DYNAMICAL PRESSURE IN A POLYATOMIC GAS:
INTERPLAY BETWEEN KINETIC THEORY AND
EXTENDED THERMODYNAMICS

MARZIA BISI
Dip. di Scienze Matematiche, Fisiche e Informatiche
Università di Parma, Parco Area delle Scienze 53/A
I-43124 Parma, Italy

TOMMASO RUGGERI
Dip. di Matematica and Alma Mater Research Center
on Applied Mathematics AM2, Via Saragozza, 8
40123 Bologna, Italy

GIAMPIERO SPIGA
Dip. di Scienze Matematiche, Fisiche e Informatiche
Università di Parma, Parco Area delle Scienze 53/A
I-43124 Parma, Italy

(Communicated by Laurent Desvillettes)

Abstract. The aim of this paper is to compare different kinetic approaches to a polyatomic rarefied gas: the kinetic approach via a continuous energy parameter $I$ and the mixture-like one, based on discrete internal energy. We prove that if we consider only 6 moments for a non-polytropic gas the two approaches give the same symmetric hyperbolic differential system previously obtained by the phenomenological Extended Thermodynamics. Both meaning and role of dynamical pressure become more clear in the present analysis.

1. Introduction. An accurate and consistent description of a rarefied gas may be obtained, as well known, by a mesoscopic approach based on a suitable kinetic equation (typically the Boltzmann equation) for the particle distribution function, which represents the density in phase space, and allows to construct all macroscopic fields of practical interest as velocity power moments with respect to the molecular velocity [17, 16]. Gas kinetic theory was originally developed for a single monatomic gas, endowed with translational degrees of freedom only: extension to mixtures or to polyatomic molecules typically encounters serious technical difficulties, because of the complicated structure of the nonlinear integro–differential collision operator. In any case, the rough monatomic approximation has been providing, to a good extent, satisfactory theoretical results as well as reliable physical outputs in applications, even for reacting mixtures [30]. More recent studies concern for instance shock

2010 Mathematics Subject Classification. Primary: 80A05, 76P05; Secondary: 82C40.
Key words and phrases. Extended thermodynamics, kinetic theory, moment equations, polyatomic gas, dynamical pressure.

* Corresponding author: T. Ruggeri.
structure [20, 22], convergence to equilibrium [11], deflagration processes [18], multi-temperature problems [12], and numerical solution schemes [13, 21].

A possible strategy for the description of a polyatomic gas consists in a kind of semi-classical approach by which the internal structure of a molecule is taken into account by a large number of discrete energy states, so that the gas might be considered as a sort of mixture of monatomic components, which interact by binary collisions with conservation of total energy, but with possible exchange of energy between its kinetic and internal (excitation) forms. Again the model can be used also in a reactive frame [23], even in the presence of its self-consistent radiation field. Apart from the intrinsic interest of the model, what people are most interested in is the corresponding hydro-dynamic (continuum) limit, which corresponds to the case when the Knudsen number, ratio of the mean free path to a macroscopic length, is very small. Such a limit is usually achieved by the Chapman–Enskog method, based on an appropriate singular asymptotic expansion with respect to that small parameter, and provides closed fluid-dynamics equations for the macroscopic fields of physical interest, which correspond, for increasing order of accuracy, to partial differential equations of Euler or Navier–Stokes type [17, 26]. Different physical regimes may lead to different interesting hydrodynamic limits [24, 12], and this is the point where kinetic theory and thermodynamics, in spite of their different algorithms and axiomatic structures, meet together, making possible a comparison of results, aiming at a better understanding of both theories, and at optimizing reliability and accuracy of their predictions. In particular, kinetic theory can provide in this respect a mesoscopic foundation of thermodynamics. The agreement is well established for monatomic gases. We are interested here in the polyatomic case, focusing on the capability of reproducing some basic features of polytropic or non-polytropic gases, with particular emphasis on a typical polyatomic effect such as the dynamical pressure.

Another crucial step towards the development of the theory of rarefied polyatomic gases was made by Borgnakke and Larsen [14]. The distribution function is assumed to depend on an additional continuous variable representing the energy of the internal modes of a molecule in order to take into account the exchange of energy (other than translational one) 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 the generalized Boltzmann equation by Bourgat, Desvillettes, Le Tallec and Perthame [15].

As a consequence of the introduction of one additional parameter $I$, the velocity distribution function $f(t, x, v, I)$ is defined on the extended domain $[0, \infty) \times R^3 \times R^3 \times [0, \infty)$ ($t, x$ and $v$ are respectively the time, the space coordinates and the microscopic velocity). Its rate of change is determined by the Boltzmann equation which has the same form as the one of monatomic gases but the collision integral takes into account the influence of the internal degrees of freedom through the collision cross section.

At level of continuum theory the methods of Rational Extended Thermodynamics (RET) were enlarged to polyatomic gas and dense gas by Arima, Taniguchi, Ruggeri and Sugiyama [8]. They adopt two parallel hierarchies (binary hierarchy) for the independent fields: the mass density $\rho$, the velocity $u \equiv (u_i)$, the internal energy $\varepsilon$, the deviatoric shear stress $\Pi_D \equiv (\pi_{ij})$, the dynamical pressure $\Pi$ and the heat flux $q \equiv (q_i)$. One hierarchy consists of balance equations for the mass density, the momentum density and the momentum flux (momentum-like hierarchy), and the
other one consists of balance equations for the energy density and the energy flux (energy-like hierarchy). These hierarchies cannot merge with each other in contrast to the case of rarefied monatomic gases because the specific internal energy (the intrinsic part of the energy density) is no longer related to the pressure (one of the intrinsic parts of the momentum flux). By means of the closure procedure of the RET theory based mainly on the compatibility with the entropy principle, the constitutive equations are determined explicitly by the thermal and caloric equations of state and in this way an hyperbolic model with 14 fields is established. The 14-field RET theory (ET\textsubscript{14}) gives us a complete phenomenological model but its differential system is rather complex. For this reason these authors construct a simplified RET theory with 6 fields (ET\textsubscript{6}) that preserves the main physical properties of the more complex ET\textsubscript{14} theory, when the bulk viscosity plays more important role than the shear viscosity and the heat conductivity. Therefore the only dissipative field is the non-equilibrium dynamical pressure $\Pi$. This situation is observed in many polyatomic gases such as rarefied hydrogen gases and carbon dioxide gases at some temperature ranges. The first model was done for rarefied polytropic fluids near equilibrium (theory linear in $\Pi$) [9]. Then a non-linear theory in $\Pi$ was presented in [36, 5] and the closure at macroscopic level has been done also for non polytropic fluids. Recently an extension for dense gas was studied [3].

The closure of RET was confirmed in 14 [29], 6 [32] and many moments [2] in the case of a polyatomic gas via the so called molecular extended thermodynamics [27] that consists in recalling that the fields are moments of an enlarged Borgnakke–Larsen distribution function and in obtaining the closure via the maximum entropy principle (MEP) or equivalently via the entropy principle.

The ET\textsubscript{14} and also ET\textsubscript{6} of polyatomic gases were very successful in particular for very good agreement, in linear waves [7] and in the shock profile [37, 35], between theoretical predictions and experiments, and with numerical simulation of the full Boltzmann equation [25]. For more details see the recent book of Ruggeri and Sugiyama [33] and the references therein.

Considering the simplest case of 6 moments, the aim of this paper is first to close the system of 6 moments via non linear MEP using the continuous distribution function for non-polytropic fluids that never was done before and to prove that the closure also in this case is in perfect agreement with the macroscopic phenomenological model. In the case of polytropic fluid we recover the previous Ruggeri results [32]. Then the goal is to verify that it is possible to construct 6 macroscopic moments using the Groppi-Spiga kinetic theory via discrete internal energy [23] and to prove that if we assume that the global heat flux and global shear stress are negligible then the corresponding differential system is closed and completely equivalent to the one obtained via continuous distribution function. The closure of the production (collision) term is of course always possible at BGK level, and it is achieved here in explicit form also at the Boltzmann (nonlinear) level in terms of integrals of the microscopic collision kernel. In this way we prove at least in the range of 6 fields the equivalence between the kinetic approach via continuous parameter $I$ and the mixture-like one, based on discrete internal energy.

The paper is organized in this way. In Section 2 we deduce the field equations obtained by the continuous MEP approach for a non-polytropic gas. In Section 3 we present the field equation using the discrete approach and in Section 4 we compare the results.
2. The continuous kinetic approach and the binary hierarchy of moments.

As we said in the introduction, in the continuum approach the distribution function $f \equiv f(t, x, v, I)$ depends on the extra variable $I$ representing the energy of the internal modes of a molecule. Its rate of change is determined by the Boltzmann equation which has the same form as in the case of monatomic gases:

$$\partial_t f + v_i \partial_i f = J(f),$$

where $\partial_t = \partial / \partial t$ and $\partial_i = \partial / \partial x_i$, and $J$ is the collision term expressing the effect of collisions between molecules. The collision term now takes into account the existence of the internal degrees of freedom through the collisional cross section.

In the present case we have two infinite hierarchies of moments that we truncate at same tensorial order (MN-System see [2], [1]):

$$\partial_t F + \partial_i F_i = 0,$$
$$\partial_t F_{k_1} + \partial_{i} F_{ik_1} = 0,$$
$$\partial_t F_{k_1 k_2} + \partial_{i} F_{ik_1 k_2} = S_{k_1 k_2},$$
$$\cdots$$
$$\partial_t G_{ll} + \partial_{i} G_{ll i} = 0,$$
$$\partial_t G_{ll i} + \partial_{i j} G_{ll ij} = T_{ll i},$$
$$\cdots$$

involving the momentum-like moments:

$$F = \int_{R^3} \int_{0}^{\infty} m f(t, x, v, I) \varphi(I) dI d\mathbf{v},$$

$$F_{k_1 k_2 \cdots k_n} = \int_{R^3} \int_{0}^{\infty} m v_{k_1} v_{k_2} \cdots v_{k_n} f(t, x, v, I) \varphi(I) dI d\mathbf{v}, \quad (n = 1, \cdots, N)$$

and the energy-like moments:

$$G_{ll} = \int_{R^3} \int_{0}^{\infty} m \left( v^2 + \frac{1}{m} \right) f(t, x, v, I) \varphi(I) dI d\mathbf{v},$$

$$G_{ll k_1 k_2 \cdots k_m} = \int_{R^3} \int_{0}^{\infty} m \left( v^2 + \frac{1}{m} \right) v_{k_1} v_{k_2} \cdots v_{k_m} f(t, x, v, I) \varphi(I) dI d\mathbf{v},$$

where the weighting function $\varphi(I)$ is determined in such way that in equilibrium we can recover the caloric equation of state. In particular for polytropic fluids it can be shown that $\varphi(I) = I^\alpha$ with $\alpha > -1$.

2.1. Balance equations of $ET_0$ and equilibrium distribution function. We consider 6 independent macroscopic field-variables: mass density, velocity, temperature and dynamical pressure $(\rho, u_i, T, \Pi)$, and therefore the previous binary
hierarchy (2) of the balance equations reduces in the present case to the following 6 moments:

\[
\begin{align*}
\partial_t F + \partial_i F_i &= 0, \\
\partial_t F_j + \partial_i F_{ji} &= 0, \\
\partial_t F_{il} + \partial_i F_{ili} &= S_{li}, \\
\partial_t G_{il} + \partial_i G_{illi} &= 0.
\end{align*}
\]

(9)

Taking into account that (9)\_1,2,4 are respectively the mass, momentum and energy conservation laws we have:

\[
F = \rho, \quad F_i = \rho u_i, \quad F_{ij} = \rho u_i u_j + (p + \Pi) \delta_{ij},
\]

\[
G_{il} = \rho u_i^2 + 2\rho \varepsilon, \quad G_{illi} = (\rho u_i^2 + 2\rho \varepsilon + 2p + 2\Pi) u_i
\]

with \( p \) and \( \varepsilon \) being, respectively, the pressure and the specific internal energy. The equation (9)\_3 is the new balance law for the dynamical pressure \( \Pi \). The deviatoric (traceless) part of the stress tensor \( \pi_{\langle ij \rangle} \) and the heat flux \( q_i \) are neglected in this theory.

On the other hand, for rarefied gases, it is possible to adopt the closure at the kinetic level that is called in [28] molecular ET (MET). In this case, the field equations are obtained by the moment-equations of the distribution function associated with the Boltzmann equation, and the closure is obtained by using the maximum entropy principle (MEP). This was done, for monatomic gases, by Dreyer [19] and by Müller and Ruggeri in the first edition of their book [27].

In the paper [32], the nonlinear MET theory with the 6 fields was constructed for polytropic gas. It was shown that this nonlinear MET is perfectly consistent with the phenomenological approach mentioned above. See also Chapter 12 of the book [33]. In fact, following the idea introduced in [29] for the 14-field theory and in [4] for the theory with any number of moments, the following generalized moments were proposed [32]:

\[
\begin{pmatrix}
F \\
F_i \\
F_{il}
\end{pmatrix} = \begin{pmatrix}
\rho \\
\rho u_i \\
\rho u_i^2
\end{pmatrix} = \int_{R^3} \int_0^\infty m \begin{pmatrix}
1 \\
\frac{v_i}{v^2}
\end{pmatrix} f_{\varphi(I)} dI dv
\]

(11)

and

\[
G_{il} = \rho u_i^2 + 2\rho \varepsilon = \int_{R^3} \int_0^\infty m(v_i^2 + 2I/m) f_{\varphi(I)} dI dv,
\]

(12)

while the production is given by:

\[
S_{il} = \int_{R^3} \int_0^\infty m v_i v_j J(f)_{\varphi(I)} dI dv.
\]

(13)

Equation (11)\_3 defines the dynamical pressure, with \( p = nk_BT \) and \( T \) equilibrium temperature and we have:

\[
\Pi = \frac{1}{3} \int_{R^3} \int_0^\infty m C^2 (f - f_E) \varphi(I) dI dC,
\]

(14)

where \( f_E \) denotes the equilibrium value of the distribution function and \( C = v - u \) is the peculiar velocity.

Note that the internal energy density can be divided into the translational part \( \varepsilon_K \) and the part of the internal degrees of freedom \( \varepsilon_I \):

\[
\rho \varepsilon_K = \int_{R^3} \int_0^\infty \frac{1}{2} m C^2 f(t, x, C, I) \varphi(I) dI dC,
\]

and
\[ \rho \varepsilon_I = \int_{R^3} \int_{0}^{\infty} I f(t, x, C, I) \varphi(I) dI dC. \]  

(15)

Pavic, Ruggeri and Simić [29] (see also [33]) firstly considered the 5 moments of Euler fluids and they proved using MEP that the distribution function in equilibrium that maximizes the entropy has the form:

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

(16)

where

\[ A(T) = \int_{0}^{\infty} \exp \left( -\frac{I}{k_B T} \right) \varphi(I) dI. \]

(17)

This generalizes the Maxwellian distribution function in the case of polyatomic gas and was obtained first with different arguments in [15].

2.2. Polytropic fluid. In the polytropic case the weighting function \( \varphi(I) \) is determined in such a way that it recovers the caloric equation of state for polyatomic gases. In fact it can be shown that the relation \( \varphi(I) = I^\alpha \) with \( \alpha > -1 \) leads to the appropriate caloric equation of state of polytropic gas:

\[ \varepsilon(T) = \frac{D}{2} k_B T, \quad \alpha = \frac{D - 5}{2}, \]

(18)

where \( D \) is the number of degrees of freedom of gas molecules. In this case (17) becomes

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

(19)

where \( \Gamma \) is the Gamma function.

The MEP in the nonlinear polytropic ET6 gives the following distribution function \( f \) that maximizes the entropy [32]:

\[ h = -k_B \int_{R^3} \int_{0}^{\infty} f \log f \varphi(I) dI d\nu \]

(20)

under the constraints (11), (12):

\[ f_{\text{Poly}} = \frac{\rho}{m} \left( \frac{m}{2\pi k_B T} \right)^{3/2} \left( \frac{1}{1 + \frac{\Pi}{p}} \right)^{1+\alpha} \exp \left\{ -\frac{1}{k_B T} \left( \frac{1}{2} m C^2 + I \right) \right\} \left( \frac{1}{1 - \frac{3}{2(1+\alpha)} \frac{\Pi}{p}} \right)^{1+\alpha}. \]

(21)

It is important to remark that the distribution function is non-linear in the dynamical pressure differently with usual closure of moments theory in which the non-equilibrium distribution function is a linear perturbation of the equilibrium one. The closed system and the non-equilibrium entropy thus obtained [32] are exactly the same as the ones obtained by the phenomenological approach [5], [33].

2.3. Non-polytropic gas and molecular ET6. In the case of ideal non-polytropic gases the specific heat \( c_v = d\varepsilon(T)/dT \) is, in general, a nonlinear function of the temperature and the caloric and thermal equations of state read:

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

(22)
As \( c_v \) can be measured by experiments as a function of the temperature \( T \) we can obtain the specific internal energy \( \varepsilon \) as

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

(23)

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

From (15), inserting the equilibrium distribution (16) and taking into account (17), we obtain the internal energy at equilibrium due to the internal motion:

\[
\varepsilon_I(T) = k_B m T^2 \frac{d \log A(T)}{dT}, \quad \varepsilon_I = \varepsilon - \varepsilon_K,
\]

(24)

with \( \varepsilon_K \) given by

\[
\varepsilon_K = \frac{3}{2} \frac{k_B}{m} T.
\]

(25)

Therefore if we know the caloric equation of state (23) we know from (24) \( \varepsilon_I \) and therefore from (24) we can obtain \( A(T) \):

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

(26)

where \( A_0 \) and \( T_0 \) are inessential constants. As it was observed in [10], the function \( A \) is, according to (17), the Laplace transform of \( \varphi \):

\[
A(T) = \mathcal{L}_a [\varphi(I)] (s), \quad s = \frac{1}{k_B T},
\]

(27)

and then we can obtain the weighting function \( \varphi \) as the inverse Laplace transform of \( A \):

\[
\varphi(I) = \mathcal{L}_a^{-1} [A(T)] (I), \quad T = \frac{1}{k_B s}.
\]

(28)

We want now to prove the following theorem about the non-equilibrium distribution function:

**Theorem 2.1.** The distribution function that maximizes the entropy (20) under the constraints (11), (12) has the form:

\[
f_{\text{Non-Poly}} = \frac{\rho}{m A(\Theta)} \left( \frac{m}{2 \pi k_B T} \frac{1}{1 + \frac{p}{\rho}} \right)^{3/2} \exp \left\{ - \frac{1}{k_B T} \left( \frac{1}{2} m \xi^2 \left( \frac{1}{1 + \frac{p}{\rho}} \right) + I \frac{T}{\Theta} \right) \right\},
\]

(29)

where the non-equilibrium temperature \( \Theta \) is related to the dynamical pressure \( \Pi \) through the relation:

\[
\frac{\varepsilon_I(T) - \varepsilon_I(\Theta)}{\varepsilon_K(T)} = \frac{\Pi}{p},
\]

(30)

and \( A(\Theta) \) is given by (26)

\[
A(\Theta) = A_0 \exp \left( \frac{m}{k_B} \int_{T_0}^{\Theta} \frac{\varepsilon_I(T')}{T'^2} dT' \right).
\]

(31)

All the moments are convergent and the bounded solutions satisfy the inequalities:

\[
-1 < \frac{\Pi}{p} < \frac{\varepsilon_I(T)}{\varepsilon_K(T)}.
\]

(32)

The distribution function is non-linear in the dynamical pressure and positive.
Proof. The proof of the theorem is accomplished with the use of the Lagrange multiplier method. Introducing the vector of the multipliers \( (\lambda, \lambda_i, \lambda_l, \mu_l) \), we define the functional:

\[
\mathcal{L} = - \int_{\mathbb{R}^3} \int_0^{\infty} k_B f \log f \varphi(I) \, dI \, dv + \lambda \left( \rho - \int_{\mathbb{R}^3} \int_0^{\infty} m f \varphi(I) \, dI \, dv \right) + \\
+ \lambda_i \left( \rho u_i - \int_{\mathbb{R}^3} \int_0^{\infty} m f v_i \varphi(I) \, dI \, dv \right) + \\
+ \lambda_l \left( \rho u^2 + 3(p + \Pi) - \int_{\mathbb{R}^3} \int_0^{\infty} m v^2 f \varphi(I) \, dI \, dv \right) + \\
+ \mu_l \left( \rho u^2 + 2 \rho \varrho - \int_{\mathbb{R}^3} \int_0^{\infty} m \left( v^2 + \frac{2 I}{m} \right) f \varphi(I) \, dI \, dv \right).
\]

As this is a functional of the distribution function \( f \) and we want to maximize it with respect to \( f \) with the given macroscopic quantities, this functional can be substituted by the following one:

\[
\mathcal{L} = - \int_{\mathbb{R}^3} \int_0^{\infty} k_B f \log f \varphi(I) \, dI \, dv - \lambda \int_{\mathbb{R}^3} \int_0^{\infty} m f \varphi(I) \, dI \, dv - \\
- \lambda_i \int_{\mathbb{R}^3} \int_0^{\infty} m f v_i \varphi(I) \, dI \, dv - \lambda_l \int_{\mathbb{R}^3} \int_0^{\infty} m v^2 f \varphi(I) \, dI \, dv - \\
- \mu_l \int_{\mathbb{R}^3} \int_{R_0}^{\infty} m \left( v^2 + \frac{2 I}{m} \right) f \varphi(I) \, dI \, dv.
\]

Since \( \mathcal{L} \) is a scalar, it must retain the same value in the case of zero hydrodynamic velocity \( u = 0 \) due to the Galilean invariance. Therefore:

\[
\mathcal{L} = - \int_{\mathbb{R}^3} \int_0^{\infty} k_B f \log f \varphi(I) \, dI \, dC - \hat{\lambda} \int_{\mathbb{R}^3} \int_0^{\infty} m f \varphi(I) \, dI \, dC - \\
- \hat{\lambda}_i \int_{\mathbb{R}^3} \int_0^{\infty} m f C_i \varphi(I) \, dI \, dC - \hat{\lambda}_l \int_{\mathbb{R}^3} \int_0^{\infty} m C^2 f \varphi(I) \, dI \, dC - \\
- \hat{\mu}_l \int_{\mathbb{R}^3} \int_{R_0}^{\infty} m \left( C^2 + \frac{2 I}{m} \right) f \varphi(I) \, dI \, dC.
\]

Comparison between (33) and (34) yields the relations between the Lagrange multipliers and the corresponding zero-velocity Lagrange multipliers indicated by hat:

\[
\lambda = \hat{\lambda} - \lambda_i u_i + (\hat{\lambda}_l + \hat{\mu}_l) u^2; \quad \lambda_i = \hat{\lambda}_i - 2 (\hat{\lambda}_l + \hat{\mu}_l) u_i; \quad \lambda_l = \hat{\lambda}_l; \quad \mu_l = \hat{\mu}_l, \quad (35)
\]

which dictate the velocity dependence of the Lagrange multipliers. We notice that these relations are in accordance with the general results, valid for a generic system of balance laws, of the Galilean invariance [31]. The Euler-Lagrange equation \( \delta \mathcal{L}/\delta f = 0 \) leads to the following form of the distribution function:

\[
f = \exp^{-1 - \frac{1}{k_B} \chi}, \quad (36)
\]

where

\[
\chi = \hat{\lambda} + \lambda_i C_i + \hat{\lambda}_l C^2 + \hat{\mu}_l \left( C^2 + \frac{2 I}{m} \right).
\]

By introducing the following new multipliers:

\[
\xi = \frac{m}{k_B} (\hat{\lambda}_l + \hat{\mu}_l), \quad \eta_i = \frac{m}{k_B} \hat{\lambda}_i, \quad \zeta = \frac{2}{k_B} \hat{\mu}_l, \quad \Omega = \exp \left( -1 - \frac{m}{k_B} \hat{\lambda} \right), \quad (37)
\]

...
the distribution function can be rewritten as
\[ f = \Omega e^{-\zeta I} e^{-\xi C^2 - \eta_i C_i}. \] (38)

Inserting (38) into the second equation of (11) evaluated at the zero velocity, we obtain immediately \( \eta_i = 0. \)

Introducing \( \Theta \) instead of \( \zeta \)
\[ \Theta = \frac{1}{k_B \zeta}, \] (39)
and recalling (27)
\[ A(\Theta) = \mathcal{L}_u \varphi(I)(\zeta) = \int_0^{\infty} e^{-I \zeta} \varphi(I) dI; \quad \zeta = \frac{1}{k_B \Theta}, \] (40)
then the remaining equations of (11) and (12) evaluated for \( u = 0 \) become
\[ \rho = \int_{R^3} \int_0^{\infty} m f(I) dI dC = m \pi^{3/2} \Omega A(\Theta) \frac{A(\Theta)}{\xi^{3/2}}, \] (41)
\[ p + \Pi = \frac{1}{3} \int_{R^3} \int_0^{\infty} m f C^2 \varphi(I) dI dC = m \pi^{3/2} \Omega A(\Theta) \frac{2 A(\Theta)}{2 \xi^{5/2}}, \]
\[ \rho \varepsilon = \int_{R^3} \int_0^{\infty} m \left( \frac{C^2}{2} + \frac{I}{m} \right) \varphi(I) dI dC = m \pi^{3/2} \Omega A(\Theta) \frac{4 A(\Theta)}{4 \xi^{5/2}} \left( 3 + \frac{4}{m} \xi k_B \Theta^2 A'(\Theta) \right), \]
where
\[ A'(\Theta) = \frac{dA(\Theta)}{d\Theta}. \] (42)

From (41) we can invert the Lagrange multipliers \( (\xi, \zeta, \Omega) \) in terms of the physical variables \( (\rho, T, \Pi) \) through the parameter \( \Theta \):
\[ \xi = \frac{\rho}{2p} \frac{1}{1 + \frac{\Pi}{p}}, \]
\[ \zeta = \frac{1}{k_B \Theta}, \] (43)
\[ \Omega = \frac{\rho}{mA(\Theta)} \left( \frac{m}{2 \pi k_B T} \frac{1}{1 + \frac{\Pi}{p}} \right)^{3/2}, \]
where the parameter \( \Theta \) depends on \( T \) and \( \Pi \) through:
\[ \Pi = \frac{2}{3} \rho \left( \varepsilon_I(T) - \varepsilon_I(\Theta) \right) \] (44)
and \( A(\Theta) \) is given by (31).

The equation (43)_1 is obtained by the ratio between (41)_1 and (41)_2. Putting the relation (43)_2, the equation (43)_3 is obtained by (41)_1, while from (41)_3 we have:
\[ (\ln A(\Theta))' = \frac{m}{2 \rho k_B \Theta^2} \left\{ 2 \rho \varepsilon - 3(p + \Pi) \right\}, \]
and rewriting (26) as (31) we obtain immediately the expression (44). Inserting (43) into the distribution function (38), we obtain (29). Concerning the inequalities (32) we observe that from the integrability conditions in (41), we have
\[ \zeta > 0, \quad \xi > 0. \] (45)
Taking into account (43)1 and (45) we obtain the left inequality of (32), while from the fact that \( \varepsilon_t \) is a strictly increasing function and that (45) require \( \Theta > 0 \), we have from (44) that for fixed \( T \) the maximum value of \( \Pi/p \) is obtained for \( \Theta \to 0 \). Since \( \varepsilon_T(0) = 0 \), we obtain the right part of the inequality (32) and the theorem is proved. When \( \Pi \to 0 \) it follows that \( \Theta \to T \) and (29) becomes the equilibrium distribution function (16).

2.4. Closure and field equations. Substituting (29) into the fluxes we obtain after some calculations

\[
\begin{align*}
F_{ik} &= \int_{R^3} \int_0^\infty m v_i v_k f(I) dI d\mathbf{v} = \rho u_i u_k + (p + \Pi) \delta_{ik}, \\
F_{llk} &= \int_{R^3} \int_0^\infty m v^2 v_k f(I) dI d\mathbf{v} = (5(p + \Pi) + \rho u^2) u_k, \\
G_{llk} &= \int_{R^3} \int_0^\infty m \left( v^2 + \frac{2I}{m} \right) v_k f(I) dI d\mathbf{v} = (\rho u^2 + 2\rho \varepsilon + 2p + 2\Pi) u_k.
\end{align*}
\]

From the balance equations of momentum and of energy in continuum mechanics, we know that

\[
F_{ik} = \rho u_i u_k + P_{ik}, \quad G_{llk} = (\rho u^2 + 2\rho \varepsilon) u_k + 2P_{l} u_i + 2q_k,
\]

where \( P_{ij} \) is called in the kinetic theory community the pressure tensor that corresponds except for the sign to the stress tensor \( t_{ij} = -P_{ij} \):

\[
P_{ij} = p \delta_{ij} + \pi_{ij} = (p + \Pi) \delta_{ij} + \pi_{<ij>},
\]

where \( \pi \equiv (\pi_{ij}) \) is except for the sign the viscous stress tensor, \( \pi^D \equiv (\pi_{<ij>}) \) denotes the deviatoric part (traceless) and \( \Pi \) is called the dynamical pressure. Comparing with the closure (46)1,3, we conclude that the closure provides \( \pi_{<ik>} = 0 \) and \( q_k = 0 \) in the 6-moment theory. This is the expected result that there exist no shear viscosity and no heat conductivity in the 6-moment theory. For what concerns (46)2, taking into account the Galilean invariance we obtain the zero-velocity of \( F_{llk} \):

\[
\tilde{F}_{llk} = \int_{R^3} \int_0^\infty m C^2 C_k f(I) dI dC = 0,
\]

and

\[
\tilde{S}_{ll} = \tilde{S}_{ll} = \int_{R^3} \int_0^\infty m C^2 J(f) \varphi(I) dI dC.
\]

Concerning the production term \( S_{ll} \), the main problem is that, in order to have explicit expression of the production, we need a model for the collision term, which is, in general, not easy to obtain in the case of polyatomic gases. With (46) we obtain that the differential system of 6 moments (9) becomes:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) &= 0, \\
\frac{\partial (\rho u_j)}{\partial t} + \frac{\partial}{\partial x_i} [(p + \Pi) \delta_{ij} + \rho u_i u_j] &= 0, \\
\frac{\partial}{\partial t} (2p \varepsilon + \rho u^2) + \frac{\partial}{\partial x_i} \left\{ [2(p + \Pi) + 2\rho \varepsilon + \rho u^2] u_i \right\} &= 0, \\
\frac{\partial}{\partial t} [3(p + \Pi) + \rho u^2] + \frac{\partial}{\partial x_i} \left\{ [5(p + \Pi) + \rho u^2] u_i \right\} &= \tilde{S}_{ll}.
\end{align*}
\]
It is more convenient, in order to obtain the limiting case of monatomic gas \([6, 4]\), to substitute the last equation in \((48)\) with the difference between \((48)_4\) and \((48)_3\), which yields the equivalent PDE’s system:

\[
\begin{align*}
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_i} (\rho u_i) &= 0, \\
\frac{\partial (\rho u_j)}{\partial t} + \frac{\partial}{\partial x_i} \left[ (p + \Pi) \delta_{ij} + \rho u_i u_j \right] &= 0, \\
\frac{\partial}{\partial t} \left[ 2(p + \Pi) + 2 \rho \varepsilon + \rho u_i^2 \right] u_i &= 0, \\
\frac{\partial}{\partial t} \left[ 3(p + \Pi) - 2 \rho \varepsilon \right] + \frac{\partial}{\partial x_i} \left[ 3(p + \Pi) - 2 \rho \varepsilon \right] u_i &= \dot{S}_H. 
\end{align*}
\]

\((49)\)

The system \((49)\) with the thermal and caloric equations of state \((22)\) is a closed system for the 6 unknowns \((\rho, u_i, T, \Pi)\), provided that we know the collision term in \((49)_4\). These results are in perfect agreement with the results derived from the phenomenological theory \([5]\). The differential system is symmetric hyperbolic and satisfies the so called K-condition \([34]\) and therefore smooth solution exists for any time provided the initial data are sufficiently small \([33]\).

2.5. **Entropy density.** Let us study the entropy density \(h\) with non-linear non-equilibrium distribution function:

\[
h = -k_B \int_{R^3} \int_0^\infty f \log f \varphi(I) dI dC. 
\]

\((50)\)

Inserting \((29)\) after some calculations we obtain the relative entropy as function of \(T\) and \(Z\) in parametric form with parameter the non-equilibrium temperature \(\Theta\), precisely:

\[
\begin{align*}
k &= \frac{h - h^{eq}}{\rho} = \int_T^{\Theta} \frac{\varepsilon_I(T')}{T'^2} dT' + \frac{3k_B}{2 m} \log(1 + Z) + \frac{\varepsilon_I(\Theta)}{\Theta} - \frac{\varepsilon_I(T)}{T}, \\
Z &= \frac{\Pi}{p} = \frac{\varepsilon_I(T) - \varepsilon_I(\Theta)}{\varepsilon_K(T)},
\end{align*}
\]

\((51)\)

where \(h^{eq}\) is the equivalent equilibrium expression of \((50)\) when \(f\) is replaced by the equilibrium distribution function given by \((16)\). It is easy to check that it is solution of the equilibrium Gibbs equation:

\[
Td \left( \frac{h^{eq}}{\rho} \right) = d\varepsilon - \frac{p}{\rho^2} d\rho.
\]

\((52)\)

It is also interesting to verify that expressions \((51)\) coincide with those obtained by the phenomenological ET approach \([5]\).

In the polytropic case \((18)\), the expressions become the ones obtained in a previous paper \([32]\). In particular the non-equilibrium distribution function \((29)\) reduces to the expression \((21)\).

2.6. **Non-equilibrium temperatures.** We have seen in \((44)\) that we can express the dynamical pressure in terms of the non-equilibrium temperature \(\Theta\). Therefore we can interpret the dynamical pressure as the one caused by the energy exchange which puts the internal modes into the non-equilibrium state with a non-equilibrium temperature \(\Theta\) different from the state with the local equilibrium temperature \(T\). For this reason we may say that \(\Theta\) is the temperature of the internal modes of a molecule.
Moreover by the analogy of (22) we can define a non equilibrium temperature \( \vartheta \) such that the total pressure \( P = p + \Pi \) has analogous expression of the equilibrium one:

\[
P = p + \Pi = \frac{k_B}{m} \rho \vartheta.
\] (53)

Therefore from (22) and (53) we can express the dynamical pressure in terms of \( \vartheta \):

\[
\Pi = \frac{k_B}{m} \rho (\vartheta - T) = p(\vartheta) - p(T).
\] (54)

Comparison between (54) and (44) gives a relation between the two non equilibrium temperatures:

\[
\varepsilon_I(T) - \varepsilon_I(\Theta) = \varepsilon_K(\vartheta) - \varepsilon_K(T).
\] (55)

We observe the two possible meanings of the dynamical pressure. In the momentum equation (49), \( \Pi \) given by (54) is the difference between the pressure corresponding to the non equilibrium temperature \( \vartheta \) and the equilibrium one. At the same time, \( \Pi \) appearing in the last equation (49) has, according to (44), the physical meaning of difference of energy due to the internal motion between equilibrium and non equilibrium. If we substitute in fact in the equation (49) the expressions (44), (22), and (24) we can rewrite the last equation as:

\[
\frac{\partial}{\partial t} [2 \rho \varepsilon_I(\Theta)] + \frac{\partial}{\partial x_i} [2 \rho \varepsilon_I(\Theta) u_i] = - \hat{S}_l.
\] (56)

A recent work [3] uses similar considerations to construct a macroscopic ET\(_6\) theory valid also for dense gas.

In the case of a polytropic gas, for which (18) holds, all previous non-polytropic gas results reduce to the one obtained in [32] and in particular we have:

\[
\varepsilon_I(T) = \frac{D - 3}{2} \frac{k_B}{m} T.
\] (57)

In this case the relations between the two non equilibrium temperatures (30) become:

\[
(D - 3)(T - \Theta) = 3(\vartheta - T),
\] (58)

while the equation (56) becomes:

\[
\frac{\partial}{\partial t} (\rho \Theta) + \frac{\partial}{\partial x_i} (\rho \Theta u_i) = - \frac{m \hat{S}_l}{k_B(D - 3)},
\] (59)

with \( \Pi \) from (44) that is now related to \( \Theta \) by the simple relation:

\[
\Pi = \frac{D - 3}{3} \frac{k_B}{m} \rho (T - \Theta).
\] (60)

3. The discrete kinetic approach. The structure of a polyatomic gas may be described in quantum/semi-classical way by a collection of \( N \) discrete energy levels \( E_s \) (with \( E_1 = 0 \)), making up a mixture of \( N \) species endowed with only translational degrees of freedom. The relevant kinetic Boltzmann equations for the distribution functions \( f_s \), depending on space, time, and molecular velocity \( \mathbf{v} \), are summarized as follows (\( \vec{f} \) denotes the column vector of the \( f_s \))

\[
\frac{\partial f_s}{\partial t} + \mathbf{v} \cdot \nabla f_s = J_s[\vec{f}] \quad s = 1, \ldots, N
\]

\[
J_s[\vec{f}] = \sum_{r,h,k} \int_{R^3} \int_{S^2} K^r_{s}^{hk}[\vec{f}](\mathbf{v}, \mathbf{w}, \hat{n}') d\mathbf{w} d\hat{n}'
\]
\[ K_{sr}^{hk}(\mathbf{v}, \mathbf{w}, \mathbf{n}') = \mathcal{H} \left( g^2 - \sigma_{sr}^{hk} \right) g^{hk}(g, \mathbf{n} \cdot \mathbf{n}') \left[ f_s(v_{sr}) f_k(w_{sr}) - f_s(v) f_r(w) \right] \]

(61)

where \( \sigma_{sr}^{hk} \) stands for microscopic differential cross section \([16]\) relevant to a collision between two molecules in states \( s \) and \( r \) putting them in states \( h \) and \( k \), \( \mathcal{H} \) denotes the Heaviside function, and

\[
\begin{align*}
g &= |\mathbf{v} - \mathbf{w}|, \quad \mathbf{n} = \frac{1}{g} (\mathbf{v} - \mathbf{w}), \\
\mathbf{v}_{sr}^{hk} &= \frac{1}{2} (\mathbf{v} + \mathbf{w} + g_{sr}^{hk} \mathbf{n}') \\
\mathbf{w}_{sr}^{hk} &= \frac{1}{2} (\mathbf{v} + \mathbf{w} - g_{sr}^{hk} \mathbf{n}') \\
\delta_{sr}^{hk} &= \frac{4}{m} \Delta E_{sr}^{hk}, \quad \Delta E_{sr}^{hk} = E_h + E_k - E_s - E_r, \quad g_{sr}^{hk} = |\mathbf{v}_{sr}^{hk} - \mathbf{w}_{sr}^{hk}|.
\end{align*}
\]

From now on, it is implicitly understood that integrations on velocity variables range all over \( \mathbb{R}^3 \) and integrations on angular variables range over the unit sphere \( S^2 \) like in (61)\( 2 \). Number densities, mass densities, mean macroscopic velocities, pressure tensors, internal energies, and heat fluxes are defined in the usual way as moments of the distribution functions (a star means excitation contributions, to be added to the thermal ones)

\[
\begin{align*}
n_s &= \int f_s \, dv, \quad \rho_s = m n_s, \quad \mathbf{u}_s = \frac{1}{n_s} \int \mathbf{v} f_s \, dv, \\
\mathbf{P}_s &= m \int (\mathbf{v} - \mathbf{u}_s) \otimes (\mathbf{v} - \mathbf{u}_s) f_s \, dv = \sum_s \mathbf{P}_s + \sum_s \rho_s (\mathbf{u}_s - \mathbf{u}) \otimes (\mathbf{u}_s - \mathbf{u}), \\
U_s &= \frac{1}{2} \text{tr}(\mathbf{P}_s) = \frac{1}{2} \sum_s \text{tr}(\mathbf{P}_s) + \frac{1}{2} \sum_s \rho_s |\mathbf{u}_s - \mathbf{u}|^2, \quad U^*_s = \sum_s E_s n_s, \\
\mathbf{q}_s &= \frac{1}{2} m \int (\mathbf{v} - \mathbf{u}_s) |\mathbf{v} - \mathbf{u}_s|^2 f_s \, dv = \sum_s \mathbf{q}_s + \sum_s \mathbf{P}_s \cdot (\mathbf{u}_s - \mathbf{u}) \\
&\quad + \sum_s U_s (\mathbf{u}_s - \mathbf{u}) + \frac{1}{2} \sum_s \rho_s (\mathbf{u}_s - \mathbf{u}) |\mathbf{u}_s - \mathbf{u}|^2, \\
\mathbf{q}_s^* &= \sum_s E_s \int (\mathbf{v} - \mathbf{u}) f_s \, dv = \sum_s E_s n_s (\mathbf{u}_s - \mathbf{u}).
\end{align*}
\]

Collision invariants are in number of \( \infty \)

\[
\begin{pmatrix}
1 \\
1 \\
\vdots \\
1
\end{pmatrix}
\quad \begin{pmatrix}
mv \\
mv \\
\vdots \\
mv
\end{pmatrix}
\quad \begin{pmatrix}
\frac{1}{2} m v^2 + E_1 \\
\frac{1}{2} m v^2 + E_2 \\
\vdots \\
\frac{1}{2} m v^2 + E_N
\end{pmatrix}
\]
representing number density $n$, momentum density $\rho u$, and total (kinetic and excitation) energy of the gas $\frac{1}{2} \rho u^2 + U + U^*$. Such quantities (or equivalently $n, u, U + U^*$) are conserved by collisions. Collision equilibria are provided by the family of Maxwellians (with 5 free parameters, $n, u, T$, and with $A$ denoting partition function)

$$f_{\text{eq}}(v) = n_{\text{eq}}^s \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left[ - \frac{m}{2k_BT} |v - u|^2 \right],$$

$$n_{\text{eq}}^s = \frac{n}{A(T)} \exp \left( - \frac{E_s}{k_BT} \right), \quad A(T) = \sum_s \exp \left( - \frac{E_s}{k_BT} \right).$$

Notice how the partition function defined here is just the discrete version of formula (17).

The kinetic temperature $\vartheta$ is defined by means of the trace of $P$ as

$$nk_B \vartheta = \frac{1}{3} \text{tr} P = \frac{2}{3} U.$$  

We shall set $p = nk_B T$ for the (equilibrium) scalar pressure, so that

$$U_{\text{eq}} = \frac{3}{2} nk_B T = \frac{3}{2} p.$$  

Taking into account (47) we have:

$$\Pi = P - nk_B T I, \quad \Pi^D = P - nk_B \vartheta I, \quad \Pi = \frac{1}{3} \text{tr}(\Pi) = nk_B (\vartheta - T).$$

Macroscopic quantities at equilibrium are

$$P_{\text{eq}} = nk_B T I, \quad U_{\text{eq}} = \frac{n}{A(T)} \sum_s E_s \exp \left( - \frac{E_s}{k_BT} \right) = nE(T),$$

$$q_{\text{eq}} = 0, \quad q^*_{\text{eq}} = 0.$$  

This defines $E(T)$ as the temperature–dependent mean value of the energy levels, averaged with weights given by the Boltzmann factors. Internal specific (per unit mass) energy, and dimensionless constant–volume specific heat are

$$\varepsilon = \frac{U + U^*}{\rho}, \quad \varepsilon_{\text{eq}} = \frac{3}{2} \frac{k_B}{m} T + \frac{1}{m} \bar{E}(T),$$

$$\hat{c}_v = \frac{m}{k_B} \frac{\partial \varepsilon_{\text{eq}}}{\partial T} = \frac{3}{2} + \frac{1}{A(T)} \sum_s \left( \frac{E_s - \bar{E}(T)}{k_BT} \right)^2 \exp \left( - \frac{E_s}{k_BT} \right) = \frac{3}{2} + \hat{\sigma}(T)$$

where the correction $\hat{\sigma}$ to the mono–atomic value $3/2$ represents the variance of the spectrum of energy levels with respect to their mean value, and depends on temperature according to the actual structure of such levels. Exact non–closed macroscopic conservation equations read as

$$\frac{\partial n}{\partial t} + \nabla \cdot (n u) = 0$$

$$\frac{\partial}{\partial t} \left( \rho u \right) + \nabla \cdot (\rho u \otimes u + P) = 0$$

$$\frac{\partial}{\partial t} \left( \frac{1}{2} \rho u^2 + U + U^* \right) + \nabla \cdot \left[ \left( \frac{1}{2} \rho u^2 + U + U^* \right) u \right] + \nabla \cdot (P \cdot u + q + q^*) = 0.$$  

(67)
For all quantities non-conserved by collisions we may rely on balance equations with collision contributions. For instance, for the excitation energy we have

$$\frac{\partial U^*}{\partial t} + \nabla \cdot \left( \sum_s E_s n_s \mathbf{u}_s \right) = S^*$$

$$S^* = \sum_{s,r,h,k} E_s Q_{srhk} = \sum_{s,r,h,k} E_s \int \int \int K_{srhk} (\mathbf{v}, \mathbf{w}, \hat{n}') d\mathbf{v} d\mathbf{w} d\hat{n}'$$.

(68)

Conservation equations may also be cast in convective form

$$\frac{\partial n}{\partial t} + \mathbf{u} \cdot \nabla n = -n \nabla \cdot \mathbf{u}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p - \nabla \cdot \mathbf{\pi}$$

$$\frac{\partial}{\partial t} (U + U^*) + \mathbf{u} \cdot \nabla (U + U^*) = -(p + U + U^*) \nabla \cdot \mathbf{u} - \mathbf{\pi} : \nabla \mathbf{u} - \nabla \cdot (\mathbf{q} + \mathbf{q}^*)$$

and, on using the specific internal energy rather than the energy density, the last one may be replaced by

$$\rho \frac{\partial \varepsilon}{\partial t} + \rho \mathbf{u} \cdot \nabla \varepsilon = -p \nabla \cdot \mathbf{u} - \mathbf{\pi} : \nabla \mathbf{u} - \nabla \cdot (\mathbf{q} + \mathbf{q}^*)$$.

(70)

Euler equations correspond to the assumption of collision equilibrium, which is quantified by the ansatz

$$\mathbf{\pi} = 0, \quad \varepsilon(T) = \frac{3}{2} \frac{k_B}{m} T + \frac{1}{m} \bar{E}(T), \quad \mathbf{q} = \mathbf{q}^* = 0$$.

(71)

yielding (with $p = nk_B T$) the closed set of PDE for $n$, $\mathbf{u}$, and $T$

$$\frac{\partial n}{\partial t} + \mathbf{u} \cdot \nabla n = -n \nabla \cdot \mathbf{u}$$

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p$$

$$\rho \frac{k_B}{m} \bar{c}_v \left( \frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) = -p \nabla \cdot \mathbf{u}$$.

(72)

### 3.1. Six moment closure

The next simplest macroscopic description with a finite number of moments that can be thought of consists probably in the addition of one non-conserved moment, which, in the frame of polyatomic gases, seems to be given by the most evident effect, the dynamical pressure $\Pi$. In a kinetic frame, this makes sense in a collision dominated regime (small Knudsen number), where, in the approach to equilibrium, relaxation to zero of the dynamical pressure is, for some reason, much slower than the same process for all other extra moments (shear stress, heat flux, diffusion velocities), namely, with respect to collision equilibrium, the viscous stress $\mathbf{\pi}$ keeps diagonal form with non-zero trace. Therefore the constitutive equation $\mathbf{\pi} = 0$ must be replaced by

$$\mathbf{\pi} = \Pi \mathbf{I} = nk_B (\hat{\vartheta} - T) \mathbf{I}$$,

(73)

all the others in (71) remaining the same. Thus, as before in Sec. 2, shear stress and heat flux are not present on the considered time scale. The set of macroscopic
conservation equations becomes
\[
\frac{\partial n}{\partial t} + u \cdot \nabla n = - n \nabla \cdot u
\]
\[
\rho \left( \frac{\partial u}{\partial t} + u \cdot \nabla u \right) = - \nabla (p + \Pi)
\]
\[
nk_B \epsilon_v \left( \frac{\partial T}{\partial t} + u \cdot \nabla T \right) = - (p + \Pi) \nabla \cdot u
\]
and we need for the closure an additional equation for \( \Pi \). This can be obtained from the balance equation for excitation energy, which reduces now to
\[
\frac{\partial U^*}{\partial t} + u \cdot \nabla U^* = - U^* \nabla \cdot u + S^*.
\]
The relation between \( U^* \) and \( \Pi \) is provided by the fact that, in the present scheme, following the rigorous singularly perturbed asymptotic procedure of [26], \( U + U^* \) remains a conserved quantity, accordingly represented (like \( n \) and \( u \)) by its equilibrium value, but the same is not true for \( U \) alone, which instead takes the non–equilibrium value \( \frac{3}{2} nk_BT + \frac{3}{2} \Pi \), so that we have to assume consistently
\[
U^* = U^*(T, \vartheta) = \bar{E}(T) - \frac{3}{2} nk_B(\vartheta - T).
\]
Since
\[
\left( \frac{\partial}{\partial t} + u \cdot \nabla \right) \left( n \bar{E}(T) \right) = - n \bar{E}(T) \nabla \cdot u - \frac{\dot{\sigma}(T)}{\epsilon_v(T)} (p + \Pi) \nabla \cdot u
\]
one is left with
\[
\frac{\partial \Pi}{\partial t} + u \cdot \nabla \Pi = - \left[ \frac{2}{3} \frac{\dot{\sigma}(T)}{\epsilon_v(T)} p + \left( 1 + \frac{2}{3} \frac{\dot{\sigma}(T)}{\epsilon_v(T)} \right) \Pi \right] \nabla \cdot u - \frac{2}{3} S^*.
\]
In order to close the collision contribution related to \( S^* \) we need to use approximate but consistent distribution functions into the collision integrals. To achieve such a goal we introduce an auxiliary non–equilibrium temperature \( \Theta \), aimed at describing the excitation energy in the same way as \( \vartheta \) describes the thermal energy, and defined by
\[
\bar{E}(\Theta) = \bar{E}(T) - \frac{3}{2} nk_B(\vartheta - T).
\]
so that \( U^* = n \bar{E}(\Theta) \). Of course \( \Theta \) is not a new variable, but a certain function of \( T \) and \( \vartheta \) determined by condition (77). Both corrections \( \vartheta - T \) and \( \Theta - T \) must vanish at equilibrium. Since \( \bar{E} \) is a monotonically increasing function of its argument, the solution \( \Theta \) of equation (77), if existing, is unique. It necessarily exists if \( \vartheta - T \) is small enough, and, more precisely, since \( \bar{E} \) is ranging in some interval \((0, E_M)\) with \( E_M \leq +\infty \), existence condition reads \( -\frac{3}{2} \frac{E_M - \bar{E}(T)}{nk_B} < \vartheta - T < \frac{2}{3} \frac{\bar{E}(T)}{nk_B} \). In general, the argument of \( \bar{E} \) may be varying all over the real axis, and \( E_M \) coincides with the maximum energy level \( E_N \). In our scheme however, in which the number \( N \) of levels is expected to tend to infinity, the argument of \( \bar{E} \) is restricted to the positive real axis only (and consequently \( \Theta \) is positive), and \( E_M \) must be identified with the arithmetic mean of all energy levels, which is of course infinite when levels have no upper bound. In addition, we must have necessarily \( \vartheta > 0 \), since such a quantity (the kinetic temperature) represents the variance for the distribution of molecular
velocities. In conclusion, existence and uniqueness of solution to the transcendental equation (77) are guaranteed for
\[
\max \left\{ 0, -\frac{2}{3} \frac{E_M - \bar{E}(T)}{k_B} + T \right\} < \vartheta < \frac{2}{3} \frac{\bar{E}(T)}{k_B} + T,
\]
(78)
where \(E_M\) may take different values according to previous discussion. In particular, the physical situation corresponding to the continuous kinetic approach corresponds to the option \(E_M = +\infty\), so that the lower bound for \(\vartheta\) is actually 0. From the present kinetic point of view both non–equilibrium temperature corrections to the positive equilibrium temperature \(T\) should be seen as “small” in some sense; it is easily seen that \(\vartheta > T\) entails \(\Theta < T\), and vice versa (of course both \(\vartheta\) and \(\Theta\) coincide with \(T\) at equilibrium). In this respect, the asymptotic expansion
\[
\bar{E}(\Theta) = \bar{E}(T) + \hat{\sigma}(T) k_B (\Theta - T) + O((\Theta - T)^2)
\]
leads to the estimate
\[
\Theta = T - \frac{3}{2 \hat{\sigma}(T)} (\vartheta - T) + O((\vartheta - T)^2) \quad \text{for} \quad \vartheta \to T.
\]
(79)
From the previous discussion, one is led to choose, for the approximate closure of the collision integrals, the family of Gaussian distributions (sort of multi–temperature Maxwellians, \(\vartheta\) for the translational degrees of freedom and \(\Theta\) for the internal ones, coinciding at equilibrium)
\[
M_s(v) = n_s^{eq}(\Theta) \left( \frac{m}{2\pi k_B \vartheta} \right)^{3/2} \exp \left[ -\frac{m|v - u|^2}{2k_B \vartheta} \right]
\]

\[
n_s^{eq}(\Theta) = \frac{n}{A(\Theta)} \exp \left[ -\frac{E_s}{k_B \Theta} \right]
\]
(80)
where everything is well defined when condition (78) is fulfilled, and in particular all velocity power moments converge since \(\vartheta > 0\). These distributions reproduce trivially number density \(n\) and mass velocity \(u\), and in addition
\[
P_{ij} = m \sum_s n \frac{n_s^{eq}(\Theta)}{A(\Theta)} \int C_i C_j \left( \frac{m}{2\pi k_B \vartheta} \right)^{3/2} \exp \left[ -\frac{m C^2}{2k_B \vartheta} \right] dC = nk_B \vartheta \delta_{ij}
\]
(81)
as well as
\[
U^* = \sum_s E_s \int M_s dv = \sum_s E_s n_s^{eq}(\Theta) = n \bar{E}(\Theta) = n \bar{E}(T) - \frac{3}{2} nk_B (\vartheta - T),
\]
(82)
namely all prescriptions for distribution functions compatible with the adopted macroscopic scheme. The main motivation for the choice (80) is however the fact that it fulfils the kinetic equivalent of the Maximum Entropy Principle, namely the so–called Gibbs lemma [16, 17], in the following sense:

**Theorem 3.1.** The standard Boltzmann H–functional
\[
H[f] = \sum_s \int f_s \log f_s dv,
\]
(83)
in the class of smooth (continuous) distribution functions subject to the 6 constraints
\[\sum_s f_s \, dv = n, \quad \sum_s vf_s \, dv = n \, u, \quad \sum_s E_s f_s \, dv = n \, \bar{E}(\Theta),\]
\[\frac{1}{2} m \sum_s \int |v - u|^2 f_s \, dv = \frac{3}{2} nk_B \vartheta,\]
(84) attains its strict minimum when the distribution function coincides with the 6–parameter family of Gaussian distributions (80).

Proof. The proof follows typical convexity arguments of kinetic theory. In fact, upon setting \(f_s = h_s M_s\), we have
\[H[f] - H[M] = \sum_s h_s M_s \log h_s \, dv + \sum_s \int M_s (f_s - M_s) \, dv\]
\[= \sum_s h_s M_s \log h_s \, dv + \sum_s \int \left( f_s - M_s \right) \log \left( \frac{n}{A(\Theta)} \left( \frac{m}{2\pi k_B \vartheta} \right)^{3/2} \right) \, dv + \frac{E_s}{k_B \Theta} - \frac{m|v - u|^2}{2k_B \vartheta} \}
\]
so that, bearing in mind that \(\sum_s \int (h_s - 1) M_s \, dv = \sum_s \int (f_s - M_s) \, dv = n - n = 0\),
we may write
\[H[f] - H[M] = \sum_s \int \left[ h_s \log h_s - (h_s - 1) \right] M_s \, dv \geq 0\]
(85) since, by convexity, \(x \log x - (x - 1) \geq 0, \forall x > 0\), with equal sign iff \(x = 1\). Now equal sign in the previous equation applies only if \(h_s(v) = 1\) identically, for any \(s\). Otherwise there would be a point in one of the integration domains in which the integrand is positive, thus it would be positive in a neighborhood of it, and the result would be necessarily positive. Therefore
\[H[f] - H[M] = 0 \quad \text{iff} \quad f_s(v) = M_s(v) \quad \forall s,\]
and the considered Gaussians actually minimize the \(H\)--functional among the admissible distribution functions. \(\square\)

One can notice how (80) is just the discrete version of the continuous distribution function (29), or viceversa. They both exhibit separated factors in their dependence on molecular velocity and on internal energy, factors that are characterized by the two non–equilibrium temperatures \(\vartheta\) and \(\Theta\). The translational temperature \(\vartheta\) appears in (29) via the dynamical pressure \(\Pi = nk_B(\vartheta - T)\).

3.2. Field equations. With the choice (80) discussed above the collision integrals become, with reference to (68) and (61),
\[Q_{srhk} = \iiint \mathcal{H}(g^2 - \delta_{sr}^{hk}) g \delta_{sr}^{hk}(g, \hat{n}, \hat{n}') \left( \frac{m}{2\pi k_B \vartheta} \right)^3 \]
\[\times \left\{ n_{rh}^e(\Theta) n_{rk}^e(\Theta) \exp \left[ - \frac{m}{2k_B \vartheta} \left( |v_{sr}^{hk} - u|^2 + |w_{sr}^{hk} - u|^2 \right) \right] \right\} \]
or negative, labeled by the corresponding symbol $S^*$ satisfying the micro–reversibility condition

$$\Theta = \Theta_{eq}$$

For simple collision models the averaged collision kernels can also be made explicit. An example is given by a Maxwell molecule assumption on all endothermic collisions, namely [16]

$$\gamma_{sr}^{hk}(\vartheta) = \left(\frac{m}{2\pi k_B\vartheta}\right)^\frac{3}{2} \int \int H(g^2 - \delta_{sr}^h) g \sigma_{sr}^{hk}(g, \hat{n} \cdot \hat{n}') \exp \left[ -\frac{m(v^2 + w^2)}{2k_B\vartheta} \right] d\vartheta d\vartheta'$$

satisfying the micro–reversibility condition

$$\gamma_{sr}^{hk}(\vartheta) = \exp \left( \frac{\Delta E_{sr}^{hk}}{k_B\vartheta} \right) \gamma_{sr}^*(\vartheta),$$

we can write

$$Q_{sr}^{enk} = n_s^{en}(\Theta) n_r^{en}(\Theta) \gamma_{sr}^{hk}(\vartheta) \left[ \exp \left( \frac{\Delta E_{sr}^{hk}}{k_B\vartheta} \vartheta - \Theta \right) \right] - 1,$$

where, in near equilibrium conditions, $\Theta$ is provided by (79) and

$$\vartheta = \Theta + \left( 1 + \frac{3}{2\sigma(T)} \right) (\vartheta - \Theta) + O((\vartheta - \Theta)^2).$$

For simple collision models the averaged collision kernels $\gamma_{sr}^{hk}$ can also be made explicit. An example is given by a Maxwell molecule assumption on all endothermic collisions, namely [16]

$$\int g \sigma_{sr}^{hk}(g, \hat{n} \cdot \hat{n}') d\vartheta' = B_{sr}^{hk}, \quad \text{for } \Delta E_{sr}^{hk} > 0$$

from which

$$\gamma_{sr}^{hk}(T) = \frac{2}{\sqrt{\pi}} B_{sr}^{hk} \Gamma \left( \frac{3}{2}, \frac{\Delta E_{sr}^{hk}}{k_B T} \right), \quad \Delta E_{sr}^{hk} > 0$$

in terms of an incomplete Euler Gamma function.

From (91) it is clear that $Q_{sr}^{enk}$ vanishes when $\Delta E_{sr}^{hk} = 0$ and in the sum making up $S^*$ we can split the addends in the two classes for which such quantity is positive or negative, labeled by the corresponding symbol

$$S^* = \left( \sum_+ + \sum_- \right) E_s n_s^{en}(\Theta) n_r^{en}(\Theta) \gamma_{sr}^{hk}(\vartheta) \left[ \exp \left( -\frac{\Delta E_{sr}^{hk}}{k_B} \vartheta - \Theta \right) \right] - 1$$
and, upon using micro–reversibility, the \( \sum_s \) part may be rewritten as
\[
\sum_> E_h n^e_h(\Theta) n^e_k(\Theta) \gamma^{hk}_{sr}(\vartheta) \exp \left( \frac{\Delta E^{hk}_{sr}}{k_B} \vartheta \right) \exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) - 1 \],
\]
so that we end up with
\[
S^* = \frac{1}{2} \sum_> \gamma^{hk}_{sr}(\vartheta) n^e_s(\Theta) n^e_r(\Theta) \left\{ (E_s + E_r) \exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) - 1 \right\} + (E_h + E_k) \exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) \exp \left( \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) - 1 \right\} \tag{95}
\]
\[
= \frac{1}{2} \sum_> \gamma^{hk}_{sr}(\vartheta) n^e_s(\Theta) n^e_r(\Theta) \Delta E^{hk}_{sr} \left[ 1 - \exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) \right].
\]
It can be noticed that, if \( \vartheta > T \) (thus \( \vartheta > \Theta \) and \( \Pi > 0 \)), then \( S^* > 0 \) and the collision contribution to the balance equation for \( \Pi \) is negative, and conversely the contribution is positive when \( \vartheta < T \), so that, as expected, collisions work on the gas to have dynamical pressure vanish.

The 6–moment closure to the balance equation for \( \Pi \) is then explicitly
\[
\frac{\partial \Pi}{\partial t} + \mathbf{u} \cdot \nabla \Pi = - \left[ \frac{2}{3} \frac{\vartheta(T)}{\vartheta(T)} T + \frac{3}{2} \frac{\vartheta(T)}{\vartheta(T)} \right] \nabla \cdot \mathbf{u} \tag{96}
\]
\[
- \frac{1}{3} \sum_{s,r,h,k} \gamma^{hk}_{sr}(\vartheta) n^e_s(\Theta) n^e_r(\Theta) \Delta E^{hk}_{sr} \left[ 1 - \exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) \right],
\]
with \( \vartheta = T + \Pi/(\rho n k_B) \), to be coupled to the 5 conservation equations. Everything is explicit in terms of cross sections (collision kernels), determination of \( \Theta \) requires the solution of the transcendental equation (77), involving \( \bar{E} \). The temperature dependence of such a monotonic function is determined by the structure of the discrete levels.

3.3. **Linearization near equilibrium.** It is worth considering linearization with respect to \( \vartheta \) of the produc- tion term \( S^* \) near equilibrium. This leads to
\[
\frac{\vartheta - \Theta}{\vartheta} = \frac{1}{T} \left( 1 + \frac{3}{2} \frac{\vartheta}{\vartheta(T)} T \right) \frac{\vartheta - T}{T} + O((\vartheta - T)^2) \tag{97}
\]
from which
\[
\exp \left( - \frac{\Delta E^{hk}_{sr}}{k_B} \frac{\vartheta - \Theta}{\vartheta} \right) = 1 - \frac{\Delta E^{hk}_{sr}}{k_B T} \left( 1 + \frac{3}{2} \frac{\vartheta}{\vartheta(T)} T \right) \frac{\vartheta - T}{T} + O((\vartheta - T)^2)
\]
and then
\[
S^* = \frac{1}{2 k_B T} \left( 1 + \frac{3}{2} \frac{\vartheta}{\vartheta(T)} T \right) \left( \sum_> \gamma^{hk}_{sr} \left( T n^e_s(T) n^e_r(T) \left( \Delta E^{hk}_{sr} \right)^2 \right) \frac{\vartheta - T}{T} + O((\vartheta - T)^2) \right). \tag{98}
\]
Collision contribution to the equation for \( \Pi \) becomes
\[
- \frac{2}{3} S^* = - \frac{1}{3 k_B T} \left( 1 + \frac{3}{2} \frac{\vartheta}{\vartheta(T)} T \right) \left( \sum_> \gamma^{hk}_{sr} \left( T n^e_s(T) n^e_r(T) \left( \Delta E^{hk}_{sr} \right)^2 \right) \frac{\vartheta - T}{T} + O((\vartheta - T)^2) \right) \frac{\Pi}{p} + O(\Pi^2) \tag{99}
\]
DYNAMICAL PRESSURE IN A POLYATOMIC GAS

which defines the relaxation time

\[
\tau = \left[ \frac{1}{3n} \left( 1 + \frac{3}{2\sigma(T)} \right) \sum_{\Delta E_{sr} > 0} \frac{\sigma_{hk}(T) n_{s}^{\text{eq}}(T) n_{r}^{\text{eq}}(T)}{k_{B} T} \right]^{-1} = \tau(n, T).
\]

\((100)\)

3.4. Diffusive limit. From the 6–moment equations it is possible to derive a 5–dimensional fluid–dynamic limit for dominant collisions by an asymptotic Chapman–Enskog procedure. Adimensionalization simply introduces a small Knudsen number \(Kn = \epsilon\) as scaling parameter into the unique balance equation (relevant to \(\Pi\))

\[
\frac{\partial \Pi}{\partial t} + \mathbf{u} \cdot \nabla \Pi = -\frac{2}{3} \frac{\hat{\sigma}(T)}{c_{v}(T)} p \nabla \cdot \mathbf{u} - \left( 1 + \frac{2}{3} \frac{\hat{\sigma}(T)}{c_{v}(T)} \right) \Pi \nabla \cdot \mathbf{u} - \frac{2}{3} \frac{1}{\epsilon} S^{*}
\]

\((101)\)

which, to leading order, yields \(S^{*} = 0\). This is obviously solved by \(\theta = T\) (\(\Pi = 0\)). Other possible solutions can not be excluded by the expression of \(S^{*}\), but would be spurious, namely not compatible with the kinetic level, which prescribes \(U = \frac{3}{2} nk_{B} T\) and \(U^{*} = nE(T)\) at collision equilibrium, ruling out any possible \(\theta \neq T\).

The only quantity to be expanded in asymptotic power series of the small parameter is \(\Pi\), all other quantities being conserved by collisions. Therefore

\[
\Pi \equiv \Pi(\epsilon) = \Pi^{(0)} + \epsilon \Pi^{(1)} + \ldots \quad \Pi^{(0)} = 0
\]

\((102)\)

and then

\[
-\frac{2}{3} \frac{1}{\epsilon} S^{*} = -\frac{1}{\tau} \Pi^{(1)} + O(\epsilon).
\]

The scaled balance equation for \(\Pi\) becomes

\[
\epsilon \left[ \frac{\partial \Pi^{(1)}}{\partial t} + \mathbf{u} \cdot \nabla \Pi^{(1)} + \left( 1 + \frac{2}{3} \frac{\hat{\sigma}(T)}{c_{v}(T)} \right) \Pi^{(1)} \nabla \cdot \mathbf{u} \right] = -\frac{2}{3} \frac{\hat{\sigma}(T)}{c_{v}(T)} p \nabla \cdot \mathbf{u} - \frac{1}{\tau} \Pi^{(1)} + O(\epsilon)
\]

\((103)\)

and yields, to leading order, a linear algebraic equation for \(\Pi^{(1)}\)

\[
\Pi^{(1)} = -\frac{2}{3} \frac{\hat{\sigma}(T)}{c_{v}(T)} \tau p \nabla \cdot \mathbf{u}.
\]

\((104)\)

This provides (again to leading order) the constitutive equation for \(\Pi\), which, as expected, is first order in \(\epsilon\) and proportional to \(-\nabla \cdot \mathbf{u}\). The bulk viscosity is

\[
\nu = \frac{2}{3} \frac{\sigma^{*}(T)}{c_{v}^{*}(T)} p \tau = \nu(T).
\]

\((105)\)

Using this constitutive equation into the conservation equations leads to parabolic fluid–dynamic equations of (reduced) Navier–Stokes type, where the only dissipative (and \(O(\epsilon)\)) effect is due to the dynamical pressure.

3.5. Entropy. Another consideration is relevant to the \(H\)–functional corresponding to the Gaussian distribution functions satisfying the present Gibbs’ lemma, a non–equilibrium value depending also on \(\theta\)

\[
H = n \log \left[ \frac{n}{A(\Theta)} \left( \frac{n}{2\pi k_{B} \theta} \right)^{3/2} \right] - n \frac{\hat{E}(\Theta)}{k_{B} \Theta} - \frac{3}{2} \frac{n}{\theta}.
\]

\((106)\)

For the specific entropy \(s = -k_{B} H/\rho\), getting rid of additive constants

\[
s = -\frac{k_{B}}{m} \log \left[ \frac{n}{A(\Theta) \bar{\theta}^{3/2}} \exp \left( -\frac{\hat{E}(\Theta)}{k_{B} \Theta} \right) \right] = s(n, T, \theta),
\]

\((107)\)
and at equilibrium \((\vartheta = \Theta = T)\)

\[
s^a = -k_B \frac{m}{2} \log \left[ \frac{n}{A(T)T^{3/2}} \exp \left( -\frac{\overline{E}(T)}{k_BT} \right) \right]. \tag{108}
\]

### 3.6. Linear approximation and comparison to the polytropic case.

The previous nonlinear theory can be specialized to the simplified linear case in which the structure of the energy levels is such that \(\overline{E}\) turns out to be, or may be reasonably approximated by, a linear function of its argument, which corresponds to assuming that \(\hat{\sigma}\) is a constant. This is the case of a polytropic gas, in which \(\hat{\sigma}\) must be identified with \((D - 3)/2\), where \(D > 3\) is the number of degrees of freedom of the molecule. In other words

\[
\overline{E}(T) = \hat{\sigma}k_BT, \quad \hat{\sigma} = \frac{D - 3}{2}, \quad \hat{c}_v = \frac{3}{2} + \hat{\sigma} = \frac{D}{2}. \tag{109}
\]

The transcendental equation (77) defining \(\Theta\) becomes linear, with explicit solution

\[
\Theta = T - \frac{3}{2\hat{\sigma}}(\vartheta - T) = \frac{DT - 3\vartheta}{D - 3}, \quad \tag{110}
\]

and the consistency/compatibility conditions quoted there take the form

\[
0 < \vartheta < \frac{D}{3}T. \tag{111}
\]

The same conditions hold for the Gaussian distributions (80) to be well defined. Similar simplifications occur for the relaxation time (100), and for the bulk viscosity (105), which reduces to

\[
\nu = \frac{2}{3} \frac{D - 3}{D} p\tau. \tag{112}
\]

### 4. Conclusions.

We have proved in the present paper a complete equivalence concerning the 6 moment system of a non polytropic gas obtained by the kinetic theory with continuous energy parameter and by the kinetic theory via discrete energy levels. It is also remarkable that the differential system is the same of the one obtained by using the phenomenological theory of extended thermodynamics [5, 33].

Indeed moment equations (9) coincide with the weak forms of the Boltzmann equations (67) and (68), where \(U = p\varepsilon_K\) and \(U^* = p\varepsilon_I\), with \(S_{II} = -2S^*\). The non–equilibrium temperatures \(\vartheta\) (translational) and \(\Theta\) (internal), coinciding at equilibrium, spontaneously arise in both algorithms, the latter being defined by (30) in one case, or equivalently by (77) in the other. Similar correspondence occurs for the solvability conditions (32) and (78), respectively. Field equations provided by the two approaches, (49) and (74) plus (76), also coincide exactly in the differential part, which is in several respects the most important part in the system of six moment equations. The expression of the source term takes the explicit form (95) in the discrete kinetic case. It is generally very complicated, if not impossible, to compute the production term explicitly in the continuous kinetic approach, due to the complexity of the collision mechanism [15]. This problem could be matter of future investigation. Manipulations can be done at the BGK level, namely for linearized production term, by introducing a suitable relaxation time \(\tau_{BGK}\). An easy calculation shows that

\[
S_{II} = \frac{1}{\tau_{BGK}} \int \int mC^2 [f_E - f_{Non-Poly}] \varphi(I) dI dv = -\frac{3\Pi}{\tau_{BGK}}, \tag{113}
\]
so that the relaxation time for $\Pi$ in the continuous BGK approach, for comparison to the result (100) of the discrete kinetic approach, is just $\tau_{BGK}$. So, the expression (100), or any experimental value, could be used to tune the relaxation BGK parameter.

The coincidence of the outputs of the two approaches is also evident if one compares (56) to (75). In addition, it is easy to check that the fourth of (48) coincides, apart from the source term, with (96). Finally, even results for entropy, (51) and (107) plus (108), are easily seen to be equal, bearing in mind that

$$h = -k_B H = \rho s, \quad k = \frac{h - h^{eq}}{\rho} = s - s^{eq}. \quad (114)$$

The equivalence between the two approaches permits to interpret better the dynamical pressure, strictly related to two natural non-equilibrium temperatures. In fact the dynamical pressure has simultaneously the meaning of difference between the scalar pressure relevant to the non equilibrium (kinetic) temperature $\vartheta$ and to the equilibrium one $T$ (see (54), (64)), and the meaning of difference of the energy due to the internal motion evaluated at the equilibrium temperature $T$ and at the other non-equilibrium temperature $\Theta$ (see (44), (77)).

Moreover the discrete kinetic approach permits to calculate the explicit production term in the balance law governing the dynamical pressure.

Of course at present the equivalence between the two kinetic approaches in the case of more moments is an open problem, and this will be subject of future investigation. In any case the present work gives another indication that Kinetic theory and Extended thermodynamics, in spite of their different philosophies and methodologies, support each other in a rigorous description of physical realities.

Acknowledgments. This work was supported by National Group of Mathematical Physics (GNFM) of INdAM.

REFERENCES

[1] T. Arima, A. Mentrelli and T. Ruggeri, Extended thermodynamics of rarefied polyatomic gases and characteristic velocities, Rend. Lincei Mat. Appl., 25 (2014), 275–291.
[2] T. Arima, A. Mentrelli and T. Ruggeri, Molecular extended thermodynamics of rarefied polyatomic gases and wave velocities for increasing number of moments, Ann. Physics, 345 (2014), 111–140.
[3] T. Arima, T. Ruggeri and M. Sugiyama, Duality principle from rarefied to dense gas and extended thermodynamics with 6 fields, Phys. Rev. Fluids, 2 (2017), 013401, 22 pp.
[4] T. Arima, T. Ruggeri, M. Sugiyama and S. Taniguchi, Monatomic gas as a singular limit of polyatomic gas in molecular extended thermodynamics with many moments, Ann. Physics, 372 (2016), 83–109.
[5] T. Arima, T. Ruggeri, M. Sugiyama and S. Taniguchi, Nonlinear extended thermodynamics of real gases with 6 fields, Int. J. Non–Linear Mech., 72 (2015), 6–15.
[6] T. Arima, T. Ruggeri, S. Taniguchi and M. Sugiyama, Monatomic rarefied gas as a singular limit of polyatomic gas in extended thermodynamics, Phys. Lett. A, 377 (2013), 2136–2140.
[7] T. Arima, S. Taniguchi, T. Ruggeri and M. Sugiyama, Dispersion relation for sound in rarefied polyatomic gases based on extended thermodynamics, Contin. Mech. Thermodyn., 25 (2013), 727–737.
[8] T. Arima, S. Taniguchi, T. Ruggeri and M. Sugiyama, Extended thermodynamics of dense gases, Contin. Mech. Thermodyn., 24 (2012), 271–292.
[9] T. Arima, S. Taniguchi, T. Ruggeri and M. Sugiyama, Extended thermodynamics of real gases with dynamic pressure: An extension of Meixner’s theory, Phys. Lett. A, 376 (2012), 2799–2803.
[10] T. Arima, T. Ruggeri, M. Sugiyama and S. Taniguchi, Recent results on nonlinear extended thermodynamics of real gases with six fields. Part I: general theory, Ric. Mat., 65 (2016), 263–277.

[11] M. Bisi, L. Desvillettes and G. Spiga, Exponential convergence to equilibrium via Lyapunov functionals for reaction-diffusion equations arising from non reversible chemical kinetics, M2AN Math. Model. Numer. Anal., 43 (2009), 151–172.

[12] M. Bisi, G. Martač and G. Spiga, Multi-temperature fluid-dynamic model equations from kinetic theory in a reactive gas: the steady shock problem, Comput. Math. Appl., 66 (2013), 1403–1417.

[13] M. Bisi, A. Rossani and G. Spiga, A conservative multi-group approach to the Boltzmann equations for reactive gas mixtures, Phys. A, 438 (2015), 603–611.

[14] C. Borgnakke and P. S. Larsen, Statistical collision model for Monte Carlo simulation of polyatomic gas mixture, J. Comput. Phys., 18 (1975), 405–420.

[15] J. F. Bourgat, L. Desvillettes, P. Le Tallec and B. Perthame, Microreversible collisions for polyatomic gases, Eur. J. Mech. B/Fluids, 13 (1994), 237–254.

[16] C. Cercignani, Rarefied Gas Dynamics. From Basic Concepts to Actual Calculations, University Press, Cambridge, 2000.

[17] J. F. Bourgat, L. Desvillettes, P. Le Tallec and B. Perthame, Microreversible collisions for polyatomic gases, Eur. J. Mech. B/Fluids, 13 (1994), 237–254.

[18] C. Cercignani, Rarefied Gas Dynamics. From Basic Concepts to Actual Calculations, University Press, Cambridge, 2000.

[19] S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge University Press, Cambridge, 1970.

[20] W. Dreyer, Maximization of the entropy in non-equilibrium, J. Phys. A: Math. Gen., 20 (1987), 6505–6517.

[21] M. Groppi, K. Aoki, G. Spiga and V. Tritsch, Shock wave structure analysis in chemically reacting gas mixtures by a relaxation-time kinetic model, Phys. Fluids, 20 (2008), 117103, 11pp.

[22] M. Groppi, P. Lichtenberger, F. Schuerrer and G. Spiga, Conservative approximation schemes of kinetic equations for chemical reactions, Eur. J. Mech. B/Fluids, 27 (2008), 202–217.

[23] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[24] M. Groppi and G. Spiga, Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas, J. Math. Chem., 26 (1999), 197–219.

[25] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[26] M. Groppi and G. Spiga, Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas, J. Math. Chem., 26 (1999), 197–219.

[27] C. Borgnakke and P. S. Larsen, Statistical collision model for Monte Carlo simulation of polyatomic gas mixture, J. Comput. Phys., 18 (1975), 405–420.

[28] M. Groppi, K. Aoki, G. Spiga and V. Tritsch, Shock wave structure analysis in chemically reacting gas mixtures by a relaxation-time kinetic model, Phys. Fluids, 20 (2008), 117103, 11pp.

[29] M. Groppi, P. Lichtenberger, F. Schuerrer and G. Spiga, Conservative approximation schemes of kinetic equations for chemical reactions, Eur. J. Mech. B/Fluids, 27 (2008), 202–217.

[30] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[31] M. Groppi and G. Spiga, Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas, J. Math. Chem., 26 (1999), 197–219.

[32] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[33] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[34] M. Groppi and G. Spiga, Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas, J. Math. Chem., 26 (1999), 197–219.

[35] M. Groppi, S. Rjasanow and G. Spiga, A kinetic relaxation approach to fast reactive mixtures: Shock wave structure, J. Stat. Mech.-Theory Exp., (2009), P10010, 15 pp.

[36] M. Groppi and G. Spiga, Kinetic approach to chemical reactions and inelastic transitions in a rarefied gas, J. Math. Chem., 26 (1999), 197–219.
[36] S. Taniguchi, T. Arima, T. Ruggeri and M. Sugiyama, Overshoot of the non-equilibrium temperature in the shock wave structure of a rarefied polyatomic gas subject to the dynamic pressure, *Int. J. Non-Linear Mech.*, 79 (2016), 66–75.

[37] S. Taniguchi, T. Arima, T. Ruggeri and M. Sugiyama, Thermodynamic theory of the shock wave structure in a rarefied polyatomic gas: Beyond the Bethe-Teller theory, *Phys. Rev. E*, 89 (2014), 013025, 11 pp.

Received November 2016; 1st revision February 2017; 2nd revision March 2017.

E-mail address: marzia.bisi@unipr.it
E-mail address: tommaso.ruggeri@unibo.it
E-mail address: giampiero.spiga@unipr.it