



**HAL**  
open science

## An ES-BGK model for diatomic gases with correct relaxation rates for internal energies

Julien Mathiaud, Luc Mieussens, M. Pfeiffer

► **To cite this version:**

Julien Mathiaud, Luc Mieussens, M. Pfeiffer. An ES-BGK model for diatomic gases with correct relaxation rates for internal energies. *European Journal of Mechanics - B/Fluids*, 2022, 96, pp.65-77. 10.1016/j.euromechflu.2022.07.003 . hal-03960779

**HAL Id: hal-03960779**

**<https://hal.science/hal-03960779v1>**

Submitted on 27 Jan 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# An ES-BGK model for diatomic gases with correct relaxation rates for internal energies

J. Mathiaud<sup>1</sup>, L. Mieussens<sup>2</sup>, M. Pfeiffer<sup>3</sup>

<sup>1</sup>CEA-CESTA, 15 avenue des sablières - CS 60001, 33116 Le Barp Cedex, France,  
Univ. Bordeaux, CNRS, CELIA, UMR 5107, F-33400 Talence, France.  
(julien.mathiaud@u-bordeaux.fr)

<sup>2</sup>Univ. Bordeaux, Bordeaux INP, CNRS, IMB, UMR 5251, F-33400 Talence, France.  
(Luc.Mieussens@math.u-bordeaux.fr)

<sup>3</sup>Institute of Space Systems, University of Stuttgart, Pfaffenwaldring 29, D-70569 Stuttgart, Germany.  
(mpfeiffer@irs.uni-stuttgart.de)

## Abstract

We propose a new ES-BGK model for diatomic gases which allows for translational-rotational and translational-vibrational energy exchanges, as given by Landau-Teller and Jeans relaxation equations. This model is consistent with the general definition of the vibrational and rotational collision numbers that are also commonly used in DSMC solvers. It is proved to satisfy the H-theorem and to give the correct transport coefficients, up to the volume viscosity.

## Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
<b>2</b>	<b>Internal energies of diatomic gases</b>	<b>3</b>
2.1	The different macroscopic internal energies at equilibrium . . . . .	3
2.2	Mathematical properties of the energy functions . . . . .	4
<b>3</b>	<b>Distribution functions, moments, and temperatures</b>	<b>4</b>
3.1	Distribution function . . . . .	4
3.2	Internal temperatures . . . . .	5
3.3	Macroscopic relaxation phenomena . . . . .	5
3.4	Some remarks on the collision time $\tau_C$ . . . . .	6
<b>4</b>	<b>ES-BGK model and its mathematical properties</b>	<b>6</b>
4.1	Construction of the model . . . . .	6
4.2	Definition of the model . . . . .	8
4.3	Conservation properties . . . . .	10
4.4	Entropy . . . . .	10
4.5	Discussion on the conditions for positiveness of relaxation energies, positive definiteness of $\Pi$ , and H-theorem . . . . .	14
4.6	Comparison with the ES-BGK model of Andriès et al. [1] . . . . .	15
<b>5</b>	<b>Hydrodynamic asymptotics</b>	<b>16</b>
5.1	Euler asymptotics . . . . .	17
5.2	Compressible Navier-Stokes asymptotics . . . . .	17
<b>6</b>	<b>Reduced ES-BGK model</b>	<b>18</b>

<b>7</b>	<b>Numerical results</b>	<b>19</b>
7.1	Comparison with analytical Results . . . . .	20
7.2	Comparison with DSMC Results . . . . .	20
<b>8</b>	<b>Conclusion</b>	<b>22</b>
<b>A</b>	<b>Convexity of the vibrational energy</b>	<b>22</b>
<b>B</b>	<b>Inequality for <math>\det(\Theta)/\det(\Pi)</math></b>	<b>22</b>
<b>C</b>	<b>Elements of proof for the Chapman-Enskog expansion</b>	<b>23</b>

## 1 Introduction

In Rarefied Gas Dynamic problems, it is often useful to replace the complicated Boltzmann equation by simplified models, both for analytical calculations and numerical simulations. These model equations describe intermolecular collisions by drift and diffusion in the velocity space (Fokker-Plank models, see [2, 3, 4]) or by relaxation to a local equilibrium: this latter approach, first proposed by Bathnagar et al. [5] and Welander [6] leads to the so called BGK equation.

The BGK equation describes the evolution of a rarefied monoatomic flow, and is designed to satisfy several properties of the Boltzmann equation, like conservation laws, H-theorem, and correct shear viscosity coefficient in the compressible Navier-Stokes asymptotics as obtained by the Chapman-Enskog expansion. However, the BGK equation contains a single free parameter (the relaxation time) which is not sufficient to independently fit the correct value of the heat transfer coefficient, which leads to a constant Prandtl number equal to 1.

Several modifications of the BGK equation have been proposed to fix this problem, like the Ellipsoidal-Statistical (ES-BGK) [7] and the Shakhov [8] models that are the most popular (see [9, 10] for other models). While the ES-BGK model was already extended to polyatomic gases in [7], this is the more recent extension of Andriès et al. [1] to polyatomic gases with rotational energy that is mostly used in the litterature [11, 12]. In the same paper, the authors also proved for the first time that the ES-BGK model satisfies the H-theorem. While the Shakhov model has also been extended to polyatomic gases [13, 14], it cannot satisfy the H-theorem, since it is a perturbative model in which the distribution function can take negative values. Several extensions of the BGK equation have also been proposed for discrete internal energy levels [15, 16, 17] or thermally perfect gases [18].

In [17], the approach of Andriès et al. [1] was applied to extend the ES-BGK model to diatomic gases in which a discrete vibrational energy is taken into account. This model was designed to obtain the correct Prandtl number, as well as the correct relaxation times of internal energies, as defined by Landau-Teller and Jeans equations. However, first simulations [19] show some discrepancies with DSMC simulations, especially for the rotational and vibrational temperature profiles, which suggests that energy exchanges are not taken into account in the same way in the ES-BGK model and in the DSMC solver.

Recently, Pfeiffer [20] proposed an ES-BGK based particle simulation of diatomic rarefied flows in which he proposed a specific treatment of internal energy exchanges. His results show very good agreement with DSMC. However, the algorithm used in [20] is not derived from a complete kinetic model.

In this paper, we propose an ES-BGK model which is consistent with the numerical method of [20], and based on the theoretical framework of [17]. The main modifications with respect to the model of [17] are the following ingredients, taken from [20]:

1. The energy relaxation time scale is proportional to the mean collision time  $\tau_C$  rather than to the relaxation time  $\tau$ , as opposed to what is done in [17]. This corresponds to the

common definition of the relaxation time of inner degrees of freedom and the associated definition of the vibrational and rotational collision numbers [21, 22, 23].

2. The Landau-Teller and Jeans equations are used to define translational-rotational and translational-vibrational energy exchanges, and induce a relaxation of rotational and vibrational temperatures to the *translational* temperature, as described and discussed in detail in Haas et al. [23] for the DSMC method. Again, this is different to what is done in [17], where the model induces a relaxation of internal temperatures to the overall temperature.

Numerical tests in space homogeneous cases illustrate the excellent agreement between our new model and DSMC simulations.

Note that this new approach can also be used even if the vibration modes are not taken into account: we obtain an ES-BGK model for diatomic gases in rotational non-equilibrium which is different from the ES-BGK model of Andriès et al. [1]. However, both models are proved to be equivalent up to a correction factor of the relaxation time, or equivalently of the collision number  $Z_{rot}$ , but this correction factor can be quite large.

Moreover, our new ES-BGK model is proved to satisfy the H-theorem, with a proof that is more involved than that for [17]. A Chapman-Enskog expansion gives the corresponding transport coefficients, and we obtain the following strong result: the volume viscosity is shown to be the same as that obtained in the Boltzmann equation with two fast and slow energy modes.

The outline of our paper is the following. Sections 2 and 3 are devoted to the definition of internal energies and temperature, relaxation times, and distribution functions. Our ES-BGK model is derived and analyzed in Section 4. The results of Chapman-Enskog expansion is given in Section 5. A reduced model is proposed in Section 6 to reduce its computational complexity. Finally, the properties of our model are illustrated by some numerical results in section 7.

## 2 Internal energies of diatomic gases

### 2.1 The different macroscopic internal energies at equilibrium

In this paper we consider diatomic 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, rotational and vibrational (in case of the harmonic oscillator model) modes, the corresponding specific energies are

$$e_{tr}(T) = \frac{3}{2}RT, \quad e_{rot}(T) = \frac{\delta}{2}RT, \quad e_{vib}(T) = \frac{RT_0}{\exp(T_0/T) - 1}, \quad (1)$$

where the specific total energy is

$$e(T) = e_{tr}(T) + e_{rot}(T) + e_{vib}(T). \quad (2)$$

Here,  $\delta = 2$  is the number of degrees of freedom of rotation,  $R$  is the gas constant per unit mass and  $T_0$  is the characteristic vibrational temperature.

Note that polyatomic molecules could be considered here with  $\delta > 2$  and a vibration energy as given by a sum over all harmonic oscillators of the molecule [24]. However, this would change some details in our mathematical proofs, so that an extension of our approach to polyatomic molecules is deferred to future work.

## 2.2 Mathematical properties of the energy functions

For each energy mode, a temperature can be defined as follows. We denote by  $e_i^{-1}$  the function that maps any given energy  $E$  to the corresponding temperature. That is to say the temperature  $T$  corresponding to a given energy  $E$  is such that  $e_\alpha(T) = E$ , where  $\alpha$  stands for *tr*, *rot*, and *vib*, and is denoted by  $T = e_\alpha^{-1}(E)$ . Simple computations give

$$e_{tr}^{-1}(E) = \frac{2}{3R}E, \quad e_{rot}^{-1}(E) = \frac{2}{\delta R}E, \quad e_{vib}^{-1}(E) = T_0 / \log\left(1 + \frac{RT_0}{E}\right). \quad (3)$$

The total energy function, which is clearly invertible, cannot be inverted analytically, and we simply set

$$T = e^{-1}(E) \quad \text{such that} \quad E = \frac{3 + \delta}{2}RT + \frac{RT_0}{\exp(T_0/T) - 1}. \quad (4)$$

For each energy mode, we can also define a specific heat at constant volume  $c_v^\alpha(T) = \frac{de_\alpha(T)}{dT}$ . For translational and rotational energies, the specific heats are constant:

$$c_v^{tr} = \frac{3}{2}R, \quad c_v^{rot} = \frac{\delta}{2}R, \quad (5)$$

while for vibrational energy, we find

$$c_v^{vib}(T) = R \frac{T_0^2}{T^2} \frac{\exp(T_0/T)}{(\exp(T_0/T) - 1)^2}. \quad (6)$$

Note that  $c_v^{vib}$  can be proved to be an increasing function of  $T$  which is bounded by  $R$ . This also implies that  $e_{vib}$  is a convex function (see appendix A).

Finally, we also define for each mode a specific entropy  $s_\alpha$  such that  $\frac{ds_\alpha(E)}{dE} = \frac{1}{e_\alpha^{-1}(E)}$ . This gives, up to any arbitrary constant

$$s_{tr}(E) = \frac{3}{2}R \log E, \quad s_{rot}(E) = \frac{\delta}{2}R \log E, \quad s_{vib}(E) = R \left( \log\left(1 + \frac{E}{RT_0}\right) + \frac{E}{RT_0} \log\left(1 + \frac{RT_0}{E}\right) \right), \quad (7)$$

and we define the total entropy (at constant density)

$$\mathcal{S}(E_1, E_2, E_3) = s_{tr}(E_1) + s_{rot}(E_2) + s_{vib}(E_3). \quad (8)$$

## 3 Distribution functions, moments, and temperatures

### 3.1 Distribution function

The state of any gas molecule is described by its position  $x$ , its velocity  $v$ , its rotational energy  $\varepsilon$ , and its discrete vibrational energy  $iRT_0$ , where  $i$  is the  $i$ th vibrational energy level and  $T_0$  is the characteristic vibrational temperature of the gas, in the case of the usual simple harmonic oscillator model.

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  $\varepsilon$  centered in  $d\varepsilon$  and the discrete vibrational energy  $iRT_0$ . The macroscopic densities of mass  $\rho$ , momentum  $\rho u$ , and internal energy  $\rho E$  are

$$\rho = \langle f \rangle_{v, \varepsilon, i}, \quad \rho u = \langle v f \rangle_{v, \varepsilon, i}, \quad \rho E(f) = \left\langle \left( \frac{1}{2} |v - u|^2 + \varepsilon + iRT_0 \right) f \right\rangle_{v, \varepsilon, i}. \quad (9)$$

The dependence of  $E$  on  $f$  is intentionally 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  $\phi$ . The specific internal energy  $E(f)$  can be decomposed into

$$E(f) = E_{tr}(f) + E_{rot}(f) + E_{vib}(f), \quad (10)$$

where specific energies  $E_{tr}(f)$ ,  $E_{rot}(f)$  and  $E_{vib}(f)$  are respectively associated with translational motion of particles, rotational mode and vibrational mode through:

$$\rho E_{tr}(f) = \left\langle \frac{1}{2} |v - u|^2 f \right\rangle_{v,\varepsilon,i}, \quad \rho E_{rot}(f) = \langle \varepsilon f \rangle_{v,\varepsilon,i}, \quad \rho E_{vib}(f) = \langle iRT_0 f \rangle_{v,\varepsilon,i}. \quad (11)$$

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

$$P(f) = \langle (v - u) \otimes (v - u) f \rangle_{v,\varepsilon,i}, \quad q(f) = \left\langle \left( \frac{1}{2} |v - u|^2 + \varepsilon + iRT_0 \right) (v - u) f \right\rangle_{v,\varepsilon,i} \quad (12)$$

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

### 3.2 Internal temperatures

For a given distribution function  $f$ , the translational, rotational, and vibrational temperatures are defined by

$$T_{tr} = e_{tr}^{-1}(E_{tr}(f)), \quad T_{rot} = e_{rot}^{-1}(E_{rot}(f)), \quad T_{vib} = e_{vib}^{-1}(E_{vib}(f)), \quad (13)$$

so that we have

$$E_{tr}(f) = e_{tr}(T_{tr}) = \frac{3}{2}RT_{tr}, \quad E_{rot}(f) = e_{rot}(T_{rot}) = \frac{\delta}{2}RT_{rot}, \quad E_{vib}(f) = e_{vib}(T_{vib}) = \frac{RT_0}{\exp(T_0/T_{vib}) - 1}, \quad (14)$$

see section 2. A number of degrees of freedom  $\delta_v(T_{vib})$  for the vibration mode can be defined such that  $E_{vib}(f) = \frac{\delta_v(T_{vib})}{2}RT_{vib}$ , which leads to

$$\delta_v(T_{vib}) = \frac{2T_0/T_{vib}}{\exp(T_0/T_{vib}) - 1}. \quad (15)$$

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

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

$$T_{eq} = e^{-1}(E(f)), \quad (16)$$

and  $T_{eq}$  can be obtained by numerically solving

$$E(f) = \frac{3 + \delta}{2}RT_{eq} + \frac{RT_0}{\exp(T_0/T_{eq}) - 1}. \quad (17)$$

### 3.3 Macroscopic relaxation phenomena

The common description of the relaxation of internal energies with Jeans and Landau-Teller equations [21] as also typically used in DSMC codes (see [23, 22, 20]) is given as:

$$\frac{d}{dt} e_{rot}(T_{rot}) = \frac{1}{Z_{rot}\tau_C} (e_{rot}(T_{tr}) - e_{rot}(T_{rot})), \quad (18)$$

$$\frac{d}{dt} e_{vib}(T_{vib}) = \frac{1}{Z_{vib}\tau_C} (e_{vib}(T_{tr}) - e_{vib}(T_{vib})), \quad (19)$$

where  $Z_{rot}$  and  $Z_{vib}$  are the mean number of collisions necessary to have an exchange of rotational and vibrational energy, respectively, and  $\tau_C$  is a characteristic time of collision (see section 3.4). The equation for translational energy is

$$\frac{d}{dt}e_{tr}(T_{tr}) = -\frac{(e_{rot}(T_{tr}) - e_{rot}(T_{rot}))}{Z_{rot}\tau_C} - \frac{e_{vib}(T_{tr}) - e_{vib}(T_{vib})}{Z_{vib}\tau_C}. \quad (20)$$

which is deduced from the conservation of total energy. Our ES-BGK model will be designed to satisfy these relaxation equations.

**Remark 3.1.** These equations are different from those used in [17]. Indeed, first, they induce a relaxation of  $T_{rot}$  and  $T_{vib}$  to  $T_{tr}$ , while a relaxation to the overall temperature  $T_{eq}$  was imposed in [17], and second the relaxation time used here is the collision time  $\tau_C$ , while the ES-BGK relaxation time  $\tau$  was used in [17] (see sections 3.4 and 4.6). The use of  $\tau_C$  and the relaxation to translation temperature  $T_{tr}$  instead of equilibrium temperature  $T_{eq}$  corresponds to the most frequently used definition of the Landau-Teller and Jeans equation. A detailed discussion of the relaxation to the translation temperature instead of the equilibrium temperature can be found in Haas et al. [23].

### 3.4 Some remarks on the collision time $\tau_C$

The collision numbers  $Z_{rot}$  and  $Z_{vib}$  describe the average required number of collisions of the gas during which it undergoes a relaxation process in the rotational and vibratory degrees of freedom, respectively. Therefore, the characteristic time  $\tau_C$  should be chosen at the mean collision time of the gas [20] and is generally not equal to the relaxation time of the ES-BGK model which is chosen to represent the correct viscosity (as opposed to what is done in [1] and [17]). The difference between the relaxation time  $\tau$  and the collision time  $\tau_C$  depends on the molecular model used. For example, if we look at the Variable Soft Sphere model (VSS) often used in DSMC, the collision time is given by [25]:

$$\tau_C^{VSS} = \frac{\alpha(5-2\omega)(7-2\omega)}{5(\alpha+1)(\alpha+2)} \frac{\mu}{p} = \frac{\alpha(5-2\omega)(7-2\omega)}{5(\alpha+1)(\alpha+2)} \tau Pr, \quad (21)$$

with  $\alpha$  the diffusion factor of the VSS model,  $\omega$  the exponential factor of the temperature dependency in the viscosity, and  $Pr$  is the Prandtl number. Here, we have used the usual relation  $\tau = \mu/(pPr)$  for ES-BGK, which will be proved below. The variable hard sphere (VHS) model can simply be achieved by setting  $\alpha = 1$  which gives:

$$\tau_C^{VHS} = \frac{(5-2\omega)(7-2\omega)}{30} \frac{\mu}{p} = \frac{(5-2\omega)(7-2\omega)}{30} \tau Pr. \quad (22)$$

And finally we get the HS model from it when  $\omega = 0.5$ :

$$\tau_C^{HS} = \frac{4}{5} \frac{\mu}{p} = \frac{4}{5} \tau Pr. \quad (23)$$

## 4 ES-BGK model and its mathematical properties

### 4.1 Construction of the model

The evolution equation for  $f$  is the Boltzmann equation

$$\partial_t f + v \cdot \nabla f = Q(f), \quad (24)$$

where  $Q(f)$  is the collision operator (see [26]). The corresponding local Maxwellian equilibrium in velocity and energy is defined by

$$\mathcal{M}[f](v, \varepsilon, i) = \mathcal{M}_{tr}[f](v) \mathcal{M}_{rot}[f](\varepsilon) \mathcal{M}_{vib}[f](i), \quad (25)$$

with

$$\begin{aligned} \mathcal{M}_{tr}[f](v) &= \frac{\rho}{(2\pi RT_{eq})^{3/2}} \exp\left(-\frac{|v-u|^2}{2RT_{eq}}\right), & \mathcal{M}_{rot}[f](\varepsilon) &= \frac{\Lambda(\delta)\varepsilon^{\frac{\delta-2}{2}}}{(RT_{eq})^{\delta/2}} \exp\left(-\frac{\varepsilon}{RT_{eq}}\right), \\ \mathcal{M}_{vib}[f](i) &= (1 - \exp(-T_0/T_{eq})) \exp\left(-i\frac{T_0}{T_{eq}}\right), \end{aligned}$$

where  $\Lambda(\delta) = 1/\Gamma(\frac{\delta}{2})$ , with  $\Gamma$  the usual gamma function.

This Maxwellian distribution can be used to define the BGK approximation [27], where  $Q(f)$  is replaced by  $\frac{1}{\tau}(\mathcal{M}[f] - f)$ , where  $\tau$  is a relaxation time. This approximation has the same conservation and entropy properties as the original Boltzmann operator, but is simpler for deterministic numerical simulations. However, 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  $\text{Pr} = 1$ .

Additional relaxation times can be added in this model by using the ES-BGK approach exposed in [17]: the idea is to modify the equilibrium temperature  $T_{eq}$  in  $\mathcal{M}_{tr}$ ,  $\mathcal{M}_{rot}$ , and  $\mathcal{M}_{vib}$  so as to obtain the correct relaxation times. Indeed, our ES-BGK collision operator is

$$Q(f) = \frac{1}{\tau}(\mathcal{G}[f] - f), \quad (26)$$

with  $\mathcal{G}[f](v, \varepsilon, i) = \mathcal{G}_{tr}[f](v) \mathcal{G}_{rot}[f](\varepsilon) \mathcal{G}_{vib}[f](i)$ , where

$$\begin{aligned} \mathcal{G}_{tr}[f](v) &= \frac{\rho}{\sqrt{\det(2\pi\Pi)}} \exp\left(-\frac{1}{2}(v-u)^T \Pi^{-1} (v-u)\right), \\ \mathcal{G}_{rot}[f](\varepsilon) &= \frac{\Lambda(\delta)}{(RT_{rot}^{rel})^{\delta/2}} \varepsilon^{\frac{\delta-2}{2}} \exp\left(-\frac{\varepsilon}{RT_{rot}^{rel}}\right), \\ \mathcal{G}_{vib}[f](i) &= (1 - \exp(-T_0/T_{vib}^{rel})) \exp\left(-i\frac{T_0}{T_{vib}^{rel}}\right), \end{aligned} \quad (27)$$

are distributions associated to the energies of translation, rotation and vibration of the molecules. The relaxation tensor  $\Pi$  and temperatures  $T_{rot}^{rel}$  and  $T_{vib}^{rel}$  are defined as follows.

First, note the following integral properties

$$\int_{\mathbb{R}^3} \mathcal{G}_{tr}[f](v) dv = \rho, \quad \int_{\mathbb{R}^3} v \mathcal{G}_{tr}[f](v) dv = \rho u, \quad \int_{\mathbb{R}^3} (v-u) \otimes (v-u) \mathcal{G}_{tr}[f](v) dv = \rho \Pi \quad (28)$$

$$\int_0^{+\infty} \mathcal{G}_{rot}[f](\varepsilon) d\varepsilon = 1, \quad \int_0^{+\infty} \varepsilon \mathcal{G}_{rot}[f](\varepsilon) d\varepsilon = e_{rot}(T_{rot}^{rel}), \quad (29)$$

$$\sum_{i=0}^{+\infty} \mathcal{G}_{vib}[f](i) = 1, \quad \sum_{i=0}^{+\infty} i R T_0 \mathcal{G}_{vib}[f](i) = e_{vib}(T_{vib}^{rel}). \quad (30)$$

Now,  $T_{rot}^{rel}$  and  $T_{vib}^{rel}$  are defined so that our ES-BGK model (24)–(27) satisfies (in the space homogeneous case) the Landau-Teller and Jeans equations (18)–(19). This gives

$$e_{rot}(T_{rot}^{rel}) = e_{rot}(T_{rot}) + \frac{\tau}{Z_{rot}\tau_C} (e_{rot}(T_{tr}) - e_{rot}(T_{rot})), \quad (31)$$

$$e_{vib}(T_{vib}^{rel}) = e_{vib}(T_{vib}) + \frac{\tau}{Z_{vib}\tau_C} (e_{vib}(T_{tr}) - e_{vib}(T_{vib})), \quad (32)$$



We also need a relaxation translational temperature  $T_{tr}^{rel}$ , defined by

$$\rho e_{tr}(T_{tr}^{rel}) = \int_{\mathbb{R}^3} \frac{1}{2} |v - u|^2 \mathcal{G}_{tr}[f](v) dv \quad (33)$$

which reads  $e_{tr}(T_{tr}^{rel}) = \frac{1}{2} \text{Trace}(\Pi)$ , or equivalently  $T_{tr}^{rel} = \frac{1}{3R} \text{Trace}(\Pi)$ . Then, the conservation of total energy of our model requires  $\langle (\frac{1}{2}|v - u|^2 + \varepsilon + iRT_0)\mathcal{G}[f] \rangle_{v,\varepsilon,i} = \rho E(f)$ , which gives the following definition of  $T_{tr}^{rel}$ :

$$e_{tr}(T_{tr}^{rel}) = e_{tr}(T_{tr}) - \frac{\tau}{Z_{rot}\tau_C} (e_{rot}(T_{tr}) - e_{rot}(T_{rot})) - \frac{\tau}{Z_{vib}\tau_C} (e_{vib}(T_{tr}) - e_{vib}(T_{vib})). \quad (34)$$

Now, the relaxation tensor  $\Pi$  is defined as follows. In the homogeneous case, our ES-BGK model makes the heat flux relax exponentially fast to 0 with relaxation time  $\tau$ . We impose that the deviation of  $\Theta$  to its trace value  $RT_{tr}I$  relaxes to zero too, with relaxation time  $\tau \text{Pr}$ . This gives

$$\Pi = RT_{tr}^{rel}I + \frac{\text{Pr} - 1}{\text{Pr}} (\Theta - RT_{tr}I). \quad (35)$$

The relaxation time  $\tau$  is defined so that our ES-BGK model is consistent with the compressible Navier-Stokes equations with shear viscosity  $\mu$  (see section 5): this gives

$$\tau = \frac{\mu}{\rho RT_{tr} \text{Pr}}. \quad (36)$$

Moreover, note that a temperature power law dependence of  $\mu$  is generally chosen, which is related to the intermolecular collision model of the Boltzmann equation (see [25] for instance).

Finally, note that collision numbers  $Z_{rot}$  and  $Z_{vib}$  might be temperature dependant (models of Parker and Millikan-White): in this case, they have to be defined at the translational temperature  $T_{tr}$ . In the same way,  $\mu$  should also be defined at  $T_{tr}$  in (36), so that  $\tau$  depends on  $T_{tr}$ , like  $\tau_C$ . However, to make notations simpler, the dependence on  $T_{tr}$  of  $Z_{rot}$ ,  $Z_{vib}$ ,  $\tau$ , and  $\tau_C$  is not made explicit in the remaining of this paper.

## 4.2 Definition of the model

Our model is not always well defined: indeed, it requires that the relaxation energies are positive, and that the relaxation tensor  $\Pi$  is positive definite. These constraints are analyzed in the following two propositions, where it is shown that they depend on the translational temperature only via values of  $Z_{rot}$ ,  $Z_{vib}$ ,  $\tau$ ,  $\tau_C$ , and  $c_v^{vib}$ .

**Proposition 4.1** (Positiveness of relaxation energies). *For positive  $T_{tr}$ ,  $T_{rot}$  and  $T_{vib}$ , the relaxation energies defined by (31), (32), and (34), are positive if*

$$\frac{\tau}{Z_{rot}\tau_C} < 1, \quad \frac{\tau}{Z_{vib}\tau_C} < 1, \quad \text{and} \quad \frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} + \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_{tr})}{c_v^{tr}} < 1. \quad (37)$$

*Proof.* The positivity of  $e_{rot}(T_{rot}^{rel})$  and  $e_{vib}(T_{vib}^{rel})$  is obtained by writing relations (31) and (32) as linear combinations that are clearly strictly convex under the necessary and sufficient conditions  $\frac{\tau}{Z_{rot}\tau_C} < 1$  and  $\frac{\tau}{Z_{vib}\tau_C} < 1$ .

For  $e_{tr}(T_{tr}^{rel})$ , we rewrite (34) as

$$T_{tr}^{rel} = T_{tr} - \frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} (T_{tr} - T_{rot}) - \frac{\tau}{Z_{vib}\tau_C} \frac{1}{c_v^{tr}} (e_{vib}(T_{tr}) - e_{vib}(T_{vib})),$$

see (14) and (5). Then we use the mean value theorem applied to the function  $e_{vib}$  to get

$$T_{tr}^{rel} = T_{tr} - \frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} (T_{tr} - T_{rot}) - \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_1)}{c_v^{tr}} (T_{tr} - T_{vib}), \quad (38)$$

where  $T_1$  lies between  $T_{tr}$  and  $T_{vib}$  and is such that  $e_{vib}(T_{tr}) - e_{vib}(T_{vib}) = c_v^{vib}(T_1)(T_{tr} - T_{vib})$ , and we remind we have used  $c_v^{vib}(T) = de_{vib}(T)/dT$ .

Now, for the positiveness of  $T_{tr}^{rel}$ , the most restrictive case is when  $T_{tr} - T_{rot} \geq 0$  and  $T_{tr} - T_{vib} \geq 0$ , that we assume now. Moreover, the positiveness of  $T_{tr}^{rel}$  and hence of  $e_{tr}(T_{tr}^{rel})$ , is obtained by writing (38) as a linear combination of  $T_{tr}$ ,  $T_{rot}$ , and  $T_{vib}$  which is strictly convex under the condition

$$\frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} + \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_1)}{c_v^{tr}} < 1. \quad (39)$$

Since  $c_v^{vib}$  is an increasing function (see section 2.2), and since we assumed  $T_{tr} \geq T_{vib}$ , therefore  $c_v^{vib}(T_1) \leq c_v^{vib}(T_{tr})$ , which gives the last condition of (37).

For the other cases, it can easily be proved that this condition is sufficient too: in the case ( $T_{tr} - T_{rot} \leq 0$  and  $T_{tr} - T_{vib} \leq 0$ ), (38) is always true, and in the cases ( $T_{tr} - T_{rot} \geq 0$  and  $T_{tr} - T_{vib} \leq 0$ ) and ( $T_{tr} - T_{rot} \leq 0$  and  $T_{tr} - T_{vib} \geq 0$ ), (38) is true under conditions  $1 - \frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} \geq 0$  and  $1 - \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_{tr})}{c_v^{tr}} \geq 0$ , respectively.  $\square$

**Proposition 4.2** (Positiveness of tensor  $\Pi$ ). *Let  $T_{tr}$ ,  $T_{rot}$  and  $T_{vib}$  be three positive temperatures, and a Prandtl number  $\frac{2}{3} < \text{Pr} \leq 1$ . We assume (37) holds, then the tensor  $\Pi$  defined by (35) is positive definite under the assumption*

$$\frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} + \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_{tr})}{c_v^{tr}} < \frac{3}{\text{Pr}} \left( \text{Pr} - \frac{2}{3} \right). \quad (40)$$

*Proof.* First, note that  $\Pi$  and  $\Theta$  have the same eigenvectors, and hence relation (35) written in this eigenvector basis reads

$$\lambda_i(\Pi) = RT_{tr}^{rel} + \left(1 - \frac{1}{\text{Pr}}\right)(\lambda_i(\Theta) - RT_{tr}),$$

where  $\lambda_i(\Pi)$  and  $\lambda_i(\Theta)$  are the eigenvalues of  $\Pi$  and  $\Theta$  for  $i = 1, 2, 3$ . By (13) and (12), we have  $RT_{tr} = \frac{1}{3}(\lambda_1(\Theta) + \lambda_2(\Theta) + \lambda_3(\Theta))$ , and since the  $\lambda_i(\Theta)$  are positive (note that (12) implies  $\Theta$  is positive definite), we get  $\lambda_i(\Theta) \leq 3RT_{tr}$ . Finally, the assumption  $\text{Pr} \leq 1$  implies

$$\lambda_i(\Pi) \geq RT_{tr}^{rel} + \left(1 - \frac{1}{\text{Pr}}\right)2RT_{tr}. \quad (41)$$

Consequently, a sufficient condition for  $\Pi$  to be positive definite is that the right-hand side of (41) is positive.

Now, we inject the expression of  $T_{tr}^{rel}$  (38) into (41), and we find that the right-hand side of (41) is positive if

$$\frac{3}{\text{Pr}} \left( \text{Pr} - \frac{2}{3} \right) T_{tr} - \frac{\tau}{Z_{rot}\tau_C} \frac{c_v^{rot}}{c_v^{tr}} (T_{tr} - T_{rot}) - \frac{\tau}{Z_{vib}\tau_C} \frac{c_v^{vib}(T_1)}{c_v^{tr}} (T_{tr} - T_{vib}) \geq 0. \quad (42)$$

The same analysis as for the proof of proposition 4.1 gives the final condition (40).  $\square$

**Remark 4.1.** Condition (40) is clearly not optimal, since the directional temperatures  $\lambda_i(\Theta)/R$  are generally close to  $T_{tr}$  and the non zero values of  $T_{rot}$  and  $T_{vib}$  help in getting (42) (see [4] for an optimal condition obtained in the monoatomic case).

### 4.3 Conservation properties

**Proposition 4.3.** *The collision operator (26) of the ES-BGK model satisfies the conservation of mass, momentum, and energy:*

$$\left\langle (1, v, \frac{1}{2}|v-u|^2 + \varepsilon + iRT_0) \frac{1}{\tau} (\mathcal{G}[f] - f) \right\rangle_{v,\varepsilon,i} = 0. \quad (43)$$

*Proof.* This is a simple consequence of the definition of the relaxation variables  $T_\alpha^{rel}$  and  $\Pi$  (see (31–35)), and of the integral relations (27–30).  $\square$

### 4.4 Entropy

The use of a single rotational energy with  $\delta$  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 any macroscopic values  $(\rho, u, \Theta, T_{rot}, T_{vib})$ , we define the following set of distribution functions that realizes these values, namely

$$\begin{aligned} \mathcal{X}_{\rho,u,\Theta,T_{rot},T_{vib}} = \{ & \phi \geq 0, \quad \left\langle (1 + |v|^2 + \varepsilon + i + |\log(\phi/\varepsilon^{\frac{\delta}{2}-1})|) \phi \right\rangle_{v,\varepsilon,i} < +\infty, \\ & \langle (1, v, (v-u) \otimes (v-u), \varepsilon, iRT_0) \phi \rangle_{v,\varepsilon,i} = (\rho, \rho u, \rho \Theta, \rho e_{rot}(T_{rot}), \rho e_{vib}(T_{vib})) \}. \end{aligned} \quad (44)$$

Now we state the H-theorem for our model.

**Proposition 4.4.** *We assume  $\frac{2}{3} < \text{Pr} \leq 1$  and conditions (37) and (40) are satisfied. Our ES-BGK model (24)-(26) satisfies*

$$\partial_t \mathbb{H}(f) + \nabla \cdot \left\langle v(f \log(f/\varepsilon^{\frac{\delta}{2}-1}) - f) \right\rangle_{v,\varepsilon,i} = \left\langle \frac{1}{\tau} (\mathcal{G}[f] - f) \log(f/\varepsilon^{\frac{\delta}{2}-1}) \right\rangle_{v,\varepsilon,i} \leq 0, \quad (45)$$

under the additional condition

$$\frac{\tau}{Z_{rot}\tau_C} + \frac{\tau}{Z_{vib}\tau_C} \leq \frac{3}{5}. \quad (46)$$

Moreover, the right-hand side of (45) is zero if, and only if  $f = \mathcal{M}[f]$ .

*Proof.* We remind elements of proof already proved in [17] that apply here too:

1. The Gaussian distribution  $\mathcal{G}[f]$  defined by (26) is the unique minimizer of the entropy functional  $\mathbb{H}(f)$  on the set  $\mathcal{X}_{\rho,u,\Pi,T_{rot}^{rel},T_{vib}^{rel}}$ , defined according to (44).
2. By convexity of  $\mathbb{H}$ , the right-hand side of (45) is non positive under the sufficient condition

$$\mathbb{H}(\mathcal{G}[f]) \leq \mathbb{H}(f). \quad (47)$$

This condition is not obvious, since  $f$  is not in  $\mathcal{X}_{\rho,u,\Pi,T_{rot}^{rel},T_{vib}^{rel}}$ .

3. For any macroscopic quantities  $(\rho, u, \Theta, T_{rot}, T_{vib})$ , we denote by  $S(\rho, u, \Theta, T_{rot}, T_{vib})$  the minimum value of  $\mathbb{H}$  on  $\mathcal{X}_{\rho,u,\Theta,T_{rot},T_{vib}}$ , and we have

$$S(\rho, u, \Theta, T_{rot}, T_{vib}) = \rho \log \rho + C\rho - \frac{\rho}{R} \mathcal{S} \left( \frac{3}{2} (\det \Theta)^{\frac{1}{2}}, e_{rot}(T_{rot}), e_{vib}(T_{vib}) \right) \quad (48)$$

where  $\mathcal{S}$  is the entropy at constant density defined in section 2, and  $C$  is a constant that depends on  $\delta$  and  $R$  only.

4. By point 1, we have  $\mathbb{H}(\mathcal{G}[f]) = S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel})$ .
5. Since  $f$  is in  $\mathcal{X}_{\rho, u, \Theta, T_{rot}, T_{vib}}$ , then we have  $S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel}) \leq \mathbb{H}(f)$ .
6. A sufficient condition for (47) is therefore

$$S(\rho, u, \Pi, T_{rot}^{rel}, T_{vib}^{rel}) \leq S(\rho, u, \Theta, T_{rot}, T_{vib}). \quad (49)$$

7. We have

$$\frac{\det \Theta}{\det \Pi} \leq \left( \frac{e_{tr}(T_{tr})}{e_{tr}(T_{tr}^{rel})} \right)^3. \quad (50)$$

The proof of this inequality is slightly different from that shown in [17] and is given in appendix B.

8. With points 3, 6, and 7, a sufficient condition for (49) is

$$\begin{aligned} & \mathcal{S}(e_{tr}(T_{tr}), s_{rot}(e_{rot}(T_{rot})), s_{vib}(e_{vib}(T_{vib}))) \\ & \leq \mathcal{S}(e_{tr}(T_{tr}^{rel}), s_{rot}(e_{rot}(T_{rot}^{rel})), s_{vib}(e_{vib}(T_{vib}^{rel}))), \end{aligned} \quad (51)$$

The proof of this last inequality is the only part which is different from [17], and a bit more involved. Our proof is divided into 5 steps.

**Step 1: parametrization of  $\mathcal{S}$ .** We consider  $(e_{tr}(T_{tr}^{rel}), e_{rot}(T_{rot}^{rel}), e_{vib}(T_{vib}^{rel}))$  as (affine) functions of parameters  $Z_{rot}$  and  $Z_{vib}$ , and we set

$$h(\theta_{rot}, \theta_{vib}) = \mathcal{S}(e_{tr}(T_{tr}^{rel}), e_{rot}(T_{rot}^{rel}), e_{vib}(T_{vib}^{rel})), \quad (52)$$

where  $\theta_{rot} = \frac{\tau}{Z_{rot}\tau_C}$  and  $\theta_{vib} = \frac{\tau}{Z_{vib}\tau_C}$ . With these new parameters, we have

$$e_{tr}(T_{tr}^{rel}) = e_{tr}(T_{tr}) + \theta_{rot}(e_{rot}(T_{rot}) - e_{rot}(T_{tr})) + \theta_{vib}(e_{vib}(T_{vib}) - e_{vib}(T_{tr})) \quad (53)$$

$$e_{rot}(T_{rot}^{rel}) = \theta_{rot}e_{rot}(T_{tr}) + (1 - \theta_{rot})e_{rot}(T_{rot}), \quad (54)$$

$$e_{vib}(T_{vib}^{rel}) = \theta_{vib}e_{vib}(T_{tr}) + (1 - \theta_{vib})e_{vib}(T_{vib}). \quad (55)$$

Now it is clear that for  $(\theta_{rot}, \theta_{vib}) = (0, 0)$ , the relaxation energies reduce to the initial energies, that is to say

$$(e_{tr}(T_{tr}^{rel}), e_{rot}(T_{rot}^{rel}), e_{vib}(T_{vib}^{rel}))|_{(\theta_{rot}, \theta_{vib})=(0,0)} = (e_{tr}(T_{tr}), e_{rot}(T_{rot}), e_{vib}(T_{vib})).$$

Consequently, our entropy inequality (51) reads

$$h(0, 0) \leq h(\theta_{rot}, \theta_{vib}). \quad (56)$$

While the domain of definition of  $h$  is given by positiveness condition (37), here we need to reduce it to condition (46) given in the proposition. With our new parameters, it reads

$$\theta_{rot} + \theta_{vib} \leq \frac{3}{5}. \quad (57)$$

In fact, numerical tests suggest (56) can be false if this condition is not fulfilled.

Finally, note that  $h$  is concave, as composed of an affine function and the concave function  $\mathcal{S}$ .

**Step 2: relaxation temperatures as convex combinations** Here we use the same argument as used in the proof of proposition 4.1: we linearize (53)–(55) by using the mean value theorem, and we get

$$\begin{aligned} T_{tr}^{rel} &= (1 - \theta_{rot} \frac{c_v^{rot}}{c_v^{tr}} - \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}}) T_{tr} + \theta_{rot} \frac{c_v^{rot}}{c_v^{tr}} T_{rot} + \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}} T_{vib}, \\ T_{rot}^{rel} &= \theta_{rot} T_{tr} + (1 - \theta_{rot}) T_{rot}, \\ T_{vib}^{rel} &= \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} T_{tr} + (1 - \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)}) T_{vib}, \end{aligned} \quad (58)$$

where  $T_1$  and  $T_2$  are some temperatures between  $T_{tr}$  and  $T_{vib}$ , and  $T_{vib}^{rel}$  and  $T_{vib}$ , respectively, defined by

$$c_v^{vib}(T_1) = \frac{e_{vib}(T_{tr}) - e_{vib}(T_{vib})}{T_{tr} - T_{vib}}, \quad \text{and} \quad c_v^{vib}(T_2) = \frac{e_{vib}(T_{vib}) - e_{vib}(T_{vib}^{rel})}{T_{vib} - T_{vib}^{rel}}. \quad (59)$$

**Step 3: minimization of  $h$ .** In the plane  $(\theta_{rot}, \theta_{vib})$ , condition (57) defines a triangle  $\mathcal{T}$  of vertices  $(0, 0)$ ,  $(0, \frac{3}{5})$ ,  $(\frac{3}{5}, 0)$ . Since  $h$  is concave, its minimum on  $\mathcal{T}$  is reached at one vertex of  $\mathcal{T}$ . Therefore

$$h(\theta_{rot}, \theta_{vib}) \geq \min(h(0, 0), h(0, \frac{3}{5}), h(\frac{3}{5}, 0)).$$

for every  $(\theta_{rot}, \theta_{vib})$  in  $\mathcal{T}$ .

Then a sufficient condition for (56) is that the minimum is reached at  $(0, 0)$ , that is to say

$$h(0, 0) \leq h(0, \frac{3}{5}) \quad \text{and} \quad h(0, 0) \leq h(\frac{3}{5}, 0). \quad (60)$$

Now, we prove the first inequality of (60). In fact, it is simpler to prove a stronger property, namely

$$h(0, 0) \leq h(0, \theta_{vib}) \quad (61)$$

for every  $\theta_{vib} \leq \frac{3}{5}$ . We start by using that  $h$  is concave but also that it is differentiable to get

$$h(0, \theta_{vib}) \geq h(0, 0) + \theta_{vib} \partial_{\theta_{vib}} h(0, \theta_{vib}),$$

and now a sufficient condition to get (61) is  $\partial_{\theta_{vib}} h(0, \theta_{vib}) \geq 0$ . But the chain rule gives

$$\begin{aligned} \partial_{\theta_{vib}} h(\theta_{rot}, \theta_{vib}) &= \nabla \mathcal{S}(e_{tr}(T_{tr}^{rel}), e_{rot}(T_{rot}^{rel}), e_{vib}(T_{vib}^{rel})) \cdot \frac{\partial}{\partial \theta_{vib}} \begin{pmatrix} e_{tr}(T_{tr}^{rel}) \\ e_{rot}(T_{rot}^{rel}) \\ e_{vib}(T_{vib}^{rel}) \end{pmatrix} \\ &= \left( \frac{1}{T_{tr}^{rel}} - \frac{1}{T_{vib}^{rel}} \right) (e_{vib}(T_{vib}) - e_{vib}(T_{tr})). \end{aligned}$$

Now for  $\theta_{rot} = 0$  this reads

$$\partial_{\theta_{vib}} h(0, \theta_{vib}) = \left( \frac{1}{T_{tr}^{rel,0}} - \frac{1}{T_{vib}^{rel}} \right) (e_{vib}(T_{vib}) - e_{vib}(T_{tr})), \quad (62)$$

where the exponent 0 indicates that  $T_{tr}^{rel,0}$  is defined by (53) with  $\theta_{rot} = 0$ .

This quantity can be proved to be non negative if we are able to show that  $T_{vib}^{rel} - T_{tr}^{rel,0} = \alpha(T_{vib} - T_{tr})$  with  $\alpha \geq 0$ . Indeed, if the second bracket of (62) is positive, then  $T_{vib} - T_{tr} \geq 0$  since  $e_{vib}$  is an increasing function, and hence  $T_{vib}^{rel} - T_{tr}^{rel,0} \geq 0$  too, and the first bracket of (62)

is positive as well, which gives the sign of  $\partial_{\theta_{vib}} h(0, \theta_{vib})$ . The proof is the same in the opposite case.

The relation  $T_{vib}^{rel} - T_{tr}^{rel,0} = \alpha(T_{vib} - T_{tr})$  is obtained with (58). With  $\theta_{rot} = 0$ , these relations give

$$T_{vib}^{rel} - T_{tr}^{rel,0} = \left(1 - \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} - \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}}\right) (T_{vib} - T_{tr}).$$

Our coefficient  $\alpha$  is clearly non negative under the condition

$$\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} + \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}} \leq 1. \quad (63)$$

Now, this condition is analyzed with two different cases.

**First case:**  $T_{tr} \leq T_{vib}$ . Since  $T_{vib}^{rel}$  is a convex combination of  $T_{tr}$  and  $T_{vib}$ , we have  $T_{tr} \leq T_{vib}^{rel} \leq T_{vib}$ . Then the intermediate temperatures  $T_1$  and  $T_2$  are in intervals  $[T_{tr}, T_{vib}]$  and  $[T_{vib}^{rel}, T_{vib}]$ , respectively. Now, the convexity of  $e_{vib}$  implies  $c_v^{vib}(T_2) \geq c_v^{vib}(T_1)$  (see appendix A). Consequently, the first term of the left-hand side of (63) satisfies

$$\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} \leq \theta_{vib}.$$

Moreover, the second term satisfies  $\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}} \leq \frac{2}{3}\theta_{vib}$  (since  $c_v^{vib}$  is bounded by  $R$ , see section 2.2). Finally, the left-hand side of (63) satisfies

$$\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} + \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}} \leq \frac{5}{3}\theta_{vib}$$

which is indeed lower than 1, since  $\theta_{vib} \leq 3/5$ . Therefore (63) is satisfied.

**Second case:**  $T_{tr} \geq T_{vib}$ . Now we have  $T_{vib} \leq T_{vib}^{rel} \leq T_{tr}$ . This case is more delicate, since in the first term of (63),  $\frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)}$  now is greater than 1. Thus we must work on the product  $\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)}$ . By using (59), we have

$$\begin{aligned} \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} &= \theta_{vib} \left( \frac{e_{vib}(T_{tr}) - e_{vib}(T_{vib})}{e_{vib}(T_{vib}) - e_{vib}(T_{vib}^{rel})} \right) \left( \frac{T_{tr} - T_{vib}}{T_{vib} - T_{vib}^{rel}} \right) \\ &= \frac{T_{vib}^{rel} - T_{vib}}{T_{tr} - T_{vib}} = 1 - \frac{T_{tr} - T_{vib}^{rel}}{T_{tr} - T_{vib}}, \end{aligned} \quad (64)$$

where we have used (55) to simplify the energy ratio.

Now, note that  $e_{vib}(T_{tr}) - e_{vib}(T_{vib}^{rel}) \leq c_v^{vib}(T_{tr})(T_{tr} - T_{vib}^{rel})$ , since  $c_v^{vib}$  is bounded by  $c_v^{vib}(T_{tr})$  in  $[T_{vib}, T_{tr}]$ , and hence

$$\begin{aligned} T_{tr} - T_{vib}^{rel} &\geq \frac{e_{vib}(T_{tr}) - e_{vib}(T_{vib}^{rel})}{c_v^{vib}(T_{tr})} \\ &= \frac{(1 - \theta_{vib})(e_{vib}(T_{tr}) - e_{vib}(T_{vib}))}{c_v^{vib}(T_{tr})} = (1 - \theta_{vib}) \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_{tr})} (T_{tr} - T_{vib}), \end{aligned}$$

from (55) and (59). Consequently, we go back to (64) and we get

$$\theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_2)} \leq 1 - (1 - \theta_{vib}) \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_{tr})},$$

which is now clearly lower than 1. Therefore, a sufficient condition for (63) is

$$1 - (1 - \theta_{vib}) \frac{c_v^{vib}(T_1)}{c_v^{vib}(T_{tr})} + \theta_{vib} \frac{c_v^{vib}(T_1)}{c_v^{tr}} \leq 1,$$

which is equivalent to

$$\theta_{vib} \leq \frac{1}{1 + \frac{c_v^{vib}(T_{tr})}{c_v^{tr}}}.$$

Now, since the ratio  $\frac{c_v^{vib}(T_{tr})}{c_v^{tr}}$  is lower than  $2/3$ , this last inequality is satisfied if  $\theta_{vib} \leq 1/(1 + 2/3) = 3/5$ , which is what we wanted to prove, and hence (63) is now proved for every cases. This proves (61) for every  $\theta_{vib} \leq \frac{3}{5}$  and hence the first inequality of (60) is proved.

The second inequality of (60) is proved in a similar way, but much more easily, since  $e_{rot}$  is linear. Indeed, the ratio  $c_v^{rot}(T_1)/c_v^{rot}(T_2)$  in the equivalent of (63) is equal to 1, and the inequality is obviously satisfied for every  $\theta_{rot} \leq 3/5$ .

This long analysis proves (60), and hence (56) and in turn (51). The proof of the proposition is now almost complete: the equilibrium part is proved like in [17] and is left to the reader.  $\square$

## 4.5 Discussion on the conditions for positiveness of relaxation energies, positive definiteness of $\Pi$ , and H-theorem

**Hierarchy of conditions.** Propositions 4.1, 4.2, and 4.4 hold for different conditions that are in fact not completely independent.

For instance condition (40) for positive definiteness of  $\Pi$  implies the third constraint of condition (37) for the positiveness of relaxation energies: indeed, the right-hand side of (40) is lower than 1 for  $\text{Pr} \leq 1$ .

Moreover, in proposition 4.4, condition (46) clearly implies the first two constraints of (37). However, it does not always implies the third constraint of (37), since it is temperature dependent.

This means that the number of conditions could be reduced in our propositions. Nevertheless, we find that the current redundancy is clearer, since there is a clear hierarchy: for the H-theorem to hold, we should first assume that the relaxation energies are positive, and then that  $\Pi$  is positive definite.

**Physical validity.** Now, we discuss the physical validity of these conditions. As an example, we consider a flow of nitrogen, for which the characteristic vibrational temperature is  $T_0 = 3.371\text{K}$ , and the molecular VSS parameters are  $\omega = 0.74$  and  $\alpha = 1.36$ . With the Eucken formula  $\text{Pr} = 2(5 + \delta + \delta_v)/(15 + 2(\delta + \delta_v))$  and definitions (6) and (21), we can compute all the terms of conditions (37), (40), and (46), for any arbitrary temperature, and hence we can check for what range of temperature these conditions are satisfied. For  $Z_{vib}$ , we use the Millikan-White formula as given in [25, 28]. For  $Z_{rot}$ , its usual value in aerodynamics is  $Z_{rot} = 5$ , but we also use its value as given by the Parker formula [25, 21]. Our observations are as follows.

For  $Z_{rot} = 5$ , all the conditions are satisfied up to a temperature of 40.000 K. For larger temperatures, the constraint  $\tau/Z_{vib}\tau_C < 1$  of (37) fails, and the vibrational energy becomes negative. This upper bound is clearly sufficient here, since the model is not designed for so large temperatures, for which other physical phenomenon have to be taken into account (dissociation for instance). In addition, the model of Millikan and White [28] is an empirical model which in the original paper itself is only defined in a temperature range between  $280\text{K} < T < 8000\text{K}$ , so that the physical suitability at  $T = 40.000\text{K}$  may be doubted. In general, the physical suitability of the model for very high temperatures is doubtful, since  $Z_{vib}$  then approaches 0. However, a

$Z_{vib} < 1$  would be problematic from a purely physical point of view, since the relaxation time would then be smaller than the collision time itself.

For  $Z_{rot}$  as given by Parker formula, note that  $Z_{vib}$  and  $Z_{rot}$  behave very differently, since  $Z_{rot}$  increases with the temperature, while  $Z_{vib}$  decreases very fast, and is infinitely large for small temperatures. Then we observe that all the conditions are satisfied for temperatures between 60 and 42.000 K. Again, the upper bound is clearly sufficient. The lower bound is due to the constraint  $\tau/Z_{rot}\tau_C < 1$  of (37): for lower temperatures, this constraint is not satisfied, and the rotational energy becomes negative (the other conditions fail for small temperatures a bit smaller, between 20 and 32, which is less restrictive). Here the same problem arises as already described for the vibration, since  $Z_{rot}$  goes towards 0 for decreasing temperatures. Again,  $Z_{rot} < 1$  is difficult from a purely physical point of view. The model is therefore not suitable for such low temperatures. There is another problem: the characteristic rotational temperature of  $N_2$  is  $T_{0,rot} = 2.88$  K. For hydrogen  $H_2$ , for example, this is already  $T_{0,rot} = 87.6$  K. At such low temperatures, one can no longer necessarily assume that the rotational degree of freedom is fully excited, which means that the number of degrees of freedom of the rotation and thus  $c_v^{rot}$  also become temperature-dependent for very low temperatures, comparable with the vibration in the considered temperature range. In the model proposed here, however, this effect was not taken into account, as these temperatures are lower than the smallest temperatures generally met in aerodynamics. Therefore, this effect is typically also neglected in DSMC codes and the rotational temperature is assumed to be continuous. In general, very little information can be found in the literature about the relaxation time of rotation at very low temperatures. However, in Riabov [29] one can find a discussion about the discrepancy between the classical consideration of Parker's model and the technique of Lebed and Riabov [30] for the relaxation times of rotation for  $T < 100$  K. It becomes clear that the Parker model can no longer be used for these low temperatures.

## 4.6 Comparison with the ES-BGK model of Andriès et al. [1]

If the vibration modes are neglected, our model reduces to the following translation-rotation ES-BGK model:

$$\partial_t f + v \cdot \nabla_x f = \frac{1}{\tau} (\mathcal{G}[f] - f), \quad (65)$$

where now  $f$  does not depend on  $i$ , while the Gaussian is  $\mathcal{G}[f] = \mathcal{G}_{tr}[f]\mathcal{G}_{rot}[f]$ , with  $\Pi$  and  $T_{rot}^{rel}$  are still defined by (35) and (31), and  $T_{tr}^{rel}$  is now defined by

$$e_{tr}(T_{tr}^{rel}) = e_{tr}(T_{tr}) - \frac{\tau}{Z_{rot}\tau_C} (e_{rot}(T_{tr}) - e_{rot}(T_{rot})), \quad (66)$$

while  $T_{vib}^{rel}$  is not used anymore. The macroscopic quantities are defined as in (9)–(12) without the series in  $i$ . Here, the model is not restricted to diatomic gases anymore, and  $\delta$  can take any integer values greater than or equal to 2.

For such polyatomic gases, the first ES-BGK model was proposed by Andriès et al [1], and is often used in the literature (see for instance [12]). This model reads as above with relaxation tensor

$$\Pi = (1 - \theta)((1 - \nu)RT_{tr}I + \nu\Theta) + \theta RT_{eq}, \quad (67)$$

and the relaxation rotational temperature is

$$T_{rot}^{rel} = \theta T_{eq} + (1 - \theta)T_{rot}, \quad (68)$$

where the equilibrium temperature is

$$T_{eq} = \frac{3T_{tr} + \delta T_{rot}}{3 + \delta}. \quad (69)$$



Note that in [1],  $T_{rot}$  is denoted by  $T_{int}$ ,  $T_{rot}^{rel}$  by  $T_{rot}^{rel}$ , and  $\Pi$  by  $\mathcal{T}$ . Moreover, the variable  $I = \varepsilon^{\delta/2}$  is used instead of  $\varepsilon$ , which does not change our analysis and conclusions below. Finally, the parameters  $\theta$  and  $\nu$  are defined by

$$\theta = \frac{1}{Z_{rot}}, \quad \text{and} \quad (1 - \theta)\nu = \frac{1}{Pr} - 1. \quad (70)$$

First, we show that our model can be written under the same form as the Andriès et al. model, with modified coefficients.

**Proposition 4.5.** *The relaxation tensor  $\Pi$  and rotational temperature of model (65)-(66) can be written under form (67) and (68) with modified coefficients  $\tilde{\theta}$  and  $\tilde{\nu}$  defined by*

$$\tilde{\theta} = \frac{3 + \delta}{3} \frac{\tau}{\tau_C} \theta \quad \text{and} \quad (1 - \tilde{\theta})\tilde{\nu} = \frac{1}{Pr} - 1.$$

This proposition is readily proved with a direct calculation in which  $T_{tr}$  is written as a function of  $T_{eq}$  and  $T_{rot}$  by using (69). This is left to the reader.

It is interesting to compare coefficients  $\theta$  and  $\tilde{\theta}$  of both models. For instance, for a diatomic gas ( $\delta = 2$ ) with a ratio  $\tau/\tau_C \approx 1.7$  in case of the HS collision model (see section 3.4 with the value  $Pr \approx 0.74$  for a diatomic gas without vibration modes), we find  $\tilde{\theta}$  is approximately  $3\theta$ . This shows that these two models have very different coefficients.

Another way to compare these models is to look at energy relaxations. The following proposition compares relaxation times for both models.

**Proposition 4.6.** *For both ES-BGK models, in the space homogeneous case, the rotational temperature relaxes according to*

$$\frac{d}{dt} T_{rot} = \frac{1}{\tau_{rot}} (T_{tr} - T_{rot}). \quad (71)$$

where the relaxation time is

$$\begin{aligned} \tau_{rot} &= Z_{rot} \tau_C && \text{for our model (65)-(66), and} \\ \tau_{rot} &= Z_{rot} \tau (3 + \delta) / 3 && \text{for Andriès et al. model.} \end{aligned}$$

This proposition is proved by a direct integration of the homogeneous kinetic equation times  $\varepsilon$ , and then by using the definition of  $T_{rot}^{rel}$ . This result shows that both models give different exchange rates of energy between rotational and translational modes. This can be seen more clearly with the previous example of a diatomic gas, since we find  $\tau_{rot}|_{Andriès} \approx 3\tau_{rot}$ , which means that the rotational energy of Andriès et al. model relaxes three times as fast as with our model. If the correct relaxation rate is  $\tau_{rot}$  (as it is used in some DSMC codes, see [22, 20, 23, 21]), then the energy exchange rate as given by Andriès et al. model is much too large.

## 5 Hydrodynamic asymptotics

To obtain the conservation laws, we multiply (24) by the vector  $1$ ,  $v$ , and  $\frac{1}{2}|v|^2 + \varepsilon + iRT_0$  and we integrate to get:

$$\begin{aligned} \partial_t \rho + \nabla \cdot (\rho u) &= 0, \\ \partial_t (\rho u) + \nabla \cdot (\rho u \otimes u) + \nabla \cdot P(f) &= 0, \\ \partial_t \mathcal{E} + \nabla \cdot (\mathcal{E} u) + \nabla \cdot (P(f) u) + \nabla \cdot q(f) &= 0, \end{aligned} \quad (72)$$

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 (12). If we have some characteristic values of length, time, velocity, density, and temperature, our ES-BGK model (24)–(26) can be non-dimensionalized. This equation reads

$$\partial_t f + v \cdot \nabla f = \frac{1}{\text{Kn} \tau} (\mathcal{G}[f] - f), \quad (73)$$

where  $\text{Kn}$  is the Knudsen number which is the ratio between the mean free path and a macroscopic length scale. For simplicity, we use the same notations for the non-dimensional and dimensional variables. Note that we assume here that the three relaxation times have the same asymptotic order of magnitude with respect to  $\text{Kn}$  (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, leading to compressible Euler equations and compressible Navier-Stokes equations, respectively.

## 5.1 Euler asymptotics

We get the following proposition, that can be proved as in [17].

**Proposition 5.1.** *The moments of  $f$ , solution of the ES-BGK model (24), satisfy the compressible Euler equations up to  $O(\text{Kn})$ :*

$$\begin{aligned} \partial_t \rho + \nabla \cdot (\rho u) &= 0, \\ \partial_t (\rho u) + \nabla \cdot (\rho u \otimes u) + \nabla p &= O(\text{Kn}), \\ \partial_t \mathcal{E} + \nabla \cdot ((\mathcal{E} + p)u) &= O(\text{Kn}), \end{aligned} \quad (74)$$

where  $p = \rho R T_{eq}$  is the pressure at equilibrium. The non-conservative form of these equations is

$$\begin{aligned} \partial_t \rho + u \cdot \nabla \rho + \rho \nabla \cdot u &= 0, \\ \partial_t u + (u \cdot \nabla)u + \frac{1}{\rho} \nabla p &= O(\text{Kn}), \\ \partial_t T_{eq} + u \cdot \nabla T_{eq} + (\gamma - 1)T_{eq} \nabla \cdot u &= O(\text{Kn}), \end{aligned} \quad (75)$$

where  $\gamma = c_p(T_{eq})/c_v(T_{eq})$  is the ratio of specific heats, with  $c_p(T_{eq}) = c_v(T_{eq}) + R$  and  $c_v(T_{eq}) = \frac{de(T_{eq})}{dT} = c_v^{tr} + c_v^{rot} + c_v^{vib}(T_{eq})$  is the specific heat at constant volume.

## 5.2 Compressible Navier-Stokes asymptotics

Our main result is the following.

**Proposition 5.2.** *The moments of  $f$ , solution of the ES-BGK model (24), satisfy the compressible Navier-Stokes equations up to  $O(\text{Kn}^2)$ :*

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

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

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

and the viscosity, heat transfer and volume viscosity coefficients are

$$\mu = \tau p \text{Pr}, \quad \kappa = \frac{\mu c_p(T_{eq})}{\text{Pr}}, \quad \zeta = pR \left( \tau_{rot} \frac{c_v^{rot}}{c_v(T_{eq})^2} + \tau_{vib} \frac{c_v^{vib}(T_{eq})}{c_v(T_{eq})^2} \right),$$

with  $\tau_{rot} = Z_{rot} \tau_{\mathcal{C}}$  and  $\tau_{vib} = Z_{vib} \tau_{\mathcal{C}}$ , while  $Z_{rot}$ ,  $Z_{vib}$ ,  $\tau_{\mathcal{C}}$ , and  $\tau$  are defined at  $T_{eq}$ .

For the proof of proposition 5.2, most of the calculations are very similar to that given in [17]. The only difference is the first order expansion of the temperatures and of the tensor  $\Pi$  required to compute the Chapman-Enskog expansion. The corresponding procedure and results are given in appendix C.

**Remark 5.1.** The volume viscosity  $\zeta$  is the same as that found by Bruno and Giovangigli in [31] for a one temperature Navier-Stokes asymptotics derived from a Boltzmann equation for a diatomic gas with two internal modes. Indeed, in [31], when we assume that the vibrational and rotational modes are independent and that  $\tau_{vib}$  and  $\tau_{rot}$  are of the same order as  $\tau_{\mathcal{C}}$ , then equation (A2) of [31] with  $rap = vib$ ,  $sl = rot$ ,  $K^{vib,rot} = 0$ , and  $\tau_{vib}$  and  $\tau_{rot}$  as given by relation before (70) of [31] (with equilibrium temperatures), we find exactly  $\zeta$ .

Our second result is the Chapman-Enskog distribution for our model.

**Proposition 5.3.** *The first order expansion of  $f$  is*

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

with

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

This result can be obtained exactly as in [17].

## 6 Reduced ES-BGK model

For numerical simulations with a deterministic solver, our ES-BGK model may be too expensive, since it 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 [32] (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 (9)–(12) now depend on  $F$ ,  $G$  and  $H$  through:

$$\begin{aligned} \rho &= \langle F \rangle_v, & \rho u &= \langle vF \rangle_v, \\ \rho E_{tr}(f) &= \left\langle \frac{1}{2} |v|^2 F \right\rangle_v, & \rho E_{rot}(f) &= \langle G \rangle_v, & \rho E_{vib}(f) &= \langle H \rangle_v, \\ \rho \Theta &= \langle (v-u) \otimes (v-u) F \rangle_v, & q &= \left\langle \left( \frac{1}{2} |v-u|^2 F + G + H \right) (v-u) \right\rangle_v, \end{aligned} \quad (76)$$

where  $\langle \cdot \rangle_v$  denotes integrals with respect to  $v$  only. The reduced ES-BGK is obtained by multiplying our kinetic model (24)-(26) by the vector  $(1, \varepsilon, iRT_0)^T$  and by summing and integrating w.r.t to  $i$  and  $\varepsilon$ , respectively: it is written

$$\partial_t \mathbf{F} + v \cdot \nabla \mathbf{F} = \frac{1}{\tau} (\mathcal{G}[\mathbf{F}] - \mathbf{F}). \quad (77)$$

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

By using the same argument as in [17] and the result of proposition 4.4, we can prove the following H-theorem for this reduced model. The proof is left to the reader.

**Proposition 6.1.** *The functional  $\mathcal{H}(\mathbf{F}) = \langle h(\mathbf{F}) \rangle_v$ , where*

$$h(\mathbf{F}) = F \left[ \left( 1 + \frac{\delta}{2} \right) \log \left( \frac{F}{G^{\frac{\delta}{2+\delta}}} \right) + \log \left( \frac{RT_0 F}{RT_0 F + H} \right) \right] + \frac{H}{RT_0} \log \left( \frac{H}{RT_0 F + H} \right) \quad (78)$$

*is an entropy for the reduced ES-BGK system (77) and we have*

$$\partial_t \mathcal{H}(\mathbf{F}) + \nabla \cdot \langle v h(\mathbf{F}) \rangle_v = \left\langle \nabla_{\mathbf{F}} h(\mathbf{F}) \cdot \left( \frac{1}{\tau} \mathcal{G}[\mathbf{F}] - \mathbf{F} \right) \right\rangle_v \leq 0, \quad (79)$$

*under conditions of propositions 4.1, 4.2, and 4.4. The equilibrium is reached (the right-hand side of (79) 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 modes (see section 4.1).*

## 7 Numerical results

To test the ES-BGK model presented here, we will choose a Monte Carlo approach. For this purpose, relaxation processes to the equilibrium state in an adiabatic box will be investigated and compared with analytical solutions and results of the DSMC method. In the homogeneous test cases, the equation to be solved simplifies to

$$\partial_t f = \frac{1}{\tau} (\mathcal{G}[f] - f). \quad (80)$$

In the Monte Carlo method, the distribution function is represented by a linear combination of  $N$  delta functions in phase space with a numerical weighting  $w$ . The points in the phase space

are often interpreted as particles, where  $w$  corresponds to the number of real particles that a simulation particle represents. For the Monte Carlo method, (80) is integrated analytically for a time step  $\Delta t = t^{n+1} - t^n$  [33]:

$$f^{n+1} = (1 - \exp(-\Delta t/\tau))\mathcal{G}[f^n] + \exp(-\Delta t/\tau)f^n. \quad (81)$$

The idea is that each of the  $N$  particles relaxes with probability  $(1 - \exp(-\Delta t/\tau))$ , i.e. a new state is sampled from the distribution function  $\mathcal{G}[f^n]$ . Different ways to efficiently sample velocities from the ES-BGK distribution are described in [33]. The new rotational energy is sampled using an exponential distribution depending on  $T_{rot}^{rel}$ . The new vibrational quantum state is sampled using a standard Acceptance-Rejection method as described in [25] depending on  $T_{vib}^{rel}$ . Since energy and momentum are only preserved in the mean here, we choose a large number of particles  $N$  and small time steps  $\Delta t/\tau < 0.1$ . This reduces the statistical noise and ensures stability.

## 7.1 Comparison with analytical Results

To compare the model with an analytical solution, the translational-rotational and translational-vibrational relaxation are first considered separately, i.e.  $Z_{vib} = \infty$  and  $Z_{rot} = \infty$  respectively. If one also assumes an isothermal relaxation ( $T_{tr}(t) = T_{tr}(t = \infty)$ ), i.e. the thermal velocities do not relax, the characteristic time  $\tau_C$  is constant (since it depends on the translation temperature) and it is possible to define an analytical solution of the Landau-Teller equation

$$\frac{E_i(t = \infty) - E_i(t)}{E_i(t = \infty) - E_i(t = 0)} = e^{-t/Z_i\tau_C} \quad (82)$$

with  $i$  being the rotational or vibrational part.

The simulations are done with nitrogen  $N_2$  with a characteristic vibrational temperature of  $T_0^{N_2} = 3395$  K using a VHS collision model. This means an exponential ansatz is used for the viscosity depending on the VHS parameters  $T_{dref}^{VHS} = 273$  K,  $d_{dref}^{VHS} = 4.17 \cdot 10^{-10}$  m and  $\omega_{VHS} = 0.74$  as described in [20]. Thus, the analytical value for  $\tau_C$  can be calculated with the fixed translational temperature as described in Sec. 3.4.

The particle density in the simulations was chosen to be  $n = 2 \cdot 10^{22} \text{ m}^{-3}$  which corresponds to about 4 million particles in our simulation. The translational temperature is fixed to  $T_{tr} = T_{eq} = 16000$  K, the initial temperatures of the rotational and vibrational states are  $T_{rot} = T_{vib} = 8000$  K. The collision numbers are chosen to  $Z_{rot} = 5$  and  $Z_{vib} = 10$ . The results for the normalized energy difference (left hand side of (82)) are depicted in Fig. 1 showing a very good agreement for the rotational as well as vibrational relaxation.

## 7.2 Comparison with DSMC Results

In this test case, a simultaneous relaxation of the translational, rotational and vibrational temperature is demonstrated and compared with DSMC. Furthermore, the difference is shown when it is assumed that there is only one relaxation time, i.e.  $\tau_C = \tau$ . For this simulation the same parameters have been used as before with the exception of  $T_{tr} = 16000$  K,  $T_{vib} = 8000$  K,  $T_{rot} = 12000$  K,  $Z_{rot} = 5$  and  $Z_{vib} = 50$ . The DSMC simulation was carried out with the identical VHS parameters. In addition, the prohibiting double relaxation method was used to reproduce the Landau-Teller equation as described in various studies [34, 35]. The results are depicted in Fig. 2 and excellent agreement is found between DSMC and the proposed ES-BGK model. Furthermore, it is easy to see that the model with only one relaxation time does not produce the correct Landau-Teller relaxation curves when the same  $Z_{rot}$  and  $Z_{vib}$  are used: this clearly proves the improvement of our new model.

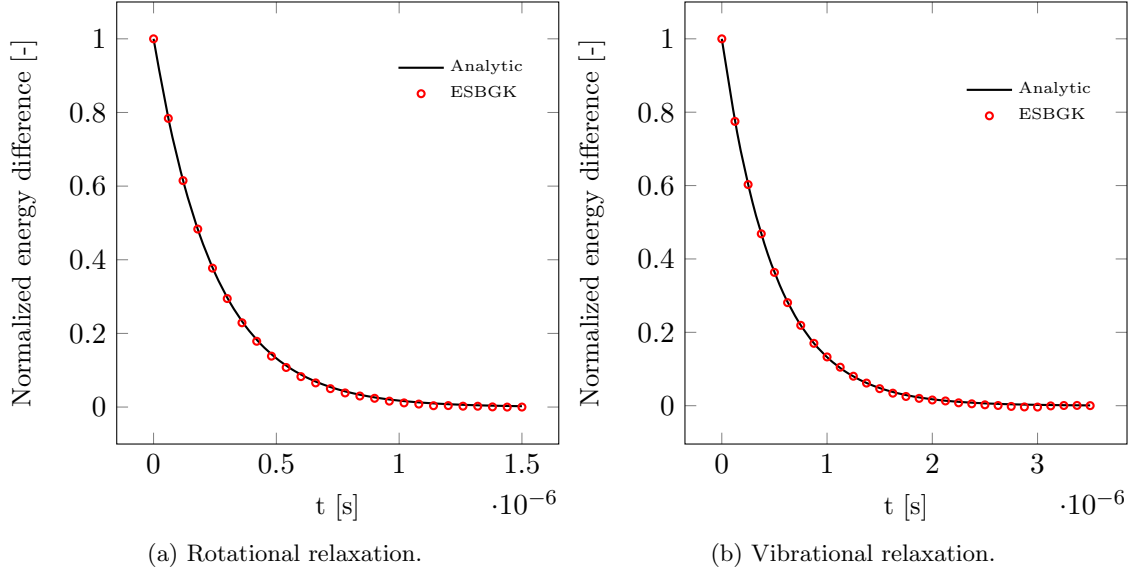


Figure 1: Comparison of ES-BGK simulation results with analytical Landau-Teller solution.

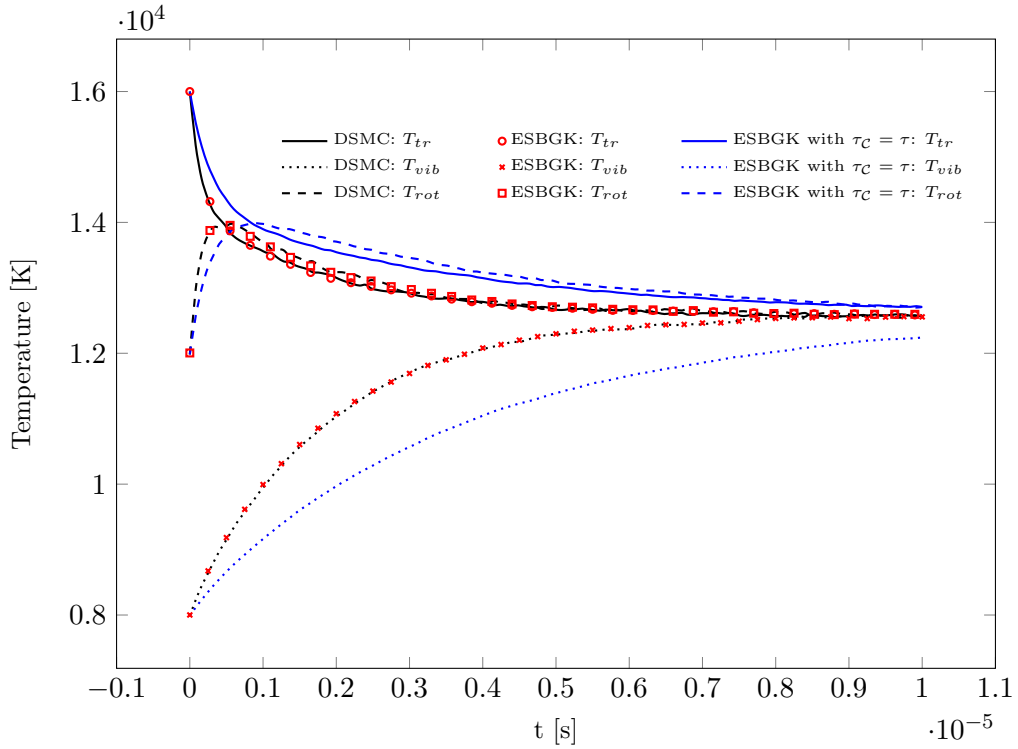


Figure 2: Comparison of relaxation process of  $T_{tr}$ ,  $T_{rot}$  and  $T_{vib}$  between DSMC and ES-BGK as well as ES-BGK with only one relaxation time  $\tau_C = \tau$ .

## 8 Conclusion

In this paper, we have proposed an ES-BGK model for diatomic gases that accounts for translational-rotational and translational-vibrational energy exchanges. It is consistent with the general definition of the vibrational and rotational collision numbers that are also commonly used in DSMC solvers to reproduce the Landau-Teller and Jean equations.

Our model is based on a correction of a previous model [17] and is induced by the numerical method of [20]. We have proved this model satisfies the H-theorem and fits the correct transport coefficients. Even the volume viscosity is consistent with that obtained for a Boltzmann equation with two internal energy modes in [31].

In the purely translational-rotational case, our model also gives a correction of the standard ES-BGK model of Andriès et al. [1] with a correction factor of the collision number that can be as large as 3.

A reduced version of our model has been derived to eliminate the dependency to the internal energy variables: the reduced model should make it possible numerical simulations of diatomic gas flows with a computational cost of same order of magnitude as for a monoatomic gas.

This model will be extended to polyatomic molecules with more than two atoms in a forthcoming work.

## A Convexity of the vibrational energy

Differentiation of (6) with respect to  $T$  gives

$$\frac{d}{dT} c_v^{vib}(T) = \frac{2RT_0^2}{T^3 e^{T_0/T} (e^{T_0/T} - 1)^2} \left( \frac{T_0}{2T} \coth\left(\frac{T_0}{2T}\right) - 1 \right),$$

which is positive, from the known inequality  $\coth(x) \geq 1/x$  for every positive  $x$ . This proves that  $c_v^{vib}$  is an increasing function, and hence that  $e_{vib}$  is convex. Passing to the limit  $T = 0$  in (6) shows that  $c_v^{vib}$  is bounded by  $R$ .

We come to the proof of the assertion made in first case of step 3 for the proof of proposition 4.4. We have  $T_{tr} \leq T_1 \leq T_{vib}$  and  $T_{vib}^{rel} \leq T_2 \leq T_{vib}$ , while  $T_{vib}^{rel}$  is between  $T_{tr}$  and  $T_{vib}$ , and we want to prove that  $c_v^{vib}(T_2) \geq c_v^{vib}(T_1)$ . This is a simple consequence of the convexity of  $e_{vib}$ , as it is shown below.

It is well known that for every convex function  $\phi$ , the ratio  $(\phi(y) - \phi(x))/(y - x)$  is increasing in  $x$  for every fixed  $y$ . This result applied to  $\phi = e_{vib}$ ,  $y = T_{vib}$  and  $x = T_{tr}$  then  $x = T_{vib}^{rel}$  gives

$$(e_{vib}(T_{vib}) - e_{vib}(T_{vib}^{rel})) / (T_{vib} - T_{vib}^{rel}) \geq (e_{vib}(T_{vib}) - e_{vib}(T_{tr})) / (T_{vib} - T_{tr}).$$

Then we remind that  $T_1$  and  $T_2$  are defined by (59): the previous inequality is then exactly  $c_v^{vib}(T_2) \geq c_v^{vib}(T_1)$ .

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

This proof is very close to that given in [1]. First, note that (50) is equivalent to

$$\det\left(\frac{\Theta}{RT_{tr}}\right) \leq \det\left(\frac{\Pi}{RT_{tr}^{rel}}\right). \quad (83)$$

Then as remarked in the proof of proposition 4.1, we can work in the same basis in which  $\Theta$  and  $\Pi$  are diagonal tensors, and we denote by  $\mu_i$  the three positive eigenvalues of  $\Theta/RT_{tr}$ , whose

sum is 3. Then by using definition (35) of  $\Pi$ , (83) reads

$$\prod_{i=1}^3 \mu_i \leq \prod_{i=1}^3 (1 + \alpha(\mu_i - 1)), \quad (84)$$

where we set  $\alpha = \frac{\text{Pr}-1}{\text{Pr}} \frac{T_{tr}}{T_{tr}^{rel}}$ . We remind that  $\Pi$  is positive definite under assumption (40), so that each terms in the product of the right-hand side of (84) is positive. Therefore, we can apply the log function to this inequality to get

$$\sum_{i=1}^3 \log \mu_i \leq \sum_{i=1}^3 \log(1 + \alpha(\mu_i - 1)). \quad (85)$$

This is the inequality we prove now.

As usual, the idea is to use convexity properties. However, since  $\alpha$  is negative for Pr between 2/3 and 1, the right-hand side of (85) is rewritten by using  $(\mu_1 + \mu_2 + \mu_3)/3 = 1$ . Indeed, we get

$$\begin{aligned} \sum_{i=1}^3 \log(1 + \alpha(\mu_i - 1)) &= \sum_{i=1}^3 \log\left(\frac{1}{3}(\mu_1 + \mu_2 + \mu_3) + \alpha\left(\mu_i - \frac{1}{3}(\mu_1 + \mu_2 + \mu_3)\right)\right) \\ &= \sum_{i=1}^3 \log\left(\frac{1}{3}(1 - \alpha)(\mu_{i_1} + \mu_{i_2}) + \frac{1}{3}(1 + 2\alpha)\mu_i\right), \end{aligned} \quad (86)$$

where  $i_1$  and  $i_2$  are the indices that follow  $i$  in the circular permutation of  $\{1, 2, 3\}$ . Now we assume  $\alpha > -1/2$  (see below), so that the argument of the log function above is a convex combination of the  $\mu_i$ . Since log is concave, the Jensen inequality gives

$$\begin{aligned} \sum_{i=1}^3 \log\left(\frac{1}{3}(1 - \alpha)(\mu_{i_1} + \mu_{i_2}) + \frac{1}{3}(1 + 2\alpha)\mu_i\right) &\geq \sum_{i=1}^3 \frac{1}{3}(1 - \alpha)(\log(\mu_{i_1}) + \log(\mu_{i_2})) + \frac{1}{3}(1 + 2\alpha)\log(\mu_i) \\ &= \sum_{i=1}^3 \log \mu_i = \det\left(\frac{\Theta}{RT_{tr}}\right). \end{aligned} \quad (87)$$

This proves (85).

It remains to prove  $\alpha > -1/2$ : this is actually a consequence of assumption (40) that guarantees that  $\Pi$  is positive definite (see the proof of proposition 4.2: the positivity of  $\alpha$  is equivalent to that of the right-hand side of (41), which is given by (42), and hence by (40)).

## C Elements of proof for the Chapman-Enskog expansion

Integration of (73) multiplied by  $\frac{1}{2}|v|^2$ ,  $\varepsilon$ , and  $iRT_0$ , respectively, gives macroscopic evolution equations of  $e_{tr}(T_{tr})$ ,  $e_{rot}(T_{rot})$ , and  $e_{vib}(T_{vib})$ . Linearization of these equations by using  $\partial_t e_\alpha(T_\alpha) = c_v^\alpha(T_\alpha) \partial_t T_\alpha$  give first order expansions of  $e_{tr}(T_{tr}^{rel})$ ,  $e_{rot}(T_{rot}^{rel})$ , and  $e_{vib}(T_{vib}^{rel})$ . The definition of the relaxation energies (31)–(34) and other successive linearizations lead to the



following first order expansions:

$$\begin{aligned}
T_{rot}^{rel} &= T_{eq} \left( 1 - \text{Kn}\tau_{\mathcal{C}}(\gamma - 1) \left( Z_{rot} \left( \frac{c_v^{rot}}{c_v(T_{eq})} - 1 \right) + Z_{vib} \frac{c_v^{vib}(T_{eq})}{c_v(T_{eq})} + \frac{\tau}{\tau_{\mathcal{C}}} \right) \nabla \cdot u \right) + O(\text{Kn}^2), \\
T_{vib}^{rel} &= T_{eq} \left( 1 - \text{Kn}\tau_{\mathcal{C}}(\gamma - 1) \left( Z_{vib} \left( \frac{c_v^{vib}(T_{eq})}{c_v(T_{eq})} - 1 \right) + Z_{rot} \frac{c_v^{rot}}{c_v(T_{eq})} + \frac{\tau}{\tau_{\mathcal{C}}} \right) \nabla \cdot u \right) + O(\text{Kn}^2), \\
T_{tr}^{rel} &= T_{eq} \left( 1 - \text{Kn}\tau_{\mathcal{C}}(\gamma - 1) \left( Z_{vib} \frac{c_v^{vib}(T_{eq})}{c_v(T_{eq})} + Z_{rot} \frac{c_v^{rot}}{c_v(T_{eq})} + \frac{\tau}{\tau_{\mathcal{C}}} \left( 1 - \frac{c_v(T_{eq})}{c_v^{tr}} \right) \right) \nabla \cdot u \right) + O(\text{Kn}^2).
\end{aligned}$$

These relations give the first order expansion of the relaxation tensor

$$\begin{aligned}
\Pi &= \frac{RT_{eq}}{\text{Pr}} I + \frac{\text{Pr} - 1}{\text{Pr}} \Theta \\
&\quad + \text{Kn}\tau R(\gamma - 1) T_{eq} \left( \left( \frac{c_v(T_{eq})}{c_v^{tr}} - 1 \right) - \frac{1}{\text{Pr}} \frac{\tau_{\mathcal{C}}}{\tau} \left( Z_{vib} \frac{c_v^{vib}(T_{eq})}{c_v(T_{eq})} + Z_{rot} \frac{c_v^{rot}}{c_v(T_{eq})} \right) \right) \nabla \cdot u I \\
&\quad + O(\text{Kn}^2).
\end{aligned}$$

The other calculations are standard and can be found in [17].

## Acknowledgments

”Marcel Pfeiffer has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No. 899981 MEDUSA)”

## References

- [1] P. Andriès, P. Le Tallec, J.-F. Perlat, and B. Perthame. The Gaussian-BGK model of Boltzmann equation with small Prandtl number. *Eur. J. Mech. B/Fluids*, 2000.
- [2] C. Cercignani. *The Boltzmann Equation and Its Applications*, volume 68. Springer-Verlag, Lectures Series in Mathematics, 1988.
- [3] M.H. Gorji, M. Torrilhon, and P. Jenny. Fokker-Planck model for computational studies of monatomic rarefied gas flows. *Journal of fluid mechanics*, 680:574–601, August 2011.
- [4] J. Mathiaud and L. Mieussens. A Fokker-Planck model of the Boltzmann equation with correct Prandtl number. *Journal of Statistical Physics*, 162(2):397–414, Jan 2016.
- [5] E.P. Gross, P.L. Bhatnagar, and M. Krook. A model for collision processes in gases. *Physical review*, 94(3):511–525, 1954.
- [6] P. Welander. On the temperature jump in a rarefied gas. *Arkiv für Fysik*, 7(44):507–553, 1954.
- [7] Jr. Lowell H. Holway. New statistical models for kinetic theory: Methods of construction. *Physics of Fluids*, 9(9):1658–1673, 1966.
- [8] E. M. Shakhov. Generalization of the Krook relaxation kinetic equation. *Izv. Akad. Nauk SSSR. Mekh. Zhidk. Gaza*, pages 142–145, 1968.

- [9] H. Struchtrup. The BGK-Model with Velocity-Dependent Collision Frequency. *Continuum Mech. Thermodyn.*, 9:23–31, 1997.
- [10] Guangjun Liu. A method for constructing a model form for the boltzmann equation. *Physics of Fluids A: Fluid Dynamics*, 2(2):277–280, 1990.
- [11] P. Andriès, J.-F. Bourgat, P. le Tallec, and B. Perthame. Numerical comparison between the Boltzmann and ES-BGK models for rarefied gases. *Computer Methods in Applied Mechanics and Engineering*, 191(31):3369–3390, 2002.
- [12] S. Kosuge, H.-W. Kuo, and K. Aoki. A kinetic model for a polyatomic gas with temperature-dependent specific heats and its application to shock-wave structure. *Journal of Statistical Physics*, 177(2):209–251, Oct 2019.
- [13] V. A. Rykov. A model kinetic equation for a gas with rotational degrees of freedom. *Fluid Dynamics*, 10(6):959–966, 1975.
- [14] Z. Wang, H. Yan, Q. Li, and K. Xu. Unified gas-kinetic scheme for diatomic molecular flow with translational, rotational, and vibrational modes. *Journal of Computational Physics*, 350:237 – 259, 2017.
- [15] T. F. Morse. Kinetic model for gases with internal degrees of freedom. *Phys. Fluids*, 7(159), 1964.
- [16] M. Bisi and M.J. Cáceres. A BGK relaxation model for polyatomic gas mixtures. *Commun. Math. Sci.*, 14(2):297–325, October 2016.
- [17] Y. Dauvois, J. Mathiaud, and L. Mieussens. An ES-BGK model for polyatomic gases in rotational and vibrational nonequilibrium. *European Journal of Mechanics - B/Fluids*, 88:1–16, 2021.
- [18] J. Mathiaud and L. Mieussens. Mesoscopic Boltzmann model equations for thermally perfect gases. *Physics of Fluids*, 33(12):127112, 2021.
- [19] C. Baranger, J.-P. Braeunig, Y. Dauvois, J. Mathiaud, and L. Mieussens. Validation of ES-BGK solvers. unpublished.
- [20] M. Pfeiffer. Extending the particle ellipsoidal statistical Bhatnagar-Gross-Krook method to diatomic molecules including quantized vibrational energies. *Physics of Fluids*, 30:116103, 11 2018.
- [21] J. G. Parker. Rotational and vibrational relaxation in diatomic gases. *The Physics of Fluids*, 2(4):449–462, 1959.
- [22] I. Boyd and T. E. Schwartzentruber. *Nonequilibrium Gas Dynamics and Molecular Simulation*. Cambridge Aerospace Series. Cambridge University Press, 2017.
- [23] Brian L. Haas, David B. Hash, Graeme A. Bird, Forrest E. Lumpkin, and H. A. Hassan. Rates of thermal relaxation in direct simulation monte carlo methods. *Physics of Fluids*, 6(6):2191–2201, 1994.
- [24] Marcel Pfeiffer, Paul Nizenkov, and Stefanos Fasoulas. Extension of particle-based bgk models to polyatomic species in hypersonic flow around a flat-faced cylinder. In *AIP Conference Proceedings*, volume 2132, page 100001. AIP Publishing LLC, 2019.

- [25] G. A. Bird. *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*. Oxford Engineering Science Series, 2003.
- [26] V. Giovangigli. *Multicomponent Flow Modeling*. Birkhäuser Boston, Boston, MA, 1999.
- [27] J. Mathiaud and L. Mieussens. BGK and Fokker-Planck models of the Boltzmann equation for gases with discrete levels of vibrational energy. *Journal of Statistical Physics*, 178(5):1076–1095, 2020.
- [28] Roger C. Millikan and Donald R. White. Systematics of vibrational relaxation. *The Journal of Chemical Physics*, 39(12):3209–3213, 1963.
- [29] Vladimir V. Riabov. Estimations of rotational relaxation parameters in diatomic gases. *AIP Conference Proceedings*, 1333(1):1257–1262, 2011.
- [30] IV Lebed and VV Riabov. Quantum effects in rotational relaxation of a freely expanding gas. *PMTF Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki*, 20(1):3–6, 1979.
- [31] D. Bruno and V. Giovangigli. Relaxation of internal temperature and volume viscosity. *Physics of Fluids*, 23(9):093104, 2011.
- [32] C. K. Chu. Kinetic-theoretic description of the formation of a shock wave. *Phys. Fluids*, 8(1):12, 1965.
- [33] M. Pfeiffer. Particle-based fluid dynamics: Comparison of different Bhatnagar-Gross-Krook models and the direct simulation monte carlo method for hypersonic flows. *Physics of Fluids*, 30(10):106106, 2018.
- [34] C. Zhang and T. E. Schwartzentruber. Inelastic collision selection procedures for direct simulation monte carlo calculations of gas mixtures. *Physics of Fluids (1994-present)*, 25(10):–, 2013.
- [35] M. Pfeiffer, P. Nizenkov, A. Mirza, and S. Fasoulas. Direct simulation Monte Carlo modeling of relaxation processes in polyatomic gases. *Physics of Fluids*, 28(2):027103, feb 2016.