

Multiscale Phenomena in Continuum Mechanics: Mesoscopic Justification of Rational Extended Thermodynamics of Gases with Internal Structure



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Abstract In many physical systems one encounters situations where phenomena occur at different scales. An example is the modeling of a rarefied gas at varying Knudsen number (Kn). Large Kn corresponds to a case where the Boltzmann equation is the most appropriate model while, for small Kn, one can obtain the Euler or Navier–Stokes–Fourier system. At intermediate regime, using the mathematical methods of Rational Extended Thermodynamics (RET), one can obtain the closure of hyperbolic moment system associated with the Boltzmann equation for monatomic gas. This methodology can be extended to polyatomic gas by considering a distribution function depending on an extra variable that takes into account the internal motion of polyatomic molecule (rotation and vibration). In this survey paper we consider first the state-of-the-art of RET and at the end we give a summary on the recent results about more refined version of RET of polyatomic gas in which molecular rotational and vibrational relaxation processes are treated individually.

1 Thermodynamics of Irreversible Processes

A continuous medium is a continuous distribution of material points which occupy a region of the Euclidean space Ω with boundary Σ . The typical unknown fields depending on space $\mathbf{x} \equiv (x_i)$ ($i = 1, 2, 3$) and time t are the mass density ρ , the velocity $\mathbf{v} \equiv (v_i)$, the temperature T , the specific internal energy ε , the heat flux $\mathbf{q} \equiv (q_i)$, and the stress tensor $\mathbf{t} \equiv (t_{ij})$ that in the case of a fluid can be decomposed into the equilibrium and non-equilibrium parts:

$$t_{ij} = -p \delta_{ij} + \sigma_{ij} = -(p + \Pi) \delta_{ij} + \sigma_{\langle ij \rangle}, \quad (1)$$

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where p is the equilibrium pressure, δ_{ij} is the Kronecker symbol, and $\boldsymbol{\sigma} \equiv (\sigma_{ij})$ is the viscous stress tensor that is decomposed furthermore into isotropic and deviatoric parts: Π is called the dynamical pressure and $\sigma_{\langle ij \rangle}$ is the deviatoric (traceless) shear viscosity tensor.

These fields obey two kinds of equations: the *universal balance laws* (valid for all materials) which are typically: Conservation of mass; Balance law of momentum; Balance laws of energy; and the so-called *constitutive equations* that are necessary to close the system and to characterize the constitutive properties of the material in question.

For example in the case of one-component fluid we have:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \frac{\partial \rho v_i}{\partial x_i} &= 0, \\ \frac{\partial \rho v_j}{\partial t} + \frac{\partial}{\partial x_i} (\rho v_i v_j - t_{ij}) &= \rho b_j, \\ \frac{\partial E}{\partial t} + \frac{\partial}{\partial x_i} (E v_i + q_i - t_{ij} v_j) &= \rho b_j v_j + r, \end{aligned} \quad (2)$$

where $E = \rho v^2/2 + \rho \varepsilon$ is the total energy that is the sum of the kinetic energy density and the internal energy density, $\mathbf{b} \equiv (b_i)$ and r are, respectively, the external body force and the heat supply. If \mathbf{b} and r vanish, the balance laws become conservation laws.

As is well known the previous system (2) in the absence of external sources can be rewritten, for classical solutions, in the form:

$$\begin{aligned} \dot{\rho} + \rho \frac{\partial v_j}{\partial x_j} &= 0, \\ \rho \dot{v}_i - \frac{\partial t_{ij}}{\partial x_j} &= 0, \\ \rho \dot{\varepsilon} - t_{ij} \frac{\partial v_i}{\partial x_j} + \frac{\partial q_i}{\partial x_i} &= 0, \end{aligned} \quad (3)$$

where a dot on a quantity denotes the material time derivative operator:

$$\frac{\partial}{\partial t} + v_i \frac{\partial}{\partial x_i}.$$

The specific internal energy ε and the pressure p are considered to be functions of ρ and T that are prescribed by the thermal and caloric equations of state of equilibrium thermodynamics

$$p \equiv p(\rho, T), \quad \varepsilon \equiv \varepsilon(\rho, T). \quad (4)$$

In order to close the system (3), we need the constitutive relations of σ_{ij} and q_i in terms of the independent fields ρ , v_i , and T . In TIP, such relations are derived in a heuristic manner from the entropy balance equation that is based on the Gibbs equation of the concept of *local equilibrium*.

First of all we need to recall the important contribution by the mathematician Constantin Carathéodory with his fundamental work on the *axiomatic approach of thermodynamics*. He postulated the so-called *principle of inaccessibility* that states [1] (see also [2, 3]): “*In the neighborhood of any equilibrium state of a system (of any number of thermodynamic coordinates), there exist states that are inaccessible by reversible adiabatic processes*”.

Starting with this axiom and using some properties of Pfaffian forms Carathéodory showed how to derive the absolute temperature as integral factor and he justify rigorously the famous Gibbs equation in thermostatics:

$$T ds = d\varepsilon - \frac{p}{\rho^2} d\rho, \quad (5)$$

where s is the specific entropy density.

In non-equilibrium according to the procedure TIP the concept of local equilibrium is introduced and the Gibbs relation (5) is assumed to be valid. From (5) we have

$$\dot{s} = \frac{1}{T} \left(\dot{\varepsilon} - \frac{p}{\rho^2} \dot{\rho} \right). \quad (6)$$

Elimination of $\dot{\varepsilon}$ and $\dot{\rho}$ in (6) by using (3) gives

$$\rho \dot{s} + \frac{\partial}{\partial x_i} \left(\frac{q_i}{T} \right) = \frac{1}{T} \sigma_{(ij)} \frac{\partial v_{(i}}{\partial x_{j)}} - \frac{1}{T} \Pi \frac{\partial v_i}{\partial x_i} - \frac{1}{T^2} q_i \frac{\partial T}{\partial x_i},$$

or equivalently:

$$\frac{\partial \rho s}{\partial t} + \frac{\partial}{\partial x_i} \left(\rho s v_i + \frac{q_i}{T} \right) = \frac{1}{T} \sigma_{(ij)} \frac{\partial v_{(i}}{\partial x_{j)}} - \frac{1}{T} \Pi \frac{\partial v_i}{\partial x_i} - \frac{1}{T^2} q_i \frac{\partial T}{\partial x_i},$$

which can be seen as a balance equation of the entropy with the following interpretation:

$$\text{intrinsic entropy flux : } \Phi_i = \frac{q_i}{T},$$

$$\text{entropy production: } \Sigma = \frac{1}{T} \sigma_{(ij)} \frac{\partial v_{(i}}{\partial x_{j)}} - \frac{1}{T} \Pi \frac{\partial v_i}{\partial x_i} - \frac{1}{T^2} q_i \frac{\partial T}{\partial x_i}.$$

The entropy production is a sum of products of:

Dissipative fluxes	Thermodynamic forces
shear stress $\sigma_{(ij)}$	deviatoric velocity gradient $\frac{1}{T} \frac{\partial v_{<i}}{\partial x_{j>}}$,
dynamic pressure Π	divergence of velocity $-\frac{1}{T} \frac{\partial v_i}{\partial x_i}$,
heat flux q_i	temperature gradient $-\frac{1}{T^2} \frac{\partial T}{\partial x_i}$.

From the second law of thermodynamics, the entropy production must be non-negative. Assuming linear relations between the dissipative fluxes and the thermodynamic forces, we have the constitutive equations (phenomenological equations) of the type:

$$\begin{aligned}
 \sigma_{(ij)} &= 2\mu \frac{\partial v_{<i}}{\partial x_{j>}} & \mu &\geq 0, \\
 \Pi &= -\nu \frac{\partial v_i}{\partial x_i} & \nu &\geq 0, \\
 q_i &= -\kappa \frac{\partial T}{\partial x_i} & \kappa &\geq 0.
 \end{aligned} \tag{7}$$

These are known as the constitutive laws of Navier-Stokes and Fourier with μ and ν being the shear and bulk viscosities and κ the thermal conductivity. All of these coefficients may be functions of ρ and T .

Along with the thermal and caloric equations of state, the equations (7) are adopted as the constitutive equations of the thermodynamical of irreversible processes (TIP), and the differential system (3) is closed, i.e., 5 equations for 5 unknowns [4]. The system formed by the balance laws (2) and the constitutive laws (4), (7) is called briefly *Navier–Stokes–Fourier system* and if isothermal *Navier–Stokes system*.

1.1 Equations of Heat and Heat Paradox

In the simplified case of a rigid heat conductor the system of balance equations (3) reduces to that of energy:

$$\rho \dot{\varepsilon} + \frac{\partial q_j}{\partial x_j} = 0, \tag{8}$$

which, combined with the Fourier equation (7)₃ and the caloric equation $\varepsilon \equiv \varepsilon(T)$, provides the classic heat equation, a prototype of a parabolic equation:

$$\frac{\partial T}{\partial t} = \mathcal{D}\Delta T, \quad \left(\mathcal{D} = \frac{\kappa}{\rho c_V}, \quad c_V = \frac{d\varepsilon}{dT} \right) \quad (9)$$

that, in the simple case of constant \mathcal{D} , has the following solution of the Cauchy problem:

$$T(\mathbf{x}, t) = \frac{1}{(4\pi\mathcal{D}t)^{3/2}} \int_{-\infty}^{\infty} T(\mathbf{y}, 0) e^{-\frac{(\mathbf{y}-\mathbf{x})^2}{4\mathcal{D}t}} d\mathbf{y}. \quad (10)$$

We notice that $T(\mathbf{x}, t)$ is nonzero for any \mathbf{x} if $t > 0$ even though the initial value $T(\mathbf{x}, 0)$ is nonzero only in a bounded domain. This phenomenon has been sometimes called a paradox, because the temperature perturbations propagate with infinitely large speed. From a mathematical point of view, this is due to the parabolic character of the basic equation (9).

The assertion of infinite speed is, of course, beyond the validity range of TIP. We cannot describe properly such a rapid change by TIP because TIP is based on the local equilibrium assumption. On the other hand, it is well known that Eqs. (9) and (10) have been utilized quite successfully in various practical situations. Indeed, if we take carefully its validity range into account, and if we do not care about its unphysical predictions, we would have useful results from a practical point of view.

There is, however, a situation where the infinite speed should be avoided strictly. It is a relativistic thermodynamic case where propagation speed of a wave should be less or equal to the light speed. How can we construct a new thermodynamic theory that predicts only finite speed of waves by generalizing TIP? Carlo Cattaneo addressed this paradox, and proposed in 1948 a modified Fourier equation which is known as Cattaneo equation [5]:

$$\tau \dot{q}_i + q_i = -\chi \frac{\partial T}{\partial x_i}. \quad (11)$$

Combining (8) with (11) we obtain instead of the classical heat equation an hyperbolic equation called the *telegraph equation*:

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} = \mathcal{D}\Delta T.$$

The importance of hyperbolic equations has its experimental evidence in the so-called second sound, which is a perturbation wave of temperature observed firstly in liquid helium at low temperatures [6] and subsequently in crystals [7]. However Cattaneo equation has several weak points: it can predict negative value

of the temperature and the entropy principle is not satisfied for processes far from equilibrium (see [8] and references therein on this subject).

On the other hand, Cattaneo equation has an empirical genesis and is oversimplified. To find a theoretical justification for hyperbolic systems for heat propagation need the approach of extended thermodynamics as we shall see in Sect. 3.

2 Successive Approach

After the pioneering work of Cattaneo the most fundamental improvements on this subject were done:

- 1949—Grad [9] constructed by kinetic methods the so-called 13 moments fields theory that give a system of hyperbolic type for monatomic rarefied gases.
- 1966—Müller [10] determined, via a continuum approach, a hyperbolic system for a generic gas abandoning the local equilibrium assumption and modifying the Gibbs equations using as extended fields the heat flux and the viscous stress tensor. This was the first version and the begin of *Extended Thermodynamics theory*. This point of view has been adopted by several authors and is the starting point of Extended Irreversible Thermodynamics (EIT), which has gained popularity through the book of Jou et al. [11].
- 1983—Following some criticism of Ruggeri in [12] a revision of ET was proposed by Liu and Müller [13] in a classic context, and by Liu, Müller and Ruggeri in a relativistic framework [14]. This new approach was named *Rational Extended Thermodynamics* (RET) and the main results obtained at that time were summarized in the two editions of the book by Müller and Ruggeri [15, 16].
- 2012—The previous RET theory, being strictly connected with the kinetic theory, suffers from nearly the same limitations as the Boltzmann equation. Indeed, the theory is valid only for rarefied monatomic gases, where the specific internal energy ε and the pressure p are connected by the relation $2\rho\varepsilon = 3p$, and the dynamic pressure Π vanishes identically. In the case of polyatomic gases, on the other hand, the rotational and vibrational degrees of freedom of a molecule, which are not present in monatomic gases, come into play. After several tentative theories, a satisfactory *14-field* ET theory for rarefied polyatomic ones was recently developed by Arima et al. [17]. The recent book of Ruggeri and Sugiyama summarizes this new extension of RET [8].

This list reflects the personal opinion of the present author but of course it is not exhaustive because it is well known that several different approaches on non-equilibrium thermodynamics are present in the literature. A first tentative of comparison between different theories was done in [18].

3 Rational Extended Thermodynamics of Rarefied Monatomic Gas

The kinetic theory describes a state of a rarefied gas through the phase density $f(\mathbf{x}, t, \mathbf{c})$, where $f(\mathbf{x}, t, \mathbf{c})d\mathbf{c}$ is the number density of atoms at point \mathbf{x} and time t that have velocities between \mathbf{c} and $\mathbf{c} + d\mathbf{c}$. The phase density obeys the Boltzmann equation that in the case of absence of external forces reads:

$$\frac{\partial f}{\partial t} + c_i \frac{\partial f}{\partial x_i} = Q, \quad (12)$$

where Q represents the collisional term. Most macroscopic thermodynamic quantities are identified as moments of the phase density

$$F_{k_1 k_2 \dots k_j} = \int_{\mathbb{R}^3} m f c_{k_1} c_{k_2} \dots c_{k_j} d\mathbf{c},$$

where m is the mass of a molecule. Due to the Boltzmann equation (12), the moments satisfy an infinite hierarchy of balance laws in which the flux in one equation becomes the density in the next one:

$$\begin{aligned} \partial_t F + \partial_i F_i &= 0 \\ &\swarrow \\ \partial_t F_{k_1} + \partial_i F_{ik_1} &= 0 \\ &\swarrow \\ \partial_t F_{k_1 k_2} + \partial_i F_{ik_1 k_2} &= P_{\langle k_1 k_2 \rangle} \\ &\swarrow \\ \partial_t F_{k_1 k_2 k_3} + \partial_i F_{ik_1 k_2 k_3} &= P_{k_1 k_2 k_3} \\ &\vdots \\ \partial_t F_{k_1 k_2 \dots k_n} + \partial_i F_{ik_1 k_2 \dots k_n} &= P_{k_1 k_2 \dots k_n}, \\ &\vdots \end{aligned} \quad (13)$$

where

$$\partial_t = \frac{\partial}{\partial t}, \quad \partial_i = \frac{\partial}{\partial x_i}$$

and $\langle \dots \rangle$ indicates the deviatoric part of a tensor, $(i, k_1, k_2, \dots = 1, 2, 3)$.

Taking into account that $P_{kk} = 0$, the first five equations are conservation laws and coincide with the mass, momentum, and energy conservation, respectively, while the remaining ones are balance laws.

Remark ET with this hierarchy structure is valid only for *monatomic gases*. In fact due to the previous structure we have from (13)₂ that the momentum flux:

$$F_{ik} = \rho v_i v_k - t_{ik},$$

while the trace of (13)₃ is the conservation of energy with:

$$F_{ll} = 2\rho\varepsilon + \rho v^2$$

then taking into account (1) we have

$$3p = 2\rho\varepsilon, \quad \Pi = 0. \quad (14)$$

The first of (14) gives

$$\gamma = \frac{c_p}{c_v} = \frac{5}{3},$$

i.e. monatomic gas; while the second of (14) implies that in monatomic gas the dynamical pressure is identical zero.

When we cut the hierarchy at the density with tensor of rank n , we have the problem of closure because the last flux and the production terms are not in the list of the densities. The first idea of Rational Extended Thermodynamics [16] was, by assumptions to adopt, as differential system, the one with the structure of moments (13) but forgetting that the fields are moments of a distribution function. Then the truncated system at tensorial index n is considered as a phenomenological system of continuum mechanics. As usual in continuum mechanics we consider the quantities (last flux and the production terms) that are not in the list of densities as constitutive functions:

$$F_{k_1 k_2 \dots k_n k_{n+1}} \equiv F_{k_1 k_2 \dots k_n k_{n+1}} (F, F_{k_1}, F_{k_1 k_2}, \dots, F_{k_1 k_2 \dots k_n})$$

$$P_{k_1 k_2 \dots k_j} \equiv P_{k_1 k_2 \dots k_j} (F, F_{k_1}, F_{k_1 k_2}, \dots, F_{k_1 k_2 \dots k_n}), \quad (2 \leq j \leq n).$$

According to the continuum theory, the restrictions on the constitutive equations come only from *universal principles*, i.e.: *Entropy principle*, *Objectivity Principle*,

and *Causality and Stability* (convexity of the entropy). The most interesting physical cases were the 13 fields theory [13]:

$$\begin{aligned}\partial_t F + \partial_i F_i &= 0 \\ \partial_t F_{k_1} + \partial_i F_{ik_1} &= 0 \\ \partial_t F_{k_1 k_2} + \partial_i F_{ik_1 k_2} &= P_{<k_1 k_2>} \\ \partial_t F_{k_1 j j} + \partial_i F_{ik_1 j j} &= P_{k_1 j j}.\end{aligned}$$

The surprising result is that the closure adopted by the Rational Extended Thermodynamics via phenomenological approach gives the same differential system obtained by Grad using the well known 13 moments perturbation method of the Maxwellian in terms of Hermite polynomials [16].

4 Closure via the Maximum Entropy Principle and Molecular RET of Monatomic Gases

If the number of moments increases, it is too difficult to adopt the pure continuum approach for a system with such a large number of field variables. Therefore it is necessary to recall that the field variables are the moments of a distribution function truncated at some order. And then the closure of the balance equations of the moments, which is known as the *Maximum Entropy Principle* (MEP), should be introduced. This approach was called by Müller and Ruggeri *Molecular Extended Thermodynamics* [15]. The principle of maximum entropy has its root in statistical mechanics. It is developed by Jaynes [19] in the context of the theory of information basing on the Shannon entropy. Nowadays the importance of MEP is recognized fully due to the numerous applications in many fields, for example, in the field of computer graphics.

MEP states that the probability distribution that represents the current state of knowledge in the best way is the one with the largest entropy.

Another way of stating this is as follows: *Take precisely stated prior data or testable information about a probability distribution function. Then consider the set of all trial probability distributions that would encode the prior data. Of those, one with maximal information entropy is the proper distribution, according to this principle.*

Concerning the applicability of MEP in non-equilibrium thermodynamics, this was originally by the observation made by Kogan [20] that Grad's distribution function maximizes the entropy. The MEP closure was proposed in RET for the first time by Dreyer in 1987 [21]. In this way the closure of 13-moment theory can be obtained in three different ways: RET, Grad, and MEP. A remarkable point is that all closures are equivalent to each other!

In 1993 the MEP procedure was then generalized by Müller and Ruggeri to the case of any number of moments in the first edition of their book [15] proving that the system is symmetric hyperbolic if the Lagrange multipliers are chosen as field variables. The complete equivalence between the entropy principle closure and the MEP ones in molecular extended thermodynamics was finally proved by Boillat and Ruggeri in 1997 [22] who proved that the Lagrange multipliers coincide with the so-called *main field* that symmetrize any hyperbolic system compatible with a convex entropy law [23, 24].

The RET has been successful because several experiments are in agreement with the theory (sound waves in high frequencies, light scattering, shock waves) [16]. Nevertheless it has two limitations:

1. The theory is valid only for monatomic rarefied gas.
2. The theory is substantially valid only near equilibrium.

5 Polyatomic Gases

In 2012 Arima et al. [17] deduced a 14-fields phenomenological theory for polyatomic rarefied gas using the universal principles of RET postulating a double hierarchy of equations. We do not discuss here this macroscopic theory. The interested reader may consult the original paper [17] or the book [8]. Instead we want to recall the molecular approach in the present case of polyatomic gas. The first question is that “does a macroscopic system have a kinetic counterpart?” The idea first developed by Borgnakke and Larsen [25] and successively reconsidered in more mathematical aspects by Bourgat et al. [26] to have a kinetic theory of polyatomic gas is to assume that the distribution function $f(t, \mathbf{x}, \mathbf{c}, I)$ defined on extended domain $[0, \infty) \times \mathbb{R}^3 \times \mathbb{R}^3 \times [0, \infty)$ depends on an additional continuous variable I representing the energy of the internal mode. Its rate of change is determined by the Boltzmann equation which has the same form as for monatomic gas (12), but collision integral $Q(f)$ takes into account the influence of internal degrees of freedom through collisional cross section.

5.1 Equilibrium Distribution Function for Polyatomic Gases

In the present approach the collision invariants form a vector with five components:

$$\boldsymbol{\psi}(\mathbf{c}, I) = \left(m, mc_i, \frac{1}{2}mc^2 + I \right)^T,$$

which lead to hydrodynamic variables in the form:

$$\begin{pmatrix} \rho \\ \rho v_i \\ \frac{1}{2}\rho v^2 + \rho\varepsilon \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty \boldsymbol{\psi}(\mathbf{c}, I) f(t, \mathbf{x}, \mathbf{c}, I) \varphi(I) dI d\mathbf{c}. \quad (15)$$

Here $\varphi(I)dI$ represents the number of internal modes between I and $I+dI$. Entropy is defined by the following relation:

$$h = \rho s = -k_B \int_{\mathbb{R}^3} \int_0^\infty f \log f \varphi(I) dI d\mathbf{c}, \quad (16)$$

where k_B is the Boltzmann constant. We shall introduce the peculiar velocity $\mathbf{C} \equiv (C_i)$:

$$\mathbf{C} = \mathbf{c} - \mathbf{v}, \quad C^2 = C_i C_i$$

and rewrite the Eq. (15) in terms of it. Then

$$\begin{pmatrix} \rho \\ 0_i \\ 2\rho\varepsilon \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty m \begin{pmatrix} 1 \\ C_i \\ C^2 + 2I/m \end{pmatrix} f(t, \mathbf{x}, \mathbf{C}, I) \varphi(I) dI d\mathbf{C}.$$

Note that the internal energy density can be divided into the translational part $\rho\varepsilon_K$ and the part related to the internal degrees of freedom $\rho\varepsilon_I$:

$$\begin{aligned} \rho\varepsilon_K &= \int_{\mathbb{R}^3} \int_0^\infty \frac{1}{2} m C^2 f(t, \mathbf{x}, \mathbf{C}, I) \varphi(I) dI d\mathbf{C}, \\ \rho\varepsilon_I &= \int_{\mathbb{R}^3} \int_0^\infty I f(t, \mathbf{x}, \mathbf{C}, I) \varphi(I) dI d\mathbf{C}. \end{aligned} \quad (17)$$

The former can be related to the kinetic temperature in the following way:

$$\varepsilon_K = \frac{3}{2} \frac{k}{m} T, \quad (18)$$

whereas the latter is the energy contribution of internal degrees of freedom to the internal energy, which is determined by

$$\varepsilon_I = \varepsilon - \varepsilon_K. \quad (19)$$

Pavic et al. [27]¹ firstly considered the five moments of Euler fluids and they proved using MEP that the distribution function in equilibrium that maximizes the entropy has the form:

$$f_E = \frac{\rho}{m A(T)} \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left\{ -\frac{1}{k_B T} \left(\frac{1}{2} m C^2 + I \right) \right\}, \quad (20)$$

where

$$A(T) = \int_0^\infty \exp \left(-\frac{I}{k_B T} \right) \varphi(I) dI. \quad (21)$$

This is a generalization of the Maxwellian distribution function to the case of polyatomic gas and was obtained first with different arguments in [26].

Non-polytropic Gas In the case of ideal non-polytropic gases the specific heat $c_v = d\varepsilon(T)/dT$ is, in general, a non-linear function of the temperature and the caloric and thermal equations of state read:

$$\varepsilon \equiv \varepsilon(T), \quad p = \frac{k_B}{m} \rho T = \frac{2}{3} \rho \varepsilon_K.$$

As c_v can be measured by experiments as a function of the temperature T we can obtain the specific internal energy ε as

$$\varepsilon(T) = \frac{k_B}{m} \int_{T_0}^T \hat{c}_v(T') dT', \quad (22)$$

where $\hat{c}_v = (m/k_B)c_v$ is the dimensionless specific heat and T_0 is an inessential reference temperature.

From (17), inserting the equilibrium distribution (20) and taking into account (21), we obtain the internal energy at equilibrium due to the internal motion:

$$\varepsilon_I(T) = \frac{k_B}{m} T^2 \frac{d \log A(T)}{dT}, \quad (23)$$

with ε_K given by (18).

Therefore if we know the caloric equation of state (22) we know from (19) the expression of ε_I and from (23) we can obtain $A(T)$:

$$A(T) = A_0 \exp \left(\frac{m}{k_B} \int_{T_0}^T \frac{\varepsilon_I(T')}{T'^2} dT' \right),$$

¹In this paper there are some misprints and therefore interested reader can check also Chapter 6 of the book [8].

where A_0 and T_0 are inessential constants. As it was observed in [28] and in [29], the function A is, according to (21), the Laplace transform of φ :

$$A(s) = \mathcal{L}[\varphi(I)](s) = \int_0^\infty e^{-sI} \varphi(I) dI, \quad s = \frac{1}{k_B T},$$

and then we can obtain the weighting function φ as the inverse Laplace transform of A :

$$\varphi(I) = \mathcal{L}^{-1}[A(s)].$$

Polytropic Gas In the polytropic case c_v is constant and the internal energy is linear in the temperature:

$$\varepsilon(T) = \frac{D}{2} \frac{k_B}{m} T,$$

where D is the number of degrees of freedom of a molecule. This is a particular case of the previous non-polytropic case and we obtain the following weighting function:

$$\varphi(I) = I^\alpha, \quad \text{with} \quad \alpha = \frac{D-5}{2} > -1$$

and

$$A(T) = (k_B T)^{1+\alpha} \Gamma(1+\alpha),$$

where Γ is the gamma function.

Observe that model for a monatomic gas ($D = 3$) cannot be recovered from the one with continuous internal energy, since the value of parameter α in monatomic case violates the overall restriction $\alpha > -1$ but can be considered only as singular limit for $\alpha \rightarrow -1$.

5.2 The Closure of 14-Field Model of Polyatomic Gas

Pavić, Ruggeri and Simić after they considered the case of 14 moments in the case of polytropic gas [27] considering the same binary hierarchy proposed in the macroscopic approach [30]:

$$\begin{aligned} \partial_t F + \partial_k F_k &= 0, \\ \partial_t F_i + \partial_k F_{ik} &= 0, \\ \partial_t F_{ij} + \partial_k F_{ijk} &= P_{ij}, & \partial_t G_{ll} + \partial_k G_{llk} &= 0, \\ & & \partial_t G_{lli} + \partial_k G_{llik} &= Q_{lli}, \end{aligned}$$

where F is the mass density, F_i is the momentum density, G_{ii} is the energy density, F_{ij} is the momentum flux, and G_{lli} is the energy flux. And F_{ijk} and G_{llik} are the fluxes of F_{ij} and G_{lli} , respectively, and P_{ij} and Q_{lli} are the productions with respect to F_{ij} and G_{lli} , respectively. In the present case they take into account that the fields are moments of the generalized distribution function in this way:

$$\begin{pmatrix} F \\ F_{i1} \\ F_{i1i2} \\ F_{i1i2i3} \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty m \begin{pmatrix} 1 \\ c_{i1} \\ c_{i1}c_{i2} \\ c_{i1}c_{i2}c_{i3} \end{pmatrix} f(t, \mathbf{x}, \mathbf{c}, I) \varphi(I) dI d\mathbf{c},$$

$$\begin{pmatrix} G_{ll} \\ G_{llk_1} \\ G_{llk_1k_2} \end{pmatrix} = \int_{\mathbb{R}^3} \int_0^\infty m \begin{pmatrix} c^2 + 2\frac{I}{m} \\ (c^2 + 2\frac{I}{m})c_{k_1} \\ (c^2 + 2\frac{I}{m})c_{k_1}c_{k_2} \end{pmatrix} f(t, \mathbf{x}, \mathbf{c}, I) \varphi(I) dI d\mathbf{c}.$$

For the entropy defined by (16), 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 $h \rightarrow \max.$, being subjected to the constraints of prescribed 14 moments. The solution near an equilibrium state is that the distribution function, which maximizes the entropy with weighting function $\varphi(I) = I^\alpha$, has the form:

$$\begin{aligned} f = f_E \left\{ 1 - \frac{\rho}{p^2} q_i C_i + \frac{\rho}{p^2} \left[-\sigma_{(ij)} + \left(\frac{5}{2} + \alpha \right) (1 + \alpha)^{-1} \Pi \delta_{ij} \right] C_i C_j \right. \\ \left. - \frac{3}{2(1 + \alpha)} \frac{\rho}{p^2} \Pi \left(\frac{1}{2} C^2 + \frac{I}{m} \right) + \left(\frac{7}{2} + \alpha \right)^{-1} \frac{\rho^2}{p^3} q_i \left(\frac{1}{2} C^2 + \frac{I}{m} \right) C_i \right\}, \end{aligned} \quad (24)$$

where f_E is the equilibrium distribution (20). The non-equilibrium distribution (24) reduces to the velocity distribution obtained by Mallinger for gases composed of diatomic molecules ($\alpha = 0$). Again as in the monatomic case also in polyatomic gas for any $\alpha > -1$, the closure gives exactly the same equations obtained previously by using the macroscopic approach [17]:

$$\begin{aligned} \dot{\rho} + \rho \frac{\partial v_k}{\partial x_k} &= 0, \\ \rho \dot{v}_i + \frac{\partial p}{\partial x_i} + \frac{\partial \Pi}{\partial x_i} - \frac{\partial \sigma_{(ij)}}{\partial x_j} &= 0, \\ \dot{T} + \frac{2}{D \frac{k_B}{m} \rho} (p + \Pi) \frac{\partial v_k}{\partial x_k} - \frac{2}{D \frac{k_B}{m} \rho} \frac{\partial v_i}{\partial x_k} \sigma_{(ik)} + \frac{2}{D \frac{k_B}{m} \rho} \frac{\partial q_k}{\partial x_k} &= 0, \end{aligned}$$

$$\begin{aligned}
\dot{\sigma}_{\langle ij \rangle} + \sigma_{\langle ij \rangle} \frac{\partial v_k}{\partial x_k} - 2\Pi \frac{\partial v_{\langle i}}{\partial x_j \rangle} + 2 \frac{\partial v_{\langle i}}{\partial x_k} \sigma_{\langle j \rangle k} - \frac{4}{D+2} \frac{\partial q_{\langle i}}{\partial x_j \rangle} - 2p \frac{\partial v_{\langle i}}{\partial x_j \rangle} &= -\frac{1}{\tau_S} \sigma_{\langle ij \rangle}, \\
\dot{\Pi} + \frac{5D-6}{3D} \Pi \frac{\partial v_k}{\partial x_k} - \frac{2(D-3)}{3D} \frac{\partial v_{\langle i}}{\partial x_k} \sigma_{\langle ik \rangle} + \frac{4(D-3)}{3D(D+2)} \frac{\partial q_k}{\partial x_k} + \frac{2(D-3)}{3D} p \frac{\partial v_k}{\partial x_k} &= -\frac{1}{\tau_\Pi} \Pi, \\
\dot{q}_i + \frac{D+4}{D+2} q_i \frac{\partial v_k}{\partial x_k} + \frac{2}{D+2} q^k \frac{\partial v_k}{\partial x_i} + \frac{D+4}{D+2} q^k \frac{\partial v_i}{\partial x_k} \\
+ \frac{k_B}{m} T \frac{\partial \Pi}{\partial x_i} - \frac{k_B}{m} T \frac{\partial \sigma_{\langle ik \rangle}}{\partial x_k} + \Pi \left[-\frac{k_B}{m} T \frac{\partial \rho}{\partial x_i} + \frac{D+2}{2} \frac{k_B}{m} \frac{\partial T}{\partial x_i} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_i} + \frac{1}{\rho} \frac{\partial \sigma_{\langle ik \rangle}}{\partial x_k} \right] \\
- \sigma_{\langle ik \rangle} \left[-\frac{k_B}{m} T \frac{\partial \rho}{\partial x_k} + \frac{D+2}{2} \frac{k_B}{m} \frac{\partial T}{\partial x_k} - \frac{1}{\rho} \frac{\partial \Pi}{\partial x_k} + \frac{1}{\rho} \frac{\partial \sigma_{\langle pk \rangle}}{\partial x_p} \right] \\
+ \frac{D+2}{2} \left(\frac{k_B}{m} \right)^2 \rho T \frac{\partial T}{\partial x_i} &= -\frac{1}{\tau_q} q_i, \tag{25}
\end{aligned}$$

where τ_S , τ_Π , and τ_q are the relaxation times. The Navier–Stokes Fourier theory is contained in the present theory as a limit of small relaxation times (the Maxwellian iteration [31]) as shown in [17].

The monatomic gas limit $D \rightarrow 3$ is a singular limit. It is possible to prove that the 14 equations (25) and the solutions of the system converge to the 13 equations and solutions of monatomic gas with $\Pi = 0$, respectively, provided that the initial data are chosen in such a way that the data are compatible with a monatomic gas, i.e., $\Pi(\mathbf{x}, 0) = 0$ [32].

6 The General Hierarchy of Moment Equations for Polyatomic Gases

In non-equilibrium motivated by the idea of phenomenological ET, we shall generalize the moment equations for polyatomic gases by constructing two independent hierarchies. One will be much alike classical “*momentum*” hierarchy of monatomic gases (*F-hierarchy*); the other one, “*energy*” hierarchy, commences with the moment related to the energy collision invariant and proceeds with standard increase of the order through multiplication by velocities (*G-hierarchy*). They read [27, 33]:

$$\partial_t F + \partial_i F_i = 0,$$

$$\partial_t F_{k_1} + \partial_i F_{ik_1} = 0,$$

$$\begin{aligned}
\partial_t F_{k_1 k_2} + \partial_i F_{i k_1 k_2} &= P_{k_1 k_2}, & \partial_t G_{kk} + \partial_i G_{ikk} &= 0, \\
\vdots & & \partial_t G_{kkj_1} + \partial_i G_{k k i j_1} &= Q_{kkj_1}, \\
\vdots & & \vdots & \\
\partial_t F_{k_1 k_2 \dots k_N} + \partial_i F_{i k_1 k_2 \dots k_N} &= P_{k_1 k_2 \dots k_N}, & \vdots & \\
& & \partial_t G_{kkj_1 j_2 \dots j_M} + \partial_i G_{k k i j_1 j_2 \dots j_M} & \\
& & = Q_{kkj_1 j_2 \dots j_M}. &
\end{aligned}$$

The particular case are ($N = 1, M = 0$) and ($N = 2, M = 1$), which correspond to the Euler system and the 14-field system, respectively. The interested reader can see the results in this general case in [8, 33, 34].

7 RET with Different Molecular Relaxations Processes

It is evident, however, that the ET theory of polyatomic gases with the binary hierarchy has the limitation of its applicability, although the theory has been successfully utilized to analyze various non-equilibrium phenomena. In fact, we have many experimental data showing that the relaxation times of the rotational mode and of the vibrational mode are quite different to each other. In such a case, more than one molecular relaxation processes should be taken into account to make the ET theory more precise. In order to describe the relaxation processes of rotational and vibrational modes separately, Arima, Ruggeri and Sugiyama, first in the case of 7 fields [35] and then in the general case of 15 fields [36], proposed to decompose the energy of internal modes I as the sum of the energy of rotational mode I^R and the energy of vibrational mode I^V :

$$I = I^R + I^V.$$

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

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

$$\begin{aligned}
F_{i_1 \dots i_j} &= \int_{R^3} \int_0^\infty \int_0^\infty m c_{i_1} \dots c_{i_j} f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
H_{ll i_1 \dots i_k}^R &= \int_{R^3} \int_0^\infty \int_0^\infty 2I^R c_{i_1} \dots c_{i_k} f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
H_{ll i_1 \dots i_l}^V &= \int_{R^3} \int_0^\infty \int_0^\infty 2I^V c_{i_1} \dots c_{i_l} f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c},
\end{aligned}$$

where $j, k, l = 1, 2, \dots$. From the Boltzmann equation (12), we obtain three hierarchies (a triple hierarchy) of balance equations, i.e., F , H^R , and H^V -hierarchies in the following form:

$$\begin{aligned}
 \partial_t F + \partial_i F_i &= 0, \\
 \partial_t F_{i_1} + \partial_i F_{i_1} &= 0, \\
 \partial_t F_{i_1 i_2} + \partial_i F_{i_1 i_2} &= P_{i_1 i_2}^K, & \partial_t H_{ll}^R + \partial_i H_{lli}^R &= P_{ll}^R, & \partial_t H_{ll}^V + \partial_i H_{lli}^V &= P_{ll}^V, \\
 \partial_t F_{i_1 i_2 i_3} + \partial_i F_{i_1 i_2 i_3} &= P_{i_1 i_2 i_3}^K, & \partial_t H_{lli_1}^R + \partial_i H_{llii_1}^R &= P_{lli_1}^R, & \partial_t H_{lli_1}^V + \partial_i H_{llii_1}^V &= P_{lli_1}^V, \\
 \vdots & & \vdots & & \vdots &
 \end{aligned}
 \tag{26}$$

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

$$\begin{aligned}
 P_{i_1 \dots i_j}^K &= \int_{R^3} \int_0^\infty \int_0^\infty m c_{i_1} \dots c_{i_j} Q(f) \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 P_{lli_1 \dots i_k}^R &= \int_{R^3} \int_0^\infty \int_0^\infty 2I^R c_{i_1} \dots c_{i_k} Q(f) \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 P_{lli_1 \dots i_l}^V &= \int_{R^3} \int_0^\infty \int_0^\infty 2I^V c_{i_1} \dots c_{i_l} Q(f) \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}.
 \end{aligned}$$

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

$$Q_{ll} = P_{ll}^K + P_{ll}^R + P_{ll}^V = 0.$$

In each of the three hierarchies, the flux in one equation appears as the density in the next equation. Here $\varphi(I^R)$ and $\psi(I^V)$ are the state densities corresponding to I^R and I^V , i.e., $\varphi(I^R) dI^R (\psi(I^V) dI^V)$ represents the number of internal rotational (vibrational) state between I^R and $I^R + dI^R$ (I^V and $I^V + dI^V$).

7.1 Entropy Law

The entropy density $h = \rho s$, the entropy flux h_i , and the entropy production Σ are defined by

$$\begin{aligned}
h &= -k_B \int_{R^3} \int_0^\infty \int_0^\infty f \log f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
h_i &= -k_B \int_{R^3} \int_0^\infty \int_0^\infty c_i f \log f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
\Sigma &= -k_B \int_{R^3} \int_0^\infty \int_0^\infty Q(f) \log f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}.
\end{aligned} \tag{27}$$

Then we have the entropy law: $\partial_t h + \partial_i h_i = \Sigma$.

7.2 Equilibrium Distribution Function

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

$$G_{II} = \int_{R^3} \int_0^\infty \int_0^\infty (mc^2 + 2I^R + 2I^V) f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}. \tag{28}$$

It is easy to see, from (28), that the specific internal energy ε is composed of the kinetic, rotational, and vibrational parts, ε^K , ε^R , and ε^V , i.e.,

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

The equilibrium distribution function f_E , which maximizes the entropy density (27)₁ under the constraints that the first five moments are prescribed, is given by

$$f_E = f_E^{(K)} f_E^{(R)} f_E^{(V)} \tag{29}$$

with

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

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

$$A^R(T) = \int_0^\infty \varphi(I^R) e^{-\beta_E I^R} dI^R, \quad A^V(T) = \int_0^\infty \psi(I^V) e^{-\beta_E I^V} dI^V. \quad (30)$$

Here $\beta_E = 1/(k_B T)$ and T is the equilibrium temperature. For the proof see [29, 35, 37].

Using the equilibrium distribution function f_E , we obtain the caloric and thermal equations of state. The caloric equation of state is given by

$$\varepsilon = \varepsilon_E(T) = \varepsilon_E^K(T) + \varepsilon_E^R(T) + \varepsilon_E^V(T),$$

and we have

$$\varepsilon_E^K(T) \equiv \frac{3k_B}{2m} T, \quad \varepsilon_E^R(T) \equiv \frac{k_B}{m} T^2 \frac{d \log A^R(T)}{dT}, \quad \varepsilon_E^V(T) \equiv \frac{k_B}{m} T^2 \frac{d \log A^V(T)}{dT}. \quad (31)$$

If the partition functions A^R and A^V are given, for example, by a statistical-mechanical analysis, we obtain the equilibrium energies of rotational and vibrational modes from (31). Vice versa, if we know the caloric equations of state $\varepsilon_E^K(T)$ and $\varepsilon_E^R(T)$, we can obtain, by integration of (31)_{2,3}, the partition functions. We remark that the knowledge of the partition functions permits us to obtain, from (30), the measures $\varphi(I^R)$ and $\psi(I^V)$ via the inverse Laplace transform. The thermal equation of state is given by

$$p = p^K(\rho, T) \equiv \frac{k_B}{m} \rho T = \frac{2}{3} \rho \varepsilon_E^K(T).$$

The specific entropy density in equilibrium $s_E = h_E/\rho$ is given by

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

where

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

$$\begin{aligned}
s_E^R(T) &\equiv -\frac{k_B}{\rho} \int_{R^3} \int_0^\infty \int_0^\infty f_E \log f_E^{(R)} \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
&= \frac{k_B}{m} \log A^R(T) + \frac{\varepsilon_E^R(T)}{T}, \\
s_E^V(T) &\equiv -\frac{k_B}{\rho} \int_{R^3} \int_0^\infty \int_0^\infty f_E \log f_E^{(V)} \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
&= \frac{k_B}{m} \log A^V(T) + \frac{\varepsilon_E^V(T)}{T}.
\end{aligned}$$

7.3 Molecular ET Theory with 7 Independent Fields (ET₇)

The simplest RET theory with the triple hierarchy is the theory with 7 fields (ET₇); mass density, velocity, internal energy of translational mode, internal energy of rotational mode, and internal energy of vibrational mode [35]. The system of balance equations is the system of (26) but truncated at the second-order tensor:

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

The closure in this simple case is very interesting because as in the previous ET₆ [29, 37] can be done in full non-linear way and therefore is not necessary to assume that the processes are near an equilibrium state [35]. On the basis of this theory, it was revealed that the internal energies of the three modes can be characterized by the three non-equilibrium temperatures and the non-equilibrium entropy is expressed in terms of these non-equilibrium temperatures. It was also shown that the dispersion relation derived by ET₇ is in excellent agreement with the experimental data of CO₂, Cl₂, and Br₂ gases [35].

7.4 Molecular ET Theory with 15 Independent Fields (ET₁₅)

Because the ET₇ theory describes the relaxation processes of molecular rotational and vibrational modes satisfactorily, but it ignores the effect of shear stress and heat

flux, a more realistic theory including all these dissipative fluxes was established in [36]. In this case the starting moments are:

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

where $(F_{ijk}, H_{lli}^R, H_{lli}^V, G_{llik})$ and $(P_{ij}^K, P_{ll}^R, P_{ll}^V, Q_{lli})$ are, respectively, the fluxes and productions of the densities $(F_{ij}, H_{ll}^R, H_{ll}^V, G_{lli})$. It is worth emphasizing again that the ET₁₄ theory adopts $F, F_i, F_{ij}, G_{ll}(= F_{ll} + H_{ll}^R + H_{ll}^V)$ and G_{lli} as independent fields and the internal modes of a molecule are treated as a unit. On the other hand, ET₁₅ describes the rotational and vibrational modes individually. The densities of the system (32) are related to the following conventional field variables:

$$\begin{aligned}
 \rho &\equiv \int_{R^3} \int_0^\infty \int_0^\infty m f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 v_i &\equiv \frac{1}{\rho} \int_{R^3} \int_0^\infty \int_0^\infty m c_i f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 \varepsilon^K &\equiv \frac{1}{2\rho} \int_{R^3} \int_0^\infty \int_0^\infty m C^2 f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 \varepsilon^R &\equiv \frac{1}{\rho} \int_{R^3} \int_0^\infty \int_0^\infty m I^R f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 \varepsilon^V &\equiv \frac{1}{\rho} \int_{R^3} \int_0^\infty \int_0^\infty m I^V f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 \sigma_{(ij)} &\equiv - \int_{R^3} \int_0^\infty \int_0^\infty m C_{(i} C_{j)} f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}, \\
 q_i &\equiv \frac{1}{2} \int_{R^3} \int_0^\infty \int_0^\infty (m C^2 + 2I^R + 2I^V) C_i f \varphi(I^R) \psi(I^V) dI^R dI^V d\mathbf{c}.
 \end{aligned} \tag{33}$$

We define three new variables θ^K, θ^R , and θ^V associated with the specific energies $\varepsilon^K, \varepsilon^R$, and ε^V in (33)_{3,4,5} through the caloric equations of state given in (31) [35]:

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

Because of the monotonicity of $\varepsilon_E^{K,R,V}$, these are one-to-one relations between the new variables $\theta^{K,R,V}$ and the specific energies $\varepsilon^{K,R,V}$. From (29), the temperature T is determined in an implicit way by the relation:

$$\varepsilon_E(T) = \varepsilon_E^K(\theta^K) + \varepsilon_E^R(\theta^R) + \varepsilon_E^V(\theta^V).$$

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

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

The dynamic pressure is expressed as [37, 38]:

$$\Pi = p^K(\rho, \theta^K) - p^K(\rho, T) = \frac{2}{3}\rho \left(\varepsilon_E^K(\theta^K) - \varepsilon_E^K(T) \right). \quad (34)$$

It is convenient to introduce the following variables, i.e., energy deviations of the three modes from the state with the common temperature T [35, 38–40]:

$$\Delta^K = \varepsilon_E^K(\theta^K) - \varepsilon_E^K(T), \quad \Delta^R = \varepsilon_E^R(\theta^R) - \varepsilon_E^R(T), \quad \Delta^V = \varepsilon_E^V(\theta^V) - \varepsilon_E^V(T).$$

Then, from (34), the dynamic pressure Π is expressed as

$$\Pi = \frac{2}{3}\rho \Delta^K.$$

Proceeding with the usual technique of MEP we obtain for processes near the equilibrium the following closed differential system written with the usual physical symbols:

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

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

$$\frac{\partial}{\partial t} \{ 2\rho \varepsilon_E(T) + \rho v^2 \} + \frac{\partial}{\partial x_i} \{ 2q_i + 2[\rho \varepsilon(T) + p(\rho, T) + \Pi] v_i - 2\sigma_{(li)} v_l + \rho v^2 v_i \} = 0,$$

$$\frac{\partial}{\partial t} \{ 2\rho [\varepsilon_E^R(T) + \Delta^R] \} + \frac{\partial}{\partial x_i} \left\{ 2\rho [\varepsilon_E^R(T) + \Delta^R] v_i + \frac{2c_v^R(T)}{\frac{k_B}{m} + c_v(T)} q_i \right\} = \hat{P}_{ll}^R,$$

$$\frac{\partial}{\partial t} \{ 2\rho [\varepsilon_E^V(T) + \Delta^V] \} + \frac{\partial}{\partial x_i} \left\{ 2\rho [\varepsilon_E^V(T) + \Delta^V] v_i + \frac{2c_v^V(T)}{\frac{k_B}{m} + c_v(T)} q_i \right\} = \hat{P}_{ll}^V,$$

$$\begin{aligned}
& \frac{\partial}{\partial t} \left(-\sigma_{(ij)} + \rho v_{(i} v_{j)} \right) + \frac{\partial}{\partial x_k} \left\{ \frac{2 \frac{k_B}{m}}{\frac{k_B}{m} + c_v(T)} q_{(i} \delta_{j)k} + 2[p(\rho, T) + \Pi] v_{(i} \delta_{j)k} \right. \\
& \quad \left. - \sigma_{(ij)} v_k - 2\sigma_{(k(i} v_{j)} + \rho v_{(i} v_{j)} v_k \right\} = \hat{P}_{(ij)}^K, \\
& \frac{\partial}{\partial t} \left\{ 2q_i + 2[\rho \varepsilon_E(T) + p(\rho, T) + \Pi] v_i - 2\sigma_{(li} v_l + \rho v^2 v_i \right\} + \\
& \quad + \frac{\partial}{\partial x_k} \left\{ 2 \left[p(\rho, T) \left(\varepsilon_E(T) + \frac{p(\rho, T)}{\rho} \right) + \Pi \left(\varepsilon_E(T) + 2 \frac{p(\rho, T)}{\rho} \right) \right] \delta_{ik} \right. \\
& \quad - 2 \left[\varepsilon_E(T) + 2 \frac{p(\rho, T)}{\rho} \right] \sigma_{(ik)} + \frac{2 \frac{k_B}{m}}{\frac{k_B}{m} + c_v(T)} q_l v_l \delta_{ik} \\
& \quad + 2 \left[1 + \frac{\frac{k_B}{m}}{\frac{k_B}{m} + c_v(T)} \right] (q_i v_k + q_k v_i) + [p(\rho, T) + \Pi] v^2 \delta_{ik} \\
& \quad \left. + 2[\rho \varepsilon_E(T) + 2p(\rho, T) + 2\Pi] v_i v_k - v^2 \sigma_{(ik)} - 2v_l v_i \delta_{(lk)} - 2v_l v_k \sigma_{(il)} + \rho v^2 v_i v_k \right\} \\
& = 2v_l \hat{P}_{il}^K + \hat{Q}_{lli}.
\end{aligned}$$

7.5 Three Relaxation Times

In polyatomic gases, we may introduce three characteristic times corresponding to three relaxation processes caused by the molecular collision:

1. Relaxation time τ_K : This characterizes the relaxation process within the translational mode (mode K) of molecules. The process shows the tendency to approach an equilibrium state of the mode K.
2. Relaxation time τ_{bc} : There are energy exchanges among the three modes: mode K, rotational mode (mode R), and vibrational mode (mode V). The relaxation process occurs in such a way that two of the three modes (say (bc) = (KR), (KV), (RV)) approach, after the relaxation time τ_{bc} , an equilibrium state characterized by a common temperature θ^{bc} .
3. Relaxation time τ of the last stage: after the relaxation process between b and c, all modes, K, R, and V, eventually approach a local equilibrium state characterized by f_E with a common temperature T .

7.6 Generalized BGK Collision Term

The generalized BGK collision term for (bc)-process ((bc) = (KR), (KV), (RV)) is proposed as follows:

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

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

$$\begin{aligned} f_{K:E} &= \frac{\rho^{RV}(I^R, I^V)}{m} \left(\frac{m}{2\pi k_B \theta^K} \right)^{3/2} \exp\left(-\frac{mC^2}{2k_B \theta^K}\right), \\ f_{KR:E} &= \frac{\rho^V(I^V)}{m A^R(\theta^{KR})} \left(\frac{m}{2\pi k_B \theta^{KR}} \right)^{3/2} \exp\left\{-\frac{1}{k_B \theta^{KR}} \left(\frac{mC^2}{2} + I^R \right)\right\}, \\ f_{KV:E} &= \frac{\rho^R(I^R)}{m A^V(\theta^{KV})} \left(\frac{m}{2\pi k_B \theta^{KV}} \right)^{3/2} \exp\left\{-\frac{1}{k_B \theta^{KV}} \left(\frac{mC^2}{2} + I^V \right)\right\}, \\ f_{RV:E} &= \frac{\rho}{m A^R(\theta^{RV}) A^V(\theta^{RV})} \left(\frac{m}{2\pi k_B \theta^K} \right)^{3/2} \exp\left(-\frac{mC^2}{2k_B \theta^K} - \frac{I^R + I^V}{k_B \theta^{RV}}\right), \end{aligned}$$

with

$$\begin{aligned} \rho^{RV}(I^R, I^V) &= \int_{\mathbb{R}^3} m f d\mathbf{c}, \\ \rho^V(I^V) &= \int_{\mathbb{R}^3} \int_0^\infty m f \varphi(I^R) dI^R d\mathbf{c}, \quad \rho^R(I^R) = \int_{\mathbb{R}^3} \int_0^\infty m f \varphi(I^V) dI^V d\mathbf{c}. \end{aligned}$$

Several works are now in progress with the new ET₁₅ theory in particular comparison of dispersion relation between theoretical prediction and experimental data, and the analysis of shock waves.

Acknowledgement This work was supported by National Group of Mathematical Physics GNFM-INdAM.

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