Ruggeri [64].

Another point worth mentioning is that the same conclusion of the singular limit explained in Sect. 5 is also true for the ET6 theory [61]. That is, rarefied monatomic gases can be identified as a singular limit of rarefied polyatomic gases. This case is particularly interesting because, in the limit $D \to 3$, the system of ET6, which is a hyperbolic dissipative system of equations, approaches the Euler system with 5 fields that is a conservative hyperbolic system.

Because of the simplicity of the ET6 theory, thorough mathematical studies of its hyperbolic system of equations seem to be quite interesting as future works.

8 Molecular Extended Thermodynamics of Rarefied Polyatomic Gases with Many Moments

We study the case of a generic number of moments. We can proceed in the same way as for 14 fields (29).

8.1 Binary Hierarchy of Moments

We can define a binary hierarchy of moments as follows [20, 22]: By introducing the moments

$$\begin{aligned} F_A &= \int_{\mathbb{R}^3}\int_0^\infty m f c_A I^\alpha \, dI d\mathbf{c}, \qquad F_{iA} = \int_{\mathbb{R}^3}\int_0^\infty m f c_i c_A I^\alpha \, dI d\mathbf{c}, \\ P_A &= \int_{\mathbb{R}^3}\int_0^\infty m Q(f) c_A I^\alpha \, dI d\mathbf{c}, \end{aligned} \tag{37}$$

and the additional moments [20]

$$\begin{aligned} G_{llA'} &= \int_{\mathbb{R}^3}\int_0^\infty m f \left(c^2 + \frac{2I}{m}\right) c_{A'} I^\alpha \, dI d\mathbf{c}, \\ G_{illA'} &= \int_{\mathbb{R}^3}\int_0^\infty m f \left(c^2 + \frac{2I}{m}\right) c_i c_{A'} I^\alpha \, dI d\mathbf{c}, \\ Q_{llA'} &= \int_{\mathbb{R}^3}\int_0^\infty m Q(f) \left(c^2 + \frac{2I}{m}\right) c_{A'} I^\alpha \, dI d\mathbf{c}, \end{aligned} \tag{38}$$

it is possible to build two hierarchies of moments that, after truncation, read as follows ("(N, M)-system"):

$$\begin{aligned} &\partial_t F_A + \partial_i F_{iA} = P_A, &&\partial_t G_{llA'} + \partial_i G_{lliA'} = Q_{llA'}, \\ &(0 \le A \le N) &&\big(0 \le A' \le M\big). \end{aligned} \tag{39}$$

The following multi-index notations are introduced for the sake of compactness:

$$F_A = \begin{cases} F & \text{for } A = 0 \\ F_{i_1\cdots i_A} & \text{for } 1 \le A \le N \end{cases}, \qquad F_{iA} = \begin{cases} F_i & \text{for } A = 0 \\ F_{i\, i_1\cdots i_A} & \text{for } 1 \le A \le N \end{cases},$$

$$P_A = \begin{cases} 0 & \text{for } A = 0 \\ 0 & \text{for } A = 1 \\ P_{i_1\cdots i_A} & \text{for } 2 \le A \le N \text{ (with } P_{ll} = 0) \end{cases},$$

$$G_{llA'} = \begin{cases} G_{ll} & \text{for } A' = 0 \\ G_{lli_1\cdots i_{A'}} & \text{for } 1 \le A' \le M \end{cases}, \qquad G_{lliA'} = \begin{cases} G_{lli} & \text{for } A' = 0 \\ G_{llii_1\cdots i_{A'}} & \text{for } 1 \le A' \le M \end{cases},$$

$$Q_{llA'} = \begin{cases} 0 & \text{for } A' = 0 \\ Q_{lli_1\cdots i_{A'}} & \text{for } 1 \le A' \le M \end{cases},$$

and

$$c_A = \begin{cases} 1 & \text{for } A = 0 \\ c_{i_1} \cdots c_{i_A} & \text{for } 1 \le A \le N \end{cases},$$

where the indices i and $i_1 \le i_2 \le \cdots \le i_A$ assume the values $1, 2, 3$. The truncation order N of the F-hierarchy (*momentum-like* hierarchy) and M order of the G-hierarchy (*energy-like* hierarchy) are a priori independent of each other. It is worth noting that the first and second equations of the F-hierarchy represent the conservation of mass and momentum, respectively ($P \equiv 0$, $P_i \equiv 0$), while the first equation of the G-hierarchy represents the conservation of energy ($Q_{ll} \equiv 0$), and in each of the two hierarchies the flux in one equation appears as the density in the following equation—a feature in common with the single hierarchy of monatomic gases.

We note that the Euler 5 moments system is a particular case of (39) with $N = 1$, $M = 0$, and the 14 moments case (2) is a particular case of (39) with $N = 2$, $M = 1$.

The variational problem from which the distribution function $f_{(N,M)}$ is obtained is connected to the functional:

$$\mathcal{L}_{(N,M)}(f) = -k \int_{\mathbb{R}^3} \int_0^\infty f \log f \, I^\alpha \, dI d\mathbf{c} + u'_A \left(F_A - m \int_{\mathbb{R}^3} \int_0^\infty c_A f I^\alpha \, dI d\mathbf{c} \right)$$

$$+ v'_{A'} \left(G_{llA'} - m \int_{\mathbb{R}^3} \int_0^\infty \left(c^2 + \frac{2I}{m} \right) c_{A'} f I^\alpha dI d\mathbf{c} \right),$$

where u'_A and $v'_{A'}$ are the Lagrange multipliers. The distribution function $f_{(N,M)}$ which maximizes the functional $\mathcal{L}_{(N,M)}$ is given by [22]:

$$f_{(N,M)} = \exp\left(-1 - \frac{m}{k} \chi_{(N,M)} \right), \quad \chi_{(N,M)} = u'_A c_A + \left(c^2 + \frac{2I}{m} \right) v'_{A'} c_{A'}. \tag{40}$$

By inserting (40) into $(37)_1$ and $(38)_1$, the Lagrange multipliers u'_A and $v'_{A'}$ are evaluated in terms of the densities F_A and $G_{llA'}$. By using the distribution function expressed by the densities, the constitutive functions which close the truncated fluxes and productions in (37) and (38) with respect to the densities are obtained.

Then, the system (39) may be rewritten as follows:

$$\begin{pmatrix} J^0_{AB} & J^1_{AB'} \\ J^1_{A'B} & J^2_{A'B'} \end{pmatrix} \partial_t \begin{pmatrix} u'_B \\ v'_{B'} \end{pmatrix} + \begin{pmatrix} J^0_{iAB} & J^1_{iAB'} \\ J^1_{iA'B} & J^2_{iA'B'} \end{pmatrix} \partial_i \begin{pmatrix} u'_B \\ v'_{B'} \end{pmatrix} = \begin{pmatrix} P_A \\ Q_{llA'} \end{pmatrix}, \tag{41}$$

where

$$\begin{aligned} J^0_{AB} &= -\frac{m^2}{k} \int_{\mathbb{R}^3} \int_0^\infty f c_A c_B I^\alpha \, dI d\mathbf{c}, \\ J^1_{AB'} &= -\frac{m^2}{k} \int_{\mathbb{R}^3} \int_0^\infty f c_A c_{B'} \left(c^2 + \frac{2I}{m} \right) I^\alpha \, dI d\mathbf{c}, \\ J^2_{A'B'} &= -\frac{m^2}{k} \int_{\mathbb{R}^3} \int_0^\infty f c_{A'} c_{B'} \left(c^2 + \frac{2I}{m} \right)^2 I^\alpha \, dI d\mathbf{c}. \end{aligned} \tag{42}$$

It has been proved that the truncation indices N and M of the two hierarchies are, in reality, not independent because of the physical reasons; Galilean invariance of field equations and the fact that the characteristic velocities depend on the degrees of freedom of the particles. And we have arrived at the conclusion that the relation $M = N - 1$ should be satisfied [22]. Moreover it has also been proved that, for any generic number of moments, the closure procedures of EP and MEP are equivalent to each other.

The system (41) is symmetric hyperbolic according with the general theory of systems of balance laws with a concave entropy density (see [30, 64–66]).

8.2 Characteristic Velocities

The characteristic velocities $\lambda^{(k)}_{(N,M)}$ of the system (41) in the direction of propagation having unit vector $\mathbf{n} \equiv (n^i)$ are the roots of the characteristic polynomial $T_{(N,M)}$:

$$T_{(N,M)} = \det\left[\begin{pmatrix} J^0_{iAB} & J^1_{iAB'} \\ J^1_{iA'B} & J^2_{iA'B'} \end{pmatrix} n^i - \lambda_{(N,M)} \begin{pmatrix} J^0_{AB} & J^1_{AB'} \\ J^1_{A'B} & J^2_{A'B'} \end{pmatrix}\right] = 0.$$

In particular, the wave speeds for disturbances propagating in an equilibrium state are the solutions of the characteristic polynomial $T^E_{(N,M)}$:

$$T^E_{(N,M)} = \det\left[\begin{pmatrix} J^{0|E}_{iAB} & J^{1|E}_{iAB'} \\ J^{1|E}_{iA'B} & J^{2|E}_{iA'B'} \end{pmatrix} n^i - \lambda^E_{(N,M)} \begin{pmatrix} J^{0|E}_{AB} & J^{1|E}_{AB'} \\ J^{1|E}_{A'B} & J^{2|E}_{A'B'} \end{pmatrix}\right] = 0,$$

where the superscript "E" denotes that all the quantities are evaluated by using the local equilibrium distribution function f^E given by (27).

In a recent paper by Arima, Mentrelli and Ruggeri [22], they have shown that it is possible to compare the characteristic velocities for a polyatomic gas and a monatomic one for any index of truncation. In particular, using the convexity arguments and the sub-characteristic conditions for principal subsystems, they have proven that the lower bound estimate for the equilibrium maximum characteristic velocity (in sound speed unity) established for monatomic gases by Boillat and Ruggeri [30]:

$$\frac{\lambda^{\max}_{(N)}}{c_0} \geq \sqrt{\frac{6}{5}\left(N - \frac{1}{2}\right)} \quad \left(c_0 = \sqrt{\frac{5}{3}\frac{k}{m}T}\right) \tag{43}$$

is universal and independent of the degrees of freedom of a molecule. Therefore, also in the case of polyatomic gases, the maximum characteristic velocity is unbounded when $N \to \infty$.

9 Summary

We have explained the present status of ET of dense gases by reviewing the recent results. Many open problems remained have also been pointed out. It is obvious that this research field is still at infancy and that many things are remained to be studied further.

Lastly we make two remarks here. As is pointed out in the preceding sections, the concavity of entropy density and the related stability problem at $D = 3$ is not yet completely solved. In order to include the case of monatomic dense gases into the validity range of the ET6, ET14 or ETn theory, we should generalize the system of field equations. One possible way in this direction will soon be reported elsewhere.

In connection with this remark, it should be emphasized that the present ET theory of dense gases is valid up to moderately dense gases [19]. If we want to analyze nonequilibrium properties in more dense gases, we will encounter the same stability problem mentioned above. We should generalize the system of field equations. This is, we believe, a fundamentally important problem worthy of the next study.

Another challenge will be to construct the relativistic counterpart of dense and rarefied polyatomic gas theory.

Acknowledgements The authors thank T. Arima, E. Barbera, F. Brini, A. Mentrelli, M. Pavić, S. Simić, and S. Taniguchi for sharing the pleasant joint works. This work was partially supported by the National Group of Mathematical Physics GNFM-INdAM and by University of Bologna: FARB 2012 Project *Extended Thermodynamics of Non-Equilibrium Processes from Macro- to Nano-Scale* (T.R.) and by Japan Society of Promotion of Science (JSPS) No. 25390150 (M.S.).

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