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An ES-BGK model for polyatomic gases in rotational and vibrational nonequilibrium

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Abstract

We propose an extension of the Ellipsoidal-Statistical BGK model to account for discrete levels of vibrational energy in a rarefied polyatomic gas. This model satisfies an H-theorem and contains parameters that allow to fit almost arbitrary values for the Prandtl number and the relaxation times of rotational and vibrational energies. With the reduced distribution technique, this model can be reduced to a three distribution system that could be used to simulate polyatomic gases with rotational and vibrational energy for a computational cost close to that of a simple monoatomic gas.

Contents

1 Introduction

During atmospheric reentry, a space vehicle encounters several atmospheric layers at high velocity so that very large fluxes are generated and may destroy the vehicle: estimating heat fluxes to design its heat shield becomes critical. At high altitudes, air is in rarefied regime and usual macroscopic fluid dynamics equations become non valid. Instead the Boltzmann equation is used to describe transport and collisions of molecules at a microscopic scale. The Direct Simulation Monte Carlo method (DSMC) [1, 2] is generally used but its computational cost is known to become very large close to dense regimes (even if accelerated methods like the one in [3] can partially solve this problem). In this case, it can be more efficient to use deterministic solvers based on discretizations of BGK like models of the Boltzmann equation: the Boltzmann collision operator is replaced by a simple relaxation operator towards Maxwellian equilibrium which satisfies conservation of macroscopic quantities and second principle of thermodynamics. However, by construction, the simple BGK model [4] (derived for monoatomic gases) induces a Prandtl number equal to 1 and cannot predict the correct transport coefficients. This can be corrected by models that include another parameter to uncouple the thermal relaxation from the viscosity relaxation, like the ES-BGK model [5] and the Shakhov model [6]. Both models have been extended to polyatomic gases with degrees of freedom of rotation [7, 8]. However, up to our knowledge, only the ES-BGK model can be proved to satisfy the second principle of thermodynamics (also called H-theorem in kinetic theory). This was proved and extended to polyatomic gases with rotational energy by Andries et al. [8]. We also mention another model where the Boltzmann collision operator is replaced by a Fokker-Planck operator in velocity variable that allows for efficient stochastic simulations: this model has been recently extended for polyatomic gases by Jenny et al. [9, 10, 11, 12] and also by Mathiaud and Mieussens [13, 14, 15].

Here we want to extend the ES-BGK model of [8] to take into account vibration energy of molecules. Indeed, at high temperature, there are exchanges of energy between translational, rotational, and vibration modes. Taking into account vibration energy has a strong influence on the parietal heat flux and shock position [16, 17]. In recent literature, one can find models that take into account vibrations of molecules by assuming a continuous distribution of the vibrational energy [18, 19, 20, 21, 17]. However, up to our knowledge, it is not possible so far to prove any H-theorem for these models.

Moreover, while transitional and rotational energies in air can be considered as continuous for temperature larger than 1K and 10K, respectively, vibrational energy can be considered as continuous only for much larger temperatures (2000K for oxygen and 3300K for nitrogen). For flows up to 3000K around reentry vehicles, discrete levels of vibrational energy must be used [22]. While discrete vibrational energy levels are generally used in Boltzmann equation for polyatomic gases [23, 24, 25], this is less usual for BGK models. Such BGK model is the one proposed by Morse [26], but we mention that the idea of discrete internal energy levels have also been recently used in a BGK model by Bisi and Caceres in [27]. We used the idea of Morse to derive a new BGK model with discrete vibrational energy levels in [15], as given by the simple harmonic oscillator model, for which we were able to prove a H-theorem. In this paper, we use this model and the methodology of [8] to propose an ES-BGK extension, for which we are also able to prove a H-theorem too. This model contains some free parameters that can be adjusted to recover any relaxation times for rotation and vibration modes (as given by Jeans and Landau-Teller equations, for instance), as well as the correct value of the Prandtl number. Note that since the vibration energy is a non linear function of temperature, this extension is not trivial: while [8] is based on convex combinations of temperatures, we have found more natural to work with convex combinations of energies.

At a computational level, note that even if the computational cost of a deterministic solver based on a model with so many variables (velocity, energy of rotation and vibration) is necessarily very large, the great advantage of the BGK approach is that this cost can be drastically reduced. Indeed, like every BGK models, the computational complexity of our new model can be reduced by the standard reduced distribution technique [30]: this gives a model that has the same computational cost as a model for monoatomic gas (the only kinetic variable is the velocity), while it still accounts for rotation and vibration energy exchanges. Moreover, a H-theorem also holds for this reduced model.

The outline of our paper is as follows. The next two sections are necessary to prepare the introduction of our model: in section 2 we detail the different energies at macroscopic scale as functions of temperature, and we give their mathematical properties; the description, at the kinetic level, of a polyatomic gas with energy of translation, rotation, and vibration is given in section 3. We define our new ES-BGK model in section 4, in which we also prove a H-theorem. In section 5, we show how the parameters of our model can be adjusted to fit the correct relaxation times of rotation and vibration. In section 6 we derive the hydrodynamic limits of our model by the usual Chapman-Enskog expansion. The reduced ES-BGK model is derived and analyzed in section 7. Finally, some preliminary numerical results are shown in section 8 to illustrate the capability of our model to capture correct relaxation times.

2 Internal energies of polyatomic gases

2.1 The different macroscopic internal energies at equilibrium

In this paper we consider polyatomic perfect gases for which each molecule has several degrees of freedom: translation, rotation and vibration. At the macroscopic level, a gas in thermodynamical equilibrium at temperature T has different specific energies associated to each mode. For translational and rotational modes, the translational and rotational energies are

$$e_{tr}(T) = \frac{3}{2}RT, \quad \text{and} \quad e_{rot}(T) = \frac{\delta}{2}RT, \tag{1}$$

where δ is the number of degrees of freedom of rotation and R is the gas constant per unit mass. For the vibrational mode, in case of the harmonic oscillator model, the vibrational energy is

$$e_{vib}(T) = \frac{RT_0}{\exp{(T_0/T)} - 1}, \tag{2}$$

where T_0 is the characteristic vibrational temperature ($T_0 = 2256K$ for dioxygen for instance).

The total internal energy is denoted by $e(T)$ and is simply the sum of the three previous energies:

$$e(T) = e_{tr}(T) + e_{rot}(T) + e_{vib}(T). \tag{3}$$

Finally, we also define the joint translational-rotational energy function

$$e_{tr,rot}(T) = e_{tr}(T) + e_{rot}(T) = \frac{3+\delta}{2}RT, \tag{4}$$

that will be useful for the derivation of our model.

2.2 Mathematical properties of the energy functions

For the construction of our model, it is useful to study the specific internal energies defined in the previous section, as functions of the temperature. The property needed here is the invertibility, since it will be used to define an equivalent temperature for each mode in non-equilibrium regimes.

We denote by e_i^{-1} the function that maps any given energy E to the corresponding temperature. In other words, $e_i^{-1}(E) = T$ such that $e_i(T) = E$, where i stands for tr, rot, vib, and tr, rot. Since e_{tr}, e_{rot}, and $e_{tr,rot}$ are linear functions of T (see (1) and (4)), they are clearly invertible, and we have

$$e_{tr}^{-1}(E) = \frac{2}{3R}E, \qquad e_{rot}^{-1}(E) = \frac{2}{\delta R}E, \qquad \text{and} \qquad e_{tr,rot}^{-1}(E) = \frac{2}{(3+\delta)R}E. \tag{5}$$

For e_{vib}, which is a non linear function of T, it can be proved it is increasing, thus invertible, and we have

$$e_{vib}^{-1}(E) = T_0 / \log\left(1 + \frac{RT_0}{E}\right). \tag{6}$$

The total internal energy e is also an increasing function (see (3)), thus invertible, but its inverse $e^{-1}(E)$ cannot be written analytically. In other words

$$e^{-1}(E) = T \qquad \text{such that} \qquad E = \frac{3+\delta}{2}RT + \frac{RT_0}{\exp(T_0/T) - 1}. \tag{7}$$

3 Distribution functions, moments, and temperatures

3.1 Distribution function

The state of any gas molecule will be described by its position x, its velocity v, its rotational energy ε, and its discrete vibrational energy. In the case of the usual simple harmonic oscillator model, this energy is given by iRT_0, where i is the ith vibrational energy level and T_0 is the characteristic vibrational temperature of the gas. This model is the simplest model for vibrations, but extensions for more complex models is more difficult and will be studied in a future work.

The distribution function of the gas is the mass density $f(t, x, v, \varepsilon, i)$ of molecules that at time t are located in a elementary volume dx centered in x, have the velocity v in a elementary volume dv, have the rotational energy ε centered in $d\varepsilon$ and the discrete vibrational energy iRT_0.

The macroscopic densities of mass ρ, momentum ρu, and internal energy ρE are defined by the first five moments of f:

$$\rho = \langle f \rangle_{v,\varepsilon,i}, \qquad \rho u = \langle v f \rangle_{v,\varepsilon,i}, \qquad \rho E(f) = \left\langle \left(\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0\right) f \right\rangle_{v,\varepsilon,i}. \tag{8}$$

In this paper, to clarify the notations, the dependence of E on f is made explicit, and we denote by $\langle\phi\rangle_{v,\varepsilon,i}(t,x) = \sum_{i=0}^{+\infty}\int_{\mathbb{R}^3}\int_{\mathbb{R}}\phi(t,x,v,\varepsilon,i)d\varepsilon dv$ the integral of any function ϕ.

The specific internal energy $E(f)$ can be decomposed into

$$E(f) = E_{tr}(f) + E_{rot}(f) + E_{vib}(f), \tag{9}$$

which is the sum of the energy $E_{tr}(f)$ associated with the translational motion of particles, the energy $E_{rot}(f)$ associated with the rotational mode, and the energy $E_{vib}(f)$ associated with the vibrational mode, defined by

$$\rho E_{tr}(f) = \left\langle \frac{1}{2}|v-u|^2 f \right\rangle_{v,\varepsilon,i}, \qquad \rho E_{rot}(f) = \langle \varepsilon f\rangle_{v,\varepsilon,i}, \qquad \rho E_{vib}(f) = \langle iRT_0 f\rangle_{v,\varepsilon,i}. \tag{10}$$

We also define the pressure tensor $P(f)$ and the heat flux $q(f)$ by

$$P(f) = \langle (v-u)\otimes(v-u)f\rangle_{v,\varepsilon,i} \quad , \quad q(f) = \left\langle \left(\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0\right)(v-u)f \right\rangle_{v,\varepsilon,i} \tag{11}$$

and we denote by Θ the tensor such that $P(f) = \rho\Theta$.

3.2 Internal temperatures

When the gas is in a non-equilibrium state, as described by the distribution f, a temperature can be defined for each mode, by using the specific energy functions and their inverse as defined in section 2. Indeed, the translational, rotational, and vibrational temperatures are defined by

$$T_{tr} = e_{tr}^{-1}(E_{tr}(f)), \quad T_{rot} = e_{rot}^{-1}(E_{rot}(f)), \quad T_{vib} = e_{vib}^{-1}(E_{vib}(f)), \tag{12}$$

so that we have the following relations

$$E_{tr}(f) = \frac{3}{2}RT_{tr}, \quad E_{rot}(f) = \frac{\delta}{2}RT_{rot}, \quad E_{vib}(f) = \frac{RT_0}{\exp(T_0/T_{vib})-1}. \tag{13}$$

The equilibrium temperature T_{eq} is the temperature corresponding to the total internal energy, that is to say

$$T_{eq} = e^{-1}(E(f)). \tag{14}$$

In other words, T_{eq} can be obtained by numerically solving

$$E(f) = \frac{3+\delta}{2}RT_{eq} + \frac{RT_0}{\exp\left(T_0/T_{eq}\right)-1}. \tag{15}$$

Note that (11) and (13) give $\mathrm{Tr}(\Theta) = 3RT_{tr}$. Moreover, each diagonal component of Θ can be associated to a directional translational temperature: indeed, the translational temperature $T_{j,j}$ in direction j can be defined by $\Theta_{jj} = RT_{j,j}$, where $j = 1,2,3$. Consequently, the previous relation gives $T_{tr} = (T_{1,1} + T_{2,2} + T_{3,3})/3$.

Finally, it is useful for the following to define the intermediate translational-rotational temperature by

$$\begin{aligned} T_{tr,rot} &= e_{tr,rot}^{-1}(E_{tr}(f) + E_{rot}(f)) \\ &= \frac{3T_{tr} + \delta T_{rot}}{3+\delta}. \end{aligned} \tag{16}$$

3.3 Vibrational number of degrees of freedom

By analogy with the relation between $E_{rot}(f)$ and T_{rot} (see (13)), a number of degrees of freedom $\delta_v(T_{vib})$ for the vibration mode can be defined such that $E_{vib}(f) = \frac{\delta_v(T_{vib})}{2} RT_{vib}$, so that we have

$$\delta_v(T_{vib}) = \frac{2T_0/T_{vib}}{\exp(T_0/T_{vib}) - 1}. \tag{17}$$

This number is not an integer, is temperature dependent, and tends to 2 for large T_{vib}.

3.4 Relaxation times

The exchanges of energy between the different modes and their relaxation to equilibrium are characterized by the relaxation times τ, τ_{rot}, τ_{vib}. The first one is the translation relaxation time, that can be written as $\tau = 1/\nu$, where ν is the collision frequency of molecules. The two others are the rotational and vibrational relaxation times. They can be written as functions of τ by $\tau_{rot} = \tau Z_{rot}$ and $\tau_{vib} = \tau Z_{vib}$, where Z_{rot} and Z_{vib} can be viewed as average numbers of collisions needed to enforce a change in rotational and vibrational energy.

In most cases $1 < Z_{rot} < Z_{vib}$ and relaxation processes occur in a specific sequence (see [1] for empirical laws that are temperature dependent): first, the translational temperatures $T_{j,j}$ in the three directions $j = 1, 2, 3$ relax towards the mean translational temperature T_{tr}, then the translational and rotational temperatures T_{tr} and T_{rot} relax towards the intermediate temperature $T_{tr,rot}$, and for longer times this temperature and the vibrational temperature T_{vib} relax towards the equilibrium temperature T_{eq} (see figure 1 in section 8 for an illustration).

This type of relaxation model for temperatures is the simplest one and seems the best suited for BGK models. However, we mention that real energy exchanges are sometimes more complex, with relaxation times of very different order of magnitude, see [24, 25] for instance.

4 ES-BGK model

In this section, our new ES-BGK model that accounts for vibrations of molecules is presented, and its main properties are stated and discussed.

4.1 Construction of the model

The evolution of the mass density of a gas in non-equilibrium is described by the Boltzmann equation (in which $Q(f)$ is the Boltzmann collision operator):

$$\partial_t f + v \cdot \nabla f = Q(f), \tag{18}$$

A simpler relaxation BGK like model can be derived, as proposed in [15], where $Q(f)$ is replaced by $\frac{1}{\tau}(\mathcal{M}[f] - f)$, where τ is a relaxation time and $\mathcal{M}[f]$ is the generalized Maxwellian in velocity and energy, as defined by

$$\mathcal{M}[f](v, \varepsilon, i) = \mathcal{M}_{tr}[f](v)\mathcal{M}_{rot}[f](\varepsilon)\mathcal{M}_{vib}[f](i), \tag{19}$$

with

$$\mathcal{M}_{tr}[f](v) = \frac{\rho}{(2\pi RT_{eq})^{3/2}} \exp\left(-\frac{|v-u|^2}{2RT_{eq}}\right), \qquad \mathcal{M}_{rot}[f](\varepsilon) = \frac{\Lambda(\delta)\varepsilon^{\frac{\delta-2}{2}}}{(RT_{eq})^{\delta/2}} \exp\left(-\frac{\varepsilon}{RT_{eq}}\right),$$

$$M_{vib}[f](i) = (1 - \exp(-T_0/T_{eq})) \exp\left(-i\frac{T_0}{T_{eq}}\right),$$

where $\Lambda(\delta) = 1/\Gamma(\frac{\delta}{2})$, with Γ the usual gamma function. This generalized Maxwellian is the natural equilibrium for an entropy functional $\mathbb{H}(f)$, see section 4.3.

However, this model is too simple, since the single relaxation time cannot account for the various time scales of the original problem. Indeed, such a model gives the same value for rotational and vibrational relaxation times, and the same value for relaxation times of viscous and thermal fluxes, leading to the usual incorrect Prandtl number $\mathrm{Pr} = 1$.

This problem can be fixed by using additional parameters in the model (at least 3 in this case). The correct Prandtl number for a monoatomic gas can be obtained by the ES-BGK approach [5], which has been extended later in [8] to account for a correct rotational time scale for polyatomic gases. Here, we extend this model to account for a correct vibrational time scale. Note that in this case, since the relation between temperature and energy is non linear, we find it more relevant to make an intensive use of the energy variable, that makes the derivation a bit different from that of [8]. Our ES-BGK collision operator is the following:

$$Q(f) = \frac{1}{\tau}(\mathcal{G}[f] - f) = \frac{1}{\tau}(\mathcal{G}_{tr}[f](v)\mathcal{G}_{rot}[f](\varepsilon)\mathcal{G}_{vib}[f](i) - f), \tag{20}$$

with

$$\begin{aligned}
\mathcal{G}_{tr}[f](v) &= \frac{\rho}{\sqrt{\det(2\pi\Pi)}} \exp\left(-\frac{1}{2}(v-u)^T\,\Pi^{-1}\,(v-u))\right), \\
\mathcal{G}_{rot}[f](\varepsilon) &= \frac{\Lambda(\delta)}{(RT_{rot}^{rel})^{\delta/2}}\varepsilon^{\frac{\delta-2}{2}} \exp\left(-\frac{\varepsilon}{RT_{rot}^{rel}}\right), \\
\mathcal{G}_{vib}[f](i) &= (1-\exp(-T_0/T_{vib}^{rel}))\exp\left(-i\frac{T_0}{T_{vib}^{rel}}\right).
\end{aligned} \tag{21}$$

Note that $\mathcal{G}_{tr}[f]$, $\mathcal{G}_{rot}[f]$ and $\mathcal{G}_{vib}[f]$ are distributions associated to the energies of translation, rotation and vibration of the molecules. The covariance matrix Π and the temperatures T_{rot}^{rel} and T_{vib}^{rel} are modifications of tensor Θ and temperatures T_{rot}, T_{vib} so as to fit different relaxation times.

First, the corrected tensor Π is defined by (with I the identity matrix):

$$\Pi = \eta RT_{eq}I + (1-\eta)\left[\theta RT_{tr,rot}I + (1-\theta)(\nu\Theta + (1-\nu)RT_{tr}I)\right], \tag{22}$$

so that the hierarchy of relaxation processes explained in section 3.4 holds: (1) the directional temperatures $T_{j,j}$ (diagonal elements of Θ) first relax to T_{tr} (governed by parameter ν); (2) the translational temperature T_{tr} relaxes to the intermediate temperature $T_{tr,rot}$ (governed by parameter θ); (3) this temperature relaxes to the final equilibrium temperature T_{eq}, as governed by parameter η.

Now the relaxation temperatures T_{rot}^{rel} and T_{vib}^{rel}, used in distributions $\mathcal{G}_{rot}$ and $\mathcal{G}_{vib}$, are defined with the same idea as the covariance matrix Π, except that we first write the relaxations in term of energies. Indeed, we define the relaxation energies for rotation and vibration by

$$\begin{aligned}
e_{rot}^{rel} &= \eta e_{rot}(T_{eq}) + (1-\eta)\left[\theta e_{rot}(T_{tr,rot}) + (1-\theta)E_{rot}(f)\right], \\
e_{vib}^{rel} &= \eta e_{vib}(T_{eq}) + (1-\eta)E_{vib}(f),
\end{aligned} \tag{23}$$

and the corresponding relaxation temperatures are

$$T_{rot}^{rel} = e_{rot}^{-1}(e_{rot}^{rel}), \qquad \text{and} \qquad T_{vib}^{rel} = e_{vib}^{-1}(e_{vib}^{rel}). \tag{24}$$

These definitions account for the relaxation of T_{rot} to $T_{tr,rot}$ then to T_{eq}, and for the relaxation of T_{vib} to T_{eq} with rates that are consistent with the definition of Π.

Note that the relaxation rotational temperature T_{rot}^{rel} can be equivalently defined by $T_{rot}^{rel} = \eta T_{eq} + (1-\eta)\left[\theta T_{tr,rot} + (1-\theta)T_{rot}\right]$, which is a simple extension of the definition given in [8].

However, the relaxation vibrational temperature T_{vib}^{rel} cannot be defined in the same way: indeed, the nonlinearity of the function e_{vib} would make the simpler definition $T_{vib}^{rel} = \eta T_{eq} + (1-\eta) T_{vib}$ not consistent with the energy conservation (see section 4.2).

For the analysis of the conservation properties of our model, it is also useful to define the relaxation energy of translation

$$e_{tr}^{rel} = \frac{1}{2}\,\mathrm{Tr}(\Pi) = \eta \frac{3}{2} R T_{eq} + (1-\eta)(\theta \frac{3}{2} R T_{tr,rot} + (1-\theta) \frac{3}{2} R T_{tr}),$$

and the corresponding relaxation temperature of translation which is

$$T_{tr}^{rel} = e_{tr}^{-1}(e_{tr}^{rel}), \tag{25}$$

that will be used later.

This derivation shows that parameter θ is associated with transfers between translational and rotational energies and η with transfers between translational-rotational and vibrational energies. It will be shown in section 5.1 that these parameters are related to Z_{rot} and Z_{vib} by the relations

$$\eta = \frac{1}{Z_{vib}}, \quad \text{and} \quad \theta = \frac{1/Z_{rot} - 1/Z_{vib}}{1 - 1/Z_{vib}}. \tag{26}$$

where we remind that Z_{rot} and Z_{vib} are defined in section 3.3. Moreover, parameter ν will be used to fit the correct Prandtl number. It will be shown in section 5.2 that ν has to be set so that the Prandtl number Pr is

$$\mathrm{Pr} = \frac{1}{1 - (1-\eta)(1-\theta)\nu}. \tag{27}$$

Finally, the relaxation time τ of the model can be related to the shear viscosity of the gas by a Chapman-Enskog analysis: it will be shown in section 6.3 that our ES-BGK model is consistent with the compressible Navier-Stokes equations with shear viscosity μ, if the relaxation time is set to

$$\tau = \frac{\mu}{p}(1 - (1-\eta)(1-\theta)\nu).$$

Note that a temperature power law dependance of μ is generally chosen, which is related to the intermolecular collision model of the Boltzmann equation (see [1] for instance).

4.2 Conservation properties

The relation (25) on T_{tr}^{rel} and the definition (23) of relaxation energies of rotation and vibration can be rewritten under the compact form

$$\begin{pmatrix} e_{tr}^{rel} \\ e_{rot}^{rel} \\ e_{vib}^{rel} \end{pmatrix} = \eta \begin{pmatrix} e_{tr}(T_{eq}) \\ e_{rot}(T_{eq}) \\ e_{vib}(T_{eq}) \end{pmatrix} + (1-\eta) \begin{pmatrix} 1 - \frac{\delta\theta}{3+\delta} & \frac{3\theta}{3+\delta} & 0 \\ \frac{\delta\theta}{3+\delta} & 1 - \frac{3\theta}{3+\delta} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix}. \tag{28}$$

Now, we state what are the first moments of $\mathcal{G}[f]$ that can be computed by standard integrals and series (see appendix A).

Proposition 4.1. *The Gaussian $\mathcal{G}[f]$ satisfies*

$$\langle \mathcal{G}[f] \rangle_{v,\varepsilon,i} = \rho, \tag{29}$$

$$\langle v\mathcal{G}[f] \rangle_{v,\varepsilon,i} = \rho u, \tag{30}$$

$$\left\langle \frac{1}{2}|v-u|^2 \mathcal{G}[f] \right\rangle_{v,\varepsilon,i} = \rho e_{tr}^{rel}, \quad \langle \varepsilon \mathcal{G}[f] \rangle_{v,\varepsilon,i} = \rho e_{rot}^{rel}, \quad \langle i R T_0 \mathcal{G}[f] \rangle_{v,\varepsilon,i} = \rho e_{vib}^{rel}. \tag{31}$$

Then these properties can be used to prove the conservations properties of our kinetic model.

Proposition 4.2. *The collision operator of the ES-BGK model satisfies the conservation of mass, momentum, and energy:*

$$\left\langle (1, v, \frac{1}{2}|v-u|^2 + \varepsilon + iRT_0)\frac{1}{\tau}(\mathcal{G}[f] - f) \right\rangle_{v,\varepsilon,i} = 0.$$

Proof. The conservation of mass and momentum are obvious consequences of relations (29) and (30). For the conservation of energy, note that (31) and (28) imply

$$\begin{aligned}
&\left\langle (\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0)\mathcal{G}[f] \right\rangle_{v,\varepsilon,i} = \rho(e^{rel}_{tr} + e^{rel}_{rot} + e^{rel}_{vib}) \\
&= \rho\eta(e_{tr}(T_{eq}) + e_{rot}(T_{eq}) + e_{vib}(T_{eq})) + \rho(1-\eta)(E_{tr}(f) + E_{rot}(f) + E_{int}(f)) \\
&= \rho\eta E(f) + \rho(1-\eta)E(f) \\
&= \left\langle (\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0)f \right\rangle_{v,\varepsilon,i},
\end{aligned}$$

where we have used relations (13)–(15) and (8). □

4.3 Entropy

The use of a single rotational energy with δ degrees of freedom requires to define the Boltzmann entropy functional as

$$\mathbb{H}(f) = \langle f \log(f/\varepsilon^{\frac{\delta}{2}-1}) - f \rangle_{v,\varepsilon,i}.$$

For the following, we will consider the set $\mathcal{X}$ of non negative and integrable distributions that realize the same moments as that used to define $\mathcal{G}[f]$, that is to say

$$\begin{aligned}
\mathcal{X} = \{\phi \geq 0, \quad &\left\langle (1 + |v|^2 + \varepsilon + i + |\log(\phi/\varepsilon^{\frac{\delta}{2}-1})|)\phi \right\rangle_{v,\varepsilon,i} < +\infty, \\
&\langle \mathbf{m}\phi \rangle_{v,\varepsilon,i} = \big(\rho, \rho u, \rho(u \otimes u + \Pi), \rho e^{rel}_{rot}, \rho e^{rel}_{vib}\big)\},
\end{aligned}$$

where $\mathbf{m} = (1, v, v \otimes v, \varepsilon, iRT_0)$. We can now state our main result.

Proposition 4.3. *For parameters $-1/2 \leq \nu < 1$, $0 \leq \theta < 1$, and $0 \leq \eta < 1$ we have:*

1. *For symmetric positive definite tensor Θ and positive temperatures $T_{tr,rot}$ and T_{tr}, the tensor Π defined by (22) is symmetric positive definite.*
2. *(Entropy minimization) The Gaussian distribution $\mathcal{G}[f]$ defined by (20) is the unique minimizer of the entropy functional $\mathbb{H}(f)$ on the set $\mathcal{X}$.*
3. *(H-theorem) The ES-BGK model (18)-(20) satisfies*

$$\partial_t \mathbb{H}(f) + \nabla \cdot \left\langle v(f\log(f/\varepsilon^{\frac{\delta}{2}-1}) - f) \right\rangle_{v,\varepsilon,i} = \left\langle \frac{1}{\tau}(\mathcal{G}[f] - f)\log(f/\varepsilon^{\frac{\delta}{2}-1}) \right\rangle_{v,\varepsilon,i} \leq 0,$$

4. *(Equilibrium) If $f = \mathcal{G}[f]$, then $f = \mathcal{M}[f]$.*

Proof of Property 1.
We first rewrite Π as follows: we define the intermediate tensor $A = \nu\Theta + (1-\nu)RT_{tr}I$ associated to the relaxation phenomenon for the translation mode, and the tensor $B = (1-\theta)A + \theta RT_{tr,rot}I$ associated to the relaxation of the rotational mode, such that (22) reads $\Pi = (1-\eta)B + \eta RT_{eq}I$.

Since $\mathrm{Tr}(\Theta) = 3RT_{tr}$ (see section 3.2), then A is positive definite if $(1+2\nu)\lambda_i + (1-\nu)(\lambda_j + \lambda_k)$ is nonegative, where λ_i, λ_j, λ_k are the (positive) eigenvalues of Θ. A sufficient condition is clearly $1 + 2\nu \geq 0$ and $1 - \nu \geq 0$, which gives $\nu \in [-1/2, 1]$. Now, for $\theta \in [0,1]$, since B is a convex combination of A and $RT_{tr,rot}I$, it is also symmetric and positive definite. Finally, for $\eta \in [0,1]$, Π is a convex combination of B and $RT_{eq}I$, and hence is symmetric and positive definite too. □

Proof of Property 2.
First, note that by construction, $\mathcal{G}[f]$ is in set $\mathcal{X}$. Then, since the functional $f \mapsto \mathbb{H}(f)$ is convex, then we have

$$\mathbb{H}(\mathcal{G}[f]) \leq \mathbb{H}(\phi) - \mathbb{H}'(\mathcal{G}[f])(\phi - \mathcal{G}[f])$$

for every ϕ in $\mathcal{X}$. Moreover, we have

$$\begin{aligned}\mathbb{H}'(\mathcal{G}[f])(\phi - \mathcal{G}[f]) &= \left\langle (\phi - \mathcal{G}[f]) \log(\mathcal{G}[f]/\varepsilon^{\frac{\delta}{2}-1}) \right\rangle_{v,\varepsilon,i} \\ &= \left\langle (\phi - \mathcal{G}[f]) \boldsymbol{\alpha}^T \mathbf{m} \right\rangle_{v,\varepsilon,i} \\ &= 0,\end{aligned}$$

with:

$$\boldsymbol{\alpha} = \left(\log\left(\frac{2}{\delta} \frac{\rho\Lambda(\delta)(1-\exp(-T_0/T_{vib}^{rel}))}{\sqrt{\det(2\pi\Pi)}(RT_{rot}^{rel})^{\delta/2}} \right) - \frac{1}{2}u^T\Pi^{-1}u, \Pi^{-1}u, -\frac{1}{2}\Pi^{-1}, -\frac{1}{RT_{rot}^{rel}}, -\frac{1}{RT_{vib}^{rel}} \right).$$

since both $\mathcal{G}[f]$ and ϕ are in $\mathcal{X}$. Consequently $\mathbb{H}(\mathcal{G}[f]) \leq \mathbb{H}(\phi)$ for every ϕ in $\mathcal{X}$, which concludes the proof.

□

Proof of property 3.

This proof is decomposed into 4 steps.

Step 1: entropy inequality. First, note that with elementary calculus, (20) implies

$$\partial_t \mathbb{H}(f) + \nabla \cdot \left\langle v(f \log(f/\varepsilon^{\frac{\delta}{2}-1}) - f) \right\rangle_{v,\varepsilon,i} = \frac{1}{\tau}\mathbb{H}'(f)(\mathcal{G}[f] - f).$$

Then, since $\mathbb{H}$ is convex, the right-hand side of the previous equality satisfies

$$\mathbb{H}'(f)(\mathcal{G}[f] - f \leq \mathbb{H}(\mathcal{G}[f]) - \mathbb{H}(f).$$

Consequently, the H-theorem is obtained if we can prove that

$$\mathbb{H}(\mathcal{G}[f]) \leq \mathbb{H}(f). \tag{32}$$

Note that this is not obvious, since f is not in $\mathcal{X}$.

Step 2: entropy minima on different sets. It is convenient to define, for every macroscopic quantities ρ, u, Π, T_{rot}^{rel} and T_{vib}^{rel} the minimum of entropy $\mathbb{H}$ on $\mathcal{X}$, and we set

$$S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel}) = \min\left\{ \mathbb{H}(\phi), \phi \geq 0 \text{ s.t. } \langle \mathbf{m}\phi \rangle_{v,I,i} = \left(\rho, \rho u, \rho(u \otimes u + \Pi), \rho e_{rot}^{rel}, \rho e_{vib}^{rel}\right) \right\}.$$

Property 2 implies

$$S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel}) = \mathbb{H}(\mathcal{G}[f]).$$

Now we define a second entropy minimization problem, based on the moments of g. Namely

$$S(\rho,u,\Theta,T_{rot},T_{vib}) = \min\left\{\mathbb{H}(\phi), \phi \geq 0 \text{ s.t. } \langle \mathbf{m}\phi\rangle_{v,I,i} = (\rho, \rho u, \rho(u\otimes u+\Theta), \rho E_{rot}(f), \rho E_{vib}(f))\right\}.$$

Here, by definition g belongs to the minimization set, and therefore

$$S(\rho,u,\Theta,T_{rot},T_{vib}) \leq \mathbb{H}(f).$$

Therefore, a sufficient condition to have (32) is $S(\rho,u,\Pi,T_{rot}^{rel},T_{vib}^{rel}) \leq S(\rho,u,\Theta,T_{rot},T_{vib})$, which is rewritten as

$$\Delta S = S(\rho,u,\Pi,T_{rot}^{rel},T_{vib}^{rel}) - S(\rho,u,\Theta,T_{rot},T_{vib}) \leq 0. \tag{33}$$

This entropy difference is now analyzed in the following.

Step 3: entropy difference A direct calculation gives

$$S(\rho,u,\Pi,T_{rot}^{rel},T_{vib}^{rel}) = \rho\log\left(\rho\frac{2}{\delta}\frac{\Lambda(\delta)(1-\exp(-T_0/T_{vib}^{rel}))}{\sqrt{\det(2\pi\Pi)}(RT_{rot}^{rel})^{\delta/2}}\right) - \rho\frac{5+\delta+\delta_v(T_{vib}^{rel})}{2}.$$

A similar relation is deduced for $S(\rho,u,\Theta,T_{rot},T_{vib})$ and we get

$$\begin{aligned}\Delta S &= \frac{1}{2}\rho\log\left(\frac{\det\Theta}{\det\Pi}\left(\frac{T_{rot}}{T_{rot}^{rel}}\right)^{\delta}\left(\frac{(1-\exp(-T_0/T_{vib}^{rel}))}{(1-\exp(-T_0/T_{vib}))}\right)^2\right) - \rho\frac{\delta_v(T_{vib}^{rel})-\delta_v(T_{vib})}{2},\\ &= \frac{1}{2}\rho\log\left(\frac{\det\Theta}{\det\Pi}\left(\frac{E_{rot}(f)}{e_{rot}^{rel}}\right)^{\delta}\left(\frac{RT_0+E_{vib}(f)}{RT_0+e_{vib}^{rel}}\right)^2\right) - \rho\frac{\delta_v(T_{vib}^{rel})-\delta_v(T_{vib})}{2}\end{aligned}$$

where we have used relations (2), (12), and (23) to obtain the last equality.

First, the following result is admitted (see the proof in appendix B):

$$\frac{\det\Theta}{\det\Pi} \leq \left(\frac{E_{tr}(f)}{e_{tr}^{rel}}\right)^3. \tag{34}$$

This allows us to write the following inequality, as function of energies only:

$$\Delta S \leq \frac{1}{2}\rho\log\left(\left(\frac{E_{tr}(f)}{e_{tr}^{rel}}\right)^3\left(\frac{E_{rot}(f)}{e_{rot}^{rel}}\right)^{\delta}\left(\frac{RT_0+E_{vib}(f)}{RT_0+e_{vib}^{rel}}\right)^2\right) - \rho\frac{\delta_v(T_{vib}^{rel})-\delta_v(T_{vib})}{2}.$$

After expansion, this inequality reads as

$$\Delta S \leq \frac{\rho}{R}\left(\mathcal{S}(E_{tr}(f),E_{rot}(f),E_{vib}(f)) - \mathcal{S}(e_{tr}^{rel},e_{rot}^{rel},e_{vib}^{rel})\right), \tag{35}$$

where we have introduced the new energy functional $\mathcal{S}$, defined for every energy triplet (e_1,e_2,e_3) by

$$\mathcal{S}(e_1,e_2,e_3) = R\left(\frac{3}{2}\log(e_1) + \frac{\delta}{2}\log(e_2) + \log\left(1+\frac{e_3}{RT_0}\right) + \frac{e_3}{RT_0}\log\left(1+\frac{RT_0}{e_3}\right)\right).$$

Note that to obtain (35), we also have replaced δ_v by its definition (17) and the temperatures of vibration have been replaced by their corresponding energies.

Now it is clear that a sufficient condition to have $\Delta S \leq 0$ is

$$\mathcal{S}(E_{tr}(f),E_{rot}(f),E_{vib}(f)) \leq \mathcal{S}(e_{tr}^{rel},e_{rot}^{rel},e_{vib}^{rel}), \tag{36}$$

which is proved in the last step.

Step 4: proof of (36) The usual argument to conclude an entropy inequality is a convexity property. Here, our functional $\mathcal{S}$ can easily be seen to be concave (see appendix C). However, since the right-hand side of (36) is not at equilibrium, a direct use of the convexity inequality does not work here. Instead, we find it simpler, and physically relevant, to use successively two paths, based on parameters θ and η. Indeed, note that relaxation energies $(e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel})$ depend on θ and η (see (28)). Then we set

$$s(\theta,\eta) = \mathcal{S}(e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel}).$$

From (28), it is clear that $s(0,0) = \mathcal{S}(E_{tr}(f), E_{rot}(f), E_{vib}(f))$ since the relaxation energies reduce to the internal energies of f for such values of θ and η. Consequently, inequality (36) reduces to

$$s(0,0) \leq s(\theta,\eta). \tag{37}$$

The idea is now to decompose inequality (37) into two embedded inequalities

$$s(0,0) \leq s(\theta,0) \leq s(\theta,\eta). \tag{38}$$

We start with the second inequality and consider the variation of s with respect to η. Elementary calculus shows that

$$\begin{aligned}\frac{\partial s}{\partial \eta}(\theta,\eta) = {} & \frac{1}{T_{tr}^{rel}}\left(e_{tr}(T_{eq}) - \left(1-\frac{\delta\theta}{3+\delta}\right)E_{tr}(f) - \frac{3\theta}{3+\delta}E_{rot}(f)\right) \\ & + \frac{1}{T_{rot}^{rel}}\left(e_{rot}(T_{eq}) - \left(1-\frac{3\theta}{3+\delta}\right)E_{rot}(f) - \frac{\delta\theta}{3+\delta}E_{tr}(f)\right) \\ & + \frac{1}{T_{vib}^{rel}}\left(e_{vib}(T_{eq}) - E_{vib}(f)\right),\end{aligned} \tag{39}$$

and

$$\begin{aligned}\frac{\partial^2 s}{\partial \eta^2}(\theta,\eta) = {} & \partial_{1,1}\mathcal{S}(e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel})\left(e_{tr}(T_{eq}) - \left(1-\frac{\delta\theta}{3+\delta}\right)E_{tr}(f) - \frac{3\theta}{3+\delta}E_{rot}(f)\right)^2 \\ & + \partial_{2,2}\mathcal{S}(e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel})\left(e_{rot}(T_{eq}) - \left(1-\frac{3\theta}{3+\delta}\right)E_{rot}(f) - \frac{\delta\theta}{3+\delta}E_{tr}(f)\right)^2 \\ & + \partial_{3,3}\mathcal{S}(e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel})\left(e_{vib}(T_{eq}) - E_{vib}(f)\right)^2,\end{aligned}$$

and the reader is referred to appendix C for the computation of the partial derivatives of $\mathcal{S}$. The previous relation shows that s is a concave function of η. Moreover, note that for $\eta = 1$, relation (28) shows that all the relaxation energies are equal to the equilibrium energy, and hence all the relaxation temperatures are equal to T_{eq}. When this is used into (39), we find that $\frac{\partial s}{\partial \eta}(\theta,1) = 0$. With the concavity property, this proves that s is an increasing function of η on the interval $[0,1]$, and this proves the second inequality of (38).

For the first inequality of (38), we set η to 0, and we study the variation of $s(\theta,0)$ with respect to θ. Again, elementary calculus shows that $\frac{\partial^2 s}{\partial \theta^2}(\theta,0) \leq 0$, and hence $s(\theta,0)$ is a concave function of θ. Moreover, we find

$$\frac{\partial s}{\partial \theta}(\theta,0) = -\frac{3\delta}{2(3+\delta)}R(T_{tr} - T_{rot})\left(\frac{1}{(1-\theta)T_{tr} + \theta T_{tr,rot}} - \frac{1}{(1-\theta)T_{rot} + \theta T_{tr,rot}}\right), \tag{40}$$

and hence $\frac{\partial s}{\partial \theta}(1,0) = 0$, which implies that $s(\theta,0)$ is a non decreasing function of θ. Consequently, this gives the first inequality of (38) which concludes the proof of (36), and hence of (32), and the proof of the H-theorem is now complete.

$\square$

Proof of property 4. At equilibrium $f = \mathcal{G}[f]$ and hence $\Theta = \Pi$, $E_{rot}(f) = e_{rot}^{rel}$, and $E_{vib}(f) = e_{vib}^{rel}$. Then it is easy to see that relations (22)–(23) imply $T_{tr} = T_{rot} = T_{vib} = T_{tr,rot} = T_{rot}^{rel} = T_{vib}^{rel} = T_{eq}$ and then $\Theta = RT_{eq}I$. Consequently, $\mathcal{G}[f] = \mathcal{M}[f]$ and then $f = \mathcal{M}[f]$. □

5 Relaxation phenomena

In this section, we solve the local relaxation equations for energies, pressure tensor, and heat flux. This give us the relations between parameters η, θ, and ν of our model and the vibrational and rotation collision numbers Z_{vib}, Z_{rot}, and the Prandtl number.

5.1 Relaxation rates of translational, rotational and vibrational energies

The energy of translation, rotation and vibration are transferred from one mode to another one during inter-molecular collisions. These transfers are described by local relaxations obtained as moments of our ES-BGK model (in a space homogeneous case). Indeed, our model (18)–(20) is multiplied by $\frac{1}{2}|v-u|^2$, ε, iRT_0, and integrated w.r.t v, ε, and i, and we use closure relations (28) to find

$$\frac{d}{dt}\begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} = \frac{\eta}{\tau}\begin{pmatrix} e_{tr}(T_{eq}) - E_{tr}(f) \\ e_{rot}(T_{eq}) - E_{rot}(f) \\ e_{vib}(T_{eq}) - E_{vib}(f) \end{pmatrix} + \frac{1-\eta}{\tau}\begin{pmatrix} -\frac{\delta\theta}{3+\delta} & \frac{3\theta}{3+\delta} & 0 \\ \frac{\delta\theta}{3+\delta} & -\frac{3\theta}{3+\delta} & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} \tag{41}$$

The last equation has to be consistent with the Landau-Teller relaxation equation that describes the relaxation of the macroscopic energy of vibration to equilibrium, at a relaxation rate $\tau_{vib} = \tau Z_{vib}$. The second equation has to be consistent with the Jeans relaxation equation, which plays the same role for rotational energy, at the rate $\tau_{rot} = \tau Z_{rot}$. Moreover, this equation should also be consistent with the fast relaxation of T_{tr} and T_{rot} towards $T_{tr,rot}$ (see section 3.4).

Now we assume parameters τ, η, and θ are constant, and we solve these equations to find the relaxation times of this system.

The third equation of (41) directly shows that $E_{vib}(f)$ relaxes to its equilibrium value with time scale τ/η. This relaxation time is indeed $\tau_{vib} = \tau Z_{vib}$ if η is such that

$$Z_{vib} = \frac{1}{\eta}, \tag{42}$$

that is to say $\eta = 1/Z_{vib}$.

Since the equations for $E_{tr}(f)$ and $E_{rot}(f)$ are coupled, their relaxation to equilibrium involve two time scales. Instead of solving these equations separately, we find it more relevant to derive the relaxation of $T_{tr,rot}$ to T_{eq}, that should be with time scale τ_{vib}, and of T_{tr} and T_{rot} to $T_{tr,rot}$, that should hold with time scale $\tau_{rot} = \tau Z_{rot}$. By combining the first two equations of (41), we get

$$\frac{d}{dt}T_{tr,rot} = \frac{\eta}{\tau}(T_{eq} - T_{tr,rot}), \tag{43}$$

which shows that $T_{tr,rot}$ indeed relaxes to T_{eq} with time scale $\tau/\eta = \tau_{vib}$ if $\eta = 1/Z_{vib}$, which is coherent with the relaxation found for E_{vib}.

Then we use (43) and the first equation of (41) to find

$$\frac{d}{dt}(T_{tr} - T_{tr,rot}) = -\frac{1-(1-\eta)(1-\theta)}{\tau}(T_{tr} - T_{tr,rot}), \tag{44}$$

which shows that T_{tr} relaxes to $T_{tr,rot}$ with relaxation time $\tau/(1-(1-\eta)(1-\theta)) = \tau_{rot}$ if θ is such that

$$Z_{rot} = \frac{1}{1-(1-\eta)(1-\theta)}, \tag{45}$$

which gives $\theta = (Z_{vib} - Z_{rot})/((Z_{vib}-1)Z_{rot})$. With the same analysis, we also find that T_{rot} relaxes to $T_{tr,rot}$ with the same relaxation time.

Since we want the rotational and vibrational collision numbers such that $1 < Z_{rot} < Z_{vib}$ (see section 3.4), then the previous definition gives the restriction $0 \leq \theta < 1$ and $0 \leq \eta < 1$. Case $\theta = 0$ gives $Z_{rot} = Z_{vib}$ which means that vibration modes relax as fast as rotation modes.

Note that even if the relations on Z_{rot} and Z_{vib} have been obtained under the assumption of constant parameters η, θ, and τ, they will be used to define our model in a general case. More precisely, once we know the (temperature) laws for Z_{rot} and Z_{vib}, then parameters θ and η are defined so that (42) and (45) hold.

5.2 Relaxation of pressure tensor and heat flux

Relaxation equations for pressure tensor and heat flux are obtained by multiplying the kinetic equation (18) by $(v-u)\otimes(v-u)$ and $(\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0)(v-u)$ and integrating w.r.t v,ε and i to get, in the space homogeneous case :

$$\frac{d}{dt}\Theta = \frac{1}{\tau}((1-\eta)(1-\theta)(1-\nu)(RT_{tr}I - \Theta) + (1-\eta)\theta(RT_{tr,rot}I - \Theta) + \eta(RT_{eq}I - \Theta)), \tag{46}$$

$$\frac{d}{dt}q = -\frac{1}{\tau}q. \tag{47}$$

Since $\mathrm{Tr}(\Theta) = 3RT_{tr}$, taking the trace of (46) gives

$$\frac{d}{dt}RT_{tr} = \frac{1}{\tau}\left((1-\eta)\theta(RT_{tr,rot} - RT_{tr}) + \eta(RT_{eq} - RT_{tr})\right).$$

This equation is subtracted to (46) to get

$$\frac{d}{dt}(\Theta - RT_{tr}I) = -\frac{1}{\tau}(1-(1-\theta)(1-\eta)\nu)(\Theta - RT_{tr}I).$$

This shows that for large times, tensor Θ tends to $RT_{tr}I$, while the heat flux tends to 0. More precisely, for ν, θ, η and τ constant, we have the analytic solutions:

$$\Theta(t) - RT_{tr}(t)I = (\Theta(0) - RT_{tr}(0)I)\exp\left(-(1-(1-\eta)(1-\theta)\nu)\frac{t}{\tau}\right),$$

$$q(t) = q(0)\exp\left(-\frac{t}{\tau}\right).$$

The Prandtl number can be viewed as the ratio between the relaxation times of these two processes, and we get:

$$\mathrm{Pr} = \frac{1}{1-(1-\eta)(1-\theta)\nu}.$$

Incidentally, this value will be checked numerically in section 8 by computing the ratio

$$\frac{\log(|q_i(t)/q_i(0)|)}{\log(|(\Theta_{ii}(t) - RT_{tr}(t))/(\Theta_{ii}(0) - RT_{tr}(0))|)} \tag{48}$$

for $i = 1, 2, 3$.

6 Chapman-Enskog analysis

The conservation laws are obtained by multiplying (18) by the vector 1, v, and $\frac{1}{2}|v|^2+\varepsilon+iRT_0$ and then by integrating we get:

$$\begin{aligned}&\partial_t\rho+\nabla\cdot(\rho u)=0,\\&\partial_t(\rho u)+\nabla\cdot(\rho u\otimes u)+\nabla\cdot P(f)=0,\\&\partial_t\mathcal{E}+\nabla\cdot(\mathcal{E}u)+\nabla\cdot(P(f)u)+\nabla\cdot q(f)=0,\end{aligned}\tag{49}$$

where $\mathcal{E}=\langle(\frac{1}{2}|v|^2+\varepsilon+iRT_0)f\rangle_{v,\varepsilon,i}=\frac{1}{2}\rho|u|^2+\rho E(f)$ is the total energy density, while the pressure tensor $P(f)$ and the heat flux $q(f)$ have been defined by (11).

If we have some characteristic values of length, time, velocity, density, and temperature, our ES-BGK model (18)–(20) can be non-dimensionalized. This equation reads

$$\partial_t f+v\cdot\nabla f=\frac{1}{\mathrm{Kn}\,\tau}(\mathcal{G}[f]-f),\tag{50}$$

where Kn is the Knudsen number which is the ratio between the mean free path and a macroscopic length scale. For simplicity, here we use the same notations for the non-dimensional variables as for the dimensional ones. Note that we assume here that the three relaxation times have the same asymptotic order of magnitude with respect to Kn (even if their values can be very different).

The Chapman-Enskog analysis consists in approximating the pressure tensor and the heat flux at zero and first order with respect to the Knudsen number, which gives compressible Euler equations and compressible Navier-Stokes equations, respectively.

6.1 Euler asymptotics

At equilibrium, f is equal to the equilibrium Maxwellian distribution. Even in non-equilibrium, when Kn is very small the gas is very close to its equilibrium state: indeed, (50) induces

$$f=\mathcal{G}[f]+O(\mathrm{Kn}),\tag{51}$$

if in addition f and its time and space derivatives are $O(1)$ w.r.t Kn (we exclude any initial layer and assume that the gradients lengths are larger than the mean free path). Then by using the same argument as in the proof of proposition 4.3 and the regularity of energy functions, we get

$$P(f)=pI+O(\mathrm{Kn}),\qquad q(f)=O(\mathrm{Kn}),\tag{52}$$

where we denote by $p=\rho RT_{eq}$ the pressure at equilibrium, and we also get

$$T_{tr}=T_{eq}+O(\mathrm{Kn}),\ T_{rot}=T_{eq}+O(\mathrm{Kn}),\ T_{vib}=T_{eq}+O(\mathrm{Kn}),\ T_{tr,rot}=T_{eq}+O(\mathrm{Kn}).\tag{53}$$

These relations show that (51) finally gives

$$f=\mathcal{M}[f]+O(\mathrm{Kn}).\tag{54}$$

Relations (52) are then used into conservation laws (49) to get the compressible Euler equations with first order reminder:

$$\begin{aligned}&\partial_t\rho+\nabla\cdot(\rho u)=0,\\&\partial_t(\rho u)+\nabla\cdot(\rho u\otimes u)+\nabla p=O(\mathrm{Kn}),\\&\partial_t\mathcal{E}+\nabla\cdot((\mathcal{E}+p)u)=O(\mathrm{Kn}).\end{aligned}\tag{55}$$

The non-conservative form of these equations is

$$
\begin{aligned}
&\partial_t \rho + u \cdot \nabla \rho + \rho \nabla \cdot u = 0, \\
&\partial_t u + (u \cdot \nabla) u + \frac{1}{\rho} \nabla p = O(\mathrm{Kn}), \\
&\partial_t T_{eq} + u \cdot \nabla T_{eq} + T_{eq} C \nabla \cdot u = O(\mathrm{Kn}),
\end{aligned}
\tag{56}
$$

with $C = \frac{R}{c_v(T_{eq})}$, and $c_v(T_{eq}) = \frac{\partial e(T_{eq})}{\partial T_{eq}}$ is the heat capacity at constant volume of the gas, which is temperature dependent here due to vibration modes (see equations (14) and (15)).

The Navier-Stokes equations are obtained by looking for a first order expansion of f. In the following section, we first derive useful first order expansions of energies and tensor Π that are used in our model.

6.2 Energy and tensor relations at first order

First, (18) is multiplied by $\frac{1}{2}|v|^2$, ε, and iRT_0 and integrated w.r.t v, ε, and i. We use relations (52), (56), and (28) to get

$$
\partial_t \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} + u \cdot \nabla \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} + \begin{pmatrix} RT_{eq} \nabla \cdot u \\ 0 \\ 0 \end{pmatrix} + O(\mathrm{Kn}) = \frac{\eta}{\mathrm{Kn}\tau} \begin{pmatrix} e_{tr}(T_{eq}) \\ e_{rot}(T_{eq}) \\ e_{vib}(T_{eq}) \end{pmatrix} + \frac{1}{\mathrm{Kn}\tau} D \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix}
\tag{57}
$$

with

$$
D = \begin{pmatrix} -\frac{(1-\eta)\delta\theta}{3+\delta} - \eta & \frac{3(1-\eta)\theta}{3+\delta} & 0 \\ \frac{\delta(1-\eta)\theta}{3+\delta} & -\frac{3(1-\eta)\theta}{3+\delta} - \eta & 0 \\ 0 & 0 & -\eta \end{pmatrix}.
\tag{58}
$$

Note that the eigenvalues of D are $-\eta$, $-\eta$, and $-\eta - (1-\eta)\theta$ so that (57) is indeed a relaxation process, and also that D is invertible.

Moreover, from (12), we deduce the differential relation $dE_\alpha(f) = e'_\alpha(T_\alpha) dT_\alpha$, for $\alpha = tr, rot, vib$. Then, using (53) and the last equation of (56), we get

$$
\partial_t \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} + u \cdot \nabla \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} = - \begin{pmatrix} e'_{tr}(T_{eq}) C T_{eq} \\ e'_{rot}(T_{eq}) C T_{eq} \\ e'_{vib}(T_{eq}) C T_{eq} \end{pmatrix} \nabla \cdot u + O(\mathrm{Kn}).
\tag{59}
$$

Finally, relations (57) and (59) give the following system

$$
\eta \begin{pmatrix} e_{tr}(T_{eq}) \\ e_{rot}(T_{eq}) \\ e_{vib}(T_{eq}) \end{pmatrix} + D \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix} = -\mathrm{Kn}\tau \begin{pmatrix} e'_{tr}(T_{eq}) C T_{eq} - RT_{eq} \\ e'_{rot}(T_{eq}) C T_{eq} \\ e'_{vib}(T_{eq}) C T_{eq} \end{pmatrix} \nabla \cdot u + O(\mathrm{Kn}^2)
\tag{60}
$$

that has to be solved to get first order expansion of energies as functions of the equilibrium temperature and of the divergence of u. We only write here the relations that will be useful to derive the Navier-Stokes hydrodynamics:

$$
\begin{aligned}
E_{tr}(f) &= e_{tr}(T_{eq}) + \frac{\mathrm{Kn}\tau}{\eta} \left(\frac{3}{2} C - \frac{1}{\eta + (1-\eta)\theta} \left(\eta + \frac{3(1-\eta)\theta}{3+\delta} \right) \right) RT_{eq} \nabla \cdot u + O(\mathrm{Kn}^2), \\
E_{tr,rot}(f) &= e_{tr,rot}(T_{eq}) + \frac{\mathrm{Kn}\tau}{\eta} \left(\frac{3+\delta}{2} C - 1 \right) RT_{eq} \nabla \cdot u + O(\mathrm{Kn}^2).
\end{aligned}
$$

Similar relations are readily derived for temperatures T_{tr} and $T_{tr,rot}$ by using (12) and (16), and therefore, (22) can now be used to derive the first order expansion of tensor Π:

$$\begin{aligned}\Pi =&(1-(1-\eta)(1-\theta)\nu)RT_{eq}I + (1-\eta)(1-\theta)\nu\Theta \\ &+ (1-\eta)\theta\frac{\mathrm{Kn}\tau}{\eta}\left(C - \frac{2}{3+\delta}\right)RT_{eq}\nabla\cdot uI \\ &+ (1-\eta)(1-\theta)(1-\nu)\frac{\mathrm{Kn}\tau}{\eta}\left(C - \frac{1}{\eta+(1-\eta)\theta)}\frac{2}{3}\left(\eta + \frac{3(1-\eta)\theta}{3+\delta}\right)\right)IRT_{eq}\nabla\cdot uI \\ &+ O(\mathrm{Kn}^2).\end{aligned} \tag{61}$$

Finally, we find it convenient to define the following three quantities

$$\gamma_{tr} = \frac{5}{3}, \quad \gamma_{tr,rot} = \frac{5+\delta}{3+\delta}, \quad \gamma = 1 + \frac{R}{c_v(T_{eq})} \tag{62}$$

that are nothing but heat capacity ratios for a monoatomic gas, a polyatomic gas with rotational modes only, and the present gas with rotational and vibrational modes, respectively. Then Π can be rewritten as

$$\begin{aligned}\Pi =&(1-(1-\eta)(1-\theta)\nu)RT_{eq}I + (1-\eta)(1-\theta)\nu\Theta \\ &-\left(\frac{(1-\eta)(1-\theta)(1-\nu)}{1-(1-\eta)(1-\theta)}(\gamma_{tr}-\gamma_{tr,rot}) + \frac{(1-\eta)(1-(1-\theta)\nu)}{\eta}(\gamma_{tr,rot}-\gamma)\right)\mathrm{Kn}\tau RT_{eq}\nabla\cdot uI \\ &+ O(\mathrm{Kn}^2).\end{aligned} \tag{63}$$

6.3 Navier-Stokes limit

We first state our main result.

Proposition 6.1. *The moments of f, solution of the ES-BGK model* (18)*, satisfy the compressible Navier-Stokes equations up to $O(\mathrm{Kn}^2)$:*

$$\begin{aligned}&\partial_t\rho + \nabla\cdot(\rho u) = O(\mathrm{Kn}^2), \\ &\partial_t(\rho u) + \nabla\cdot(\rho u\otimes u) + \nabla p = \nabla\cdot\sigma + O(\mathrm{Kn}^2), \\ &\partial_t\mathcal{E} + \nabla\cdot(\mathcal{E}+p)u = -\nabla\cdot q + \nabla\cdot(\sigma u) + O(\mathrm{Kn}^2),\end{aligned}$$

where, in dimensional form, the viscous stress tensor and the heat flux are given by

$$\sigma = \mu\left(\nabla u + (\nabla u)^T - \frac{2}{3}\nabla\cdot uI\right) + \zeta\nabla\cdot uI, \quad q = -\kappa\nabla T,$$

the viscosity and heat transfer coefficients are

$$\mu = \frac{\tau p}{1-(1-\eta)(1-\theta)\nu}, \qquad \kappa = (1-(1-\eta)(1-\theta)\nu)\mu c_p,$$

the volume viscosity coefficient is $\zeta = \mu\left(\frac{2}{3}-\alpha\right)$, with

$$\alpha = (\gamma-1) - \frac{(1-\eta)(1-\theta)(1-\nu)}{1-(1-\eta)(1-\theta)}(\gamma_{tr}-\gamma_{tr,rot}) - \frac{(1-\eta)(1-(1-\theta)\nu)}{\eta}(\gamma_{tr,rot}-\gamma),$$

and the Prandtl number is

$$\mathrm{Pr} = \frac{\mu c_p}{\kappa} = \frac{1}{1-(1-\eta)(1-\theta)\nu},$$

while $c_p = \frac{\partial h}{\partial T_{eq}}$ is the heat capacity at constant pressure, where $h = e(T_{eq}) + p/\rho$ is the enthalpy. The heat capacity ratios γ, γ_{tr}, $\gamma_{tr,rot}$ are defined in (62).

Proof. First, (50) and (54) give

$$f = \mathcal{G}[f] - \tau \mathrm{Kn}(\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]) + O(\mathrm{Kn}^2) \tag{64}$$

By linearity, the pressure tensor and the heat flux are

$$\begin{aligned} P(f) &= P(\mathcal{G}[f]) - \tau \mathrm{Kn}\, P(\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]) + O(\mathrm{Kn}^2) \\ q(f) &= q(\mathcal{G}[f]) - \tau \mathrm{Kn}\, q(\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]) + O(\mathrm{Kn}^2) \end{aligned} \tag{65}$$

We first deal with the expansion of the pressure tensor. For the first term, note that (21) and (22) imply $P(\mathcal{G}[f]) = \rho\Pi$. Therefore the expression above reads

$$P(f) = \rho\Pi - \tau \mathrm{Kn}\, \langle (v-u) \otimes (v-u)(\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]) \rangle_{v,\varepsilon,i} + O(\mathrm{Kn}^2). \tag{66}$$

For the second term, tedious but standard calculations show that time derivatives can be written as functions of the space derivatives only by using Euler equations (55), and then suitable integral formula give

$$P(f) = \rho\Pi - \tau \mathrm{Kn} \rho R T_{eq} (\nabla u + (\nabla u)^T - C \nabla \cdot u I) + O(\mathrm{Kn}^2), \tag{67}$$

see some details in appendix D and A. Then combining this equation with (63) one finally gets

$$P(f) = \rho R T_{eq} I - \mathrm{Kn} \tau \rho R T_{eq} \frac{1}{1-(1-\eta)(1-\theta)\nu} (\nabla u + (\nabla u)^T - \alpha \nabla \cdot u I) + O(\mathrm{Kn}^2),$$

where α takes the value given in the proposition. Now we use the equilibrium pressure $p = \rho R T_{eq}$ and we define the viscosity coefficient $\mu = \tau p/(1-(1-\eta)(1-\theta)\nu)$ to get the value of the viscous stress tensor given in the proposition.

For the heat flux, a simple parity argument shows that $q(\mathcal{G}[f]) = 0$, so that

$$q(f) = -\tau \mathrm{Kn} \left\langle (\frac{1}{2}|v-u|^2 + \varepsilon + iRT_0)(v-u)(\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]) \right\rangle_{v,\varepsilon,i} + O(\mathrm{Kn}^2).$$

Using the same tools as for the pressure tensor, we find

$$\begin{aligned} q(f) &= -\tau \mathrm{Kn} p \left(\frac{5}{2} R + \frac{\delta}{2} R + \frac{\partial}{\partial T_{eq}} (\frac{\delta_v(T_{eq})}{2} R T_{eq}) \right) \nabla T_{eq} + O(\mathrm{Kn}^2) \\ &= -\tau \mathrm{Kn} p \frac{\partial}{\partial T_{eq}} \left(\frac{5 + \delta + \delta_v(T_{eq})}{2} R T_{eq} \right) \nabla T_{eq} + O(\mathrm{Kn}^2). \end{aligned}$$

Now we notice that $\frac{5+\delta+\delta_v(T_{eq})}{2} R T_{eq} = e(T_{eq}) + R T_{eq} = e(T_{eq}) + p/\rho = h(T_{eq})$. Consequently,

$$q(f) = -\tau \mathrm{Kn} p \frac{\partial h}{\partial T_{eq}} \nabla T_{eq} + O(\mathrm{Kn}^2) = -\mathrm{Kn} \tau p c_p \nabla T_{eq} + O(\mathrm{Kn}^2),$$

which gives the Fourier law with the value of the heat transfer coefficient $\kappa = \tau p c_p$ in dimensional variables. Then using the value of μ found above leads to the value of κ given in the proposition.

Finally, note that with this analysis, if the Prandtl number is defined as $\mathrm{Pr} = \mu c_p/\kappa$, then we find $\mathrm{Pr} = \frac{1}{1-(1-\eta)(1-\theta)\nu}$, which is the same result as found in section 5.2. □

Remark 6.1. Note that by writing ν, η and θ as functions of the Prandtl number and of Z_{rot} and Z_{vib} (see section 5.1), the volume viscosity can be simply written

$$\zeta = \mu \left(\frac{Z_{rot}}{\mathrm{Pr}} (\gamma_{tr} - \gamma_{tr,rot}) + \frac{Z_{vib}}{\mathrm{Pr}} (\gamma_{tr,rot} - \gamma) \right)$$

The volume viscosity appears to be driven by relaxation processes due to rotations and vibrations of molecules characterized by Z_{rot} and Z_{vib}. It can also be written as

$$\zeta = pR\left(\tau_{rot}\frac{c_v^{rot}}{c_v^{tr}(c_v^{tr}+c_v^{rot})}+\tau_{vib}\frac{c_v^{vib}}{c_v(c_v^{tr}+c_v^{rot})}\right)$$

where c_v^{tr}, c_v^{rot}, and c_v^{vib} are the specific heat of translation, rotation, and vibration energy, respectively.

It seems that this expression has some similarities with the volume viscosity obtained in a Boltzmann equation with two fast and slow internal energy modes by Bruno and Giovangigli in [29]. However, further studies are necessary to correctly compare these results, since the definition of the characteristic times of vibration and rotation are not exactly the same.

Remark 6.2. We can also obtain the following first order expansion of f with respect to the Knudsen number (see details in appendix D and E):

$$f = \mathcal{M}[f] - \tau\mathrm{Kn}\mathcal{M}[f]\left(A(V,J,K)\cdot\frac{\nabla(RT_{eq})}{\sqrt{RT_{eq}}}+B(V,J,K):\nabla u\right)+O(\mathrm{Kn}^2), \tag{68}$$

with

$$\begin{aligned}
&V=\frac{v-u}{\sqrt{RT_{eq}}},\quad J=\frac{\varepsilon}{RT_{eq}},\quad K=\frac{iT_0}{T_{eq}},\\
&A=A_{tr}+A_{rot}+A_{vib},\quad B=B_{tr}+B_{rot}+B_{vib},\\
&A_{tr}(V)=\left(\frac{|V|^2}{2}-\frac{5}{2}\right)V,\quad B_{tr}(V)=\mathrm{Pr}\left(V\otimes V-\left(\left(\frac{|V|^2}{2}-\frac{3}{2}\right)\alpha+1\right)I\right),\\
&A_{rot}(V,J)=\left(J-\frac{\delta}{2}\right)V,\quad B_{rot}(V,J)=-\left(Z_{vib}C-\frac{2}{3+\delta}(Z_{vib}-Z_{rot})\right)\left(J-\frac{\delta}{2}\right)I,\\
&A_{vib}(V,K)=\left(K-\frac{\delta_v(T_{eq})}{2}\right)V,\quad B_{vib}(V,K)=-Z_{vib}C\left(K-\frac{\delta_v(T_{eq})}{2}\right)I.
\end{aligned}$$

7 Reduced ES-BGK model

7.1 The reduced distribution technique

For numerical simulations with a deterministic solver, our ES-BGK model is much too expensive, since the distribution f depends on many variables: time $t\in\mathbb{R}$, position $x\in\mathbb{R}^3$, velocity $v\in\mathbb{R}^3$, rotational energy $\varepsilon\in\mathbb{R}^+$ and discrete levels of the vibrational energy $i\in\mathbb{N}$. For aerodynamic problems, it is generally sufficient to compute the macroscopic velocity and temperatures fields: a reduced distribution technique [30] (by integration w.r.t rotational and vibrational energy) permits to drastically reduce the computational cost, without any approximation (as long as boundary conditions are compatible with this reduction, like usual equilibrium inflow boundary conditions and Maxwell reflection at a solid wall, for instance) . We define the three marginal distributions

$$\begin{pmatrix}F(t,x,v)\\G(t,x,v)\\H(t,x,v)\end{pmatrix}=\sum_{i=0}^{+\infty}\int_{\mathbb{R}}\begin{pmatrix}1\\ \varepsilon\\ iRT_0\end{pmatrix}f(t,x,v,\varepsilon,i)\,d\varepsilon.$$

The macroscopic quantities defined by (8)–(11) can now be computed through F, G and H only by

$$
\begin{aligned}
&\rho = \langle F\rangle_v\,, \quad \rho u = \langle vF\rangle_v\,,\\
&\rho E_{tr}(f) = \left\langle \frac{1}{2}|v|^2 F\right\rangle_v\,, \quad \rho E_{rot}(f) = \langle G\rangle_v\,, \quad \rho E_{vib}(f) = \langle H\rangle_v\,,\\
&\rho\Theta = \left\langle \frac{1}{2}(v-u)\otimes(v-u)F\right\rangle_v\,, \quad q = \left\langle (\frac{1}{2}|v-u|^2 F + G + H)(v-u)\right\rangle_v\,,
\end{aligned}
\tag{69}
$$

where $\langle . \rangle_v$ denotes integrals with respect to v only.

The reduced ES-BGK is obtained by multiplying our kinetic model (18)-(20) by the vector $(1, \varepsilon, iRT_0)^T$ and by summing and integrating w.r.t to i and ε, respectively. We get:

$$
\partial_t \mathbf{F} + v\cdot\nabla\mathbf{F} = \frac{1}{\tau}(\boldsymbol{\mathcal{G}}[\mathbf{F}] - \mathbf{F}), \tag{70}
$$

where $\mathbf{F} = (F, G, H)$ and $\boldsymbol{\mathcal{G}}[\mathbf{F}] = (\mathcal{G}_{tr}[f], e^{rel}_{rot}\mathcal{G}_{tr}[f], e^{rel}_{vib}\mathcal{G}_{tr}[f])$.

7.2 Reduced entropy

In this section, we again use the change of variable $\varepsilon = I^{2/\delta}$. To prove the H-theorem for our reduced model, it is convenient to view it as an entropic moment closure (w.r.t variables I and i), see for instance [31, 32, 33]. Then we define $g_{\mathbf{F}}$ such that $\mathbb{H}(g_{\mathbf{F}})$ is the minimum of $\mathbb{H}$ on the set $\chi_{\mathbf{F}} = \{\phi \geq 0 \text{ such that } \left\langle (1, I^{\frac{2}{\delta}}, iRT_0)\phi\right\rangle_{I,i} = \mathbf{F}\}$, and we set $\mathcal{H}(\mathbf{F}) = \mathbb{H}(g_{\mathbf{F}})$. It is now possible to prove that $\mathcal{H}(\mathbf{F})$ is an entropy for our reduced system.

Proposition 7.1 (Reduced entropy)**.** *An explicit form of $\mathcal{H}$ is given by $\mathcal{H}(\mathbf{F}) = \langle h(\mathbf{F})\rangle_v$, where h is the strictly convex function defined by*

$$
\begin{aligned}
h(\mathbf{F}) = &F\left[\left(1+\frac{\delta}{2}\right)\left(\log\left(\frac{F}{G^{\frac{\delta}{2+\delta}}}\right) - 1\right) + \log\left(\frac{RT_0F}{RT_0F + H}\right) + \frac{\delta}{2}\log\frac{\delta}{2} + \log\Lambda(\delta)\right]\\
&+ \frac{H}{RT_0}\log\left(\frac{H}{RT_0F + H}\right).
\end{aligned}
\tag{71}
$$

Proof. First, we compute $g_{\mathbf{F}}$ by solving the minimization problem $\mathbb{H}(g_{\mathbf{F}}) = \min_{\chi_{\mathbf{F}}}\mathbb{H}$. Since $\chi_{\mathbf{F}}$ is convex, we use a Lagrange multiplier method to find the minimum of the functional $\mathcal{L}$ defined as follows:

$$
\mathcal{L}(\phi,\alpha,\beta,\eta) = \langle \phi\log\phi - \phi\rangle_{I,i} + \alpha\left(\langle\phi\rangle_{I,i} - F\right) + \beta\left(\left\langle I^{2/\delta}\phi\right\rangle_{I,i} - G\right) + \eta\left(\langle iRT_0\phi\rangle_{I,i} - H\right),
$$

where the Lagrange multipliers α, β and η are functions of v. The minimum satisfies $\dfrac{\partial\mathcal{L}}{\partial\phi}(g_{\mathbf{F}},\alpha,\beta,\eta) = 0$, which leads to

$$
g_{\mathbf{F}} = \exp(-\alpha - \beta I^{2/\delta} - \eta iRT_0). \tag{72}
$$

With the linear constraints $\left\langle (1, I^{2/\delta}, RT_0 i)g_{\mathbf{F}}\right\rangle_{I,i} = (F, G, H)$, we find explicit values for α, β, and η as functions of F, G, and H. Consequently, by using $\mathcal{H}(\mathbf{F}) = \mathbb{H}(g_{\mathbf{F}})$ and these values of α, β, and η, we find (71). □

Remark 7.1. The convexity property of h could also be proved without any explicit computation: indeed, it can be viewed as the Legendre transform of $h^*(\alpha,\beta,\eta) = \left\langle \exp(-\alpha - \beta I^{2/\delta} - \eta iRT_0)\right\rangle_v$ (where α, β, and η are such that $\mathbf{F} = \left\langle (1, I^{2/\delta}, iRT_0)\exp(-\alpha - \beta I^{2/\delta} - \eta iRT_0)\right\rangle_{I,i}$), which is clearly strictly convex (see details for a similar argument in [31]).

Proposition 7.2 (H-theorem)**.** *The reduced ES-BGK system* (70) *satisfies the following local entropy dissipation law*

$$\partial_t \mathcal{H}(\mathbf{F}) + \nabla \cdot \langle v h(\mathbf{F}) \rangle_v = \left\langle D_{\mathbf{F}} h(\mathbf{F}) (\frac{1}{\tau} \boldsymbol{\mathcal{G}}[\mathbf{F}] - \mathbf{F}) \right\rangle_v \leq 0, \tag{73}$$

and the equilibrium is reached (the right-hand side of (70) *is zero) if, and only if,*

$$\mathbf{F} = (\mathcal{M}_{tr}[f], e_{rot}(T_{eq})\mathcal{M}_{tr}[f], e_{vib}(T_{eq})\mathcal{M}_{tr}[f]),$$

where $\mathcal{M}_{tr}[f]$ is the Maxwellian for translation d.o.f (see section 4.1).

Proof. The equality in (73) is obtained with elementary calculus. Since h is convex, the right-hand side of this equality satisfies

$$\left\langle D_{\mathbf{F}} h(\mathbf{F}) (\frac{1}{\tau} \boldsymbol{\mathcal{G}}[\mathbf{F}] - \mathbf{F}) \right\rangle_v \leq \langle h(\boldsymbol{\mathcal{G}}[\mathbf{F}]) - h(\mathbf{F}) \rangle_v = \mathcal{H}(\boldsymbol{\mathcal{G}}[\mathbf{F}]) - \mathcal{H}(\mathbf{F})$$

Therefore, the H-theorem is proved if we can prove that this entropy difference is non-negative.

First, we prove that $\mathcal{H}(\boldsymbol{\mathcal{G}}[\mathbf{F}]) \leq \mathbb{H}(\mathcal{G}[g])$. Indeed, $\mathcal{G}[g]$ is clearly in $\chi_{\boldsymbol{\mathcal{G}}[\mathbf{F}]}$, and since $\mathcal{H}(\boldsymbol{\mathcal{G}}[\mathbf{F}])$ is the minimum value of $\mathbb{H}$ on this set, we have $\mathcal{H}(\boldsymbol{\mathcal{G}}[\mathbf{F}]) \leq \mathbb{H}(\mathcal{G}[g])$. It is easy to prove that we have in fact equality, but this is not necessary here.

Now it is sufficient to prove that $\mathbb{H}((\mathcal{G}[g])) \leq \mathcal{H}(\mathbf{F})$. First, remind that in the proof of Proposition 4.3 (step 2), we have obtained

$$\mathbb{H}((\mathcal{G}[g])) = S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel}) \leq S(\rho, u, \Theta, T_{rot}, T_{vib}).$$

Then we remind that $\mathcal{H}(\mathbf{F}) = \mathbb{H}(g_{\mathbf{F}})$, where $g_{\mathbf{F}}$ is in $\chi_{\mathbf{F}}$. Consequently, $g_{\mathbf{F}}$ has the same moments as g, and hence $S(\rho, u, \Theta, T_{rot}, T_{vib}) \leq \mathbb{H}(g_{\mathbf{F}}) = \mathcal{H}(\mathbf{F})$, which concludes the proof. □

Remark 7.2. The reduced entropy can be simplified by dropping out some terms that are proportional to F: if we set

$$\tilde{\mathcal{H}}(\mathbf{F}) = F \log \left(\frac{F}{G^{\frac{\delta}{2+\delta}}} \right) - F + F \log \left(\frac{RT_0 F}{RT_0 F + H} \right) + \frac{H}{RT_0} \log \left(\frac{H}{RT_0 F + H} \right),$$

then $\tilde{\mathcal{H}}$ is also strictly convex. The previous proof also leads to an entropy production term lower than $\tilde{\mathcal{H}}(\boldsymbol{\mathcal{G}}[\mathbf{F}]) - \tilde{\mathcal{H}}(\mathbf{F})$. This entropy difference is the same as that obtained with the original reduced entropy $\mathcal{H}$ up to an integral of $\boldsymbol{\mathcal{G}}[\mathbf{F}] - \mathbf{F}$ which is zero (mass conservation). This simplified reduced entropy is similar to that of [8, 33] with, in addition, the effects of vibrations ([15]).

8 Numerical test

In this section, we study the relaxation process to equilibrium in a space homogeneous polyatomic vibrating gas by using Monte Carlo simulations of the ES-BGK model presented in section 4. Our results will be used to confirm that the relaxation rates of translational, rotational, and vibrational degrees of freedom can indeed be obtained by adjusting the parameters θ and η. Moreover, we will also check that the correct Prandtl number can be obtained by adjusting the parameter ν.

In this space homogeneous case, the ES-BGK model reads

$$\partial_t f = \frac{1}{\tau}(\mathcal{G}[f] - f). \tag{74}$$

Note that by conservation property 4.1, the mass density, velocity, and equilibrium temperature, are constant in time here.

8.1 The Monte Carlo method

To observe the process of relaxation we enforce a non-equilibrium initial condition, for instance a gap between the mean of the velocities of the particles and the velocity of the gas: the model should relax velocities and internal energies towards equilibrium state. We use a large number N of numerical particles related to the real molecules by a distribution function associated to a constant numerical weight $\omega = 1/N$. We use an explicit Euler scheme for time discretization and get:

$$f^{n+1} = \left(1 - \frac{\Delta t}{\tau}\right) f^n + \frac{\Delta t}{\tau}\mathcal{G}[f^n], \tag{75}$$

with $\Delta t = t^{n+1} - t^n$ and we consider $\Delta t/\tau \leq 0.1$ to ensure stability [34]. Equation (75) models the effects of collisions on the distribution functions of velocities and energies: at time t^{n+1} the distribution function is a convex combination of the distribution function at time t^n and its corresponding local Gaussian distribution. This can be simulated with a Monte Carlo algorithm as follows: at each time step, for each particle, we decide if its velocity has to be modified by a collision (with a probability $\Delta t/\tau$). In such case, the components of its velocity v are modified by

$$v_k = u_k + A(B_1, B_2, B_3)^T, \quad e^k_{rot} = B_4, \quad e^k_{vib} = B_5, \tag{76}$$

where u is macroscopic velocity of the gas, B_1, B_2, B_3 are three random numbers generated from a standard normal law and the matrix A needs to satisfy the condition: $\Pi = AA^T$ (generally, A is given by the Cholesky decomposition due to its simplicity and its low computational cost). B_4 is generated through an exponential distribution depending on RT^{rel}_{rot} and B_5 through a Poisson distribution of parameter RT^{rel}_{vib}.

8.2 Numerical results

We consider $N = 10^7$ numerical particles of velocities initially distributed according to a Gaussian distribution of variance 500 and of mean 0 for the second and the third components and 50 for the first. The initial rotational energy is set to $1000\, r_1$ and the initial vibrational energy is set to $10\, r_2$ where the random numbers r_1 and r_2 follow an uniform law between 0 and 1. The parameters θ and η are defined by (26), so that collision numbers Z_{rot} and Z_{vib} are respectively equal to 5 and 20. Finally, we set ν according to (27) so that the Prandtl number is equal to 0.73, which is close to the tabulated value for air at $2000K$. These non-equilibrium initial conditions create energy exchanges between modes and a heat flux.

We first show in figure 1 that the temperature relaxes as expected (see section 3.4). First, the translational directional temperatures converge to the mean translational temperature T_{tr} at time τ. Then, at time 20τ, this temperature and the rotational temperature converge towards the translational-rotational temperature $T_{tr,rot}$. Finally, at time 100τ, $T_{tr,rot}$ and the vibrational temperature T_{vib} converge to the equilibrium temperature T_{eq}.

In figure 2, we show the distribution of velocities, rotational energy, and vibrational energy, obtained at steady state. This distributions are compared to the components of the Maxwellian distribution (19), and we observe a prefect agreement between them, which proves that the correct equilibrium is captured by the model.

Now we plot in figure 3 the temperature differences $T_{tr} - T_{tr,rot}$, $T_{rot} - T_{tr,rot}$, $T_{tr,rot} - T_{eq}$, and $T_{vib} - T_{eq}$. We observe that this functions converge exponentially, as expected (even if a numerical noise is observed for $t > 20\tau$ which corresponds to machine accuracy when the translational and the rotational temperatures are converged). Moreover, according to section 5.1, the slopes of these convergence curves can be used to compute Z_{rot} and Z_{vib}, a posteriori. We find $Z_{rot} = 4.878$ and $Z_{vib} = 19.61$, which is very close to the expected values.

Finally, we plot in figure 4 the evolution of the difference of the first directional temperature T_{11} and the mean translational temperature T_{tr}, as well as the evolution of the first component of the heat flux q_1. According to equation (48), it is possible to estimate the Prandtl number by evaluating the slopes of the of these quantities: we find 0.71, which is close to the input value 0.75.

9 Conclusion

In this paper, we have proposed an extension of the original polyatomic ES-BGK model to take into account discrete levels of vibrational energy. For a gas flow in non-equilibrium, for instance for a high enthalpy flow, we expect this model to capture the shock position and the parietal heat flux with more accuracy. This model satisfies the conservation properties and the H-theorem and allows to adjust correct transport coefficients and relaxation rates. It has been illustrated by numerical simulations for an homogeneous problem. Finally, a reduced model which also satisfies the conservation laws and the H-theorem has been obtained: with this model, it should be possible to make simulations at a computational cost which is of same order of magnitude as for a monoatomic gas.

A Gaussian integrals and other summation formulas

In this section, we give some summation and integrals formula that are used in the paper. First, we have $\sum_{i=0}^{+\infty} e^{-i\theta} = \frac{1}{1-e^{-\theta}}$ and $\sum_{i=0}^{+\infty} ie^{-i\theta} = \frac{e^{-\theta}}{(1-e^{-\theta})^2}$, which can be used to obtain

$$\sum_{i=0}^{+\infty} \mathcal{M}_{vib}(i)[f] = 1, \qquad \text{and} \qquad \sum_{i=0}^{+\infty} iRT_0\mathcal{M}_{vib}(i)[f] = \frac{\delta_v(T_{eq})}{2}RT_{eq}.$$

Then, we remind the gamma function $\mathbf{\Gamma}(x) = \int_0^{+\infty} s^{x-1}e^{-s}\,ds$, which is such that $\mathbf{\Gamma}(x+1) = x\mathbf{\Gamma}(x)$ and $\mathbf{\Gamma}(1) = 1$. This is used to get

$$\int_0^{+\infty} \mathcal{M}_{rot}[f](\varepsilon)\,d\varepsilon = 1 \qquad \text{and} \qquad \int_0^{+\infty} \varepsilon\mathcal{M}_{rot}[f](\varepsilon)\,d\varepsilon = \frac{\delta}{2}RT_{eq}.$$

Finally, we remind the definition of the absolute Maxwellian $M_0(V) = \frac{1}{(2\pi)^{\frac{3}{2}}}\exp(-\frac{|V|^2}{2})$. We denote by $\langle\phi\rangle_V = \int_{\mathbb{R}^3}\phi(V)\,dV$ for any function ϕ. It is standard to derive the following integral relations (see [35], for instance), written with the Einstein notation:

$$\begin{aligned}
&\langle M_0\rangle_V = 1,\\
&\langle V_iV_jM_0\rangle_V = \delta_{ij}, \qquad \langle V_i^2M_0\rangle_V = 1, \qquad \langle|V|^2M_0\rangle_V = 3,\\
&\langle V_iV_jV_kV_lM_0\rangle_V = \delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}, \qquad \langle V_i^2V_j^2M_0\rangle_V = 1 + 2\,\delta_{ij}\\
&\langle V_iV_j|V|^2M_0\rangle_V = 5\,\delta_{ij}, \qquad \langle|V|^4M_0\rangle_V = 15,\\
&\langle V_iV_j|V|^4M_0\rangle_V = 35\,\delta_{ij}, \qquad \langle|V|^6M_0\rangle = 105,
\end{aligned}$$

while all the integrals of odd power of V are zero. Note that the first relation of each line implies the other relations of the same line: these relations are given here to improve the readability of the paper. From the previous Gaussian integrals, it can be shown that for any 3×3 matrix C, we have

$$\langle V_iV_jC_{kl}V_kV_lM_0\rangle_V = C_{ij} + C_{ji} + C_{ii}\delta_{ij}.$$

B Inequality for $\det(\Theta)/det(\Pi)$

Here we prove the result for inequality (34) which is: $\frac{\det\Theta}{\det\Pi} \leq \left(\frac{E_{tr}(f)}{e_{tr}^{rel}}\right)^3$. We establish the result in a basis where Θ can be diagonalized and we note $\Theta_1, \Theta_2, \Theta_3$ its eigenvalues. Note that Π is diagonal in the same basis. Then we have

$$\frac{\det\Theta}{\det\Pi} = \frac{\prod_{i=1}^{3}\Theta_i}{\prod_{i=1}^{3}(\eta RT_{eq} + (1-\eta)(\theta(RT_{tr,rot}) + (1-\theta)(\nu\Theta_i + (1-\nu)RT_{tr})))}.$$

The proof is based on convexity arguments. However, since parameter ν can be negative (we remind that ν lies in $[-\frac{1}{2}, 1]$), we first want to obtain an lower bound for $\det\Pi$ that does not depend on ν.

First, we consider $\det\Pi$ as a function of ν, and we take its logarithm denoted by $\phi(\nu)$:

$$\phi(\nu) = \sum_{i=1}^{3}\log(\eta RT_{eq} + (1-\eta)(\theta(RT_{tr,rot}) + (1-\theta)(\nu\Theta_i + (1-\nu)RT_{tr}))).$$

By computing their second derivatives, it can easily be seen that each component of this sum is a concave function of ν, and so is the function ϕ. Moreover, a simple derivation and relation $\sum_{i=1}^{3}\Theta_i = 3RT_{tr}$ (see section 3.2) show that $\phi'(0) = 0$. These two properties imply that ϕ necessarily reaches its minimum on $[-\frac{1}{2}, 1]$ at $\nu = -\frac{1}{2}$ or at $\nu = 1$.

Now we have to determine what is the minimum between $\phi(-\frac{1}{2})$ and $\phi(1)$. In order to simplify the notations, we introduce $X = \eta RT_{eq} + (1-\eta)\theta RT_{tr,rot}$, which is positive, and $Y = (1-\eta)(1-\theta)$, which is in $[0, 1)$. Then we find

$$\phi(-\frac{1}{2}) = \log(\prod_{i=1}^{3}(X + Y\frac{\Theta_j + \Theta_k}{2})) \quad \text{and} \quad \phi(1) = \log(\prod_{i=1}^{3}(X + Y\Theta_i)),$$

where j and k in the first expression denote the two other indices different from i. A convex inequality (which is nothing but the usual inequality between arithmetic and geometric means) implies

$$\phi(-\frac{1}{2}) \geq \log(\prod_{i=1}^{3}(\sqrt{(X + Y\Theta_j}\sqrt{(X + Y\Theta_k)}) = \log(\prod_{i=1}^{3}(X + Y\Theta_i)) = \phi(1).$$

Consequently, $\phi(\nu) \geq \phi(1)$ for every ν in $[-\frac{1}{2}, 1]$: this implies $\det\Pi \geq \prod_{i=1}^{3}(X + Y\Theta_i)$ and we deduce this upper bound

$$\frac{\det\Theta}{\det\Pi} \leq \prod_{i=1}^{3}\frac{\Theta_i}{X + Y\Theta_i}, \tag{77}$$

that does not depend on ν anymore, as announced above.

In the last part, we analyze the logarithm of the right-hand side of the previous inequality: we denote by

$$g(\Theta) = \log\prod_{i=1}^{3}\frac{\Theta_i}{X + Y\Theta_i} = \sum_{i=1}^{3}f(\Theta_i),$$

where $f(s) = \log\left(\frac{s}{X+Ys}\right)$ is clearly a concave function. Then we use the Jensen inequality to get

$$\begin{aligned}\frac{1}{3}g(\Theta) = \frac{1}{3}\sum_{i=1}^{3}f(\Theta_i) &\leq f\left(\frac{1}{3}\sum_{i=1}^{3}\Theta_i\right)\\ &= f(RT_{tr}) = \log\left(\frac{RT_{tr}}{X + YRT_{tr}}\right).\end{aligned}$$

Now we note that $X + YRT_{tr} = RT_{tr}^{rel}$ (see the definition of X and Y above and the definition (25)) of T_{tr}^{rel}, so that $g(\Theta) \leq \log((\frac{RT_{tr}}{RT_{tr}^{rel}})^3)$. Finally, we use this estimate in (77) to find

$$\frac{\det \Theta}{\det \Pi} \leq \left(\frac{RT_{tr}}{RT_{tr}^{rel}} \right)^3,$$

and this gives the result, since we remind that $E_{tr}(f) = \frac{3}{2}RT_{tr}$ and $e_{tr}^{rel} = \frac{3}{2}RT_{tr}^{rel}$.

C First and second order partial derivatives of $\mathcal{S}$

We remind that

$$\mathcal{S}(e_1, e_2, e_3) = R\left(\frac{3}{2}\log(e_1) + \frac{\delta}{2}\log(e_2) + \log\left(1 + \frac{e_3}{RT_0}\right) + \frac{e_3}{RT_0}\log\left(1 + \frac{RT_0}{e_3}\right)\right).$$

The first order derivatives of S are

$$\partial_1 \mathcal{S} = \frac{3}{2}R\frac{1}{e_1}, \qquad \partial_2 \mathcal{S} = \frac{\delta}{2}R\frac{1}{e_2}, \qquad \partial_3 \mathcal{S} = \frac{1}{T_0}\log\left(1 + \frac{RT_0}{e_3}\right).$$

At $(e_1, e_2, e_3) = (e_{tr}^{rel}, e_{rot}^{rel}, e_{vib}^{rel})$, with the corresponding definitions (23) and (25) of the relaxation temperatures, the relations above give

$$\partial_1 \mathcal{S} = \frac{1}{T_{tr}^{rel}}, \qquad \partial_2 \mathcal{S} = \frac{1}{T_{rot}^{rel}}, \qquad \partial_3 \mathcal{S} = \frac{1}{T_{vib}^{rel}},$$

while the second order derivatives are

$$\partial_{1,1}\mathcal{S} = -\frac{3R}{2(e_{tr}^{rel})2}, \qquad \partial_{2,2}\mathcal{S} = -\frac{\delta R}{2(e_{rot}^{rel})^2}, \qquad \partial_{3,3}\mathcal{S} = -\frac{R}{e_{vib}^{rel}\left(RT_0 + e_{vib}^{rel}\right)},$$

and are clearly negative, while the cross derivatives are zero.

D First order expansion of $\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]$

Since $\mathcal{M}[f] = \mathcal{M}_{tr}[f]\mathcal{M}_{rot}[f]\mathcal{M}_{vib}[f]$, the expansion of $\partial_t \mathcal{M}[f] + v \cdot \nabla \mathcal{M}[f]$ requires the expansion of the transport operator applied to each component of $\mathcal{M}[f]$. We first detail how we proceed for the translation component $\mathcal{M}_{tr}[f]$. The chain rule gives

$$\begin{aligned}\partial_t \mathcal{M}_{tr}[f] + v \cdot \nabla \mathcal{M}_{tr}[f] = \Bigg[&\frac{\partial_t \rho + v \cdot \nabla \rho}{\rho} + (\partial_t u + (v \cdot \nabla)u) \cdot \frac{v-u}{RT_{eq}} \\ &+(\partial_t T_{eq} + v \cdot \nabla T_{eq})\left(\frac{|v-u|^2}{2RT_{eq}} - \frac{3}{2}\right)\frac{1}{T_{eq}}\Bigg]\mathcal{M}_{tr}[f].\end{aligned}$$

Euler equations (56) are used to replace time derivatives of ρ, u, and T_{eq} by their space derivatives, and finally, we use the changes of variables $V = \frac{v-u}{\sqrt{RT_{eq}}}$, $J = \frac{\varepsilon}{RT_{eq}}$, and $K = \frac{iT_0}{T_{eq}}$ to get

$$\partial_t \mathcal{M}_{tr}[f] + v \cdot \nabla \mathcal{M}_{tr}[f] = \frac{\rho}{(RT_{eq})^{3/2}}M_0(V)\left(A_{tr}(V) \cdot \frac{\nabla(RT_{eq})}{\sqrt{RT_{eq}}} + \tilde{B}_{tr}(V) : \nabla u\right) + O(\mathrm{Kn}),$$

with

$$A_{tr}(V) = \left(\frac{|V|^2}{2} - \frac{5}{2}\right)V, \quad \tilde{B}_{tr}(V) = V \otimes V - \left(\left(\frac{|V|^2}{2} - \frac{3}{2}\right)C + 1\right)I, \quad C = \frac{R}{c_v(T_{eq})}.$$

The same kind of computations give

$$\partial_t \mathcal{M}_{rot}[f] + v\cdot\nabla\mathcal{M}_{rot}[f] = \quad (\partial_t T_{eq} + v\cdot\nabla T_{eq})\left[\left(\frac{\varepsilon}{RT_{eq}} - \frac{\delta}{2}\right)\frac{1}{T_{eq}}\right]\mathcal{M}_{rot}[f],$$

$$\partial_t \mathcal{M}_{vib}[f] + v\cdot\nabla\mathcal{M}_{vib}[f] = \quad (\partial_t T_{eq} + v\cdot\nabla T_{eq})\left[\left(\frac{iT_0}{T_{eq}} - \frac{e_{vib}(T)}{RT_{eq}}\right)\frac{1}{T_{eq}}\right]\mathcal{M}_{vib}[f],$$

so that

$$\partial_t \mathcal{M}_{rot}[f] + v\cdot\nabla\mathcal{M}_{rot}[f] = \frac{\Lambda(\delta)J^{\frac{\delta-2}{2}}}{RT_{eq}}e^{-J}\left(A_{rot}(V,J)\cdot\frac{\nabla(RT_{eq})}{\sqrt{RT_{eq}}} + \tilde{B}_{rot}(V,J):\nabla u\right) + O(\mathrm{Kn}),$$

with

$$A_{rot}(V,J) = \left(J-\frac{\delta}{2}\right)V, \quad \tilde{B}_{rot}(V,J) = -C\left(J-\frac{\delta}{2}\right)I,$$

and

$$\partial_t \mathcal{M}_{vib}[f] + v\cdot\nabla\mathcal{M}_{vib}[f] = \left(1-e^{-\frac{T_0}{T_{eq}}}\right)e^{-K}\left(A_{vib}(V,K)\cdot\frac{\nabla(RT_{eq})}{\sqrt{RT_{eq}}} + \tilde{B}_{vib}(V,K):\nabla u\right) + O(\mathrm{Kn}),$$

with

$$A_{vib}(V,K) = \left(K-\frac{e_{vib}(T_{eq})}{RT_{eq}}\right)V, \quad \tilde{B}_{vib}(V,K) = -C\left(K-\frac{e_{vib}(T_{eq})}{RT_{eq}}\right)I.$$

Finally we get

$$\frac{\partial_t \mathcal{M}[f] + v\cdot\nabla\mathcal{M}[f]}{\mathcal{M}[f]} = \left(A(V,J,K)\cdot\frac{\nabla(RT_{eq})}{\sqrt{RT_{eq}}} + \tilde{B}(V,J,K):\nabla u\right) + O(\mathrm{Kn}), \tag{78}$$

with

$$A = A_{tr} + A_{rot} + A_{vib}, \quad \tilde{B} = \tilde{B}_{tr} + \tilde{B}_{rot} + \tilde{B}_{vib}. \tag{79}$$

E First order expansion of $\mathcal{G}[f]$

Here we detail how $\mathcal{G}[f]$ can be expanded up to $O(\mathrm{Kn}^2)$, which is required to obtain the first order expansion of f, as given by (64).

First, since Π and the relaxation temperatures are equal to their equilibrium values up to $O(\mathrm{Kn})$ (see (53)), a standard Taylor expansion gives

$$\begin{aligned}\frac{\mathcal{G}[f]}{\mathcal{M}[f]} = 1 + &\frac{(v-u)^T\left(\frac{\Pi}{RT_{eq}} - I\right)(v-u)}{2RT_{eq}} \\ &-\frac{3}{2}\left(\frac{T^{rel}_{tr}}{T_{eq}} - 1\right) + \left(\frac{\epsilon}{RT_{eq}} - \frac{\delta}{2}\right)\left(\frac{T^{rel}_{rot}}{T_{eq}} - 1\right) + \left(\frac{iRT_0}{RT_{eq}} - \frac{e_{vib}(T_{eq})}{RT_{eq}}\right)\left(\frac{T^{rel}_{vib}}{T_{eq}} - 1\right) \\ &+ O(\mathrm{Kn}^2).\end{aligned} \tag{80}$$

Now, we need to expand Π and the relaxation temperatures up to $O(\mathrm{Kn}^2)$. For Π, we use (66) and (67) to get

$$\frac{\Pi}{RT_{eq}} - I = \tau\mathrm{Kn}\left((\nabla u + (\nabla u)^T - C\nabla\cdot uI) - Pr(\nabla u + (\nabla u)^T - \alpha\nabla\cdot uI)\right) + O(\mathrm{Kn}^2). \tag{81}$$

For the relaxation temperatures, we first write them as functions of the relaxation energies

$$\frac{T_{tr}^{rel}}{T_{eq}} = \frac{e_{tr}^{rel}}{e_{tr}(T_{eq})}, \quad \frac{T_{rot}^{rel}}{T_{eq}} = \frac{e_{rot}^{rel}}{e_{rot}(T_{eq})}, \quad \frac{c_v^{vib}(T_{eq})T_{eq}}{e_{vib}(T_{eq})}\left(\frac{T_{vib}^{rel}}{T_{eq}} - 1\right) = \frac{e_{vib}^{rel}}{e_{vib}(T_{eq})} - 1 + O(\mathrm{Kn}^2), \tag{82}$$

where a first order expansion is used in the last expression, due to the non linearity of the vibration energy.

Now, we just have to expand the relaxation energies. In order to shorten this derivation, we introduce the following vectorial notations:

$$\mathcal{E} = \begin{pmatrix} E_{tr}(f) \\ E_{rot}(f) \\ E_{vib}(f) \end{pmatrix}, \quad \mathcal{E}^{eq} = \begin{pmatrix} e_{tr}(T_{eq}) \\ e_{rot}(T_{eq}) \\ e_{vib}(T_{eq}) \end{pmatrix}, \quad \mathcal{E}^{rel} = \begin{pmatrix} e_{tr}^{rel} \\ e_{rot}^{rel} \\ e_{vib}^{rel} \end{pmatrix}, \text{ and } \mathcal{X} = \begin{pmatrix} e'_{tr}(T_{eq})CT_{eq} - RT_{eq} \\ e'_{rot}(T_{eq})CT_{eq} \\ e'_{vib}(T_{eq})CT_{eq} \end{pmatrix}$$

Then relation (28) reads

$$\mathcal{E}^{rel} = \eta\mathcal{E}^{eq} + (I + D)\mathcal{E}, \tag{83}$$

where I stands here for the unit 3×3 matrix and D is defined in (58). Moreover, (60) gives

$$\mathcal{E} = -\eta D^{-1}\mathcal{E}^{eq} - \mathrm{Kn}\tau D^{-1}\mathcal{X} + O(\mathrm{Kn}^2). \tag{84}$$

It can also be seen that $\mathcal{E}^{eq}$ is an eigenvector of D with eigenvalue $-\eta$, and then (84) is simply

$$\mathcal{E} = \mathcal{E}^{eq} - \mathrm{Kn}\tau D^{-1}\mathcal{X} + O(\mathrm{Kn}^2). \tag{85}$$

Then relations (83) and (85) give the following expansion of the relaxation energies

$$\mathcal{E}^{rel} = \mathcal{E}^{eq} - \mathrm{Kn}\tau(I + D^{-1})\mathcal{X} + O(\mathrm{Kn}^2).$$

To make this relation explicit, we rewrite D as

$$D = \begin{pmatrix} -\frac{\delta}{3+\delta}\frac{1}{Z_{rot}} - \frac{3}{3+\delta}\frac{1}{Z_{vib}} & \frac{3}{3+\delta}\left(\frac{1}{Z_{rot}} - \frac{1}{Z_{vib}}\right) & 0 \\ \frac{\delta}{3+\delta}\left(\frac{1}{Z_{rot}} - \frac{1}{Z_{vib}}\right) & -\frac{3}{3+\delta}\frac{1}{Z_{rot}} - \frac{\delta}{3+\delta}\frac{1}{Z_{vib}} & 0 \\ 0 & 0 & -\frac{1}{Z_{vib}} \end{pmatrix}.$$

so that

$$D^{-1} = \begin{pmatrix} -\frac{\delta}{3+\delta}Z_{rot} - \frac{3}{3+\delta}Z_{vib} & \frac{3}{3+\delta}(Z_{rot} - Z_{vib}) & 0 \\ \frac{\delta}{3+\delta}(Z_{rot} - Z_{vib}) & -\frac{3}{3+\delta}Z_{rot} - \frac{\delta}{3+\delta}Z_{vib} & 0 \\ 0 & 0 & -Z_{vib} \end{pmatrix}.$$

Then we obtain

$$\mathcal{E}^{rel} = \mathcal{E}^{eq} - \mathrm{Kn}\tau\left((1 - Z_{vib})C\begin{pmatrix} c_v^{tr} \\ c_v^{rot} \\ c_v^{vib} \end{pmatrix} - R\begin{pmatrix} 1 - \frac{\delta}{3+\delta}Z_{rot} - \frac{3}{3+\delta}Z_{vib} \\ \frac{\delta}{3+\delta}Z_{rot} - \frac{\delta}{3+\delta}Z_{vib} \\ 0 \end{pmatrix}\right)T_{eq}\nabla\cdot u + O(\mathrm{Kn}^2).$$

It remains to use (82) to get the first order expansion of the relaxation temperatures

$$\begin{pmatrix} T_{tr}^{rel}/T_{eq} - 1 \\ T_{rot}^{rel}/T_{eq} - 1 \\ T_{vib}^{rel}/T_{eq} - 1 \end{pmatrix} = \mathrm{Kn}\tau\begin{pmatrix} -\frac{2\delta}{3(3+\delta)}Z_{rot} + (C - \frac{2}{3+\delta})Z_{vib} - C + \frac{2}{3} \\ (C - \frac{2}{3+\delta})Z_{vib} + \frac{2}{3+\delta}Z_{rot} - C \\ (Z_{vib} - 1)C \end{pmatrix}\nabla\cdot u + O(\mathrm{Kn}^2),$$

that can now be used with (81) in (80) to get the first order expansion of $\mathcal{G}[f]$:

$$\begin{aligned}\frac{\mathcal{G}[f]}{\mathcal{M}[f]} = 1 + \mathrm{Kn}\tau \Bigg(&\Big[(1-\mathrm{Pr})V\otimes V - \Big((C-\alpha\mathrm{Pr})(\frac{|V|^2}{2}-\frac{3}{2})+1\Big)I\Big] \\ &+ (J-\frac{\delta}{2})\Big[(C-\frac{2}{3+\delta})Z_{vib}+\frac{2}{3+\delta}Z_{rot}-C\Big]I \\ &+(K-\frac{\delta_v(T_{eq})}{2})\left[(Z_{vib}-1)C\right]I\Bigg) : \nabla u + O(\mathrm{Kn}^2).\end{aligned} \tag{86}$$

This last relation and (78) readily lead to (68).

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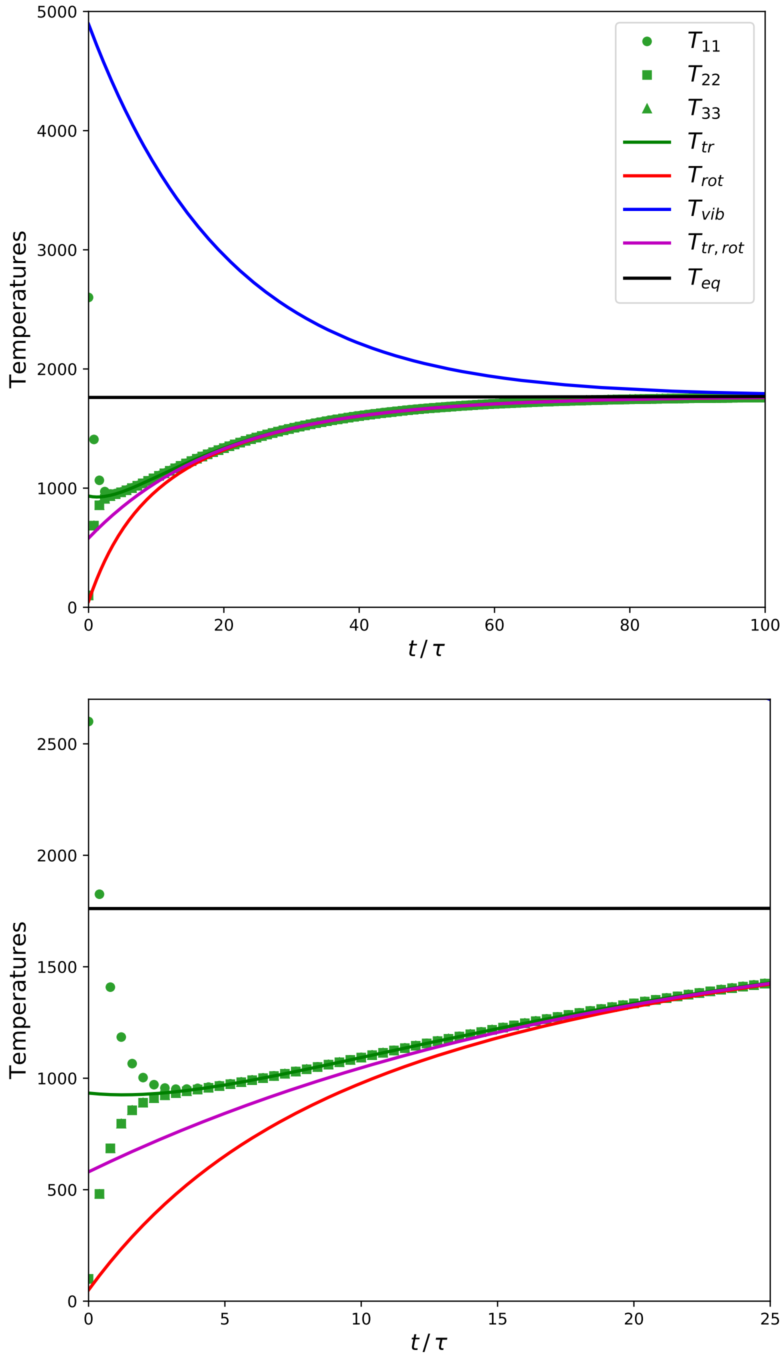

Figure 1: Relaxation of temperatures (top), and zoom between $t = 0$ and $t = 25\tau$ (bottom): (○) T_{11}, (□) T_{22} and (△) T_{33} are the components of Θ/R, T_{tr} (green), T_{rot} (red) and T_{vib} (blue) are respectively the temperatures of translation, rotation and vibration, while $T_{tr,rot}$ (purple) and T_{eq} (black) are the translational-rotational temperature and temperature at equilibrium, respectively

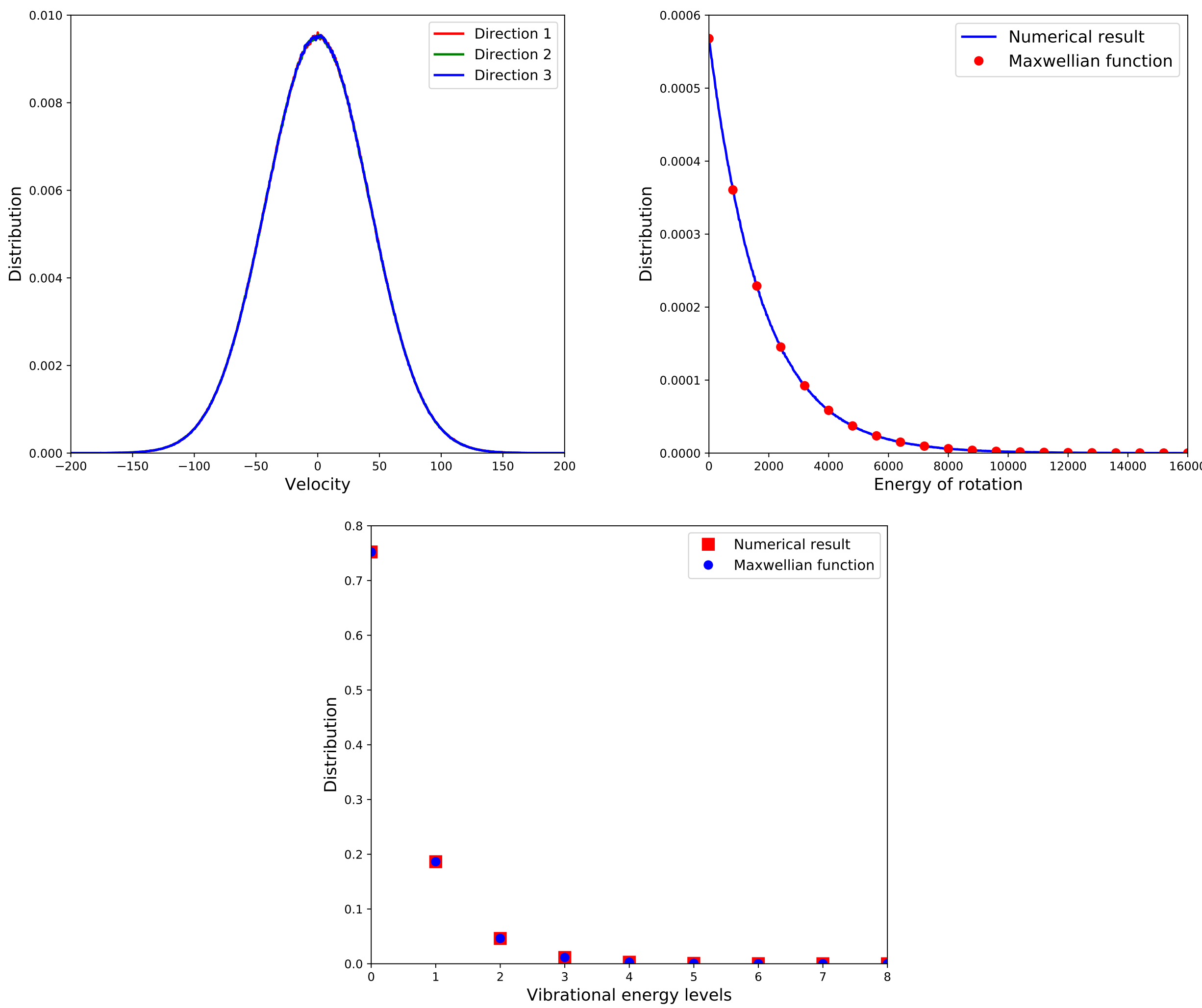

Figure 2: Top left: Distribution function of velocities at equilibrium: x direction (blue), y direction (red) and z direction (green). Top right: Distribution of the energy of rotation: numerical result (blue) and theoretical equilibrium distribution (red). Bottom: discrete distribution of the vibrational energy: numerical result (blue) and theoretical result (red).

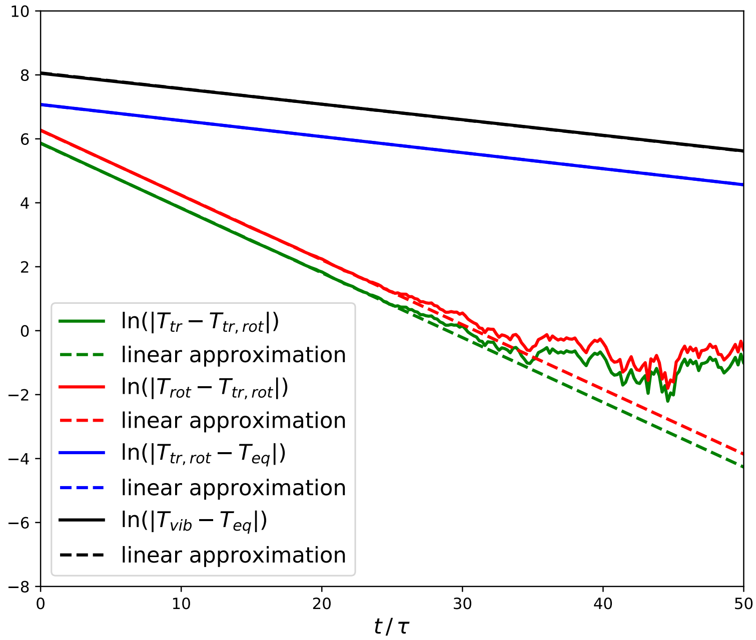

Figure 3: Relaxation of temperatures differences: $(T_{tr} - T_{tr,rot})$ (green), $(T_{rot} - T_{tr,rot})$ (red), $(T_{tr,rot} - T_{eq})$ (blue), $(T_{vib} - T_{eq})$ (black).

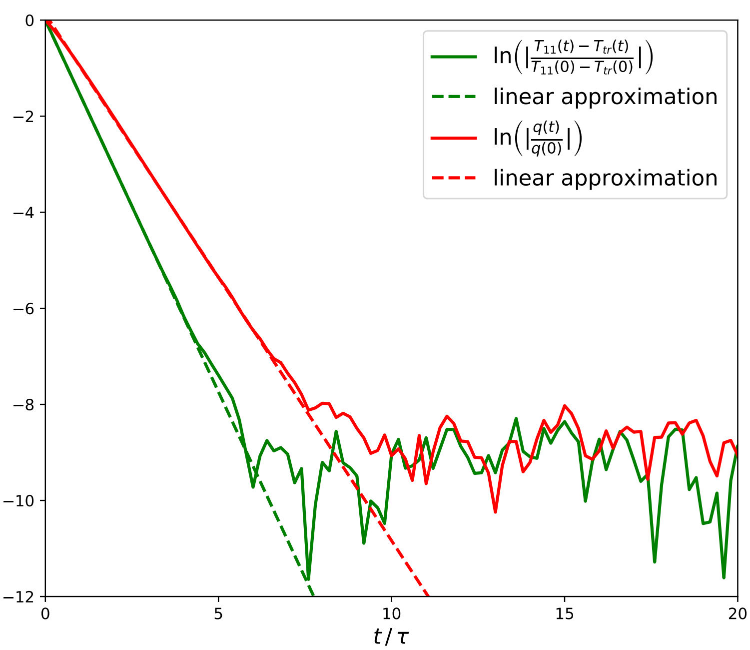

Figure 4: Relaxation of the difference of temperatures $(T_{11} - T_{tr})$ (green) and first component of the heat flux q_1 (red).