A KINETIC MODEL OF POLYATOMIC GAS
WITH RESONANT COLLISIONS

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ABSTRACT. We propose a kinetic model describing a polyatomic gas undergoing resonant collisions, in which the microscopic internal and kinetic energies are separately conserved during a collision process. This behaviour has been observed in some physical phenomena, for example in the collisions between selectively excited CO_2 molecules. We discuss the model itself, prove the related H-theorem and show that, at the equilibrium, two temperatures are expected. We eventually present a numerical illustration of the model and its main properties.

Keywords: Kinetic theory; Resonant collisions; Boltzmann equation.

1. INTRODUCTION

The Boltzmann equation [9], which is the starting point of kinetic theory, studies systems of gaseous particles at the mesoscopic level through the formalism of distribution functions defined in the phase space. Despite its importance at the theoretical level, the Boltzmann equation only describes monatomic gases, such as the noble gases. However, when dealing with polyatomic gases, e.g. nitrogen or carbon dioxide, the standard Boltzmann equation cannot properly capture all physical phenomena at the microscopic level, mainly because it does not take into account the vibrational and rotational degrees of freedom of polyatomic molecules and their effects on the internal energy of the system.

Because of the relevance of internal energy in understanding several physical and chemical phenomena, such as combustion, or when dealing with the study of gases under extreme temperatures and pressure conditions, it is necessary to provide a theoretical framework which takes into account the behaviour of the internal energy in a kinetic system.

At the level of the macroscopic description, the study of internal energy is one of the purposes of rational extended thermodynamics [33]. On the other hand, when dealing with the mesoscopic description, a first popular approach consists in dealing with systems with discrete energy levels, as in [21, 22, 32, 8]. In that case, the effects of the internal structure of a molecule are taken into account by introducing a set of distribution functions, each of them representing the (molar) fraction of the gaseous molecules at a given discrete energy level. The binary interactions conserve momentum and, when no energy is lost during the collision process, i.e. when the collisions remain elastic, the kinetic and internal energies of the colliding molecules are modified in such a way that the total energy is conserved. This choice leads to handle systems of Boltzmann-type equations, with cross interactions between the different distribution functions describing each internal energy level.

Another strategy consists in using the so-called ellipsoidal statistics (ES) model, which was first introduced in [24]. This research direction has gained much attention at the beginning of the 21st century in the context of BGK equations, see for instance [2, 1, 14], or [27] for Fokker-Planck models.

Let us also point out that, in [16], the authors works with a continuous rotational energy variable and a discrete vibrational one.

However, in the context of the full Boltzmann equation, several questions are still open. In particular, it is emphasized in [5, 4] that the kinetic modelling of carbon dioxide is quite intricate, and induces two kinds of temperatures, related to translational and rotational energies, respectively. In order to deal with the Boltzmann equation with a continuous internal energy variable, one can be led to use the phenomenological model of [10] for binary microscopic collisions in a gaseous mixture. This strategy, nowadays known as the Borgnakke-Larsen procedure, allows to handle the energy exchanges after a binary collision. The first step of the Borgnakke-Larsen strategy consists in identifying the total energy of a colliding pair in the mass center. Then a proportion of this total energy is attributed to the internal energy of the post-collisional molecules and the remainder is provided to the kinetic energy of the outgoing molecules. The internal energy of the pair is itself allocated between both molecules. This procedure and its consequences on the underlying Boltzmann equation have been widely investigated during the last thirty years, see for example [13, 17, 18, 19] which offer further physical discussions about the model, and [30, 6, 20, 3], where various mathematical properties of the Borgnakke-Larsen approach are studied.

Unfortunately, the Borgnakke-Larsen procedure cannot cover all polyatomic gas behaviours, for example the energy exchanges between selectively excited carbon dioxide molecules. In [26], the authors show that, under specific temperature and energy conditions, the role of rotational and vibrational degrees of freedom is dominant in the energy exchange, while the average contribution of translations is negligible. On the other hand, in the case of self-pressure broadening of highly polar molecules, such as hydrogen cyanide, collisions in which the rotational energy change of one molecule is exactly compensated by the rotational energy change of its collision partner play a major role [25]. Such kinds of collisions, in which the internal energy change of one molecule is compensated by the internal energy change of its collision partner and, at the same time, the kinetic energy change of one molecule is compensated by the kinetic energy change of its collision partner are known in the literature as *resonant collisions* [31].

In that situation, an alternative to the Borgnakke-Larsen procedure to work with a continuous internal energy variable is required. In order to give a first answer to this requirement, we propose a model describing a gas undergoing resonant collisions. In what follows, we consider a non-reactive polyatomic gas composed of molecules with molecular mass $m > 0$, moving in $\mathbb{R}^d$, $d = 2$ or 3.

Note that the notion of resonance studied in this article coincide with the one discussed in [23], but not exactly with the definition given in [7]. Indeed, in [7], the authors describe a reactive mixture through a finite number of densities, each of them representing a gaseous species with a given discrete internal energy level to mimic non-translational degrees of freedom. And the expression *resonant collisions* describes the interactions between particles of the same species in the case of gaseous mixtures. In this approach, the macroscopic kinetic and internal energies are treated separately, ensuring – as in our case – the existence of two distinct temperatures. However, as these two meanings have coexisted in the literature for many years, we do not see any risk of confusion in using the expression *resonant collisions* in this article.

We also highlight the recent paper [11], where the use of proper measures allows to describe polyatomic gases with rotational and vibrational energies in a general and unified way.

The structure of the article is the following. In Section 2, we describe our microscopic resonant model. Then, in Section 3, we discuss the related collision operator and the associated H-theorem, including the existence of two temperatures. Eventually, we present a numerical illustration of the model.

2. Binary resonant collisions

The first step consists in describing a collision between two molecules. In what follows, we denote by v, v_* the post-collisional velocities of the interacting particles, by I, I_* their post-collisional internal energies, and by v', v'_*, I', I'_* the corresponding pre-collisional quantities.

We assume that the collision are elastic. This hypothesis guarantees that the momentum and the total energy of the pair of molecules satisfy

$$(1) \qquad v + v_* = v' + v'_*,$$

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

When a collision is *resonant*, the sum of the post-collisional internal energies of the molecules remains equal to the sum of their pre-collisional ones [25, 26]. Consequently, because of the total energy conservation, the kinetic energy satisfies the same property. That means that (2) is replaced by the following equalities

$$(3) \qquad |v|^2 + |v_*|^2 = |v'|^2 + |v'_*|^2,$$

$$(4) \qquad I + I_* = I' + I'_*.$$

It is then clear that the velocities obey the same collision rules as in the monatomic case. Hence, we can write, for some vector $\omega \in \mathbb{S}^{d-1}$,

$$(5) \qquad v' = v - [\omega \cdot (v - v_*)]\omega, \qquad v'_* = v_* + [\omega \cdot (v - v_*)]\omega.$$

Besides, the simplest possible choice to distribute the internal energy between both particles consists in introducing an allocation parameter $r \in (0,1)$ and writing

$$(6) \qquad I' = r(I + I_*), \qquad I'_* = (1 - r)(I + I_*).$$

Eventually, for the sake of symmetry, we introduce the additional parameter r', which happens to be useful in the Jacobian computations:

$$(7) \qquad r' = \frac{I}{I + I_*}.$$

The following lemma states that both prime and non-prime variables can be seen indiscriminately as pre- or post-collisional quantities.

Lemma 1. *Let $\omega \in \mathbb{S}^{d-1}$ be fixed. Then the function $S_\omega : (v, v_*, I, I_*, r) \mapsto (v', v'_*, I', I'_*, r')$ is an involution of the set $\mathbb{R}^d \times \mathbb{R}^d \times \mathbb{R}^*_+ \times \mathbb{R}^*_+ \times (0,1)$ onto itself, and its Jacobian equals 1. Moreover, the following relationships hold:*

$$v = v' - [\omega \cdot (v' - v'_*)]\omega, \qquad v_* = v'_* + [\omega \cdot (v' - v'_*)]\omega,$$

$$I = r'(I' + I'_*), \qquad I_* = (1 - r')(I' + I'_*), \qquad r = \frac{I'}{I' + I'_*}.$$

Proof. First note that Equations (5)–(7) do not depend on each other. Since (5) exactly provides the collision rules for the velocities in the monatomic case, we already know that $(v, v_*) \mapsto (v', v'_*)$ is an involution and that its associated Jacobian equals 1. So we need to focus on the internal energies and the allocation parameters. Because of (4), $(I, I_*, r) \mapsto (I', I'_*, r')$ is clearly an involution too, and the straightforward computation of the associated Jacobian gives again 1. Then the Jacobian of S_ω equals 1, as a product of unit Jacobians. □

Remark 2.1. *A variant of this microscopic resonant collision model is discussed in Appendix 5, where the sum of the internal energies is conserved during a collision up to a small correction; and the same goes for the sum of the kinetic energies, remembering that the total energy is still conserved. Such a model can be called a quasi-resonant model and can be seen as intermediate between the resonant and Borgnakke-Larsen models.*

3. Resonant collision operator and H-theorem

The quadratic collision operator Q can be described through its weak form. More precisely, the associated bilinear operator is given by

$$(8) \quad \langle Q(f,g), \phi \rangle = \iint_{\mathbb{R}^d \times \mathbb{R}_+^*} \iint_{\mathbb{R}^d \times \mathbb{R}_+^*} \iint_{\mathbb{S}^{d-1} \times (0,1)} f(v,I) g(v_*, I_*) \left[\phi(v', I') - \phi(v, I) \right]$$

$$B(v, v_*, I, I_*, r, \omega) \, \mathrm{d}r \, \mathrm{d}\omega \, \mathrm{d}v_* \, \mathrm{d}I_* \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I,$$

where $\phi : \mathbb{R}^d \times \mathbb{R}_+^* \to \mathbb{R}$ is a suitable regular test-function. The velocities and internal energies v', I', v'_*, I'_* are defined by (5)–(6). And we must make the microreversibility assumptions on the nonnegative cross section B

$$(9) \qquad\qquad B(v, v_*, I, I_*, r, \omega) = B(v_*, v, I_*, I, 1-r, \omega),$$

$$(10) \qquad\qquad B(v, v_*, I, I_*, r, \omega) = B(v', v'_*, I', I'_*, r', \omega),$$

for any v, I, v_*, I_*. Note that (9)–(10) are automatically satisfied when B depends on $|v - v_*|$, $|(v - v_*) \cdot \omega|$ (i.e. the cosine of the angle θ between the relative velocity and ω) and $I + I_*$, since all those quantities equal their primed counterparts. That means that B should be chosen satisfying

$$(11) \qquad \beta_{lb}(r) b(\cos\theta) \tilde{B}(|v - v_*|, I + I_*) \le B(v, v_*, I, I_*, r, \omega) \le \beta_{ub}(r) b(\cos\theta) \tilde{B}(|v - v_*|, I + I_*),$$

where b is $L^1(-1,1)$ (Grad's cutoff assumption), the β functions satisfy $\beta(r) = \beta(1 - r) > 0$, and $\tilde{B}$ equals, for instance, $(m|v - v_*|^2)^\gamma + (I + I_*)^\gamma$ for $\gamma \in [0,1]$, in the same spirit as in [20], which deals with the Borgnakke-Larsen procedure.

An essential quantity of our model is the nonnegative measure $\varphi(I) \, \mathrm{d}I$, which is a parameter of the model (typically, one can take $\varphi(I) = I^a$ for some $a \ge 0$). A careful choice of the measure $\varphi(I) \, \mathrm{d}I$ makes the model automatically consistent, at the macroscopic level, with the energy law of any type of polyatomic gas [18].

Let us provide other weak formulations of the collision operator.

Lemma 2. *Let $\phi : \mathbb{R}^d \times \mathbb{R}_+^* \to \mathbb{R}$ be a function such that the following equality makes sense. Then we have*

$$(12) \quad \langle Q(f,f), \phi \rangle =$$

$$-\frac{1}{4} \iint_{\mathbb{R}^d \times \mathbb{R}_+^*} \iint_{\mathbb{R}^d \times \mathbb{R}_+^*} \iint_{\mathbb{S}^{d-1} \times (0,1)} [f(v', I') f(v'_*, I'_*) - f(v, I) f(v_*, I_*)] \times$$

$$\left[\phi(v', I') + \phi(v'_*, I'_*) - \phi(v, I) - \phi(v_*, I_*) \right] B(v, v_*, I, I_*, r, \omega) \, \mathrm{d}r \, \mathrm{d}\omega \, \mathrm{d}v_* \, \mathrm{d}I_* \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I.$$

Proof. It is enough to use in (8) the changes of variables $(v, v_*, I, I_*, r) \mapsto (v_*, v, I_*, I, 1 - r)$ and S_ω, with a fixed $\omega \in \mathbb{S}^{d-1}$. $\qquad\square$

Note that the standard conservation properties of the collision operator are consequences of (12). Indeed, if ϕ is chosen as 1, $v_{(k)}$ (the k-th coordinate of v in $\mathbb{R}^d$, $1 \le k \le d$), $|v|^2/2$ and I, we obtain the conservation of the number of molecules, the conservation of the momentum and the conservations of the kinetic and internal energies (separately) during the collision process, that is

$$\langle Q(f,f), 1 \rangle = 0, \qquad \langle Q(f,f), v_{(k)} \rangle = 0, \qquad \langle Q(f,f), |v|^2 \rangle = 0, \qquad \langle Q(f,f), I \rangle = 0.$$

We can now focus on the H-theorem corresponding to the collision operator (8). Before stating it, we need the following lemma, which is used during the proof of the H-theorem. It describes the collision invariants in the resonant case.

Lemma 3. *Let $g \in L^1_{\text{loc}}(\mathbb{R}^d \times \mathbb{R}^*_+)$ satisfying almost everywhere, for a given function $P : \mathbb{R}^d \times \mathbb{R} \times \mathbb{R}^*_+ \to \mathbb{R}$,*

$$(13) \qquad g(v, I) + g(v_*, I_*) = P(v + v_*, |v|^2 + |v_*|^2, I + I_*),$$

then there exist a, b, $c \in \mathbb{R}$ and $p \in \mathbb{R}^d$ such that

$$g(v, I) = a + p \cdot v + b|v|^2 + cI$$

for almost every v and I.

Proof. For the sake of simplicity, we assume that all the functions are smooth. However, the computations also hold in the distributional sense. Let us first differentiate (13) with respect to I to get

$$\partial_{d+1} g(v, I) = \partial_{d+2} P(v + v_*, |v|^2 + |v_*|^2, I + I_*),$$

with obvious notations, ∂_{d+1} being for instance the partial derivative with respect to the internal energy variable of g. In the same way, we differentiate (13) with respect to I_* and obtain

$$\partial_{d+1} g(v_*, I_*) = \partial_{d+2} P(v + v_*, |v|^2 + |v_*|^2, I + I_*).$$

Consequently, we have, for any v, I, v_*, I_*,

$$\partial_{d+1} g(v, I) = \partial_{d+1} g(v_*, I_*),$$

which means that $\partial_{d+1} g$ is constant. Hence there exists $c \in \mathbb{R}$ and a function h of v such that, for any v, I,

$$g(v, I) = cI + h(v).$$

Then (13) becomes

$$h(v) + h(v_*) = P(v + v_*, |v|^2 + |v_*|^2, I + I_*) - c(I + I_*).$$

Consequently, the right-hand side of the previous equality does not depend on $I + I_*$ anymore, so that h satisfies

$$h(v) + h(v_*) = \tilde{P}(v + v_*, |v|^2 + |v_*|^2)$$

for another function $\tilde{P}$. We are hence led back to the standard monatomic case [15, 34], which means that $h(v)$ has the form $a + p \cdot v + b|v|^2$, as expected. $\qquad\square$

Before writing in detail the H-theorem, we denote by q the Laplace transform of φ, that is

$$q(T) = \int_0^{+\infty} \varphi(I) \, e^{-I/(K_B T)} \, \mathrm{d}I,$$

where K_B is the Boltzmann constant.

Proposition 1. *Assume that the cross section B and the weight function φ are positive almost everywhere. Then, for any nonnegative function $g := g(v, I)$ such that the following quantity is defined, we have*

$$\iint_{\mathbb{R}^d \times \mathbb{R}^*_+} Q(g, g)(v, I) \log g(v, I) \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I \le 0.$$

Moreover, the three following properties are equivalent.

(i) $Q(M, M) = 0$.

(ii) $\displaystyle\iint_{\mathbb{R}^d \times \mathbb{R}^*_+} Q(M, M)(v, I) \log M(v, I) \, \mathrm{d}v \, \varphi(I) \, \mathrm{d}I = \langle Q(M, M), \log(M) \rangle = 0.$

(iii) There exist $n \geq 0$, $u \in \mathbb{R}^d$, T_{vel}, $T_{\mathrm{ie}} > 0$ such that, for any $v \in \mathbb{R}^d$ and $I > 0$,

$$(14) \qquad M(v, I) = \frac{n}{q(T_{\mathrm{ie}})} \left(\frac{m}{2\,\pi\,K_B T_{\mathrm{vel}}} \right)^{d/2} \exp \left(-\frac{m|v - u|^2}{2 K_B T_{\mathrm{vel}}} - \frac{I}{K_B T_{\mathrm{ie}}} \right).$$

Note that Property *(i)* of the previous proposition must first be understood in a weak sense, *i.e.* $\langle Q(M, M), \phi \rangle = 0$ for any suitable ϕ. But if we define the strong formulation of Q, it would also hold pointwise.

Proof. To obtain the inequality, we use Lemma 2 for $\phi = \log f$ and observe, as classically, that

$$[f(v', I')f(v'_*, I'_*) - f(v, I)f(v_*, I_*)][\log f(v', I') + \log f(v'_*, I'_*) - \log f(v, I) - \log f(v_*, I_*)] \geq 0.$$

Let us now focus on the equivalences. Implication *(i)* $\Rightarrow$ *(ii)* is straightforward. We obtain Implication *(iii)* $\Rightarrow$ *(i)* using Lemma 2. For the last implication, let $g := g(v, I)$ an almost everywhere positive function such that $\langle Q(g, g), \log g \rangle = 0$. The integrand in the corresponding integral in v_*, I_*, ω and r, which, as we already know, has a constant sign, is consequently zero almost everywhere. That ensures that, for almost every $(v, v_*, I, I_*, \omega, r)$,

$$\log f(v, I) + \log f(v_*, I_*) = \log f(v', I') + \log f(v'_*, I'_*).$$

Then we integrate with respect to $\omega \in \mathbb{S}^{d-1}$ and $r \in (0, 1)$ to obtain the existence of a function T such that, for almost every (v, v_*, I, I_*),

$$\log f(v, I) + \log f(v_*, I_*) = T(v + v_*, |v|^2 + |v_*|^2, I + I_*).$$

Thanks to Lemma 3, we know then that $\log f$ has the form $a + p \cdot v + b|v|^2 + cI$, for some constants a, b, $c \in \mathbb{R}$, $p \in \mathbb{R}^d$. That eventually leads to the Maxwellian form (14). $\qquad \square$

The equilibrium distribution is the product of two Gibbs distributions, which separately depend on the velocity v and on the internal energy I. In particular, each Gibbs distributions has its own temperature, which will be indicated in the following as the translational temperature and the internal temperature. The translational temperature takes into account the kinetic energy of the molecules, whereas the internal temperature includes the contributions of the rotational, vibrational and electronic excitation energies.

Because of the specific conservation laws of resonant collisions, our model does not allow any exchange between kinetic energy and internal energy at the microscopic level. Therefore, the translational temperature does not influence the internal temperature, and conversely. This behaviour, here theoretically deduced in the framework of the H-theorem, is coherent with several experimental results, such as in the shock layers over flying objects in the Earth's atmosphere, at high speeds and high altitudes [29]. In such situations, it is not possible to assume that all of the internal energy modes of the gaseous species are in equilibrium with the translational mode and therefore a one-temperature model is not adequate. Indeed, it would overestimate the rate of equilibration when compared with existing experimental data [28].

To conclude this section, we can now write down the Boltzmann equation with resonant collisions in a weak sense. The unknown of the model is the distribution function $f := f(t, x, v, I)$, depending on time $t \geq 0$, space position $x \in \mathbb{R}^d$, velocity $v \in \mathbb{R}^d$ and internal energy $I > 0$. The time evolution of f is then governed by the following partial differential equation, written in a distributional sense,

$$(15) \qquad \iint_{\mathbb{R}^d \times \mathbb{R}_+^*} (\partial_t f + v \cdot \nabla_x f)\,(t, x, v, I)\,\phi(v, I)\,\varphi(I)\,\mathrm{d}I\,\mathrm{d}v = \langle Q(f, f), \phi \rangle.$$

4. NUMERICAL ILLUSTRATION

In this last section, we just briefly present some numerical results allowing to confirm Proposition 1, *i.e.* the form of the Maxwellian equilibrium.

For the sake of simplicity, we work in a two-dimensional space-homogeneous setting, *i.e.* we drop the dependence with respect to the space variable in (15). We choose B equal to 1, which satisfies (11) with $\beta = 1$, $b = 1$, and $\gamma = 0$ in $\tilde{B}$, and $\varphi = 1$. We take $T_{\text{fin}} = 10$. We used a standard particle method involving 10^6 numerical particles to solve the homogeneous Boltzmann equation. All those particles are assumed to have the same molecular mass $m = 1$.

We choose as an initial datum for f the probability density function $f^0 := f^0(v, I) = f^0_{\text{vel}}(v) f^0_{\text{ie}}(I)$, where f^0_{vel} is the probability density of the uniform law on $v \in (-4, 4)^2$, and f^0_{ie} is the probability density of the uniform law on $I \in (0, 10)$. Note that this choice leads to a distribution with respect to the (particle) total energy $\mathfrak{E} = \frac{1}{2}|v|^2 + I$ given in Figure 1, *i.e.*

$$\mathfrak{E} \mapsto \int_{\mathbb{R}^2} f^0 \left(v, \mathfrak{E} - \frac{1}{2}|v|^2 \right) \, \mathrm{d}v.$$
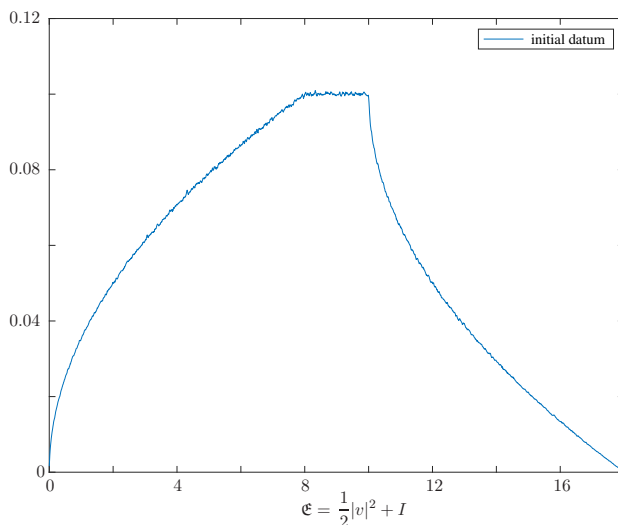

FIGURE 1.   Initial distribution w.r.t. the molecular total energy.

The distribution function f fastly reaches its equilibrium, which is described in Proposition 1. The form (14) of f is confirmed in Figure 2, where the graphs of the following functions, drawn in the semilog scale,

$$\text{(a) } I \mapsto \int_{\mathbb{R}^2} f(T_{\text{fin}}, v, I) \, \mathrm{d}v, \quad \text{(b) } \frac{|v|^2}{2} \mapsto \iint_{\mathbb{R}^*_+ \times (0, 2\pi)} f(T_{\text{fin}}, |v| \cos \alpha, |v| \sin \alpha, I) \, \mathrm{d}\alpha \, \mathrm{d}I,$$

are very close to straight lines.

Eventually, in Figure 3, we plot the semilog-scaled graph (b) of

$$\mathfrak{E} \mapsto \int_{\mathbb{R}^2} f \left(T_{\text{fin}}, v, \mathfrak{E} - \frac{1}{2}|v|^2 \right) \, \mathrm{d}v$$

.

It is clear that its graph is not close to a straight line at all. This behavior confirms that there are two distinct temperatures associated to the kinetic and internal energies in the equilibrium.
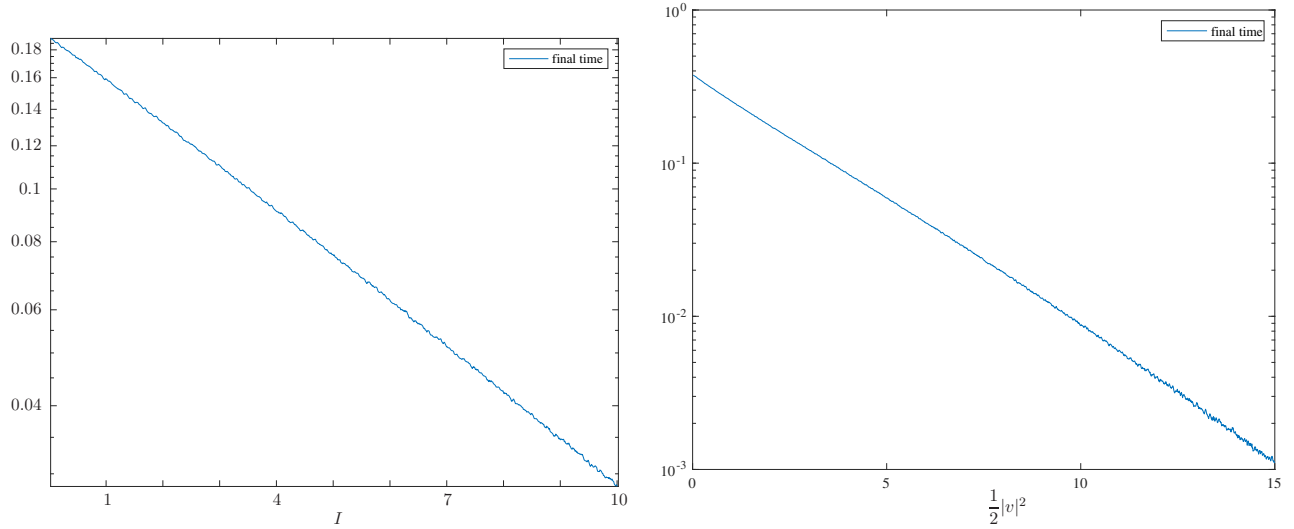
FIGURE 2. Semilog-scaled distributions w.r.t. the molecular internal (a) and kinetic
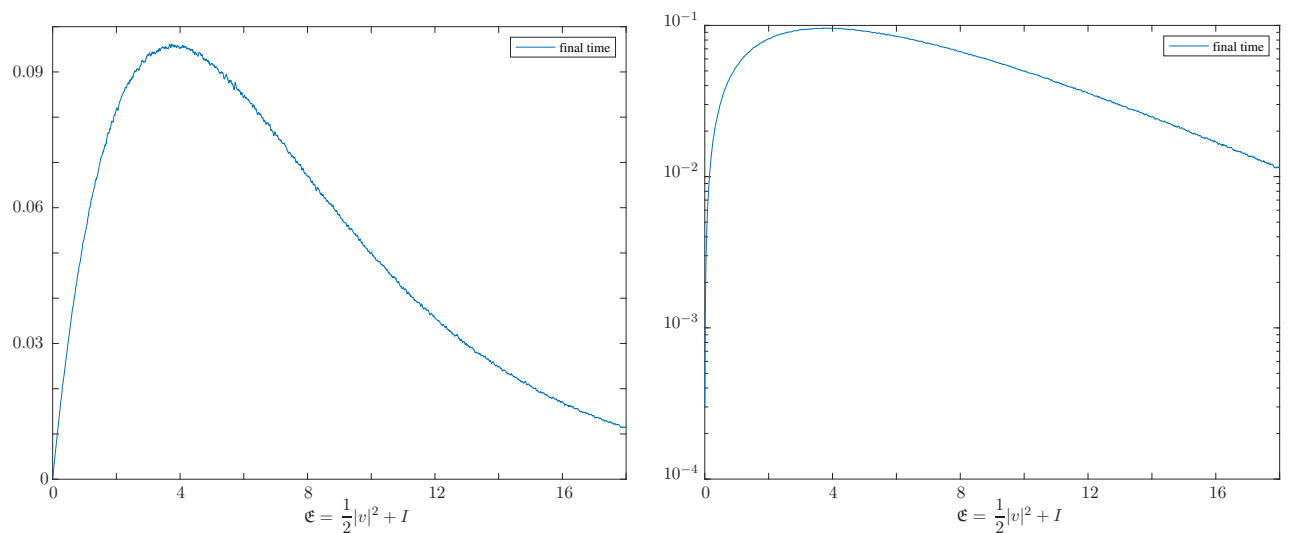(b) energies at final time.

FIGURE 3. Standard-scaled (a) and semilog-scaled (b) distributions w.r.t. the
molecular total energy at final time.

5. CONCLUSION

We proposed in this paper a new model for polyatomic gases such as carbon dioxide, where the collision process is resonant, *i.e.* the velocities and internal energies are separately conserved. That raises various mathematical questions, for instance about the perturbative setting and the study of the associated linearized collision operator. In fact, the expected compactness property of the latter operator has been studied in [12]. And the general framework built in [11] should be helpful to generalize the already known results about monatomic gases.

We can also think of natural extensions of the resonant collisions discussed in Section 2, such as quasi-resonant collisions. In that situation, the kinetic and internal energies are not separately exactly conserved any more, but only up to a small fractions of energies. More precisely, the

conservation laws of momentum and total energy for elastic collisions are still given by (1)–(2). We then compute the total energy of the colliding molecules in the mass center reference frame, *i.e.*

$$(16) \qquad \mathcal{E} = \frac{m}{4}|v - v_*|^2 + I + I_* = \frac{m}{4}|v' - v'_*|^2 + I' + I'_*.$$

When the collisions are only quasi-resonant, we consider that the sum of the internal energies of the molecules after collision equals its counterpart before collision up to a small correction, and the same goes for the sums of the kinetic energies of the two molecules. Nevertheless, of course, (16) must still hold. More precisely, for instance, we can write, for any $\eta, \nu > 0$, assumed to be small compared to 1,

$$(17) \qquad \frac{m}{4}|v' - v'_*|^2 = (1 - \nu)\frac{m}{4}|v - v_*|^2 + \eta(I + I_*) := \mathcal{E}_{1-\nu,\eta},$$

$$(18) \qquad I' + I'_* = \frac{\nu m}{4}|v - v_*|^2 + (1 - \eta)(I + I_*) := \mathcal{E}_{\nu,1-\eta}.$$

The parameters η and ν can be called the *resonance coefficients* of the model. When $\eta = \nu = 0$, we recover the model for resonant collisions. And we obviously have

$$\mathcal{E}_{1,1} = \mathcal{E} = \mathcal{E}_{\nu,1-\eta} + \mathcal{E}_{1-\nu,\eta}.$$

We need a model to allocate the energies to the two colliding particles after interaction to obtain the collision rules.

To deal with the internal energies, the simplest choice consists in introducing a parameter $r \in (0, 1)$, and then attribute the fraction r of the internal energy to one of the two outgoing particles and the remaining fraction $(1 - r)$ to the other one, that is

$$I' = r\,\mathcal{E}_{\nu,1-\eta}, \qquad I'_* = (1 - r)\mathcal{E}_{\nu,1-\eta}.$$

We can also link the pre- and post-collisional velocities by proceeding in the following way. From (17), we deduce that

$$|v' - v'_*| = 2\sqrt{\frac{\mathcal{E}_{1-\nu,\eta}}{m}}.$$

Then the pre-collisional velocity $v' - v'_*$ can be written with the help of a parameter $\omega \in \mathbb{S}^{d-1}$, so that

$$v' - v'_* = 2\sqrt{\frac{\mathcal{E}_{1-\nu,\eta}}{m}}T_\omega\left[\frac{v - v_*}{|v - v_*|}\right],$$

where $T_\omega : z \mapsto z - 2(\omega \cdot z)\omega$ is the orthogonal symmetry with respect to $\{\omega\}^\perp$. We finally find

$$v' = \frac{1}{2}(v + v_*) + \sqrt{\frac{\mathcal{E}_{1-\nu,\eta}}{m}}T_\omega\left[\frac{v - v_*}{|v - v_*|}\right], \qquad v'_* = \frac{1}{2}(v + v_*) - \sqrt{\frac{\mathcal{E}_{1-\nu,\eta}}{m}}T_\omega\left[\frac{v - v_*}{|v - v_*|}\right].$$

Unfortunately, the inversion of the previous equations, which would allow to write the non-prime quantities in terms of the prime ones, is not always possible. In fact, given the values of the post-collisional velocities and internal energies of an interacting pair of particles, it is not guaranteed that there exists an admissible pair of pre-collisional velocities and internal energies generating the considered post-collisional values. Indeed, from (17)–(18), we can deduce that

$$|v - v_*|^2 = \frac{(1 - \eta)}{1 - \eta - \nu}|v' - v'_*|^2 - \frac{4\eta}{m(1 - \eta - \nu)}(I' + I'_*),$$

and notice that the right-hand side of the previous equality becomes negative as soon as

$$|v' - v'_*|^2 < \frac{4\eta}{m(1 - \eta)}(I' + I'_*).$$

A natural way to handle this difficulty would be to work in a weak sense, which is not discussed any further here, but that already suggests difficulties related to the non-involutivity of the pre/post-collisional transformation. These quasi-resonant models will be discussed in upcoming contributions.

One interesting trail will consist in, first, properly understanding how to model the quasi-resonance, second, studying the formal convergence to the equilibrium with one temperature, and eventually, investigating if the neighbouring resonance effect provides some kind of transient equilibrium with two temperatures, as both η and ν are small with respect to 1. That possibility definitely seems quite reasonable for some scaling choices, as carbon dioxide molecules can eventually leave their selectively excited state and then satisfy another kind of microscopic model.

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