ESAIM: M2AN 60 (2026) 473–494
https://doi.org/10.1051/m2an/2026008

ESAIM: Mathematical Modelling and Numerical Analysis
www.esaim-m2an.org

A KINETIC MODEL FOR POLYATOMIC GAS WITH QUASI-RESONANT COLLISIONS LEADING TO BI-TEMPERATURE RELAXATION PROCESSES

Thomas Borsoni[1,2,*], Laurent Boudin[2], Julien Mathiaud[3] and Francesco Salvarani[4,5]

Abstract. In this article, we extend the Boltzmann framework for polyatomic gases by introducing quasi-resonant kernels, which relax resonant interactions, for which kinetic and internal energies are separately conserved and lead to equilibrium states with two temperatures. We establish an H-theorem and analyze the quasi-resonant model's asymptotic behaviour, demonstrating a two-phase relaxation process: an initial convergence towards a two-temperature Maxwellian state followed by gradual relaxation of the two temperatures towards each other. Numerical simulations validate our theoretical predictions. The notion of quasi-resonance provides the first rigorous framework of a Boltzmann dynamics for which the distribution is at all times close to a multi-temperature Maxwellian, relaxing towards a one-temperature Maxwellian.

Mathematics Subject Classification. 35Q20, 76P05, 82C40.

Received June 11, 2025. Accepted January 19, 2026.

1. Introduction

In this article, we propose a rigorous Boltzmann framework for modelling a polyatomic gas whose molecules undergo quasi-resonant collisions, relying on collision selection through the collision kernel. We discuss the behaviour of the corresponding homogeneous dynamic, for which we expect the distribution to be at all times close to a two-temperature Maxwellian, which temperatures relax towards each other, following a Landau-Teller type equation. This is finally numerically verified.

The study of polyatomic gases has garnered significant interest in recent years, with numerous researchers contributing to this field. Polyatomic gases differ from monatomic gases because their molecular structure cannot be fully described using only kinematic variables such as position and velocity. To account for these differences, an additional independent variable representing internal structure is required. The first works in this direction date back to the 1950s with Wang Chang and Uhlenbeck [40] and Taxman [39]. A significant contribution was provided by Borgnakke and Larsen in [7], introducing a numerically well-suited procedure. In this paper, we

Keywords and phrases. Boltzmann equation, polyatomic gases, resonant collisions, quasi-resonant collisions, near-resonance, Landau–Teller equations.

[1] CERMICS, École des Ponts et Chaussées – Institut Polytechnique de Paris & Inria Saclay, Champs-sur-Marne, France.

[2] Sorbonne Université, Université Paris Cité, CNRS, Laboratoire Jacques-Louis Lions, LJLL, F-75005 Paris, France.

[3] Université de Rennes, CNRS, IRMAR, UMR 6625, Rennes, France.

[4] De Vinci Higher Education, De Vinci Research Center, Paris, France.

[5] Dipartimento di Matematica "F. Casorati", Università degli Studi di Pavia, Via Ferrata 1, 27100 Pavia, Italy.

*Corresponding author: `thomas.borsoni@enpc.fr`

describe the internal structure of the polyatomic molecules through their internal energy level, denoted by I, and belonging to $\mathbb{R}_+$ endowed with a measure μ, called the internal energy law. We assume μ to have a nonnegative and continuous density φ with respect to the Lebesgue measure as in the seminal works [12, 17, 18], *i.e.*

$$\mathrm{d}\mu(I) = \varphi(I)\,\mathrm{d}I, \qquad I > 0.$$

Some typical choices of φ are $\varphi : I \mapsto I^{\delta/2-1}$, corresponding to a polytropic gas with $3+\delta$ number of degrees of freedom, and the ceiling function $\varphi : I \mapsto \lceil I \rceil$, corresponding to a diatomic molecule, whose rotation is classically described *via* a rigid-rotor model, and vibration is described *via* a quantum harmonic oscillator model, for which we refer to Bisi *et al.* [6].

Back in the 1960's, it was already shown in Sharma [36] that vibrational energy transfers between CO_2 isotopes would exhibit *near-resonance* behaviour, in the sense that collision pathways for which the post-collision vibrational energy is close to the pre-collisional one are largely dominant. This was later supported by Stephenson and Moore [38] for a mixture involving in particular CO_2 molecules. Detailed computations on collision cross-sections involving the CO_2 molecule recently conducted [27] also showed such a behaviour. Similar results for other molecules, either with experimental data or *ab initio* calculations, have also been pointed out since then [13, 37]. Early discussions on resonant vibrational energy transfers are also found in [29, 32]. *Ab initio* calculations conducted in Lanza *et al.* [26] on the rotational energy transfer in $HCl - H_2$ collisions were shown to be mostly near-resonant, and to quote the authors of the latter work, "Near resonant energy transfer process can be an important, often dominant, rotational energy transfer pathway at low temperatures".

As such, despite their broad applicability and widespread use, polyatomic Boltzmann models with standard cross-sections, such as Variable Hard Spheres, exhibit inconsistencies with experimental data and theoretical calculations in the above mentioned scenarios. As noted in [27], the kinetic modelling of carbon dioxide presents some peculiar challenges due to the emergence of two distinct temperatures associated with translational and rotational energies, which do not mutually interact. Consequently, in the mathematical models describing this framework, the kinetic and internal energy of colliding particles must be separately, or almost separately, conserved.

Advancements in this direction were made by Aoki *et al.* [25], who extended the ellipsoidal statistical model of the Boltzmann equation for a polyatomic gas with constant specific heats (proposed in Andries *et al.* [2]) to a polyatomic gas with temperature-dependent specific heats. Some other articles have then studied the complex dynamics of such gases [3, 4, 23–25] in an ES-BGK framework, highlighting several properties of resonant collisions. In [19], Djordjić, Pavić-Čolić and Torrilhon proposed a polyatomic Boltzmann model including a term of frozen collisions, for which no internal energy is exchanged, and which may be seen as a singular type of resonant collisions.

Since the 1960s, several authors have proposed kinetic models that preserve fundamental global properties of the original Boltzmann equation while neglecting detailed collision mechanisms [22, 30, 34, 35].

Indeed, transition probabilities, which are essential in the Boltzmann description, are difficult to compute *ab initio*, and can be derived from phenomenological assumptions [30] or obtained *via* molecular dynamics simulations for specific gases [31].

In [15], Bruno and Giovangigli incorporated the notion of resonant collisions in a Boltzmann framework, along with Magin, Graille and Massot [28], by considering the collision operator to be composed of a "fast" component, related to resonant collisions, and a "slow" component, encompassing standard polyatomic collisions. More recently, a Boltzmann model to describe resonant collisions has been introduced in Boudin *et al.* [11]. The equilibrium solution of the model depends on two temperatures, and several properties, including the H-theorem, have been deduced. Given the recent introduction of the corresponding model in the literature, the mathematical study of resonant collision kernels remains less developed compared to the standard Boltzmann operator. Nonetheless, significant progress has been made, including investigations into the compactness of the linearized operator [9, 10]. Let us briefly discuss that resonant model. As already stated, a collision is said to be resonant when the microscopic kinetic and internal energies are *separately* conserved during the collision together with the microscopic momentum. Hence, formally, the model rises as a singular case of polyatomic collisions exchanging momentum, kinetic energy and internal energy. Since the conservation laws are directly related to the support of the collision kernel, the resonant property of the collisions can be provided by formally putting the internal energy conservation in the collision kernel as a Dirac mass. With this viewpoint, a natural way to define quasi-resonant collision kernels is to replace the Dirac mass by a nonnegative approximation of that Dirac mass in the kernel expression.

In this work, we propose a Boltzmann model with quasi-resonant collisions, providing a more realistic framework than the resonant one, and allowing to capture slow bi-temperature relaxations, during which the distribution is at all times close to a bi-temperature Maxwellian. From a theoretical perspective, incorporating quasi-resonant kernels extends classical thermal relaxation models within the Boltzmann framework and provides insight into transitions between dynamical regimes in kinetic transport. This approach bridges the gap between idealized resonant interactions and the complexity of real molecular systems, offering a more general and physically consistent description of energy exchange. Our approach bears similarities with the ones of [15,16] and [28], with an emphasis on the collision kernel, characterization of quasi-resonant collisions and derivation of Landau-Teller equations.

The article is structured as follows.

In the next Section, we introduce the model and establish a precise definition of quasi-resonance quantified by a quasi-resonance parameter $\varepsilon > 0$. We then derive an H-theorem for this model and investigate the resonant asymptotics as ε vanishes, recovering the version of the resonant model used in Borsoni *et al.* [10] equipped with the correct internal energy measure.

In Section 3, we explore the implications of these findings and discuss the expected properties of the model. We argue that a homogeneous quasi-resonant Boltzmann dynamics likely follows a two-phase evolution. Initially, in the short-term regime, the distribution behaves similarly to the fully resonant case and relaxes toward a two-temperature Maxwellian equilibrium. Subsequently, in the long-term regime, the distribution remains in this form while the kinetic and internal temperatures gradually converge towards each other. Assuming that latter behaviour holds, we explicitly derive an ODE system which approximately governs the evolution of the kinetic and internal temperatures during the second phase. This system, valid for a broad class of collision kernels, is of Landau–Teller-type, see, for instance, [33].

Finally, in Section 4, we conduct numerical simulations to validate our theoretical predictions. Specifically, we verify that the kinetic and internal temperatures approximately follow the derived Landau–Teller-type ODE system, and conduct a preliminary quantitative study of the behaviour of the approximation as the quasi-resonance parameter ε goes to 0.

2. Boltzmann model with quasi-resonant collisions

The approach developed here is based on a polyatomic kinetic framework wherein quasi-resonant collisions are selected by truncating the cross-section.

We study a single gas composed of polyatomic molecules, which are described, at the microscopic level, by their mass $m > 0$, velocity $v \in \mathbb{R}^3$ and internal energy level $I \in \mathbb{R}_+$. We then consider two colliding molecules with respective incoming velocities v, $v_* \in \mathbb{R}^3$ and internal energies I, $I_* \in \mathbb{R}_+$ and their outgoing counterparts v', v'_*, I', I'_*. Since the momentum and total energy of the two-particle (isolated) system are conserved during the collision, the following microscopic conservation laws hold

$$v + v_* = v' + v'_*, \tag{1}$$

$$\frac{1}{2}m|v|^2 + \frac{1}{2}m|v_*|^2 + I + I_* = \frac{1}{2}m|v'|^2 + \frac{1}{2}m|v'_*|^2 + I' + I'_*. \tag{2}$$

It is important to notice that (1) and (2) imply that the total energy in the center of mass of the molecules

$$E = \frac{m}{4}|v - v_*|^2 + I + I_* = \frac{m}{4}|v' - v'_*|^2 + I' + I'_* \tag{3}$$

is conserved during the collision. Then (1) and (2) ensure the existence of $\sigma \in \mathbb{S}^2$ such that

$$v' = \frac{v + v_*}{2} + \frac{2}{\sqrt{m}}\sqrt{E - (I' + I'_*)}\,\sigma, \qquad v'_* = \frac{v + v_*}{2} - \frac{2}{\sqrt{m}}\sqrt{E - (I' + I'_*)}\,\sigma, \tag{4}$$

and $I' + I'_* \leq E$. We moreover introduce the following notations

$$R = \frac{m|v' - v'_*|^2}{4E} = 1 - \frac{I' + I'_*}{E}, \qquad R' = \frac{m|v - v_*|^2}{4E} = 1 - \frac{I + I_*}{E}, \tag{5}$$

as in the Borgnakke–Larsen description, see [12] for instance. At the microscopic level, resonant collisions, for which the kinetic and internal energy are separately conserved, can thus be characterized by the property

$$R = R'.$$

In the quasi-resonant case, both the kinetic and internal energies are separately almost conserved, *i.e.*

$$|v'|^2 + |v'_*|^2 \approx |v|^2 + |v_*|^2, \qquad I' + I'_* \approx I + I_*,$$

or equivalently,

$$R \approx R'.$$

Our approach, detailed in Subsection 2.1, consists in considering some reference polyatomic collisions, and removing the ones which are deemed too far from being resonant.

2.1. Quasi-resonance by collision kernel truncation

In the Boltzmann model, the collisional properties are embedded in the collision kernel. It is a positive function whose support (related to its domain of definition) is provided by the microscopic momentum and energy conservation laws, and whose values formally correspond to some density of probability of possible collisions. Therefore, it is equivalent to state that a collision is possible, and that the collision kernel takes a positive value on the variables involved in the latter. We consider a reference collision kernel B whose support characterizes standard polyatomic collisions. From that reference kernel, we define the family of quasi-resonant collision kernels $(B_\varepsilon)_{\varepsilon>0}$, indexed by the quasi-resonant parameter $\varepsilon > 0$, as the product of B with a cut-off function χ_ε. This function, defined below in (10), allows the removal of collisions deemed too far from being resonant relatively to the parameter ε, and is built in such a way that it approximates a Dirac mass (corresponding to the resonant case) when ε vanishes. Figure 1 provides a schematic representation of the situation.

In the standard polyatomic setting, the collision kernel seen as a measure on $(\mathbb{R}^3 \times \mathbb{R}_+)^4$ is supported on a manifold $\mathcal{C}$, as shown on Figure 1a. Then the intersection of $\mathcal{C}$ with the set of quadruplets $((v, I), (v_*, I_*), (v', I'), (v'_*, I'_*))$ such that $R = R'$ corresponds to the resonant manifold seen on Figure 1. In the quasi-resonant setting drawn on Figure 1c, the collision kernel support coincides with the support of the cut-off function χ_ε, which is a narrow strip within $\mathcal{C}$ surrounding the resonant submanifold, with a width of order ε. The quasi-resonant model is then built such that, as ε goes to 0, the quasi-resonant collision kernel measure gets closer to the resonant collision kernel measure.

To make this argument more precise, we introduce the following formalism.

Reference collision kernel

We introduce $B := B(v, v_*, I, I_*, I', I'_*, \sigma) \geq 0$ a reference polyatomic collision kernel, in the sense that it satisfies, for almost every v, $v_* \in \mathbb{R}^3$, I, I_*, I', $I'_* \in \mathbb{R}_+$, $\sigma \in \mathbb{S}^2$, a symmetry property

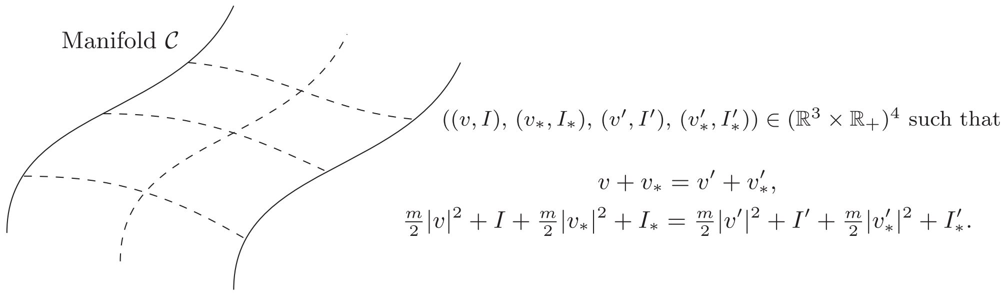
$$B(v, v_*, I, I_*, I', I'_*, \sigma) = B(v_*, v, I_*, I, I'_*, I', -\sigma), \tag{6}$$

a micro-reversibility assumption

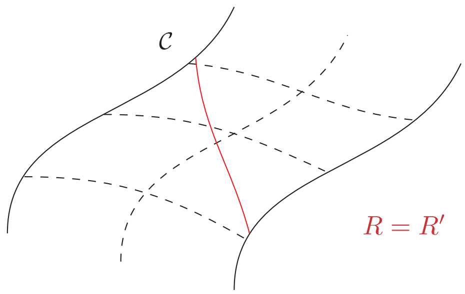
$$|v - v_*| B(v, v_*, I, I_*, I', I'_*, \sigma) = |v' - v'_*| B(v', v'_*, I', I'_*, I, I_*, \sigma'), \tag{7}$$

and a positivity condition to authorize only physical collisions, that is

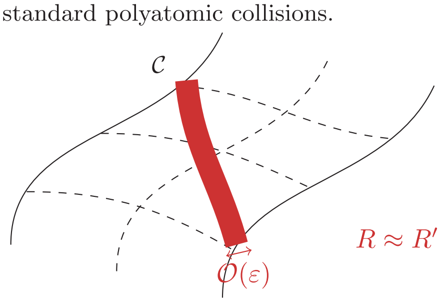
$$I' + I'_* \leq E \iff B(v, v_*, I, I_*, I', I'_*, \sigma) > 0, \tag{8}$$



(a) Manifold $\mathcal{C} \subset (\mathbb{R}^3 \times \mathbb{R}_+)^4$ of allowed standard polyatomic collisions.



(b) Resonant submanifold, one dimension less than $\mathcal{C}$.



(c) Quasi-resonant submanifold, same dimension as $\mathcal{C}$.

FIGURE 1. Standard, resonant and quasi-resonant manifolds of allowed collision quadruplets in $(\mathbb{R}^3 \times \mathbb{R}_+)^4$.

remembering that E is defined in (3). These assumptions may be found for instance in Borsoni *et al.* [8], and are compatible with other standard formulations as in [17, 20], as soon as the corresponding Boltzmann operator is defined accordingly.

A possible reference collision kernel, which we later use for explicit computations in Sections 3 and 4, would be

$$B(v, v_*, I, I_*, I', I'_*, \sigma) = C_B\, b(\sigma \cdot \sigma') \left[\frac{m}{4}|v - v_*|^2\right]^{\kappa_k - 1/2} \left[\frac{m}{4}|v' - v'_*|^2\right]^{\kappa_k} (I + I_*)^{\kappa_i} \, (I' + I'_*)^{\kappa_i} \, E^{\gamma} \, \frac{\mathbb{1}_{[I' + I'_* \leq E]}}{\mathfrak{m}_\varphi(E)},$$

where the velocities v' and v'_* are functions of the variables of B given by (4), κ_k, κ_i and γ are real numbers, $C_B > 0$ is a (dimensional) constant, and b is an angular kernel satisfying, for $\omega \in \mathbb{S}^2$,

$$\int_{\mathbb{S}^2} b(\sigma \cdot \omega) \, \mathrm{d}\sigma = 1.$$

Eventually, the notation $\mathbb{1}_X$ stands for the characteristic function of the set X, and $\mathfrak{m}_\varphi(E)$ is the L^1-norm of $\mathbb{1}_{[I' + I'_* \leq E]}$ on $(0, +\infty)^2$ with respect to the internal energy distribution measure, that is

$$\mathfrak{m}_\varphi(E) = \iint_{(0,+\infty)^2} \mathbb{1}_{[I' + I'_* \leq E]} \, \varphi(I') \, \varphi(I'_*) \, \mathrm{d}I' \, \mathrm{d}I'_*. \tag{9}$$

We emphasize again that the above explicit choice of B is not required at all in this current section.

Truncation function and quasi-resonant collision kernel

Let us now build the quasi-resonant family of kernels $(B_\varepsilon)_{\varepsilon>0}$ from the reference kernel B. In order to discriminate whether a collision is deemed quasi-resonant or not, relatively to ε, we introduce the family of cut-off functions $(\chi_\varepsilon)_{\varepsilon>0}$, defined, for all $\varepsilon > 0$, by

$$\chi_\varepsilon(R, R') = \frac{c_\eta(R, R')}{2\varepsilon}\, \mathbb{1}_{[|\eta(R)-\eta(R')|\leq\varepsilon]}, \qquad R, R' \in (0,1). \tag{10}$$

Here, η is a $\mathcal{C}^\infty$-diffeomorphism from $(0,1)$ to $\mathbb{R}$, and c_η is a $\mathcal{C}^1$ normalizing factor, satisfying a symmetry property

$$c_\eta(R, R') = c_\eta(R', R), \qquad R, R' \in (0,1), \tag{11}$$

which is required to preserve the micro-reversibility of B_ε, and a diagonal condition

$$c_\eta(R, R) = \eta'(R), \qquad R \in (0,1), \tag{12}$$

which is crucial to recover the resonant asymptotics when ε goes to 0, as we shall see below. Possible choices for c_η would be $c_\eta(R, R') = \sqrt{\eta'(R)\eta'(R')}$ or $c_\eta(R, R') = (\eta'(R) + \eta'(R'))/2$, but the upcoming computations can be carried out by keeping c_η general. Indeed, we shall see that the study of the ε-vanishing asymptotics only requires, at the first non-zero order with respect to ε, the knowledge of conditions (11) and (12).

We emphasize that the cut-off functions (χ_ε) fully characterize the notion of quasi-resonance. Indeed, at fixed $\varepsilon > 0$, the collisions deemed to be quasi-resonant are exactly the ones for which $\chi_\varepsilon(R, R') > 0$. Moreover, the support of χ_ε goes to $(0,1)^2$ (all collisions are allowed: standard polyatomic case) when $\varepsilon \to \infty$, and that χ_ε approximates the Dirac at $R = R'$ (resonant collisions) when $\varepsilon \to 0$.

Remark 1. The symmetry property of c_η implies that $\partial_1 c_\eta(R, R') = \partial_2 c_\eta(R', R)$ for any $R, R' \in (0,1)$. Besides, by differentiating (12), we get, for any $R \in (0,1)$, $\partial_1 c_\eta(R, R) + \partial_2 c_\eta(R, R) = \eta''(R)$, so that, for any $R \in (0,1)$,

$$\partial_1 c_\eta(R, R) = \partial_2 c_\eta(R, R) = \frac{\eta''(R)}{2}\cdot \tag{13}$$

In the expression (10) of the truncation function, the $\mathcal{C}^\infty$-diffeomorphism η is used to enhance the model flexibility and prevent boundary issues. Indeed, using $\mathbb{1}_{[|R-R'|\leq\varepsilon]}$ in (10) would be problematic. For instance, when $R' < \varepsilon$ is fixed, the set $\{R \in (0,1) \mid |R - R'| \leq \varepsilon\}$ becomes asymmetric due to the constraint $R > 0$. Using instead $\mathbb{1}_{[|\eta(R)-\eta(R')|\leq\varepsilon]}$ avoids this issue.

A typical choice of η, later used in the explicit computations of Sections 3 and 4, would be

$$\eta : (0,1) \to \mathbb{R}, \quad R \mapsto \log\left(\frac{R}{1-R}\right),$$

which is indeed an (increasing) $\mathcal{C}^\infty$-diffeomorphism from $(0,1)$ to $\mathbb{R}$. The distance from resonance measured through the quantity $\eta(R) - \eta(R')$ corresponds in this case to

$$\eta(R) - \eta(R') = (\log E'_k - \log E'_i) - (\log E_k - \log E_i) = (\log E'_k - \log E_k) - (\log E'_i - \log E_i).$$

That difference hence allows to simultaneously quantify the discrepancy between pre- and post-collisional energies, but also between kinetic and internal ones. Moreover, due to the presence of the log function, the comparison is made through ratios instead of differences.

We are now in a position to define the family of quasi-resonant collision kernels $(B_\varepsilon)_{\varepsilon>0}$ associated to the reference kernel B and the truncation family $(\chi_\varepsilon)_{\varepsilon>0}$, by, for any $\varepsilon > 0$, v, $v_* \in \mathbb{R}^3$, $\sigma \in \mathbb{S}^2$ and I, I_*, I', $I'_* \in \mathbb{R}_+$,

$$B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) = B(v, v_*, I, I_*, I', I'_*, \sigma)\, \chi_\varepsilon(R, R'), \tag{14}$$

where R and R' are given by (5). Thanks to (11), for any $\varepsilon > 0$, the kernel B_ε satisfies the symmetry and micro-reversibility properties, for any $v, v_*, \sigma, I, I_*, I', I'_*$,

$$B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) = B_\varepsilon(v_*, v, I_*, I, I'_*, I', -\sigma), \tag{15}$$

$$|v - v_*| B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) = |v' - v'_*| B_\varepsilon(v', v'_*, I', I'_*, I, I_*, \sigma'), \tag{16}$$

and thanks to (8), B_ε satisfies the following positivity property, which differs from (8) through the involvement of η and ε,

$$\{I' + I'_* \leq E \quad \text{and} \quad |\eta(R) - \eta(R')| \leq \varepsilon\} \iff B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) > 0. \tag{17}$$

2.2. Quasi-resonant Boltzmann operator and H-theorem

We consider a family of quasi-resonant collision kernels $(B_\varepsilon)_{\varepsilon>0}$ defined as in the previous subsection, and denote by $(Q_\varepsilon)_{\varepsilon>0}$ the associated family of Boltzmann quasi-resonant collision operators. For $\varepsilon > 0$, Q_ε is defined for any density $f \equiv f(v, I) \geq 0$ for which it makes sense, and almost every $v \in \mathbb{R}^3$, $I \in \mathbb{R}_+$, by

$$Q_\varepsilon(f, f)(v, I) = \int_{\mathbb{R}^3} \iiint_{(0,+\infty)^3} \int_{\mathbb{S}^2} (f' f'_* - f f_*) B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) \, \mathrm{d}\sigma \, \varphi(I') \, \mathrm{d}I' \, \varphi(I'_*) \, \mathrm{d}I'_* \, \varphi(I_*) \, \mathrm{d}I_* \, \mathrm{d}v_*, \tag{18}$$

where, in the above equation, we use the standard shortcuts $f \equiv f(v, I)$, $f_* \equiv f(v_*, I_*)$, $f' \equiv f(v', I')$, $f'_* \equiv f(v'_*, I'_*)$, and v', v'_* are defined by (4).

Weak form of the operator

Since the kernel B_ε satisfies the usual polyatomic symmetry and micro-reversibility conditions, we immediately obtain (see for instance [8]) that, for any test-function $\psi \equiv \psi(v, I)$ such that the following makes sense, we have

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \psi(v, I) \, Q_\varepsilon(f, f)(v, I) \, \varphi(I) \, \mathrm{d}I \, \mathrm{d}v = \frac{1}{2} \iint_{(\mathbb{R}^3)^2} \iiiint_{(0,+\infty)^4} \int_{\mathbb{S}^2} f f_* \, (\psi' + \psi'_* - \psi - \psi_*) \, B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) \, \mathrm{d}\sigma \, \varphi(I') \, \mathrm{d}I' \, \varphi(I'_*) \, \mathrm{d}I'_* \, \varphi(I) \, \mathrm{d}I \, \varphi(I_*) \, \mathrm{d}I_* \, \mathrm{d}v \, \mathrm{d}v_*, \tag{19}$$

where we use the same shortcuts as in (18). We deduce from its weak form (19) that, as usual, Q_ε conserves, at least formally, the mass, momentum and total energy. More precisely, for any $f \equiv f(v, I)$ such that it makes sense, the following property holds

$$\int_{\mathbb{R}^3} \int_0^{+\infty} Q_\varepsilon(f, f)(v, I) \begin{pmatrix} 1 \\ v \\ \frac{1}{2} m |v|^2 + I \end{pmatrix} \varphi(I) \, \mathrm{d}I \, \mathrm{d}v = 0. \tag{20}$$

Notice that the conservation properties of the quasi-resonant operators are the same as those in the non-resonant polyatomic case. On the other hand, in the resonant case, kinetic and internal energy are conserved separately.

Collision invariants and H theorem

We now focus on the basic properties of the quasi-resonant kernel.

Definition 1. A function $\psi : \mathbb{R}^3 \times \mathbb{R}_+ \to \mathbb{R}$ is said to be an ε-quasi-resonant collision invariant if ψ is measurable and satisfies, for any v, $v_* \in \mathbb{R}^3$, $\sigma \in \mathbb{S}^2$ and I, I_*, I', $I'_* \in \mathbb{R}_+$,

$$(I' + I'_* \leq E \quad \text{and} \quad |\eta(R) - \eta(R')| \leq \varepsilon) \quad \Longrightarrow \quad (\psi(v', I') + \psi(v'_*, I'_*) = \psi(v, I) + \psi(v_*, I_*)), \tag{21}$$

where E is given by (3), v', v'_* by (4), and R and R' by (5).

The definition of ε-quasi-resonant collision invariants slightly differs from the one of the usual polyatomic invariants through the additional condition $|\eta(R) - \eta(R')| \leq \varepsilon$. Therefore, the set of collisions on which the invariance property is assumed to hold is smaller than in the standard polyatomic case. As a result, we cannot directly apply the known results of characterization of the collision invariants in the generic case. We provide this characterization in the following proposition, whose proof is mostly based on Lemma 3 of [11].

Proposition 1 (Collision invariants)**.** *Assume ψ to be a continuous ε-quasi-resonant collision invariant. Then there exist $a_1 \in \mathbb{R}$, $p \in \mathbb{R}^3$ and $a_2 \in \mathbb{R}$ such that for all $(v, I) \in \mathbb{R}^3 \times \mathbb{R}_+$, we have*

$$\psi(v, I) = a_1 + p \cdot v + a_2 \Big(\frac{m}{2} |v|^2 + I \Big). \tag{22}$$

Proof. As a collision invariant in the quasi-resonant case, ψ satisfies

$$\psi\left(\frac{v + v_*}{2} + 2\sqrt{\frac{E - I' - I'_*}{m}} \sigma, I' \right) + \psi\left(\frac{v + v_*}{2} - 2\sqrt{\frac{E - I' - I'_*}{m}} \sigma, I'_* \right) = \psi(v, I) + \psi(v_*, I_*) \tag{23}$$

for any $(v, v_*, I, I_*, I', I'_*, \sigma)$ such that $B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma)$ is non-zero. In particular, (23) holds whenever $R = R'$, using the notations defined in (5), *i.e.* in the resonant case. Thanks to the computations detailed in Boudin *et al.* [11], there exist a_1, a_2, $a_3 \in \mathbb{R}$ and $p \in \mathbb{R}^3$ such that, for any (v, I),

$$\psi(v, I) = a_1 + p \cdot v + \frac{a_2}{2} m |v|^2 + a_3 I.$$

Replacing ψ by its previous expression in (23), we obtain

$$p \cdot (v' + v'_*) + \frac{a_2}{2} \big(m|v'|^2 + m|v'_*|^2 \big) + a_3 (I' + I'_*) = p \cdot (v + v_*) + \frac{a_2}{2} \big(m|v|^2 + m|v_*|^2 \big) + a_3 (I + I_*).$$

Thanks to the microscopic conservations (1) and (2) of momentum and total energy, we get

$$(a_2 - a_3)(I' + I'_* - I - I_*) = 0.$$

Finally, we can choose $(v, v_*, I, I_*, I', I'_*, \sigma)$ such that $B_\varepsilon(v, v_*, I, I_*, I', I'_*, \sigma) \neq 0$ and $R \neq R'$ simultaneously, so that $I' + I'_* \neq I + I_*$, and subsequently obtain $a_2 = a_3$. □

Let us emphasize that the collision invariants (22) are here the same as in the usual polyatomic case, rather than those of the resonant case.

Having derived the weak form of the Boltzmann collision operator and characterized the collision invariants, we are now in a position to state the H-theorem associated with the quasi-resonant model.

Theorem 1 (H-theorem)**.** *For any density $f \equiv f(v, I) > 0$, we have, at least formally,*

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \log f(v, I) \, Q_\varepsilon(f, f)(v, I) \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I \leq 0. \tag{24}$$

Moreover, the following two conditions are equivalent:

$$\int_{\mathbb{R}^3} \int_0^{+\infty} \log f(v, I) \, Q_\varepsilon(f, f)(v, I) \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I = 0 \tag{25}$$

and

$$f(v,I) = \mathcal{M}(v,I) := \frac{\rho}{m}\left(\frac{2\pi T}{m}\right)^{-3/2} Z(1/T)^{-1}\exp\left(-\frac{m|v-u|^2}{2T} - \frac{I}{T}\right), \tag{26}$$

where

$$Z(\beta) = \int_0^{+\infty} e^{-\beta I}\,\varphi(I)\,\mathrm{d}I$$

is the internal partition function, ρ, u and T are respectively the mass density, average velocity and average temperature associated with f, i.e. satisfy

$$\begin{pmatrix} \rho \\ \rho u \\ \dfrac{3+\delta(T)}{2}\rho T + \dfrac{1}{2}\rho|u|^2 \end{pmatrix} = \int_{\mathbb{R}^3}\int_0^{+\infty} f(v,I)\begin{pmatrix} 1 \\ v \\ \dfrac{1}{2}|v|^2 + I \end{pmatrix}\mathrm{d}v\,\varphi(I)\,\mathrm{d}I,$$

and where the number of internal degrees of freedom $\delta(T)$ is given by

$$\delta(T) = -\frac{2}{T}(\log Z)'\left(\frac{1}{T}\right).$$

Notice that, in the quasi-resonant case, the equilibrium distributions are, as in the usual polyatomic case, Maxwell functions with a single temperature. We recall that, in the resonant case, these distributions have two distinct temperatures (one kinetic and one internal).

The proof of Theorem 1 is straightforward once collision invariants are characterized (here, thanks to Prop. 1) and very standard, see for instance the proof of Theorem 4.1 of [8].

2.3. Resonant asymptotics

In this subsection, we investigate the consistency of the quasi-resonant collision kernels with the corresponding resonant collision kernel in the vanishing ε asymptotics.

Proposition 2. *Consider B a continuous reference collision kernel, hence satisfying (6)–(8). Let $\varepsilon > 0$, and $\psi := \psi(I', I'_*)$ be a continuous test-function with a compact support in $(0,+\infty)^2$. The tuple of variables $(v, v_*, I, I_*, \sigma) \in (\mathbb{R}^3)^2 \times (0,+\infty)^2 \times \mathbb{S}^2$ being fixed, we set*

$$\mathcal{J}_\varepsilon = \iint_{(0,+\infty)^2} B_\varepsilon(v,v_*,I,I_*,I',I'_*,\sigma)\,\psi(I',I'_*)\,\varphi(I')\,\varphi(I'_*)\,\mathrm{d}I'\,\mathrm{d}I'_*.$$

Then $(\mathcal{J}_\varepsilon)$ converges, as ε goes to 0, towards

$$\mathcal{J}_0 = \int_0^{+\infty} B^{\mathrm{res}}(v,v_*,I,I_*,I',\sigma)\,\psi(I',I+I_*-I')\,\varphi(I')\,\varphi(I+I_*-I')\,\mathrm{d}I', \tag{27}$$

where the resonant collision kernel B^{res} associated to the reference kernel B is defined by

$$B^{\mathrm{res}}(v,v_*,I,I_*,I',\sigma) = B(v,v_*,I,I_*,I',I+I_*-I',\sigma)\,E\,\mathbb{1}_{[I'\le I+I_*]}, \tag{28}$$

Proposition 2 confirms that, from a modelling viewpoint, considering a small ε in our approach indeed allows to describe the quasi-resonance phenomenon. More precisely, it is clear that B will not be the corresponding resonant cross-section, and that it is not enough to impose $I'_* = I + I_* - I'$: the measure on I' is also modified, and an additional term E rises. Hence, in (27), we obtain the resonant integration measure $\varphi(I')\,\varphi(I + I_* - I')\,\mathrm{d}I'$ used in the corrected version [10] of [9]. Moreover, B^{res} still complies with the symmetry and micro-reversibility properties. In fact, the characteristic function can be omitted, as the argument $I + I_* - I'$ of B ensures nonnegativity whenever B is non-zero.

Proof. Since v, v_*, I, I_* and σ are fixed, we set, in the following, for the sake of clarity,

$$\Psi(I', I'_*) = B(v, v_*, I, I_*, I', I'_*, \sigma)\, \psi(I', I'_*)\, \varphi(I')\, \varphi(I'_*).$$

Using (10)–(14), we get

$$\mathcal{J}_\varepsilon = \frac{1}{2\varepsilon} \iint_{(0,+\infty)^2} c_\eta(R, R')\, \mathbb{1}_{[|\eta(R)-\eta(R')|\le\varepsilon]}(R, R')\, \Psi(I', I'_*)\, \mathrm{d}I'\, \mathrm{d}I'_*.$$

Remembering that R' only depends on some of the fixed variables, and not on I' or I'_*, a convenient way to proceed is to use the Borgnakke–Larsen representation, that is to change variables (I', I'_*) into (R, r) with

$$R = 1 - \frac{I' + I'_*}{E}, \qquad r = \frac{I'}{I' + I'_*},$$

with Jacobian $(1-R)E^2$. Then we have

$$\mathcal{J}_\varepsilon = \frac{1}{2\varepsilon} \iint_{(0,1)^2} c_\eta(R, R')\, \mathbb{1}_{[|\eta(R)-\eta(R')|\le\varepsilon]}(R, R')\, \Psi(r(1-R)E, (1-r)(1-R)E)\, (1-R)E^2\, \mathrm{d}R\, \mathrm{d}r. \tag{29}$$

Consider both r and E to be fixed and denote, for any R,

$$\bar{\Psi}(R) = \Psi(r(1-R)E, (1-r)(1-R)E)\ (1-R)E^2,$$

which is clearly continuous by assumption. We now focus, in (29), on the integral in R, that is

$$\frac{1}{2\varepsilon} \int_0^1 c_\eta(R, R')\, \mathbb{1}_{[|\eta(R)-\eta(R')|\le\varepsilon]}(R, R')\, \bar{\Psi}(R)\, \mathrm{d}R.$$

We perform the change of variable $z = \eta(R)$, so that it becomes

$$\begin{aligned} &\frac{1}{2\varepsilon} \int_{\mathbb{R}} c_\eta(\eta^{-1}(z), R')\, \mathbb{1}_{[|z-\eta(R')|\le\varepsilon](\eta^{-1}(z),R')}\, \bar{\Psi}(\eta^{-1}(z))\, (\eta^{-1})'(z)\, \mathrm{d}z \\ &\qquad = \frac{1}{2\varepsilon} \int_{\eta(R')-\varepsilon}^{\eta(R')+\varepsilon} c_\eta(\eta^{-1}(z), R')\, \bar{\Psi}(\eta^{-1}(z))\, (\eta^{-1})'(z)\, \mathrm{d}z. \end{aligned} \tag{30}$$

Letting ε go to 0 in (30) and using (12), we get, at the limit,

$$c_\eta(R', R')\, \bar{\Psi}(R')\, (\eta^{-1})'(\eta(R')) = \frac{c_\eta(R', R')\, \bar{\Psi}(R')}{\eta'(R')} = \bar{\Psi}(R').$$

Hence, by dominated convergence, $(\mathcal{J}_\varepsilon)$ converges, when ε goes to 0, towards

$$\int_0^1 \Psi(r(1-R')E, (1-r)(1-R')E)\, (1-R')E^2\, \mathrm{d}r,$$

which we denote by $\mathcal{J}_0$. Remembering that $(1-R')E = I + I_*$, we finally perform the change of variable r to I' with $I' = r(I + I_*)$, leading to

$$\mathcal{J}_0 = \int_0^{I+I_*} \Psi(I', I + I_* - I')\, E\, \mathrm{d}I',$$

and then to (27). □

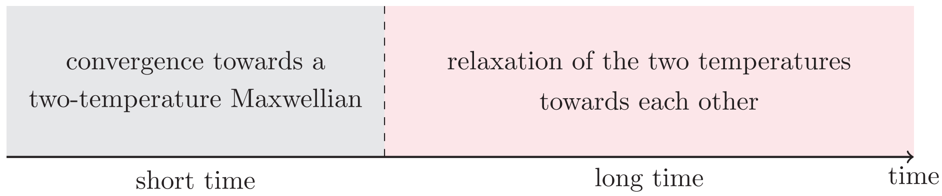


FIGURE 2. Expected behaviour of the quasi-resonant dynamics.

3. Derivation of Landau–Teller-type equations

In this section, we discuss what we can deduce from the H theorem (Thm. 1) and the resonant asymptotics (Prop. 2). We consider from now on the *homogeneous quasi-resonant Boltzmann equation*, for some $\varepsilon > 0$,

$$\partial_t f(t,v,I) = Q_\varepsilon(f(t), f(t))(v,I), \qquad f(0,v,I) = f_{\text{in}}(v,I), \tag{31}$$

for $t \geq 0$, $v \in \mathbb{R}^3$ and $I \in \mathbb{R}_+$.

Expected properties of the quasi-resonant dynamics

Let us first informally discuss the properties of the quasi-resonant model we may expect, based on the results proven earlier. The H theorem ensures that the equilibrium distributions of the quasi-resonant dynamics have a Maxwellian form, with one temperature. On the other hand, for the resonant asymptotics, Proposition 2.3 ensures that, at least formally, when ε is small, the quasi-resonant dynamics should behave almost like the associated resonant ones. But we also recall that the equilibrium distributions of the resonant dynamics are Maxwell functions with two temperatures.

Therefore, we expect the quasi-resonant dynamics to be composed of two phases, as schematically illustrated in Figure 2. In the short term, the quasi-resonant dynamics closely resembles its associated resonant dynamics, leading to a relaxation towards a two-temperature Maxwellian. Over longer time scales, since the distribution remains close to this form, the two temperatures should gradually converge towards each other. Moreover, we anticipate that the distribution will retain the structure of a two-temperature Maxwellian, as the resonant component of the quasi-resonant collision operator dominates its mixing component. This behaviour differs from the dynamics of the non-resonant polyatomic case and is a specific feature of the present model. In particular, we deduce a pair of coupled ordinary differential equations on both kinetic and internal temperatures, of Landau–Teller type, see for instance [33].

Let us now obtain explicit formulas, at the lowest non-zero order of approximation in ε, for the aforementioned two temperatures in the second, long-time, part of the dynamics. To this end, we derive ODEs of Landau–Teller type on the kinetic and internal temperatures, which are locally satisfied at time $t = 0$ by the solutions to the quasi-resonant dynamics (31) with a two-temperature Maxwellian initial distribution. The heuristic discussed above on the two phases of the dynamics allows to see those ODEs as good candidates for actually computing the two temperatures at all times: this is later highlighted by numerical experiments presented in Section 4.

Computational choices

Before stating the main result of this section, we first recall the expressions we use in the computations below. We emphasize once again that these expressions were not needed in the previous section. First, the energy law density φ is chosen as

$$\varphi(I) = I^{\delta/2-1}, \qquad I \geq 0, \tag{32}$$

with $\delta \geq 2$. This choice of energy law density corresponds to a polytropic gas with a number of internal degrees of freedom equal to δ, and is common in the literature, see [1,12].

Second, the reference collision kernel is set to

$$B(v,v_*,I,I_*,I',I'_*,\sigma) = C_B\; b(\sigma\cdot\sigma')\; E_k^{\kappa_k-\frac{1}{2}}\; {E'_k}^{\kappa_k}\; E_i^{\kappa_i}\; {E'_i}^{\kappa_i}\; E^{\gamma}\; \frac{\mathbb{1}_{[I'+I'_*\le E]}}{\mathfrak{m}_\varphi(E)}, \tag{33}$$

where we use the shortcut notations

$$E_k = \frac{m}{4}|v-v_*|^2, \qquad E_i = I + I_*, \qquad E'_k = \frac{m}{4}|v'-v'_*|^2, \qquad E'_i = I' + I'_*, \qquad E = E_k + E_i = E'_k + E'_i,$$

v' and v'_* are given by (4), κ_k, κ_i and γ are real numbers, C_B is a positive constant, and b is an angular kernel satisfying, for $\omega\in\mathbb{S}^2$,

$$\int_{\mathbb{S}^2} b(\sigma\cdot\omega)\,\mathrm{d}\sigma = 1. \tag{34}$$

Eventually, taking (32) into account in (9), and thanks to Lemma A.1, we have

$$\mathfrak{m}_\varphi(E) = \iint_{(0,+\infty)^2} \mathbb{1}_{[I'+I'_*\le E]}\,\varphi(I')\,\varphi(I'_*)\,\mathrm{d}I'\,\mathrm{d}I'_* = \frac{\Gamma(\delta/2)^2}{\Gamma(\delta+1)}\;E^{\delta}, \tag{35}$$

where Γ stands for the Gamma function.

Finally, we choose η as

$$\eta(R) = \log\left(\frac{R}{1-R}\right), \qquad R\in(0,1). \tag{36}$$

Let $\varepsilon>0$. That function η allows to define the truncation function χ_ε through (10)–(12) (with no need to specify c_η) and subsequently B_ε as

$$B_\varepsilon(v,v_*,I,I_*,I',I'_*,\sigma) = B(v,v_*,I,I_*,I',I'_*,\sigma)\,\chi_\varepsilon(R,R'). \tag{37}$$

Local Landau–Teller equations

We can now provide, in the next proposition, the first term in the expansion in ε of the derivative at time $t=0$ of the internal temperature of a solution to the homogeneous quasi-resonant Boltzmann equation (31) with a two-temperature Maxwellian initial condition.

Proposition 3. *For $\varepsilon>0$, consider f a solution to the homogeneous quasi-resonant Boltzmann equation (31) associated to φ, η and B_ε defined thanks to (32)–(37), with $\gamma=\delta+1$. Assume the initial condition f_{in} to be a* two-temperature *Maxwellian distribution associated to the energy law φ, the mass density $\rho>0$, the average velocity $u\in\mathbb{R}^3$ and the kinetic and internal temperatures $T_k^0>0$ and $T_i^0>0$. For $t\ge 0$, we set*

$$T_k(t) = \frac{m}{6\rho}\iint_{\mathbb{R}^3\times(0,+\infty)} |v-u|^2\, f(t,v,I)\,\mathrm{d}v\,\varphi(I)\,\mathrm{d}I, \quad T_i(t) = \frac{1}{\delta\rho}\iint_{\mathbb{R}^3\times(0,+\infty)} I\, f(t,v,I)\,\mathrm{d}v\,\varphi(I)\,\mathrm{d}I, \tag{38}$$

i.e. the respective kinetic and internal temperatures of f at time t. Then

$$\left.\frac{\mathrm{d}T_i}{\mathrm{d}t}\right|_{t=0} = \varepsilon^2\,\rho\, C_{\delta,\kappa_k,\kappa_i}\left(T_k^0\right)^{2\kappa_k+\frac{1}{2}}\,\left(T_i^0\right)^{2\kappa_i+\delta}\,\left(T_k^0 - T_i^0\right) + o(\varepsilon^2),$$

with

$$C_{\delta,\kappa_k,\kappa_i} = \frac{C_B}{12}\times\frac{\Gamma(2\kappa_k+3)\,\Gamma(2\kappa_i+2\delta+1)}{\Gamma(3/2)\,\Gamma(\delta)}.$$

Proof. Since f solves (31), we have

$$\left.\frac{\mathrm{d}T_i}{\mathrm{d}t}\right|_{t=0} = \frac{1}{\delta\rho}\iint_{\mathbb{R}^3\times(0,+\infty)} I Q_\varepsilon(f_{\text{in}},\, f_{\text{in}})(v,I)\,\varphi(I)\,\mathrm{d}I\,\mathrm{d}v. \tag{39}$$

Hence, we need to compute the right-hand side of (39). It comes from the weak form (19) of the operator Q_ε that

$$\frac{1}{\delta\rho}\iint_{\mathbb{R}^3\times(0,+\infty)} I Q_\varepsilon(f_{\text{in}}, f_{\text{in}})(v,I)\,\varphi(I)\,\mathrm{d}I\,\mathrm{d}v$$
$$= \frac{1}{2\delta\rho}\iint_{(\mathbb{R}^3)^2}\iiiint_{(0,+\infty)^4}\int_{\mathbb{S}^2} f_{\text{in}}\,(f_{\text{in}})_*\,(I'+I'_*-I-I_*)$$
$$B_\varepsilon(v,v_*,I,I_*,I',I'_*,\sigma)\,\mathrm{d}\sigma\,\varphi(I)\,\varphi(I_*)\,\varphi(I')\,\varphi(I'_*)\,\mathrm{d}I\,\mathrm{d}I_*\,\mathrm{d}I'\,\mathrm{d}I'_*\,\mathrm{d}v\,\mathrm{d}v_*.$$

The latter integral can be rewritten as

$$\frac{1}{2\delta\rho}\iint_{(\mathbb{R}^3)^2}\iint_{(0,+\infty)^2} f_{\text{in}}\,(f_{\text{in}})_*$$
$$\left[\iint_{(0,+\infty)^2}\int_{\mathbb{S}^2}(I'+I'_*-I-I_*)\,B_\varepsilon(v,v_*,I,I_*,I',I'_*,\sigma)\,\varphi(I')\,\varphi(I'_*)\,\mathrm{d}\sigma\,\mathrm{d}I'\,\mathrm{d}I'_*\right]$$
$$\varphi(I)\,\varphi(I_*)\,\mathrm{d}I\,\mathrm{d}I_*\,\mathrm{d}v\,\mathrm{d}v_*. \tag{40}$$

We now focus on the term between brackets in (40). Using the explicit form (33) of the reference collision kernel B as well as its angular property (34), the term becomes

$$C_B\,\frac{E_k^{\kappa_k-1/2}E_i^{\kappa_i}E^{\gamma}}{\mathfrak{m}_\varphi(E)}\iint_{(0,+\infty)^2}(E'_i-E_i)\,(E-E'_i)^{\kappa_k}\,E_i'^{\kappa_i}\,\mathbb{1}_{[E'_i\le E]}\,\chi_\varepsilon\!\left(1-\frac{E'_i}{E},1-\frac{E_i}{E}\right)\varphi(I')\,\mathrm{d}I'\,\varphi(I'_*)\,\mathrm{d}I'_*.$$

By definition (9) of $\mathfrak{m}_\varphi$, substituting $E'_i = I'+I'_*$ as an integration variable, the above term reads

$$C_B\,\frac{E_k^{\kappa_k-1/2}E_i^{\kappa_i}E^{\gamma}}{\mathfrak{m}_\varphi(E)}\int_0^E(E'_i-E_i)\,(E-E'_i)^{\kappa_k}\,E_i'^{\kappa_i}\,\chi_\varepsilon\!\left(1-\frac{E'_i}{E},1-\frac{E_i}{E}\right)\mathfrak{m}'_\varphi(E'_i)\,\mathrm{d}E'_i.$$

Then, using the explicit form (35) of $\mathfrak{m}_\varphi$, performing the change of variable $R = 1-E'_i/E$ and setting $R_0 = 1-E_i/E$, we transform the integral into

$$C_B\delta\,E_k^{\kappa_k-1/2}E_i^{\kappa_i}E^{\gamma+\kappa_k+\kappa_i+1}\int_0^1(R_0-R)\,R^{\kappa_k}\,(1-R)^{\kappa_i+\delta-1}\,\chi_\varepsilon(R,R_0)\,\mathrm{d}R. \tag{41}$$

Applying Lemma A.2 to $\psi(R) = -R^{\kappa_k}(1-R)^{\kappa_i+\delta-1}$ yields the expansion of (41) with respect to ε around 0 as

$$\varepsilon^2\,\frac{C_B(\delta+1)\,E_k^{\kappa_k-1/2}E_i^{\kappa_i}E^{\gamma+\kappa_k+\kappa_i+1}\,{R_0}^{\kappa_k}(1-R_0)^{\kappa_i+\delta-1}}{3\eta'(R_0)^2}\left[(\log\eta')'(R_0)-\frac{\kappa_k}{R_0}+\frac{\kappa_i+\delta-1}{1-R_0}\right]+o(\varepsilon^2). \tag{42}$$

Now, since we chose $\eta(R_0) = \log\frac{R_0}{1-R_0}$, we have $(\log\eta')'(R_0) = -\frac{1}{R_0}+\frac{1}{1-R_0}$ and $\frac{1}{\eta'(R_0)^2} = R_0^2(1-R_0)^2$ (see Rem. 2), the expression actually equals

$$\varepsilon^2\,\frac{C_B\delta}{3}\,E_k^{\kappa_k-1/2}E_i^{\kappa_i}E^{\gamma+\kappa_k+\kappa_i+1}\,R_0^{\kappa_k+2}(1-R_0)^{\kappa_i+\delta+1}\left(-\frac{\kappa_k+1}{R_0}+\frac{\kappa_i+\delta}{1-R_0}\right)+o(\varepsilon^2).$$

As $R_0 E = E_k$ and $(1-R_0)E = E_i$, the previous term becomes

$$\varepsilon^2 \, \frac{C_B \delta}{3} \, E_k^{2\kappa_k+\frac{1}{2}} E_i^{2\kappa_i+\delta} E^{\gamma-\delta-1}[(\kappa_i+\delta)E_k - (\kappa_k+1)E_i] + o(\varepsilon^2).$$

Finally, recalling that $\gamma = \delta+1$, the bracket term in (40) reads

$$\varepsilon^2 \, \frac{C_B \delta}{3} \, E_k^{2\kappa_k+1/2} E_i^{2\kappa_i+\delta}[(\kappa_i+\delta)E_k - (\kappa_k+1)E_i] + o(\varepsilon^2). \tag{43}$$

Therefore, (39) can be rewritten, when ε goes to 0, as

$$\begin{aligned} \left.\frac{\mathrm{d}T_i}{\mathrm{d}t}\right|_{t=0} = \varepsilon^2 \, \frac{C_B}{6\rho} \iint_{(\mathbb{R}^3)^2} \iint_{(0,+\infty)^2} & E_k^{2\kappa_k+1/2} E_i^{2\kappa_i+\delta}[(\kappa_i+\delta)E_k - (\kappa_k+1)E_i] \\ & \times f_{\text{in}}\,(f_{\text{in}})_* \, I^{\delta/2-1} \mathrm{d}I \, {I_*}^{\delta/2-1} \mathrm{d}I_* \, \mathrm{d}v \, \mathrm{d}v_* + o(\varepsilon^2). \end{aligned}$$

Recall that f_{in} is a two-temperature Maxwell function with mass density ρ, and respective kinetic and internal temperatures T_k^0 and T_i^0. The previous equation may be recast as

$$\begin{aligned} \left.\frac{\mathrm{d}T_i}{\mathrm{d}t}\right|_{t=0} = \varepsilon^2 \, \frac{C_B \rho}{6} \Big[& (\kappa_i+\delta)\mathbf{m}_k^{2\kappa_k+3/2}(T_k^0)\, \mathbf{m}_i^{2\kappa_i+\delta}(T_i^0) \\ & -(\kappa_k+1)\mathbf{m}_k^{2\kappa_k+1/2}(T_k^0)\, \mathbf{m}_i^{2\kappa_i+\delta+1}(T_i^0) \Big] + o(\varepsilon^2), \end{aligned} \tag{44}$$

where we set, for any $\beta > 0$ and $T > 0$,

$$\mathbf{m}_k^{\beta}(T) = \left(\frac{2\pi T}{m}\right)^{-3} \iint_{(\mathbb{R}^3)^2} e^{-m(|v|^2+|v_*|^2)/2T} \left[\frac{m}{4}|v-v_*|^2\right]^{\beta} \mathrm{d}v \, \mathrm{d}v_*, \tag{45}$$

$$\mathbf{m}_i^{\beta}(T) = \left[\iint_{(0,+\infty)^2} e^{-(I+I_*)/T} \, (II_*)^{\delta/2-1} \, \mathrm{d}I \, \mathrm{d}I_*\right]^{-1} \iint_{(0,+\infty)^2} e^{-(I+I_*)/T} \, (I+I_*)^{\beta} \, (II_*)^{\delta/2-1} \, \mathrm{d}I \, \mathrm{d}I_*. \tag{46}$$

We point out that the latter depends on δ too. Then we plug (A.6) and (A.7) from Lemma A.3 in (44) to get

$$\left.\frac{\mathrm{d}T_i}{\mathrm{d}t}\right|_{t=0} = \varepsilon^2 \, \frac{C_B \rho}{12} \, \frac{\Gamma(2\kappa_k+3)\Gamma(2\kappa_i+2\delta+1)}{\Gamma(3/2)\Gamma(\delta)} \, (T_k^0)^{2\kappa_k+1/2} (T_i^0)^{2\kappa_i+\delta} \big(T_k^0 - T_i^0\big) + o(\varepsilon^2),$$

which ends the proof. □

Remark 2. It may be possible to generalize the choice of η beyond (36) to carry out the computation, provided that the term in (42) remains polynomial in R_0.

Global Landau–Teller equations in the quasi-resonant case

In the previous Proposition 3, we obtained an explicit formula, for small ε, of the derivative around time $t = 0$ of the internal temperature of a solution to the homogeneous quasi-resonant Boltzmann equation (31) with a two-temperature Maxwellian initial condition. Following our discussion from the beginning of the current section, a solution to the homogeneous quasi-resonant Boltzmann equation is expected to remain close to the two-temperature Maxwellian form.

Hence, one can extrapolate that, if f solves (31) with a kernel B_ε defined in (37), for a small ε, and with an initial condition close to a two-temperature Maxwellian, we have for any time $t \geq 0$,

$$(T_i(t), \, T_k(t)) \approx (\overline{T_i}(t), \, \overline{T_k}(t)), \tag{47}$$

where $(\overline{T}_i, \overline{T}_k)$ solves the ODE system

$$\frac{\mathrm{d}\overline{T}_i}{\mathrm{d}t}(t) = \varepsilon^2 \rho\, C_{\delta,\kappa_k,\kappa_i}\ \overline{T}_k(t)^{2\kappa_k+1/2}\ \overline{T}_i(t)^{2\kappa_i+\delta}\ (\overline{T}_k(t) - \overline{T}_i(t)), \qquad t \geq 0, \tag{48}$$

$$\frac{3}{2}\frac{\mathrm{d}\overline{T}_k}{\mathrm{d}t}(t) + \frac{\delta}{2}\frac{\mathrm{d}\overline{T}_i}{\mathrm{d}t}(t) = 0, \qquad t \geq 0, \tag{49}$$

$$(\overline{T}_i(0), \overline{T}_k(0)) = (T_i(0), T_k(0)), \tag{50}$$

using the same notations as in Proposition 3. The goal of the next section is then to check, through some numerical experiments, the validity of (47).

4. Numerical experiments

In this section, we conduct a numerical experiment to check the validity of our statement (47), providing an equation on the relaxation of the kinetic and internal temperatures towards each other, in a quasi-resonant context. We highlight that it relies on the assumption that, in the quasi-resonant setting, the distribution stays at all times close to a two-temperature Maxwellian, which statement is therefore also numerically verified here.

In order to achieve this goal, we proceed as follows.

(i) We simulate the 3D space-homogeneous Boltzmann equation (31) associated to the collision kernel (37), with a two-temperature Maxwellian initial condition. We denote the kinetic and internal temperatures of the solution at time t by $T_k(t)$ and $T_i(t)$.

(ii) We numerically solve the ODE system (48)–(50) with the same initial conditions of temperature as the ones of DSMC.

(iii) We compare $t \mapsto T_i(t)$ with $t \mapsto \overline{T}_i(t)$: if the two curves globally coincide, then we observe experimentally the validity of (47) and the expected behaviour (Fig. 2).

4.1. Main experiment: a comparison between Landau-Teller and DSMC

Numerically solving (48)–(50) is straightforward. We simulate the three-dimensional homogeneous Boltzmann equation (31) associated with the collision kernel (37), with a two-temperature Maxwellian initial condition, through the DSMC method [5], where each particle is endowed with its velocity $v \in \mathbb{R}^3$ and internal energy quantile $q \in \mathbb{R}_+$. For a discussion on the use of energy quantiles q instead of energy levels I in numerical simulations, see [6]. The mass density, average velocity, average temperature, kinetic and internal temperatures of $f(t)$ are respectively denoted $\rho > 0$, $u \in \mathbb{R}^3$, $T_{\mathrm{eq}} > 0$ (these quantities are constant w.r.t. time) and $T_k(t)$ and $T_i(t)$. In particular, for all $t \geq 0$,

$$3T_k(t) + \delta T_i(t) = (3 + \delta)T_{\mathrm{eq}}.$$

In our DSMC simulation, we consider the functions φ, η and for some $\varepsilon > 0$, the kernel B_ε of the form (32)–(37), with

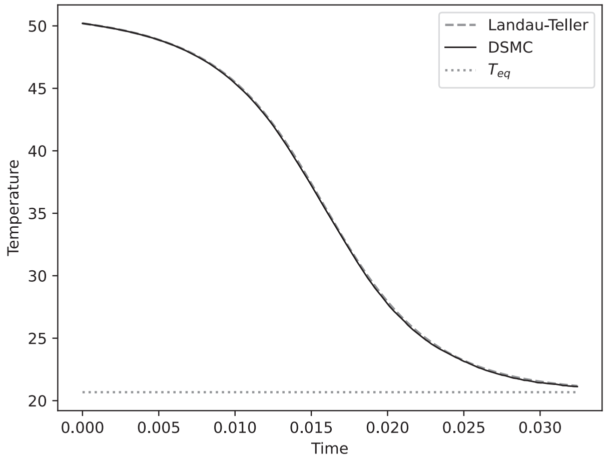
$$C_B = 2, \quad b = \frac{1}{4\pi}, \quad m = 1, \quad \rho = 1, \quad \delta = 2, \quad \kappa_k = \frac{1}{2}, \quad \kappa_i = -\frac{1}{2}, \quad \gamma = \delta + 1,$$
$$c_\eta(R, R') = \sqrt{\eta'(R)\eta'(R')}.$$

We set the initial temperatures to be

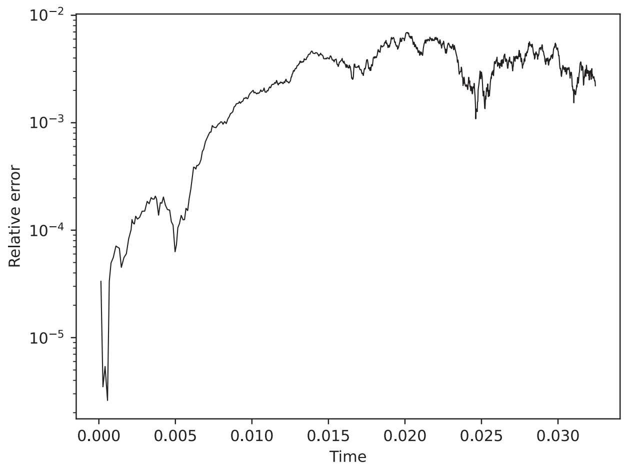
$$T_k^0 = 1, \qquad T_i^0 = 50.$$

We point out that the equilibrium temperature is $T_{\mathrm{eq}} = 20.6$ and that all values are here adimensionned. We also mention that there are no restrictions (for instance, of closeness) on the initial temperatures to consider.

Our main numerical experiment is conducted taking $\varepsilon = 10^{-1}$ (which is already in the quasi-resonant regime) and 10^5 numerical particles. We show in Figure 3 the result of the simulation. The black curve of Figure 3a



(a) Internal temperatures T_i (DSMC) and $\overline{T}_i$ (Landau–Teller) w.r.t. time.



(b) Relative error $|T_i - \overline{T}_i|/\overline{T}_i$ in semi-log scale, w.r.t. time.

FIGURE 3. Comparison of the internal temperatures T_i and $\overline{T}_i$ obtained respectively by DSMC simulation and by solving the Landau–Teller ODE system, with $\varepsilon = 10^{-1}$. (a) Internal temperatures T_i (DSMC) and $\overline{T}_i$ (Landau–Teller) w.r.t. time. (b) Relative error $|T_i - \overline{T}_i|/\overline{T}_i$ in semi-log scale, w.r.t. time.

indicates the time evolution of the internal temperature T_i of the system simulated through the DSMC algorithm, while the gray dashed curve is obtained by solving the ODE system (48)–(50) with the solver `solve_ivp` from the Python package `scipy.integrate`. The gray dotted line corresponds to the equilibrium temperature T_{eq}. We plot on Figure 3b the graph of $|T_i - \overline{T}_i|/\overline{T}_i$ in semi-log scale, the relative error between T_i (DSMC) and $\overline{T}_i$ (Landau–Teller), with respect to time.

We observe on Figure 3 a firm agreement between the DSMC-computed T_i and the Landau–Teller-solved $\overline{T}_i$ in a quasi-resonant setting with $\varepsilon = 10^{-1}$.

Remark 3. We also conducted a numerical experiment in a far-from-resonance setting, with $\varepsilon = 10$, and observed in this case, as expected, no matching between the curves of the internal temperatures given respectively by the DSMC simulation and the solving of the Landau–Teller ODE system.

Remark 4. We also conducted two experiments with initial distributions which are not two-temperature Maxwellians: a uniform distribution in both velocity and internal energy, and the product of an anisotropic distribution in velocities and a uniform one in internal energy. Using the Henze-Zikler [21] normality and Levene [14] isotropy tests for the velocity part and Kolmogorov-Smirnov test (comparing the quantile functions) for the internal part, we observed a relaxation time toward the two-temperature Maxwellian of the order of 10^{-4}, much smaller than the relaxation time of the temperatures towards each other, of the order of 10^{-2} (see Fig. 3), providing a numerical validation of the expected behaviour presented in Figure 2.

These result support, at least for our chosen set of parameters, the statements of Section 3: the kinetic and internal temperatures of a solution to the homogeneous quasi-resonant Boltzmann equation, associated to the kernel B_ε defined in (32), for some ε small and two-temperature Maxwellian initial condition, are close to the solution to the Landau–Teller ODE system (48)–(50).

This moreover somehow provides a numerical validation on the expected behaviour of the quasi-resonant dynamics schematically presented in Figure 2: it does appear reasonable to understand the latter as composed of two parts, a resonant-like dynamics in short-time making the distribution relax towards a two-temperature Maxwellian, and then a relaxation of the two temperatures towards each other driven by a Landau–Teller-type ODE system, in particular in the light of Remark 4.

4.2. Behaviour with a vanishing quasi-resonance parameter

In the previous subsection, we checked the validity of our statement (47) on a given set of parameters, validity that should be reinforced as the quasi-resonance parameter ε vanishes. In this subsection, we numerically investigate deeper the behaviour of the relative error between the internal temperatures given respectively by the DSMC simulation and the Landau–Teller system, $|T_i - \overline{T}_i|/\overline{T}_i$, in the vanishing ε limit.

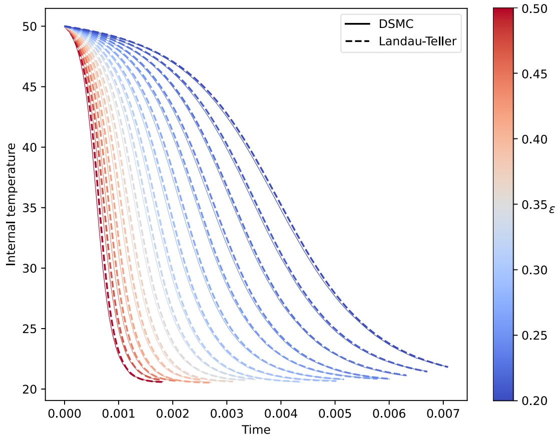
We consider the same set of physical parameters as in the previous subsection. We run the simulation for a range of values of ε, and denote for each $\varepsilon > 0$ by $t \mapsto T_i^\varepsilon(t)$ and $t \mapsto \overline{T}_i^\varepsilon(t)$ the internal temperatures obtained respectively with the DSMC simulation and solving the ODE system. We study the error between the dynamics provided by the DSMC simulation and the Landau–Teller ODE system on a complete relaxation to equilibrium. Since the time of relaxation to equilibrium depends itself on ε (it scales as ε^{-2}), we consider here, as our measure for discrepancy between the two dynamics, the average relative L^2-error between T_i^ε and $\overline{T}_i^\varepsilon$, given by

$$\left(\frac{1}{\tau_\varepsilon} \int_0^{\tau_\varepsilon} \left(\frac{|T_i^\varepsilon(t) - \overline{T}_i^\varepsilon(t)|}{\overline{T}_i^\varepsilon(t)} \right)^2 \mathrm{d}t \right)^{\frac{1}{2}},$$

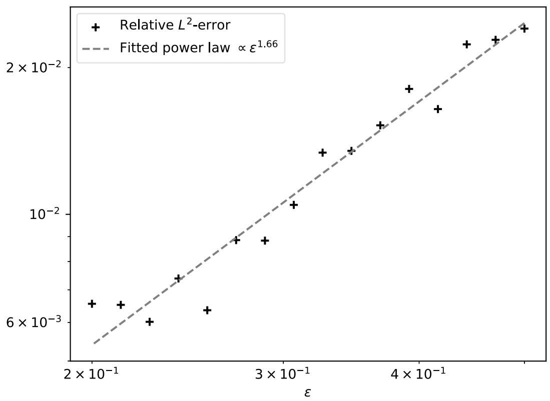
where τ_ε is the time of relaxation to equilibrium, depending on ε. We then fit the average relative L^2-error, seen as a function of ε, to a power law in ε, using a linear regression through least squares on the logarithm of the relative L^2-error.

We show on Figure 4 the graph of the relative L^2-error as a function of ε, obtained by running simulations with over 3×10^5 particles, for 16 values of ε, ranging from 0.2 to 0.5 uniformly in log-scale.

We observe on this test that the average relative L^2-error behaves like $\varepsilon^{5/3}$. Although $5/3$ is an interesting non-trivial order of convergence, we draw no definite conclusion as of the actual order of convergence, since the comparison is made here with a DSMC simulation, and we also do not exclude that the power may change for smaller values of ε.



(a) Plots of $t \mapsto T_i(t)$ (DSMC) and $t \mapsto \overline{T}_i(t)$ for various values of ε.



(b) Average relative L^2-error between T_i and $\overline{T}_i$ as a function of ε.

FIGURE 4. Result of the numerical experiment to study the behavior of the average L^2-error between T_i and $\overline{T}_i$ relatively to ε. (a) Plots of $t \mapsto T_i(t)$ (DSMC) and $t \mapsto \overline{T}_i(t)$ for various values of ε. (b) Average relative L^2-error between T_i and $\overline{T}_i$ as a function of ε.

5. Conclusion

We have numerically observed all behaviours of the quasi-resonant dynamics announced in Section 3. Namely, with our parameters and $\varepsilon = 0.1$, the typical time of convergence to a two-temperature Maxwellian is of the order of 10^{-4} (Rem. 4), which is much shorter than the typical time of convergence of the two temperatures towards each other, of the order of 10^{-2} (Fig. 3). This latter time indeed becomes larger as ε diminishes (Fig. 4a). We have also shown the validity of the Landau–Teller equation (Fig. 3), which gets all the more accurate as ε diminishes (Fig. 4b).

Acknowledgments

The authors are grateful to Professor Kazuo Aoki for useful discussions. This article has been partially funded by the Starting Grant ERC project HighLEAP (High-dimensional mathematical methods for LargE Agent and Particle systems), awarded to Virginie Ehrlacher. Partial support by INdAM-GNFM is also acknowledged.

Data availability statement

No new data/codes were created or analyzed in this study.

References

[1] R.J. Alonso, M. Čolić and I.M. Gamba, The Cauchy problem for Boltzmann bi-linear systems: the mixing of monatomic and polyatomic gases. *J. Stat. Phys.* **191** (2024) 9, 50.

[2] P. Andries, P. Le Tallec, J.-P. Perlat and B. Perthame, The Gaussian-BGK model of Boltzmann equation with small Prandtl number. *Eur. J. Mech. B Fluids* **19** (2000) 813–830.

[3] K. Aoki, M. Bisi, M. Groppi and S. Kosuge, Two-temperature Navier–Stokes equations for a polyatomic gas derived from kinetic theory. *Phys. Rev. E* **102** (2020) 023104.

[4] K. Aoki, M. Bisi, M. Groppi and S. Kosuge, A note on the steady Navier–Stokes equations derived from an ES-BGK model for a polyatomic gas. *Fluids* **6** (2021) 22.

[5] G. Bird, The DSMC Method. CreateSpace Independent Publishing Platform (2013).

[6] M. Bisi, T. Borsoni and M. Groppi, On the modelling of polyatomic molecules in kinetic theory. Preprint arXiv:2501.18207 (2025).

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

[8] T. Borsoni, M. Bisi and M. Groppi, A general framework for the kinetic modelling of polyatomic gases. *Commun. Math. Phys.* **393** (2022) 215–266.

[9] T. Borsoni, L. Boudin and F. Salvarani, Compactness property of the linearized Boltzmann operator for a polyatomic gas undergoing resonant collisions. *J. Math. Anal. Appl.* **517** (2023) 126579.

[10] T. Borsoni, L. Boudin and F. Salvarani, Corrigendum to "Compactness property of the linearized Boltzmann operator for a polyatomic gas undergoing resonant collisions" [J. Math. Anal. Appl. 517 (1) (2023) 126579]. *J. Math. Anal. Appl.*, **538** (2024) 128493, 3.

[11] L. Boudin, A. Rossi and F. Salvarani, A kinetic model of polyatomic gas with resonant collisions. *Ric. Mat.* **73** (2024) 2411–2424.

[12] J.-F. Bourgat, L. Desvillettes, P. LeTallec, and B. Perthame, Microreversible collisions for polyatomic gases and Boltzmann's theorem. *Eur. J. Mech. B Fluids* **13** (1994) 237–254.

[13] D.M. Brenner, Near resonant vibration→ vibration energy transfer under single collision conditions. *J. Chem. Phys.* **74** (1981) 494–507.

[14] M.B. Brown and A.B. Forsythe, Robust tests for the equality of variances. *J. Am. Stat. Assoc.* **69** (1974) 364–367.

[15] D. Bruno, V. Giovangigli, Relaxation of internal temperature and volume viscosity, *Physics of Fluids*, **23** (2011) 9.

[16] D. Bruno, V. Giovangigli, Internal energy relaxation processes and bulk viscosities in fluids, *Fluids*, **7**, (2022) 356.

[17] L. Desvillettes, Sur un modèle de type Borgnakke-Larsen conduisant à des lois d'énergie non linéaires en température pour les gaz parfaits polyatomiques. *Ann. Fac. Sci. Toulouse Math. (6)* **6** (1997) 257–262.

[18] L. Desvillettes, R. Monaco and F. Salvarani, A kinetic model allowing to obtain the energy law of polytropic gases in the presence of chemical reactions. *Eur. J. Mech. B Fluids* **24** (2005) 219–236.

[19] V. Djordjić, M. Pavić-Čolić, M. Torrilhon, Consistent, explicit, and accessible Boltzmann collision operator for polyatomic gases, *Phys. Rev. E*, **104** (2021) 025309.

[20] I.M. Gamba and M. Pavić-Čolić, On the Cauchy problem for Boltzmann equation modeling a polyatomic gas. *J. Math. Phys.* **64** (2023) 013303, 51.

[21] N. Henze and B. Zirkler, A class of invariant consistent tests for multivariate normality. *Commun. Statist. Theory Methods* **19** (1990) 3595–3617.

[22] L.H. Holway, New statistical models for kinetic theory: methods of construction. *Phys. Fluids* **9** (1966) 1658–1673.

[23] S. Kosuge and K. Aoki, Shock-wave structure for a polyatomic gas with large bulk viscosity. *Phys. Rev. Fluids* **3** (2018) 023401.

[24] S. Kosuge and K. Aoki, Navier–Stokes equations and bulk viscosity for a polyatomic gas with temperature-dependent specific heats. *Fluids* **8** (2023) 22.
[25] 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. *J. Stat. Phys.* **177** (2019) 209–251.
[26] M. Lanza, Y. Kalugina, L. Wiesenfeld and F. Lique, Near-resonant rotational energy transfer in HCl–H2 inelastic collisions. *J. Chem. Phys.* **140** (2014) 064316.
[27] A. Lombardi, N. Faginas-Lago, L. Pacifici and G. Grossi, Energy transfer upon collision of selectively excited CO_2 molecules: state-to-state cross sections and probabilities for modeling of atmospheres and gaseous flows. *J. Chem. Phys.* **143** (2015) 034307.
[28] T. E. Magin, B. Graille, M. Massot, Hydrodynamic model for molecular gases in thermal nonequilibrium, AIP Conference Proceedings, **1501** (2012) 231–238.
[29] B.H. Mahan, Resonant transfer of vibrational energy in molecular collisions. *J. Chem. Phys.* **46** (1967) 98–101.
[30] T. Morse, Kinetic model for gases with internal degrees of freedom. *Phys. Fluids* **7** (1964) 159–169.
[31] E. Nagnibeda and E. Kustova, *Non-equilibrium Reacting Gas Flows:. Heat and Mass Transfer*. Springer-Verlag, Berlin, 2009. Kinetic Theory of Transport and Relaxation Processes, Translated from the (2003) Russian original.
[32] E. Nikitin, Resonance and non-resonance intermolecular energy exchange in molecular collisions. *Discuss. Faraday Soc.* **33** (1962) 14–21.
[33] E.E. Nikitin and J. Troe, 70 years of Landau–Teller theory for collisional energy transfer. Semiclassical three-dimensional generalizations of the classical collinear model. *Phys. Chem. Chem. Phys.* **10** (2008) 1483–1501.
[34] J. Ross and P. Mazur, Some deductions from a formal statistical mechanical theory of chemical kinetics. *J. Chem. Phys.* **35** (1961) 19–28.
[35] V.A. Rykov, A model kinetic equation for a gas with rotational degrees of freedom. *Fluid Dyn.* **10** (1975) 959–966.
[36] R. Sharma, Near-resonant vibrational energy transfer among isotopes of CO_2. *Phys. Rev.* **177** (1969) 102.
[37] R.D. Sharma, Near-resonant vibration-to-vibration energy transfer in the NO+–N2 collisions. *J. Chem. Phys.* **125** (2006).
[38] J.C. Stephenson and C.B. Moore, Temperature dependence of nearly resonant vibration→ vibration energy transfer in CO_2 mixtures. *J. Chem. Phys.* **56** (1972) 1295–1308.
[39] N. Taxman, Classical theory of transport phenomena in dilute polyatomic gases. *Phys. Rev.* **110** (1958) 1235.
[40] C.S. Wang Chang and G.E. Uhlenbeck, Transport phenomena in polyatomic gases. Technical report, University of Michigan (1951).

Appendix A. Various technical lemmas

The first lemma is dedicated to the computation of $\mathfrak{m}_\varphi$ and its derivative, it is presented here for the sake of completeness, as it is a well-known result.

Lemma A.1. *Recall the expression* (9) *of* $\mathfrak{m}_\varphi$*, that is, for any* $E \geq 0$,

$$\mathfrak{m}_\varphi(E) = \iint_{(0,+\infty)^2} \mathbb{1}_{[I'+I'_* \leq E]}(I', I'_*)\, \varphi(I')\, \varphi(I'_*)\, \mathrm{d}I'\, \mathrm{d}I'_* = \int_0^E \int_0^J \varphi(I')\, \varphi(J-I')\, \mathrm{d}I'\, \mathrm{d}J. \tag{A.1}$$

Then, for any $E \geq 0$, we have

$$\mathfrak{m}'_\varphi(E) = \int_0^E \varphi(I')\,\varphi(E - I')\,\mathrm{d}I'. \tag{A.2}$$

Moreover, if $\varphi : I \mapsto I^{\delta/2-1}$ for some $\delta > 0$, then, for any $E \geq 0$, we have

$$\mathfrak{m}'_\varphi(E) = \frac{\Gamma(\delta/2)^2}{\Gamma(\delta)}\,E^{\delta-1}, \qquad \mathfrak{m}_\varphi(E) = \frac{\Gamma(\delta/2)^2}{\Gamma(\delta+1)}\,E^{\delta}. \tag{A.3}$$

Proof. First, (A.2) is a straightforward consequence of (A.1). Then, if $\varphi : I \mapsto I^{\delta/2-1}$, performing the change of variable $I' \to I'/E$ in (A.2), and denoting the Beta function by $\mathcal{B}$, we get, for any $E \geq 0$,

$$\mathfrak{m}'_\varphi(E) = \mathcal{B}(\delta/2, \delta/2)E^{\delta-1},$$

and eventually (A.3) thanks to the relationship between the Beta and Gamma functions. □

Then the following lemma is an intermediate result leading to relevant Taylor expansions with respect to the quasi-resonance parameter ε.

Lemma A.2. *Let $\psi \in \mathcal{C}^1((0,1))$. Then, for any $R_0 \in (0,1)$, we have*

$$\int_0^1 (R - R_0)\,\psi(R)\,\chi_\varepsilon(R, R_0)\,\mathrm{d}R \underset{\varepsilon\to 0}{=} \frac{1}{3\,\eta'(R_0)^3}\big[\eta'(R_0)\psi'(R_0) - \eta''(R_0)\,\psi(R_0)\big]\varepsilon^2 + o(\varepsilon^2), \tag{A.4}$$

where χ_ε is defined in (10).

Proof. Let $R_0 \in (0,1)$, denote by Ψ an antiderivative of $R \mapsto (R - R_0)\psi(R)c_\eta(R, R_0)$, and set, for any $x \in \mathbb{R}$,

$$g(x) = \eta^{-1}(\eta(R_0) + x).$$

That latter function g is $\mathcal{C}^\infty$ on $\mathbb{R}$, as η is itself $\mathcal{C}^\infty$ and $\eta' > 0$. We may write, for any $\varepsilon > 0$,

$$\int_0^1 (R - R_0)\,\psi(R)\,\chi_\varepsilon(R, R_0)\,\mathrm{d}R = \frac{1}{2\varepsilon}\int_{g(-\varepsilon)}^{g(\varepsilon)} (R - R_0)\,\psi(R)\,c_\eta(R, R_0)\,\mathrm{d}R.$$

We highlight that, while Ψ is only $\mathcal{C}^2$ on $(0,1)$, it is $\mathcal{C}^3$ at the point $R = R_0$. Then a straightforward Taylor expansion of $\Psi \circ g$ near 0 yields

$$\int_0^1 (R - R_0)\,\psi(R)\,\chi_\varepsilon(R, R_0)\,\mathrm{d}R = (\Psi \circ g)'(0) + \frac{\varepsilon^2}{6}\,(\Psi \circ g)'''(0) + o(\varepsilon^2). \tag{A.5}$$

The zeroth-order (in ε) term in (A.5) vanishes since $(\Psi \circ g)'(0) = \Psi'(R_0)g'(0) = 0$. The second-order term involves

$$(\Psi \circ g)'''(0) = \Psi'(R_0)\,g'''(0) + 3\Psi''(R_0)\,g'(0)\,g''(0) + \Psi'''(R_0)\,g'(0)^3.$$

By direct computations, using in particular (12) and (13), we get

$$\Psi'(R_0) = 0, \qquad \Psi''(R_0) = \psi(R_0)\,\eta'(R_0), \qquad \Psi'''(R_0) = 2\psi'(R_0)\,\eta'(R_0) + \psi(R_0)\,\eta''(R_0).$$

Moreover, we also have, remembering that $\eta' > 0$,

$$g'(0) = \frac{1}{\eta'(R_0)}, \qquad g''(0) = -\frac{\eta''(R_0)}{\eta'(R_0)^3}.$$

Putting everything together, we get (A.4). □

Remark A.1. It is worth noticing that, if the regularity of ψ is $\mathcal{C}^2$, the correction term $o(\varepsilon^2)$ in (A.4) is actually $\mathcal{O}(\varepsilon^4)$. In particular, there is no term of order ε^3.

Eventually, we need the following lemma to obtain our Landau–Teller form with explicit coefficients.

Lemma A.3. *Consider the functions* $\mathbf{m}_k^\beta$ *and* $\mathbf{m}_i^\beta$ *defined in* (45) *and* (46).

- *Assume* $\beta > -3$. *Then, for any* $T > 0$, *we have*

$$\mathbf{m}_k^\beta(T) = \frac{\Gamma(\beta + 3/2)}{\Gamma(3/2)} T^\beta. \tag{A.6}$$

- *Let* $\delta > 0$ *and assume that* $\beta > -\delta$. *Then, for any* $T > 0$, *we have*

$$\mathbf{m}_i^\beta(T) = \frac{\Gamma(\beta + \delta)}{\Gamma(\delta)} T^\beta. \tag{A.7}$$

Proof. We start by proving (A.6). We perform the change of variables $(v, v_*) \mapsto (g, G) = (v - v_*, \frac{v+v_*}{2})$ in (45) and get

$$\mathbf{m}_k^\beta(T) = \left(\frac{4\pi T}{m}\right)^{-3/2} \int_{\mathbb{R}^3} e^{-m|g|^2/4T} \left[\frac{m}{4}|g|^2\right]^\beta \mathrm{d}g.$$

Changing to polar coordinates leads to

$$\mathbf{m}_k^\beta(T) = \left(\frac{4\pi T}{m}\right)^{-3/2} |\mathbb{S}^2| \int_0^{+\infty} e^{-mr^2/4T} \left(\frac{mr^2}{4}\right)^\beta r^2 \,\mathrm{d}r.$$

Then, performing the change of variable $r \mapsto x = mr^2/4T$, we obtain

$$\mathbf{m}_k^\beta(T) = \left(\frac{4\pi T}{m}\right)^{-3/2} |\mathbb{S}^2| \int_0^{+\infty} e^{-x} (xT)^\beta \left(\frac{4T}{m}\right) x \sqrt{\frac{T}{m}} \frac{\mathrm{d}x}{\sqrt{x}} = \frac{2}{\sqrt{\pi}} T^\beta \int_0^{+\infty} e^{-x} x^{\beta+1/2} \,\mathrm{d}x,$$

which allows to recover (A.6).

To deal with (A.7), it is enough to compute the following integral, which depends on both δ and β,

$$\mathcal{I}_\beta = \iint_{(0,+\infty)^2} e^{-(I+I_*)/T} (I + I_*)^\beta (II_*)^{\delta/2-1} \,\mathrm{d}I \,\mathrm{d}I_*,$$

for any relevant β, since $\mathbf{m}_i^\beta(T) = \mathcal{I}_\beta / \mathcal{I}_0$. Thanks to Lemma A.1, the change of variable $I_* \mapsto E_i' = I + I_*$ leads to

$$\mathcal{I}_\beta = \int_0^{+\infty} e^{-E_i/T} {E_i}^\beta \,\mathfrak{m}_\varphi'(E_i) \,\mathrm{d}E_i = \frac{\Gamma(\delta/2)^2}{\Gamma(\delta)} \int_0^{+\infty} e^{-E_i/T} {E_i}^{\beta+\delta-1} \,\mathrm{d}E_i,$$

and subsequently to

$$\mathcal{I}_\beta = \frac{\Gamma(\delta/2)^2\, \Gamma(\beta + \delta)}{\Gamma(\delta)} T^{\beta+\delta}.$$

□