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BGK Models and Reaction-Diffusion Equations for Reacting Mixtures of Monatomic and Polyatomic Gases

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Abstract (English version)

The study of gas flows is an issue that nowadays responds to the necessities of various fields of research, as aerospace engineering, climate studies, energy industries, etc. For this reason, the construction of mathematical models simulating the behavior of real gas mixtures is extremely useful.

Among all possible approaches, the kinetic one, based on Boltzmann equations for species distribution functions, seems to be a very powerful tool. It allows, in fact, to describe mixtures starting from interaction among particles, with the possibility of deriving models for the behavior of the global system at observable level. The work of this thesis is devoted to considering results obtained so far for mixtures of gases and extending them considering more real-like cases, such as mixtures of monoatomic and polyatomic gas species, that may also interact inelastically or chemically.

As first, we provide an introduction in which the basic concepts and the most relevant results for kinetic description of gases are presented, along with a more detailed summary of the work carried out in the thesis.

In Chapter 1, we propose the study of a reacting mixture of four gases using the classical Boltzmann kinetic theory. This case was already analyzed when the four gases are considered to have the same number of internal energy levels. We generalize it allowing each of the gas species to have a different number of energetic levels.

Chapter 2 and Chapter 3 are devoted to the study of gas mixtures using a kinetic approach of BGK type. In particular, in Chapter 2 we provide a BGK model for an inert mixture of monatomic and polyatomic gases. We prove the consistency of the model and analyze the stability of equilibria, then we derive macroscopic equations and perform some numerical simulations being inspired by real gases. In Chapter 3, instead, we propose two BGK models for mixtures of reacting gases. In the first one we have four gas species involved in a reversible chemical reaction, in the second case eight gases react through two disjoint reactions. The same strategy is applied to both cases, the main differences are in proving the consistency of the model, since in Chapter 3 we face more complicated transcendental equations to determine all the parameters. Also in these cases, numerical simulations are performed to simulate the behavior of real reacting mixtures.

In the remaining part of the thesis, we study gas mixtures using different techniques. In Chapter 4 we consider a mixture of five gas species, three of them constituting a background medium in which the other two interact. Encounters among particles can be elastic, inelastic, or chemical and we suppose that they occur at different time scales. We write classical Boltzmann equations for the interacting components, we pass to the asymptotic diffusive limit and, by means of suitable integrations of the kinetic equations, we obtain reaction-diffusion equations for densities of the species. Specifically, we apply this procedure in three different hydrodynamic regimes, obtaining in each case a proper reaction-diffusion system.

The stability properties of these systems are then studied in Chapter 5. We investigate the possibility of having Turing instability for suitable choices of internal energy amounts and of collision frequencies.

Through numerical simulations, we verify the formation of spatial patterns in the evolution of the number densities of reactants, as predicted by Turing analysis.

We conclude with some further observations and perspectives for a future development of the present research work.

Abstract (versione italiana)

Lo studio delle miscele di gas è un tema che oggigiorno risponde alle necessità di vari campi di ricerca, come l'ingegneria aerospaziale, gli studi climatici, le industrie energetiche, ecc. Per questo motivo la costruzione di modelli matematici che simulino il comportamento di gas reali si rivela estremamente utile.

Tra tutti gli approcci possibili, quello cinetico, che si basa sulle equazioni di Boltzmann per le funzioni di distribuzione dei gas, rappresenta uno degli strumenti più validi. Esso permette, infatti, di descrivere miscele a partire dall'interazione tra particelle, per poi derivare modelli per le quantità osservabili. Il lavoro contenuto in questa tesi è volto a riprendere i risultati presenti in letteratura per miscele di gas e ad estenderli considerando casi più realistici, come miscele di specie monoatomiche e poliatomiche, che possono interagire in modo inelastico o chimico.

Per prima cosa, nell'introduzione vengono presentati i concetti basilari e i risultati più rilevanti per lo studio cinetico dei gas, insieme a una sintesi più dettagliata dei contenuti della tesi.

Nel Capitolo 1 proponiamo lo studio di una miscela reattiva costituita da quattro gas utilizzando la classica teoria cinetica di Boltzmann. Questo problema è già stato analizzato nell'ipotesi in cui i gas hanno lo stesso numero di livelli di energia interna, lo affrontiamo nel caso più generale in cui ciascuna delle specie coinvolte abbia un diverso numero di livelli energetici.

Nei due capitoli successivi vengono studiate miscele di gas utilizzando un approccio cinetico di tipo BGK. In particolare, nel Capitolo 2 forniamo un modello BGK per una miscela inerte di gas monoatomici e poliatomici. Dimostriamo la consistenza del modello e analizziamo la stabilità degli equilibri; deriviamo poi opportune equazioni macroscopiche ed eseguiamo alcune simulazioni numeriche ispirandoci ai gas reali.

Nel Capitolo 3, invece, proponiamo due modelli BGK per miscele di gas reagenti. Nel primo consideriamo quattro specie di gas coinvolte in una reazione chimica reversibile, nel secondo otto gas che partecipano a due reazioni disgiunte. La stessa procedura viene applicata in entrambi i casi, la principale differenza risiede nel dimostrare la consistenza del modello, poiché nel Capitolo 3 si ottengono equazioni trascendenti più complicate per la determinazione di tutti i parametri. Anche in questo contesto vengono eseguite simulazioni numeriche che modellizzino il comportamento di miscele reattive reali.

Nella parte restante della tesi, studiamo miscele di gas tramite tecniche ulteriori. Nel Capitolo 4 consideriamo una miscela di cinque specie di gas, di cui tre costituiscono il mezzo ospite in cui interagiscono le altre due. Gli urti tra le particelle possono essere di tipo elastico, inelastico o chimico e ci mettiamo nelle ipotesi in cui questi avvengano su scale temporali diverse. Successivamente, scriviamo le equazioni di Boltzmann classiche per le funzioni di distribuzione delle varie componenti. Dopo opportune integrazioni delle equazioni, si effettua un passaggio al limite, ottenendo equazioni di reazione-diffusione per le densità di specie. Nello specifico, applichiamo questo procedimento considerando tre diversi regimi idrodinamici, ottenendo in ciascuno di essi un diverso sistema di

reazione-diffusione.

Le proprietà di stabilità di tali sistemi vengono discusse nel Capitolo 5. Studiamo in particolare la possibilità che si verifichi il fenomeno dell'instabilità di Turing per scelte opportune dei valori di energia interna e delle frequenze di collisione. Attraverso simulazioni numeriche, verifichiamo poi la formazione di pattern nell'evoluzione delle densità dei reagenti, come previsto dall'analisi di Turing.

Concludiamo con alcune ulteriori osservazioni e prospettive per futuri sviluppi del presente lavoro di ricerca.

Contents

Introduction

The classical kinetic description of gas dynamics may be considered having its start in the Eighteenth century, when Daniel Bernoulli adopted the model of a gas as a large set of molecules moving at high speed and colliding elastically among themselves, [8]. The further development of kinetic theory of gases was due to James Clerk Maxwell, who in 1860 carried out the probability distribution for velocities at equilibrium [87]. But it was only with Boltzmann in 1872 [27] that an integro-differential equation describing the dynamical evolution of the distribution function was provided, along with a formal definition of entropy and a rigorous formulation of the second law of thermodynamics, known as H-theorem; a complete view of Boltzmann results and biography can be found in [37].

These early results were formulated for a single rarefied gas, but it is indisputable that the nature of gaseous flows in reality can be extremely various. First of all, a considerable number of components having different nature may be simultaneously present in a gaseous environment. A generalization of the Boltzmann model to a mixture of different gas species is treated in [36], where Carlo Cercignani provides a fundamental set of results concerning the study of Boltzmann equations (i.e. uniqueness of the equilibrium solution, its asymptotic stability and the relaxation to it from any initial condition) and their possible applications. Also in other books authors provided a detailed study of the kinetic theory for inert gas mixtures, as Chapman and Cowling [40], Kogan [72] or Ferziger and Kaper [52].

An important phenomenon that should also be considered in gas mixtures is that constituents may undergo chemical reactions, causing actual changes in the physical nature of the flow. Several attempts in the description of chemically reacting gas mixtures can be found in literature [10, 32, 123]. The kinetic approach seems to be one of the most suitable for this task and first results have been carried out in the Forties [74,99]. Afterwards, many advances have been obtained in this research line starting from the Sixties and Seventies and, in particular, different types of approximation have been applied in order to derive macroscopic quantities, like reaction rates or transport coefficients [90, 101, 109, 122]. Other works from the Eighties, instead, are focused on fundamental aspects, as the analysis of equilibrium [97]. A fairly exhaustive kinetic description for a mixture of four gases undergoing, apart from mechanical collisions, also a bimolecular chemical reaction can be found in [104], as by-product of previous works by the authors [25, 35, 55, 102].

Besides chemical processes, a relevant issue to be taken into account is that colliding molecules cannot always be considered perfect spheres. Polyatomic gas molecules, in particular, are more complex particles having non-translational degrees of freedom, as vibrational and rotational ones. These features may be represented by assigning to each particle a variable denoting the internal energy state, that can be considered both discrete [56, 58] or continuous [46, 105]. As a consequence of this assumption, interactions among particles in a gas mixture may also give rise to the non-conservative phenomenon of inelastic scattering. In other words, once that a binary encounter takes place, particles may change their internal energy state so that the total kinetic energy is not conserved. The phenomenological derivation of this type of scattering may be found in [55, 113], whereas the kinetic description of this framework is given in [103].

A following step in this research line consists in combining the results of [103] and [104] by considering a mixture of reacting gases endowed with discrete internal energy levels. This is, indeed, the content of many works [14, 58–60]. Despite the relevant outcomes, in all the models considered so far the gas species involved in the dynamics are assumed to have the same number N of possible discrete energy levels. This assumption surely allows more handy calculations, but does not fit any real physical environment. Molecules belonging to different species have different shape and dimension, thus the possibilities for their internal energy amount are various as well. In most situations, due to chemical dissociation and recombination reactions, gaseous elements may be found even in atomic state, that can be modeled as species having only one possible internal energy level.

Providing models for gas mixtures in which polyatomic and monatomic gas species interact through elastic, inelastic or chemical collisions is the basic purpose of this thesis. For this reason, the aim of Chapter 1 in this work is to collect and, at the same time, generalize the classical cornerstones of a Boltzmann description for a gas mixture. We analyze the case of four reacting gas species, each one allowed to have a different number (greater of equal than one) of internal energy levels l^i, $i = 1, 2, 3, 4$. Thus the mixture can be seen as made up by $L = l^1 + l^2 + l^3 + l^4$ components, indicated by C^i_j, where the superscript identifies the species which the component belongs to, while the subscript indicates the corresponding energy level. Accordingly to this notation, a generic bimolecular encounter between components can be written as follows

$$C^i_j + C^h_k \leftrightarrows C^l_m + C^n_p.$$

This encounter can be elastic if components involved do not change their chemical nature nor their energy state ($(i, j) = (l, m)$ and $(h, k) = (n, p)$), inelastic when components change their internal energy but they still belong to the same species ($i = l$, $h = n$ but $j \neq m$ or $k \neq p$ or both), chemical when there is an actual change in species ($i \neq l$ and $h \neq n$).

We further adjust this notation using, instead of a pair of indices (i, j) to indicate each component, a single index I, with $1 \leq I \leq L$. We construct then a Boltzmann equation for each distribution function f_I corresponding to a component C_I. The most relevant part is to derive the integral collision term in each equation. Indeed, in writing the inelastic and chemical contributions to the collision operators, one has to be aware that an internal energy gap is related to each encounter, so (if this gap is positive) the transition takes place only when the pre-collisional total energy is sufficient. This causes the presence of suitable energy threshold in the collision Boltzmann operators. Then we investigate the global properties of the collision operator and we present collision invariants as L-dimensional vectors constituting a 7-dimensional linear space. In this way, after defining in this context the macroscopic observables, we derive a system of seven balance equations.

Afterwards, we provide the proof of the classical Boltzmann inequality for our model, that leads to the characterization of collision equilibria that are, as expected, of Maxwellian type. In this frame, we obtain also a relation at equilibrium between number densities of each energetic component and the density of the species it belongs to, along with the classical mass action law (of Arrhenius type) relating species densities and global temperature at chemical equilibrium [5]. Finally, H-theorem provides asymptotic stability and uniqueness of the Maxwellian equilibrium.

Looking at kinetic equations of Boltzmann type, it is immediate to note that the study of the evolution of distributions as solution of an integro-differential system can be very complicated. For this reason, multiple strategies have been investigated to replace the integral collision term with a simpler one, also if this choice may lead to a loss of information at the level of microscopic two-body interactions between molecules. The most relevant collision model, taking into account only the average outcomes of collisions, is the one proposed by Bhatnagar, Gross and Krook for a single gas species in 1954 [9], known as BGK model. The idea of such kind of models comes from the fact that the dynamics of the system drives the configuration to "relax" towards a Maxwellian state, so that collisions cause a change rate for the distribution proportional to the difference between the distribution itself and a Maxwellian attractor.

The generalization of the classical BGK model to a gas mixture is not obvious (and not unique), since in the Maxwellian attractors there appear several free parameters that could be properly chosen in order to reproduce the basic features of the Boltzmann equations that one wants to approximate. The available BGK models may be divided into two classes: one assuming the kinetic equation for each species governed by a unique relaxation operator, introduced by Andries, Aoki and Perthame in [1], and the other one showing a sum of binary relaxation operators, preserving thus the "structure" of the original Boltzmann system, see for instance [63, 71, 88] and the recent paper [24].

A BGK–type description has been then adapted to gases whose particles are subject also to very simple chemical reactions, usually bimolecular and reversible; in this respect, models with a single collision operator per species have been proposed in [16, 61], while models with sums of relaxation terms may be found in [30, 75]. In general, most of the existing BGK models deal only with monatomic particles, therefore in view of physical applications their generalization to polyatomic gases through the introduction of a suitable internal energy is necessary. A BGK description in a similar situation is presented in [11] and will be the starting point of Chpaters 2 and 3 of the present thesis.

In Chapter 2 we present a BGK model for a mixture composed by $A \geq 0$ monatomic and $B \geq 0$ polyatomic species having different numbers of internal energy levels (of course a monatomic species has only one level). As usual, each polyatomic species can be considered as composed by components in number equal to that of its energy levels. We build up a set of BGK-type equations for each monatomic species and each polyatomic component of the mixture. In each of them a single BGK operator appears, depending on auxiliary parameters individuated by the auxiliary number density of each species/component, and the auxiliary mean velocity and temperature that are common to each equation.

Imposing conservation of correct (Boltzmann) collision invariants, we try to express auxiliary quantities in terms of the actual ones of the mixture. While for densities of monatomic species and for mean velocity we get an explicit relation, densities of polyatomic components result to be expressed in terms of real densities and auxiliary temperature. For the latter, we are not able to find an explicit expression as well, but it turns out to be given as the solution of a transcendental equation (coming essentially from the conservation of total energy, i.e. kinetic plus internal). We are able to prove that such a transcendental equation admits a unique solution for any values of particle masses, internal energies, and collision frequencies.

The asymptotic stability of Maxwellian equilibria in space homogeneous conditions is given by means of the H-theorem, formulated in this framework: the proof of the entropy decreasing in time strongly depends on the structure of BGK equations and of Maxwellian attractors.

In a following step, after integration of the BGK equations, macroscopic equations for observables of the mixture are derived for both monatomic and polyatomic species. Considering these equations in space-independent conditions, we perform some numerical simulations in order to analyze the trend towards equilibrium of the mixture. In a first test we consider a monatomic and a polyatomic species changing the ratios between their masses, in a second one we take two polyatomic species and we consider different sets of internal energies, as third test we take two polyatomic gases having very different masses and we observe the trend towards equilibrium taking various amounts of initial velocities.

In Chapter 3 our intention is to extend results obtained in the previous chapter to suitable reacting mixtures. As first, we consider a mixture of four gas species G^i, $i = 1, \ldots, 4$, that may undergo a reversible chemical reaction of type $G^1 + G^2 \leftrightarrows G^3 + G^4$. In this case we do not make a distinction between monatomic and polyatomic species, but we consider each one as having a number of energy levels greater or equal than one.

We write BGK equations as in the inert frame and we exploit conservation laws to recover auxiliary parameters. The main difference appearing in this frame is the fact that, since number density of each species is not preserved due to chemical reaction, the four global auxiliary densities are related not only to auxiliary temperature but also to each other. By conservation of total energy, however, is possible to express each auxiliary density in terms of actual parameters and of the auxiliary temperature. On the other hand, fictitious densities have to satisfy a constraint which is the analogous of the mass action law of chemistry. This fact provides an additional transcendental equation for the auxiliary temperature, and also in this case is possible to prove that the solution exists and is unique in an admissible set.

An analogous H-theorem in space homogeneous conditions is stated and proved in this reactive case still making use of the mass action law. Moreover, we study again the behavior in time of macroscopic quantities through numerical simulations inspired by real gas reactions.

In the second part of the chapter, the considered mixture is composed by eight gases G^i, $i = 1, , \ldots, , 8$, chemically interacting through two separate reversible chemical reactions, $G^1 + G^2 \leftrightarrows G^3 + G^4$ and $G^5 + G^6 \leftrightarrows G^7 + G^8$. In this case recovering the auxiliary parameters for the Maxwellian attractor is even more complex. From conservation of mass, indeed, we find that is possible to express fictitious number densities for the first four reacting species in terms of actual parameters, auxiliary temperature and auxiliary density of only one species involved in the same reaction. This analogously holds for the remaining four species involved in the second reaction. Conservation of total energy then provides a relation between the fictitious temperature, a fictitious density species taking part in the first reaction and another one reacting in the second. To determine these three unknowns we exploit the fact that we have a mass action law for each chemical reaction. From the first one, indeed, using the implicit function theorem, we are able to express one of the fictitious densities in terms of the temperature. Using the second mass action law, at last, we individuate the auxiliary temperature as the solution of a transcendental equation. Once that this procedure allows to determine the BGK operators and, consequently, Maxwellian equilibria, their asymptotic stability is verified by means of the H-theorem also in this case. Finally, numerical simulations show how concentrations of each component, mean velocity and temperature tend to equilibrium, taking two physical reactions as test cases.

In the remaining part of the thesis, we study mixtures of reacting monatomic and polyatomic gases using a different approach. Our task is again to build a kinetic model for a particular gas mixture and to derive and study equations for the macroscopic observables in suitable hydrodynamic limits. In this case, though, we start from the classical Boltzmann-type description of the physical setting and we aim to derive reaction-diffusion equations for the number densities of constituents of the mixture.

In many physical problems involving a huge amount of interacting objects (not only particles as in our reacting mixtures, but also cells, individuals, etc.) reaction–diffusion systems are built up starting from phenomenological considerations, therefore diffusion coefficients and parameters appearing in the reaction part are taken as arbitrary constants, and are not directly related to microscopic interactions between cells, preys and predators, etc. In this respect, kinetic theory may be useful. Indeed, it is based on a mesoscopic approach and major macroscopic fields can be recovered as suitable moments of the distribution function and, in proper hydrodynamic regimes, a closure of macroscopic equations may be obtained resorting to an asymptotic Chapman–Enskog procedure [40]. In fluid–dynamics, the most common hydrodynamic systems are Euler and Navier–Stokes equations [36]. In the frame of reacting gas mixtures, the connection between reactive kinetic equations and reaction–diffusion systems has been explored starting from BGK or Fokker–Planck models [114, 115], and also from Boltzmann operators for a single bimolecular chemical reaction [12]. Rigorous results on this kind of limit have been recently proved in [51, 94]. Under suitable assumptions on the macroscopic fields and on the distribution functions, the diffusive asymptotic limit may also lead to reaction–diffusion systems of Maxwell–Stefan type [2, 3]. Also in different physical frameworks, some attempts to derive reaction–diffusion equations from kinetic equations or as mean–field limit of interacting particle systems have been performed [41, 117].

The work presented in Chapter 4 fits into this research line. We consider a gaseous mixture with several species, undergoing elastic collisions, inelastic transitions in polyatomic particles and chemical reactions, and, following the strategy suggested in the paper [12], we derive reaction–diffusion equations from the kinetic level in different hydrodynamic limits. Specifically, we consider two species, one monatomic and the other polyatomic (diatomic) diffusing in a background medium (typically, the atmosphere). The host medium is itself a mixture, constituted by particles with different masses, and as a whole it is assumed accommodated at a Maxwellian distribution, with fixed mean velocity and temperature. The kinetic system is thus composed by three Boltzmann equations, one for the distribution of the monatomic species and the others for the distributions of the two components of the diatomic gas, each one with its value of internal energy. Intra–species and inter–species elastic scattering is allowed, as well as elastic scattering with the background medium. Inelastic transitions may also occur, where polyatomic particles pass from one energy state to the other. Moreover, two bimolecular and reversible chemical reactions are taken into account, involving the considered monatomic and polyatomic constituents and the host medium as well. In the diffusive limit, the dominant process is assumed to be, as usual, the elastic scattering with the background. Three different regimes are explored, corresponding to different scales assumed for the collisions and for chemical reactions. The first one, where all reactions have the same order of magnitude (they are all slow), leads to a system of three reaction–diffusion equations for the number densities of the monatomic gas and of the two components of the polyatomic one. In the second one, for the monatomic species the collisions with the background are supposed to be more frequent than for the other components. This assumption has as a consequence the fact that in the resulting reaction–diffusion system one of the three equations lacks the diffusive term. In the third regime, besides more frequent collisions with background for one of the species, a reaction is assumed to be faster than the other chemical and inelastic interactions. This allows to explicitly get one density in terms of the other two, so that the final reaction–diffusion system is constituted by only two equations, and it is similar to the classical Brusselator system [98]. These reductions resemble the classical quasi–steady–state approximation, a standard procedure in the study of chemical reactions kinetics in situations where certain species have a very short time of existence and therefore their variation may be neglected, reducing thus the number of equations. A detailed description of such kind of reductions can be found in [108, 112] and it is applied to the particular case of the Brusselator in [44]. The possibility of modelling auto-catalytic reactions of the Brusselator system introducing an intermediate unstable state was outlined also in [77], by one of the authors of the original paper [98]. In all the hydrodynamic limits considered in Chapter 4, we obtain that diffusion coefficients and reaction terms of our macroscopic systems explicitly depend on particle masses, background density, collision frequencies of all interaction phenomena, and internal energies of the species. This means that properties of the systems can be explored starting from the microscopic structure of the mixture.

Such properties, in particular the stability of solutions of our macroscopic systems, are discussed in Chapter 5. In particular, we recall that last system obtained in Chapter 4 is similar to the classical Brusselator, that was introduced in order to model the behavior of cross–activator–inhibitor chemical reactions for which pattern formation predicted by Turing [118] could be observed. One example of reactive models showing pattern formation is the chloriteiodide–malonic acid (CIMA) reaction [78], and other analogous models and results can be found in [57]. Analytical conditions on the parameters involved in the equations leading to Turing instability were originally given in [98]. The target is to find a homogeneous stationary state that in presence of diffusion turns into structures non–homogeneous in space. Such structures are usually obtained when the concentration of some reactants and also the diffusion coefficients of chemicals varying during the reaction fit into particular ranges.

Moreover, Turing instability has been recovered in several problems, as models for morphogenesis [81], prey–predator systems [79], epidemic models [47], models for metal growth [29], for multiple sclerosis [83], for urban crime [82] or for vegetation spots on dryland [110], just to mention some of them. In those systems, and many more, the stability properties are always discussed upon the parameters appearing in the equations. These parameters are often set starting from empirical observations or heuristic considerations. In our case, instead, coefficients appearing in the equations are explicit functions of microscopic parameters, characteristic of gas species (masses and internal energy levels) and of the mixture (collision frequencies for each reaction and for mechanical encounters). This allows us to investigate the occurrence of Turing instability for varying these microscopic parameters. More precisely, for the system of two reaction–diffusion equations we are able to find explicit conditions on the internal energies allowing (or preventing) the pattern formation; the analytical results are also validated by some numerical simulations. An analogous study is then performed also for the systems of three equations, that are much more involved, since the number of coefficients is higher and the Turing instability conditions are more complicated. In particular, for the complete three reaction-diffusion equations case, we resort also to results derived in [107], where conditions for the occurrence of Turing bifurcation in n-dimensional systems are provided. Analogies and differences between the instability properties of our three systems are commented on.

We conclude this thesis with a summary of our main results along with further considerations and perspectives for future developments of our work.

1 Preliminaries: Kinetic description of gas mixtures

The classical Boltzmann description of rarefied gas dynamics can be suitably extended to mixtures of different gases [36, 40]. In this framework, apart from elastic mechanical binary collisions among particles, also reversible chemical interactions between different gas species may occur. This case has been extensively investigated in [104]. In following works, a generalization of this kind of representation has been proposed for reacting species supposed to have an internal structure [56,58]. More precisely, a mixture of four reacting gases was considered where each one was endowed with $N > 1$ discrete quantized energy levels. This choice was performed in order to represent polyatomic molecules having translational, rotational and vibrational degrees of freedom. With this assumption, also inelastic scattering has to be taken into account, where after binary collisions particles may change their internal energy state and kinetic energy is not conserved. Nevertheless, the assumption that the number of discrete energy levels is the same for each gas species turns out to be very restrictive, since these models can hardly be applied to real physical situations. For this reason, in this first chapter, we present the kinetic description of such mixtures, with the further generalization that the number of internal energy levels can be different for each species. We also consider the possibility of non symmetric encounters, i.e. irreversible chemical reactions or inelastic transitions.

The procedure used to describe the mixture is the typical Boltzmann approach of classical kinetic theory adapted and generalized to this context. We consider thus a mixture of four gas species G^i, $i = 1, \ldots, 4$ each one having mass m^i. Writing the chemical reaction as

$$G^1 + G^2 \leftrightarrows G^3 + G^4, \tag{1.1}$$

masses have to satisfy the conservation $m^1 + m^2 = m^3 + m^4$. As already stated, each particle is endowed with an internal energy state and each gas species may have a number l^i of possible discrete values for it.. We denote each one of these values by E^i_j, $j = 1, \ldots, l^i$. As a consequence, we treat the i-th species as composed by l^i components C^i_j, $j = 1, \ldots, l^i$, being the component C^i_j characterized by the internal energy E^i_j. Energies are monotonically increasing with the index identifying the level in the frame of each species, that means $E^i_j > E^i_k$ for any $j > k$. We denote the energy gap for the ground states by $\Delta E = E^3_1 + E^4_1 - E^2_1 - E^1_1$. At this point, binary interactions between molecules are expressed by the notation

$$C^i_j + C^h_k \leftrightarrows C^l_m + C^n_p. \tag{1.2}$$

In the case of mechanical collisions, in which molecules do not change their chemical nature, we may have elastic scattering, when there is not energy dissipation due to absorption by the particles, thus the total kinetic energy is conserved before and after the impact and in the formulation (1.2) we have $(i, j) = (l, m)$ and $(h, k) = (n, p)$. If, instead, there is a variation of the internal energies of the pair of impinging particles, we have the collision (1.2) with $i = l$ and $h = n$, but $j \neq m$ and/or $k \neq p$. . In case of chemical encounters, there is also a mass transfer and particles change the gas species they belong to. When this happens we have collision (1.2) with $(i,h),(l,n) \in \{(1,2),(3,4),(2,1),(4,3)\}$, being $(i,h) \neq (l,n)$ and $i \neq n$.

For a more handy notation, we introduce the vector based on numbers of energy levels

$$\underline{\mathbf{L}} = (1,\ldots,l^1,l^1+1,\ldots,l^1+l^2,\ldots,l^1+l^2+l^3+l^4). \tag{1.3}$$

We define the partial sums of the number of energy levels $L^s = l^1 + \ldots + l^s$ for $s = 1,2,3,4$ and the total one $L = l^1 + l^2 + l^3 + l^4$; we also find it useful to define $L^0 = 0$. In this way, for any energy level E^i_j and for any component C^i_j we identify each couple of indices (i,j) with the index I given by

$$I = L^{i-1} + j. \tag{1.4}$$

The reverse relation is

$$i = \min\{k : I - L^k \leq 0,\ 1 \leq k \leq 4\}, \tag{1.5}$$

$$j = I - L^{i-1}. \tag{1.6}$$

Consequently, energy levels will be indicated with E_I and components with C_I, $I = 1,\ldots,L$. We rewrite the generic collision (1.2) as

$$C_I + C_J \leftrightarrows C_H + C_K. \tag{1.7}$$

We also consider the L-dimensional vector of masses whose entries are $m_I = m_i$ for any $1 \leq I \leq L$ with i given by relation (1.5), that we indicate by $\underline{\mathbf{m}}$. It is worth underlying the fact that the "two-indices" notation and the "single-index" one are totally equivalent. In this chapter we find it useful to adopt the latter, but in the following of this thesis we shall use the former, since it will be important to distinguish between species having one or several internal energy levels and also to easily identify the fundamental level E^i_1 of each species.

1.1 Boltzmann equation and collision operators

We are now able to describe in more detail the dynamics of each generic encounter (1.7). We will indicate with $\mathbf{v}$ and $\mathbf{w}$ the pre-collisional velocities of two impinging particles belonging to components C_I and C_J, respectively, and with $\mathbf{v}'$ and $\mathbf{w}'$ the post-collisional velocities of resulting particles of components C_H and C_K, respectively. With this notation, we have conservation of momentum, total energy and mass given by

$$\begin{cases} m_I\mathbf{v} + m_J\mathbf{w} = m_H\mathbf{v}' + m_K\mathbf{w}' \\ \frac{1}{2}m_I v^2 + E_I + \frac{1}{2}m_J w^2 + E_J = \frac{1}{2}m_H {v'}^2 + E_H + \frac{1}{2}m_K {w'}^2 + E_K \\ m_I + m_J = m_H + m_K. \end{cases} \tag{1.8}$$

We define the quantity $\Delta E^{HK}_{IJ} = E_H + E_K - E_I - E_J$ as the variation of the global internal energy of the impinging pair. In case of elastic collisions, it is obviously zero, in case of inelastic or chemical collisions, instead, it can be positive or negative. If it is greater than zero, namely the collision $C_I + C_J \to C_H + C_K$ is endothermic, it must be underlined that such interaction is possible only if the total kinetic energy before the collision is sufficient. In other words it must hold

$$\frac{1}{2}\left(m_I v^2 + m_J w^2 - m_H v'^2 - m_K w'^2\right) > \Delta E_{IJ}^{HK}. \tag{1.9}$$

This results in a threshold effect on the interaction. More specifically, taking into account the relative velocity of the two impinging particles and the velocity of the center of mass we have relations

$$\begin{cases} \mathbf{g} = \mathbf{v} - \mathbf{w} \\ \mathbf{G} = \alpha_{IJ}\mathbf{v} + \alpha_{JI}\mathbf{w} \end{cases} \qquad \begin{cases} \mathbf{g}' = \mathbf{v}' - \mathbf{w}' \\ \mathbf{G}' = \alpha_{HK}\mathbf{v}' + \alpha_{KH}\mathbf{w}', \end{cases} \tag{1.10}$$

being $\alpha_{ij} = \frac{m_i}{m_i + m_j}$. We also consider separately the absolute value and the direction of relative velocity:

$$\mathbf{g} = g\hat{\mathbf{\Omega}}, \qquad \mathbf{g}' = g'\hat{\mathbf{\Omega}}', \tag{1.11}$$

with $|\hat{\mathbf{\Omega}}| = 1$. From the conservation formulas (1.8) and condition (1.9) we deduce that $\boldsymbol{G} = \boldsymbol{G}'$ and

$$g' = \left[\frac{\mu_{IJ}}{\mu_{HK}}(g^2 - \delta_{IJ}^{HK})\right]^{\frac{1}{2}} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right), \qquad g = \left[\frac{\mu_{HK}}{\mu_{IJ}}((g')^2 - \delta_{HK}^{IJ})\right]^{\frac{1}{2}} \mathtt{H}\left((g')^2 - \delta_{HK}^{IJ}\right), \tag{1.12}$$

being

$$\delta_{IJ}^{HK} = 2\frac{\Delta E_{IJ}^{HK}}{\mu_{IJ}}, \tag{1.13}$$

with μ_{IJ} the reduced mass given by $\frac{m_I m_J}{m_I + m_J}$ and $\mathtt{H}$ the unit step Heaviside function. These transformations imply the fact that the post-collisional relative velocity g' is well defined only if the argument of the Heaviside function is positive, and this happens only, as already mentioned, if $\Delta E_{IJ}^{HK} < 0$ or if $\Delta E_{IJ}^{HK} > 0$ and the pre-collisional kinetic energy of the interacting molecules is sufficient. The same holds for the good definition of g in terms of g'.

In the following it will also turn useful to write the explicit transformations coming from (1.10) between pre and post-collision velocities provided by

$$\begin{cases} \mathbf{v}' &= \alpha_{IJ}\mathbf{v} + \alpha_{JI}\mathbf{w} + \alpha_{KH} g'\hat{\mathbf{\Omega}}', \\ \mathbf{w}' &= \alpha_{IJ}\mathbf{v} + \alpha_{JI}\mathbf{w} - \alpha_{HK} g'\hat{\mathbf{\Omega}}', \end{cases} \tag{1.14}$$

Now let us consider the distribution function relevant to the component C_I that is a function of position $\mathbf{x}$, velocity $\mathbf{v}$ and time t and we indicate it by $f_I(\mathbf{x}, \mathbf{v}, t)$. We also define the vector of all the distribution functions $\underline{\mathbf{f}} = (f_1, \ldots, f_L)$. The evolution of the whole system is given by a set of L coupled nonlinear integrodifferential equations that are a generalization of the classical Boltzmann model

$$\frac{\partial f_I}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I = \bar{Q}_I[\underline{\mathbf{f}}], \quad 1 \leq I \leq L. \tag{1.15}$$

The equation for each species I comes from the need to balance the variation (in absence of internal forces) of the number of particles within an infinitesimal volume of the phase space $d\mathbf{x}d\mathbf{v}dt$. This variation is due both to the flow of particles (each one with its molecular velocity) and to collisions which change velocities of colliding molecules. The left hand side of (1.15) describes motion in absence of collisions, while on the right hand side the collision operator $Q_I[\underline{\mathbf{f}}]$ takes into account all the possible collisions in which the component C_I can be involved. More specifically, the variation is obtained by the algebraic sum of all the particles that during collision pass from velocity $\mathbf{v}$ to velocity $\mathbf{v}'$ (loss term) and those particles that from a velocity $\mathbf{v}'$ pass to a velocity $\mathbf{v}$ (gain term). Thus we are allowed to write (neglecting higher order terms)

$$\left(\frac{\partial f_I}{\partial t} + \mathbf{v}\cdot\nabla_{\mathbf{x}} f_I\right) d\mathbf{x}d\mathbf{v}dt = (Q_I^+[\underline{\mathbf{f}}] - Q_I^-[\underline{\mathbf{f}}])d\mathbf{x}d\mathbf{v}dt, \quad 1 \le I \le L, \tag{1.16}$$

that passing to the limit $d\mathbf{x}d\mathbf{v}dt \to 0$ leads to equation (1.15).

With respect to general collision (1.7), the loss term for component C_I coming from the direct collision

$$C_I + C_J \to C_H + C_K \tag{1.17}$$

is given by ([103, 104])

$$Q_I^-[f_I, f_J, f_H, f_K](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_I(\mathbf{v}) f_J(\mathbf{w}) d\mathbf{w} d\hat{\mathbf{\Omega}}'. \tag{1.18}$$

We omit dependence on position $\mathbf{x}$ and time t in distribution functions and collision integrals in order to lighten the notation. The quantity σ_{IJ}^{HK} is the differential cross section relevant to the process in which two particles belonging to the species C_I and C_J get transformed into two particles belonging to the species C_H and C_K, respectively, and it depends on the intermolecular interaction potential [36]. It is azimuthally symmetric and depends only on the relative speed of the impinging molecules g and on the product $\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}'$. It also has to satisfy symmetry conditions

$$\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') = \sigma_{JI}^{HK}(g, -\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') = \sigma_{IJ}^{KH}(g, -\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}'). \tag{1.19}$$

On the other hand, the gain term for component C_I coming from the inverse collision

$$C_I + C_J \leftarrow C_H + C_K \tag{1.20}$$

is expressed by

$$Q_I^+[f_I, f_J, f_H, f_K](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left((g')^2 - \delta_{HK}^{IJ}\right) g'\sigma_{HK}^{IJ}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_H(\mathbf{v}') f_K(\mathbf{w}') d\mathbf{w}' d\hat{\mathbf{\Omega}}. \tag{1.21}$$

Considering the total number of collisions in the infinitesimal volume $d\mathbf{x}d\mathbf{v}'dt$ that is

$$d\mathbf{x}dt\int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left((g')^2 - \delta_{HK}^{IJ}\right) g'\sigma_{HK}^{IJ}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_H(\mathbf{v}') f_K(\mathbf{w}') d\mathbf{v}' d\mathbf{w}' d\hat{\mathbf{\Omega}} \tag{1.22}$$

and using relations (1.14) we have,

$$\mathtt{H}\left((g')^2 - \delta_{HK}^{IJ}\right) \frac{\mu_{HK}}{g'} d\mathbf{v}' d\mathbf{w}' d\hat{\mathbf{\Omega}} = \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) \frac{\mu_{IJ}}{g} d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}'. \tag{1.23}$$

Thus, passing again to the limit, the total collision term (gain minus loss) for component C_I is

$$\begin{aligned} Q_I[f_I, f_J, f_H, f_K](\mathbf{v}) &= Q_I^+ - Q_I^- \\ &= \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) \left[\frac{\mu_{IJ}}{\mu_{HK}} \frac{(g')^2}{g} \sigma_{HK}^{IJ}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_H(\mathbf{v}') f_K(\mathbf{w}') \right. \\ &\quad \left. - g\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_I(\mathbf{v}) f_J(\mathbf{w})\right] d\mathbf{w} d\hat{\mathbf{\Omega}}'. \end{aligned} \tag{1.24}$$

We now exploit the microreversibility condition [52, 80] relating the cross section of an interaction with the reverse one as

$$\mu_{IJ}^2 g^2 \sigma_{IJ}^{HK}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') = \mu_{HK}^2 (g')^2 \sigma_{HK}^{IJ}(g', \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right), \tag{1.25}$$

obtaining

$$\begin{aligned} &Q_I[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) g \sigma_{IJ}^{HK}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \left[\left(\frac{\mu_{IJ}}{\mu_{HK}} \right)^3 f_H(\mathbf{v}') f_K(\mathbf{w}') - f_I(\mathbf{v}) f_J(\mathbf{w}) \right] d\mathbf{w} d\hat{\boldsymbol{\Omega}}'. \end{aligned} \tag{1.26}$$

For future utility in this work, we compute, always referring to the collision (1.7), the collision term for components J, H, K. For the component J, it is sufficient to perform a permutation of indices $I \leftrightarrow J$ and thanks to properties (1.19) we get

$$\begin{aligned} &Q_J[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) g \sigma_{IJ}^{HK}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \left[\left(\frac{\mu_{IJ}}{\mu_{HK}} \right)^3 f_K(\mathbf{v}') f_H(\mathbf{w}') - f_J(\mathbf{v}) f_I(\mathbf{w}) \right] d\mathbf{w} d\hat{\boldsymbol{\Omega}}'. \end{aligned} \tag{1.27}$$

For components C_H and C_K we consider the collision written as

$$C_H + C_K \leftrightarrows C_I + C_J, \tag{1.28}$$

thus the collision operator for C_H reads as

$$\begin{aligned} &Q_H[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) \left[\sigma_{IJ}^{HK}(g', \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \frac{(g')^2}{g} \frac{\mu_{HK}}{\mu_{IJ}} f_I(\mathbf{v}') f_J(\mathbf{w}') \right. \\ &\quad \left. - g \sigma_{HK}^{IJ}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') f_H(\mathbf{v}) f_K(\mathbf{w}) \right] d\mathbf{w}\, d\hat{\boldsymbol{\Omega}}', \end{aligned} \tag{1.29}$$

and applying the microreversibility condition that in this case is

$$\mu_{HK}^2 g^2 \sigma_{HK}^{IJ}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') = \mu_{IJ}^2 (g')^2 \sigma_{IJ}^{HK}(g', \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right). \tag{1.30}$$

we have

$$\begin{aligned} &Q_H[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) g \sigma_{HK}^{IJ}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \left[\left(\frac{\mu_{HK}}{\mu_{IJ}} \right)^3 f_I(\mathbf{v}') f_J(\mathbf{w}') - f_H(\mathbf{v}) f_K(\mathbf{w}) \right] d\mathbf{w}\, d\hat{\boldsymbol{\Omega}}'. \end{aligned} \tag{1.31}$$

For the component C_K we again perform permutation of indices $H \leftrightarrow K$, obtaining

$$\begin{aligned} &Q_K[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) g \sigma_{HK}^{IJ}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') \left[\left(\frac{\mu_{HK}}{\mu_{IJ}} \right)^3 f_J(\mathbf{v}') f_I(\mathbf{w}') - f_K(\mathbf{v}) f_H(\mathbf{w}) \right] d\mathbf{w}\, d\hat{\boldsymbol{\Omega}}'. \end{aligned} \tag{1.32}$$

It can also be considered, instead of (1.7), an irreversible interaction between components C_I, C_J, C_H, C_K, it means that a couple of particles belonging to components C_I and C_J can be transformed in particles of components C_H and C_K, but the inverse transformation is not allowed. So we have

$$C_I + C_J \to C_H + C_K. \tag{1.33}$$

In this case, collision operators for components C_I and C_J will be composed only by a loss term, whereas for components C_H and C_K there will be only a gain one. As a result, repeating calculations done for the reversible case we have

$$Q_I[f_I, f_J, f_H, f_K](\mathbf{v}) = -\int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') f_I(\mathbf{v}) f_J(\mathbf{w}) d\mathbf{w} d\hat{\mathbf{\Omega}}', \tag{1.34}$$

$$Q_J[f_I, f_J, f_H, f_K](\mathbf{v}) = -\int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') f_J(\mathbf{v}) f_I(\mathbf{w}) d\mathbf{w} d\hat{\mathbf{\Omega}}', \tag{1.35}$$

$$Q_H[f_I, f_J, f_H, f_K](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left((g')^2 - \delta_{IJ}^{HK}\right) g'\sigma_{IJ}^{HK}(g', \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') f_I(\mathbf{v}') f_J(\mathbf{w}')\, d\mathbf{w}'\, d\hat{\mathbf{\Omega}}, \tag{1.36}$$

that becomes, using the relation between pre-collisional and post-collisional quantities that in this case provides the change

$$\mathtt{H}\left((g')^2 - \delta_{IJ}^{HK}\right) \frac{\mu_{IJ}}{g'} d\mathbf{v}' d\mathbf{w}' d\hat{\mathbf{\Omega}} = \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) \frac{\mu_{HK}}{g} d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}', \tag{1.37}$$

$$Q_H[f_I, f_J, f_H, f_K](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) \frac{\mu_{HK}}{\mu_{IJ}} \frac{(g')^2}{g} \sigma_{IJ}^{HK}(g', \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') f_I(\mathbf{v}') f_J(\mathbf{w}')\, d\mathbf{w}\, d\hat{\mathbf{\Omega}}', \tag{1.38}$$

and analogously

$$Q_K[f_I, f_J, f_H, f_K](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2 - \delta_{HK}^{IJ}\right) \frac{\mu_{HK}}{\mu_{IJ}} \frac{(g')^2}{g} \sigma_{IJ}^{HK}(g', \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') f_J(\mathbf{v}') f_I(\mathbf{w}')\, d\mathbf{w}\, d\hat{\mathbf{\Omega}}'. \tag{1.39}$$

We can now focus on a component C_I and compute its total collision operator, considering all the possible interactions with other particles of type (1.7) letting the indices J, H, K vary between 1 and L. We consider at first all possible mechanical collisions, thus we define the set of triplets

$$D_I^{ME} = \{(J, H, K), 1 \leq J, H, K \leq L : i = l, h = n\}, \tag{1.40}$$

being i, h, l, n obtained from I, J, H, K, respectively, using relation (1.5). Consequently, the collision term taking into account all the mechanical interactions of the component C_I reads as

$$Q_I^{ME}[\underline{\mathbf{f}}] = \sum_{(J,H,K) \in D_I^{ME}} Q_I[f_I, f_J, f_H, f_K]. \tag{1.41}$$

We notice that in this case operators Q_I have the formulation given in (1.26), with $\mu_{IJ} = \mu_{HK}$. In case of elastic collisions, we have that the Heaviside function is constant $\mathtt{H} \equiv 1$ and the operator is analogous to the one provided by classical Boltzmann theory [36]. Then, the possible triplets giving rise to chemical contribution for the component C_I are, instead, listed in the set

$$\begin{aligned} D_I^{CH} = \{\, &(J, H, K), 1 \leq J, H, K \leq L : (i, h) \neq (l, n),\ i \neq n, \\ &(i, h), (l, n) \in \{(1, 2), (3, 4), (2, 1), (4, 3)\}\}, \end{aligned} \tag{1.42}$$

with i, h, l, n again related to I, J, H, K by (1.5). This allows us to write the chemical collision term

$$Q_I^{CH}[\underline{\mathbf{f}}] = \sum_{(J,H,K)\in D_I^{CH}} Q_I[f_I, f_J, f_H, f_K]. \tag{1.43}$$

Finally, we have all the elements to recover the total collision operator that provides the integral term in the equation (1.15) for an index I

$$\bar{Q}_I[\underline{\mathbf{f}}] = Q_I^{ME}[\underline{\mathbf{f}}] + Q_I^{CH}[\underline{\mathbf{f}}]. \tag{1.44}$$

1.2 Collision invariants

Once defined all the collision operators for components C_I, $1 \le I \le L$, we take into account a L-dimensional vector $\underline{\varphi}$ of smooth functions defined on $\mathbb{R}^3$, $\varphi_I(\mathbf{v})$, and we define the functional

$$\mathcal{C}[\underline{\varphi}] = \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I(\mathbf{v}) \bar{Q}_I[\underline{\mathbf{f}}], \tag{1.45}$$

that explicitly reads as

$$\begin{aligned}\mathcal{C}[\underline{\varphi}] = \sum_{(I,J,H,K)\in D^G} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} &\varphi_I(\mathbf{v}) \mathbf{H}\left(g^2 - \delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \\ &\times \left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3 f_H(\mathbf{v}')f_K(\mathbf{w}') - f_I(\mathbf{v})f_J(\mathbf{w})\right] d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}',\end{aligned} \tag{1.46}$$

with $D^G = D^{ME} \cup D^{CH}$, being

$$D^{ME} = \left\{(I,J,H,K), 1 \le I,J,H,K \le L : i = l, h = n\right\}, \tag{1.47}$$

and

$$\begin{aligned}D^{CH} = \{\, &(I,J,H,K), 1 \le I,J,H,K \le L : (i,h) \ne (l,n),\ i \ne n, \\ &(i,h),(l,n) \in \{(1,2),(3,4),(2,1),(4,3)\}\},\end{aligned} \tag{1.48}$$

with i, h, l, n again coming from I, J, H, K, respectively, through relation (1.5).

We now perform in the expression for $\mathcal{C}$ one of the following operations:

i. Interchange $\mathbf{v}$ with $\mathbf{w}$ and H with K, obtaining

$$\begin{aligned}\mathcal{C}[\underline{\varphi}] = \sum_{(I,J,H,K)\in D^G} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} &\varphi_J(\mathbf{w}) \mathbf{H}\left(g^2 - \delta_{JI}^{KH}\right) g\sigma_{JI}^{HK}(g, -\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \\ &\times \left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3 f_H(\mathbf{v}')f_K(\mathbf{w}') - f_J(\mathbf{w})f_I(\mathbf{v})\right] d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}',\end{aligned} \tag{1.49}$$

this representation of $C[\underline{\varphi}]$ is equivalent to the one given in (1.46) due to the symmetry properties of the differential cross section (1.19).

ii. Renaming the variables $(\mathbf{v},\mathbf{w},\hat{\mathbf{\Omega}}') \leftrightarrow (\mathbf{v}',\mathbf{w}',\hat{\mathbf{\Omega}})$ and interchanging I with H and J with K, we have

$$\mathcal{C}[\underline{\varphi}] = \sum_{(I,J,H,K)\in D^G} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} \varphi_J(\mathbf{v}')\mathbf{H}\left((g')^2-\delta_{HK}^{IJ}\right) g'\sigma_{HK}^{IJ}(g',-\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \times \left[\left(\frac{\mu_{HK}}{\mu_{IJ}}\right)^3 f_I(\mathbf{v})f_J(\mathbf{w}) - f_H(\mathbf{v}')f_K(\mathbf{w}')\right] d\mathbf{v}'d\mathbf{w}'d\hat{\mathbf{\Omega}}'. \tag{1.50}$$

Since in this case we have the Jacobian of the transformation $(\mathbf{v}',\mathbf{w}',\hat{\mathbf{\Omega}}) \to (\mathbf{v},\mathbf{w},\hat{\mathbf{\Omega}}')$ that is

$$J = \mathbf{H}\left((g')^2-\delta_{HK}^{IJ}\right)\frac{\mu_{IJ}}{\mu_{HK}}\frac{g'}{g}, \tag{1.51}$$

and the microreversibility condition may be cast as

$$\mu_{HK}^2(g')^2\sigma_{HK}^{IJ}(g',\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') = \mathbf{H}\left((g')^2-\delta_{HK}^{IJ}\right)\mu_{IJ}^2 g^2\sigma_{IJ}^{HK}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}'), \tag{1.52}$$

we get

$$\mathcal{C}[\underline{\varphi}] = \sum_{(I,J,H,K)\in D^G} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} -\varphi_H(\mathbf{v}')\mathbf{H}\left(g^2-\delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \times \left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3 f_H(\mathbf{v}')f_K(\mathbf{w}') - f_I(\mathbf{v})f_J(\mathbf{w})\right] d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}', \tag{1.53}$$

that is again an equivalent representation for (1.46).

iii. Combining transformations i. and ii. we obtain a fourth equivalent expression for the functional $\mathcal{C}$ that is

$$\mathcal{C}[\underline{\varphi}] = \sum_{(I,J,H,K)\in D^G} \int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} -\varphi_K(\mathbf{w}')\mathbf{H}\left(g^2-\delta_{JI}^{KH}\right) g\sigma_{JI}^{KH}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \times \left[\left(\frac{\mu_{JI}}{\mu_{KH}}\right)^3 f_K(\mathbf{w}')f_H(\mathbf{v}') - f_I(\mathbf{v})f_J(\mathbf{w})\right] d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}'. \tag{1.54}$$

Those results have as consequence the fact that we can write the following expression

$$\begin{aligned}\mathcal{C}[\underline{\varphi}] = -\frac{1}{4}\sum_{(I,J,H,K)\in D^G} &\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2} \mathbf{H}\left(g^2-\delta_{IJ}^{HK}\right) g\sigma_{IJ}^{HK}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \\ &\times \left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3 f_H(\mathbf{v}')f_K(\mathbf{w}') - f_I(\mathbf{v})f_J(\mathbf{w})\right] \\ &\times \left[\varphi_H(\mathbf{v}')+\varphi_K(\mathbf{w}')-\varphi_I(\mathbf{v})-\varphi_J(\mathbf{w})\right] d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}'.\end{aligned} \tag{1.55}$$

We now consider any vector of smooth functions $\underline{\varphi}$ and provide the following definition

Definition 1.2.1. *A vector of smooth functions* $\underline{\varphi}$ *is a collision invariant for the system if it satisfies the following requirement*

$$\varphi_H(\mathbf{v}')+\varphi_K(\mathbf{w}') = \varphi_I(\mathbf{v})+\varphi_J(\mathbf{w}), \quad \forall(\mathbf{v}.\mathbf{w},\hat{\boldsymbol{\Omega}}') \in \mathbb{R}^3\times\mathbb{R}^3\times S^2, \quad \forall(I,J,H,K)\in D^G. \tag{1.56}$$

It follows that for any collision invariant $\underline{\varphi}$ it holds

$$\mathcal{C}[\underline{\varphi}] = 0 \quad \forall\underline{\mathbf{f}}. \tag{1.57}$$

It is easily verified that the scalar quantities

$$\begin{aligned}\varphi_I =& m_I, \quad 1\le I\le L,\\ \varphi_I =& m_I\mathbf{v}, \quad 1\le I\le L,\\ \varphi_I =& \frac{1}{2}m_I v^2 + E_I, \quad 1\le I\le L,\end{aligned} \tag{1.58}$$

representing mass, momentum and total energy of each component, respectively, are collision invariants, due to conservation laws (1.8).

We now give the generalization of a fundamental result in kinetic theory [36].

Theorem 1.2.2. *Collision invariants constitute a 7-dimensional linear space and they may be generically written as*

$$\underline{\varphi}(\mathbf{v}) = \underline{\mathbf{a}} + \underline{\mathbf{m}}\,\mathbf{b}\cdot\mathbf{v} + c\frac{1}{2}\underline{\mathbf{m}}v^2, \tag{1.59}$$

being $\underline{\mathbf{a}}$ *any* L*-dimensional vector with real entries,* $\mathbf{b}$ *any vector of* $\mathbb{R}^3$ *and* c *any real number such that parameters* $\underline{\mathbf{a}}$ *and* c *satisfy relations*

$$a_J - a_I = c\,(E_J - E_I) \quad \forall\, I,J \quad L^{s-1} < I,J \le L^s, \text{ for all } s = 1,2,3,4, \tag{1.60}$$

$$a_{L^2+1} + a_{L^3+1} - a_1 - a_{L^1+1} = c\Delta E. \tag{1.61}$$

In order to prove the Theorem above, we make use of the following statement.

Lemma 1.2.3. *Let* $f\,:\,\mathbb{R}^n\to\mathbb{R}$ *be a function such that*

$$f(\mathbf{x}_1) + f(\mathbf{x}_2) = f(\mathbf{x}_1+\mathbf{x}_2), \quad \forall\,\mathbf{x}_1,\mathbf{x}_2\in\mathbb{R}^n, \tag{1.62}$$

and f *is continuous in at least one point* $\mathbf{x}_0\in\mathbb{R}^n$*. Then it exists a unique value* $\mathbf{u}\in\mathbb{R}^n$ *such that*

$$f(\mathbf{x}) = \mathbf{u}\cdot\mathbf{x}. \tag{1.63}$$

For the proof of this result we address the reader to [36].

Proof of Theorem 1.2.2. First of all we observe that, if $\underline{\varphi}$ is a collision invariant, accordingly to definition (1.56) if we take sub-indices $I = J = H = K$ (simplest elastic collision) we have that, for any $(\mathbf{v}.\mathbf{w},\hat{\boldsymbol{\Omega}}')$,

$$\varphi_I(\mathbf{v}') + \varphi_I(\mathbf{w}') = \varphi_I(\mathbf{v}) + \varphi_I(\mathbf{w}). \tag{1.64}$$

We can apply a crucial result showed in [36], i.e. each function $\varphi_I(\mathbf{v})$ has the form

$$\varphi_I(\mathbf{v}) = a + \mathbf{b}\cdot\mathbf{v} + cv^2, \tag{1.65}$$

for some $a, c \in \mathbb{R}$, $\mathbf{b} \in \mathbb{R}^3$. In this peculiar case, indeed, we are in the classical conditions for which conservation of total momentum and total energy before and after the collision can be expressed as follows

$$\begin{cases} \mathbf{v} + \mathbf{w} = \mathbf{v}' + \mathbf{w}' \\ v^2 + w^2 = v'^2 + w'^2. \end{cases} \tag{1.66}$$

Definition (1.2.1) implies that if $\mathbf{v} + \mathbf{w}$ and $v^2 + w^2$ are constant, $\varphi_I(\mathbf{v}) + \varphi_I(\mathbf{w})$ must be constant too. Thus the sum $\varphi_I(\mathbf{v}) + \varphi_I(\mathbf{w})$ is indeed function of only quantities $\mathbf{v} + \mathbf{w}$ and $v^2 + w^2$, namely

$$\varphi_I(\mathbf{v}) + \varphi_I(\mathbf{w}) = \Phi_I(\mathbf{v} + \mathbf{w}, v^2 + w^2). \tag{1.67}$$

We consider the even part and the odd part of functions φ_I and Φ_I, respectively, defined as

$$\begin{aligned} \varphi_{I+}(\mathbf{v}) =& \varphi_I(\mathbf{v}) + \varphi_I(-\mathbf{v}), \\ \varphi_{I-}(\mathbf{v}) =& \varphi_I(\mathbf{v}) - \varphi_I(-\mathbf{v}), \\ \Phi_{I+}(\mathbf{v} + \mathbf{w}, v^2 + w^2) =& \Phi_I(\mathbf{v} + \mathbf{w}, v^2 + w^2) + \Phi_I(-\mathbf{v} - \mathbf{w}, v^2 + w^2), \\ \Phi_{I-}(\mathbf{v} + \mathbf{w}, v^2 + w^2) =& \Phi_I(\mathbf{v} + \mathbf{w}, v^2 + w^2) - \Phi_I(-\mathbf{v} - \mathbf{w}, v^2 + w^2). \end{aligned} \tag{1.68}$$

It is easy to verify the relations

$$\begin{aligned} \varphi_{I+}(\mathbf{v}) + \varphi_{I+}(\mathbf{w}) = \Phi_{I+}(\mathbf{v} + \mathbf{w}, v^2 + w^2), \\ \varphi_{I-}(\mathbf{v}) + \varphi_{I-}(\mathbf{w}) = \Phi_{I-}(\mathbf{v} + \mathbf{w}, v^2 + w^2), \end{aligned} \tag{1.69}$$

and this holds for any $\mathbf{v}$, $\mathbf{w} \in \mathbb{R}^3$. If we take $\mathbf{w} = -\mathbf{v}$, from the first equation of (1.69) we get $2\varphi_{I+}(\mathbf{v}) = \Phi_{I+}(2v^2, 0)$. It implies that $\varphi_{I+}(\mathbf{v}) = \psi(v^2)$, consequently,

$$\psi(v^2) + \psi(w^2) = \Phi_{I+}(\mathbf{v} + \mathbf{w}, v^2 + w^2) \tag{1.70}$$

. But in this case, to not get into contradiction, Φ_{I+} should depend only on $v^2 + w^2$, so we have $\psi(v^2) + \psi(w^2) = \Phi_{I+}(v^2 + w^2)$. On the other hand, taking $\mathbf{w} = \mathbf{0}$, we have $\psi(v^2) + \psi(0) = \Phi_{I+}(v^2)$. We are then allowed to write

$$\psi(v^2) + \psi(w^2) = \psi(v^2 + w^2) + \psi(0). \tag{1.71}$$

Let us define the function $f(v^2) = \psi(v^2) - \psi(0)$, from the equality above we obtain

$$f(v^2) + f(w^2) = f(v^2 + w^2). \tag{1.72}$$

Moreover, since $f(0) = 0$, it is possible to extend the domain of f to the whole $\mathbb{R}$ setting

$$f(-x) = -f(x) \tag{1.73}$$

for any $x = v^2 > 0$. We observe that in this way, f is continuous, being φ_I continuous, and the additivity requirement by Lemma 1.2.3 holds. As a consequence, we have $f(x) = 2cx$ for some $c \in \mathbb{R}$. Taking $a = \frac{\psi(0)}{2}$ we have

$$\phi_{I+}(\mathbf{v}) = 2a + 2cv^2, \quad a, c \in \mathbb{R}. \tag{1.74}$$

Now we observe that, choosing $\mathbf{v}$ and $\mathbf{w}$ such that $\mathbf{v}\cdot\mathbf{w} = 0$, since in this case $v^2+w^2 = |\mathbf{v}+\mathbf{w}|^2$, from the second equation in (1.69) we have $\varphi_{I-}(\mathbf{v}) + \varphi_{I-}(\mathbf{w}) = \Phi_{I-}(\mathbf{v} + \mathbf{w})$. In particular, considering $\mathbf{w} = \mathbf{0}$ it holds $\varphi_{I-}(\mathbf{v}) = \Phi_{I-}(\mathbf{v})$ and so $\varphi_{I-}(\mathbf{v} + \mathbf{w}) = \Phi_{I-}(\mathbf{v} + \mathbf{w})$. We can conclude that for any couple of orthogonal $\mathbf{v}$ and $\mathbf{w}$ it holds $\varphi_{I-}(\mathbf{v}) + \varphi_{I-}(\mathbf{w}) = \varphi_{I-}(\mathbf{v} + \mathbf{w})$. We choose now $\mathbf{v}$ and $\mathbf{w}$ such that $\mathbf{v} \cdot \mathbf{w} \neq 0$, let $\mathbf{z}$ a third vector for which $\mathbf{v} \cdot \mathbf{z} = \mathbf{0}$, $\mathbf{w} \cdot \mathbf{z} = \mathbf{0}$ and $z^2 = |\mathbf{v} \cdot \mathbf{w}|$. In particular, we can observe that for any $\mathbf{v}$, since $\mathbf{v} \cdot \mathbf{v} \geq 0$, we can write $\varphi_{I-}(2\mathbf{v}) = 2\varphi_{I-}(\mathbf{v})$. If $\mathbf{v} \cdot \mathbf{w} > 0$, it results $(\mathbf{v} + \mathbf{z}) \cdot (\mathbf{w} - \mathbf{z}) = 0$, hence the vectors $\mathbf{v} + \mathbf{z}$ and $\mathbf{w} - \mathbf{z}$ are orthogonal, thus $\varphi_{I-}(\mathbf{v} + \mathbf{z}) + \varphi_{I-}(\mathbf{w} - \mathbf{z}) = \varphi_{I-}(\mathbf{v} + \mathbf{w})$. Recalling that φ_{I-} is an odd function, we deduce

$$\varphi_{I-}(\mathbf{v}) + \varphi_{I-}(\mathbf{w}) = \varphi_{I-}(\mathbf{v} + \mathbf{w}). \tag{1.75}$$

If, instead, $\mathbf{v} \cdot \mathbf{w} < 0$, the vectors $\mathbf{v} + \mathbf{z}$ and $\mathbf{w} + \mathbf{z}$ are orthogonal, so

$$\varphi_{I-}(\mathbf{v} + \mathbf{z}) + \varphi_{I-}(\mathbf{w} + \mathbf{z}) = \varphi_{I-}(\mathbf{v} + \mathbf{w}) + \varphi_{I-}(2\mathbf{z}) \tag{1.76}$$

. Using again the orthogonality of $\mathbf{z}$ with $\mathbf{v}$ and $\mathbf{w}$ we get again the additivity property (1.75). At this point we can state that φ_{I-} satisfies hypothesis of Lemma 1.2.3, thus there exists a vector $\mathbf{b} \in \mathbb{R}^3$ such that

$$\varphi_{I-}(\mathbf{v}) = 2\mathbf{b} \cdot \mathbf{v}. \tag{1.77}$$

Finally, being $\varphi_I(\mathbf{v}) = \frac{1}{2}[\varphi_{I+}(\mathbf{v}) + \varphi_{I-}(\mathbf{v})]$, we get

$$\varphi_{I-}(\mathbf{v}) = a + \mathbf{b} \cdot \mathbf{v} + cv^2, \quad a, c \in \mathbb{R}, \mathbf{b} \in \mathbb{R}^3. \tag{1.78}$$

As consequence of this result, each collision invariant $\underline{\varphi}$ can be written as

$$\underline{\varphi}(\mathbf{v}) = \underline{\mathbf{a}} + \mathbf{B}\,\mathbf{v} + \underline{\mathbf{c}}v^2, \tag{1.79}$$

with $\underline{\mathbf{a}}, \underline{\mathbf{c}}$ two L-dimensional vectors and $\mathbf{B}$ a $3 \times L$-dimensional matrix. This means that we end up with $5L$ free coefficients. The fact that collision invariants satisfy (1.56) for any choice of vectors $(\mathbf{v}, \mathbf{w}, \hat{\mathbf{\Omega}}')$ in $\mathbb{R}^3 \times \mathbb{R}^3 \times S^2$ and indices (I, J, H, K) in D^G implies that we can make the particular choice $(\mathbf{v}, \mathbf{w}, \hat{\mathbf{\Omega}}') = (\mathbf{v}, -\mathbf{v}, -\frac{\mathbf{v}}{|\mathbf{v}|})$ and indices such that $I \neq J$, $I = H$ and $J = K$, namely we are considering elastic scattering between different components. From relations (1.14) we deduce that in this case

$$\begin{cases} \mathbf{v}' &= (\alpha_{IJ} - 3\alpha_{JI})\mathbf{v} \\ \mathbf{w}' &= (3\alpha_{IJ} - \alpha_{JI})\mathbf{v}, \end{cases} \tag{1.80}$$

thus, condition (1.56) for a collision invariant written in the form (1.79) and for this peculiar choice leads to the equations

$$8(\alpha_{IJ} - \alpha_{JI})(c_I\alpha_{IJ} - c_J\alpha_{JI})v^2 + 4(\mathbf{B}_J\alpha_{IJ} - \mathbf{B}_I\alpha_{JI}) \cdot \mathbf{v} = 0, \tag{1.81}$$

that must be satisfied for any $\mathbf{v} \in \mathbb{R}^3$, $\mathbf{v} \neq \mathbf{0}$ and for any $I \neq J$. But, just interchanging I and J, we notice that the only possibility is that both addenda in the left-hand sides must be equal to zero. Consequently, it must be

$$\begin{aligned} \frac{\mathbf{B}_I}{m_I} &= \frac{\mathbf{B}_J}{m_J} \overset{\text{def}}{=} \mathbf{b} \\ \frac{c_I}{m_I} &= \frac{c_J}{m_J} \overset{\text{def}}{=} \frac{1}{2}c, \end{aligned} \tag{1.82}$$

for any $I \neq J$, $1 \leq I, J \leq L$. We get to the same conditions when $I = J$ repeating the procedure choosing $\mathbf{w} = \mathbf{0}$ and $\hat{\mathbf{\Omega}}' = -\frac{\mathbf{v}}{|\mathbf{v}|}$. Now we consider the case in which two particles of the same component collide and after the encounter only one of them has changed its internal energy, namely we take the quadruplet (I, I, I, J) with $L^{s-1} < I, J \leq L^s$, for some $1 \leq s \leq 4$. For any choice of vectors $(\mathbf{v}, \mathbf{w}, \hat{\mathbf{\Omega}}')$ the post-collisional velocities are

$$\left\{ \begin{array}{ll} \mathbf{v}' & = \frac{1}{2}\mathbf{v} + \frac{1}{2}\mathbf{w} + \frac{1}{2}\sqrt{g^2 - \delta_{II}^{IJ}}\, \hat{\mathbf{\Omega}}' \\ \mathbf{w}' & = \frac{1}{2}\mathbf{v} + \frac{1}{2}\mathbf{w} - \frac{1}{2}\sqrt{g^2 - \delta_{II}^{IJ}}\, \hat{\mathbf{\Omega}}' \end{array} \right. . \tag{1.83}$$

In this way we have, again from (1.56), conditions

$$a_J - a_I = c(E_J - E_I), \quad L^{s-1} < I, J \leq L^s, \text{ for all } s = 1, 2, 3, 4. \tag{1.84}$$

Finally, we take into account a quadruplet (I, J, H, K) belonging to D^{CH}. From conservation laws, relations (1.56) lead to

$$a_H + a_K - a_I - a_J = c\Delta E_{IJ}^{HK}, \tag{1.85}$$

that, combined with (1.84) give the constraint

$$a_{L^2+1} + a_{L^3+1} - a_1 - a_{L^1+1} = c\Delta E. \tag{1.86}$$

This last result makes the functions defined in expression (1.79) have only 7 free coefficients. On the other hand, it is easily verified that each vector of functions $\underline{\boldsymbol{\varphi}}$ of the form

$$\underline{\boldsymbol{\varphi}}(\mathbf{v}) = \underline{\mathbf{a}} + \underline{\mathbf{m}}\, \mathbf{b} \cdot \mathbf{v} + c\frac{1}{2}\underline{\mathbf{m}} v^2, \tag{1.87}$$

with conditions (1.84) and (1.86) on coefficients, satisfies (1.56) and this concludes the proof. □

A set of seven collision invariants $\{\underline{\boldsymbol{\varphi}}^1, \ldots, \underline{\boldsymbol{\varphi}}^7\}$ that form a basis for the space defined through Theorem (1.2.2) can be constructed as follows. Taking $a_1 = a_{L^2+1} = 1$, $a_{L^1+1} = 0$, $\mathbf{b} = \mathbf{0}$, $c = 0$, we have $\underline{\boldsymbol{\varphi}}^1(\mathbf{v})$ such that

$$\varphi_I^1 = \left\{ \begin{array}{l} 1 \quad \text{if } 1 \leq I \leq L^1 \vee L^2 < I \leq L^3 \\ 0 \text{ otherwise.} \end{array} \right. \tag{1.88}$$

Taking, instead, $a_1 = 1$, $a_{L^1+1} = a_{L^2+1} = 0$, $\mathbf{b} = \mathbf{0}$, $c = 0$, we have $\underline{\boldsymbol{\varphi}}^2(\mathbf{v})$ that is

$$\varphi_I^2 = \left\{ \begin{array}{l} 1 \quad \text{if } 1 \leq I \leq L^1 \vee L^3 < I \leq L^4 \\ 0 \text{ otherwise.} \end{array} \right. \tag{1.89}$$

With $a_{L^1+1} = 1$, $a_1 = a_{L^2+1} = 0$, $\mathbf{b} = \mathbf{0}$, $c = 0$, we have $\underline{\boldsymbol{\varphi}}^3(\mathbf{v})$ equal to

$$\varphi_I^3 = \left\{ \begin{array}{l} 1 \quad \text{if } L^1 < I \leq L^2 \vee L^3 < I \leq L^4 \\ 0 \text{ otherwise.} \end{array} \right. \tag{1.90}$$

If we choose $a_1 = a_{L^1+1} = a_{L^2+1} = a_{L^3+1} = 0$, $\mathbf{b} = (1, 0, 0)$, $c = 0$ we obtain

$$\underline{\boldsymbol{\varphi}}^4(\mathbf{v}) = \underline{\mathbf{m}} v_1, \tag{1.91}$$

and, analogously, with $\mathbf{b} = (0, 1, 0)$ and $\mathbf{b} = (0, 0, 1)$ we get $\underline{\boldsymbol{\varphi}}^5(\mathbf{v}) = \underline{\mathbf{m}}v_2$ and $\underline{\boldsymbol{\varphi}}^6(\mathbf{v}) = \underline{\mathbf{m}}v_3$, respectively. Finally, picking $a_s = E_s$, for $s = 1, L^1 + 1, L^2 + 1$, $\mathbf{b} = \mathbf{0}$, $c = 1$, we find the last independent invariant $\underline{\boldsymbol{\varphi}}^7(\mathbf{v})$ corresponding to

$$\underline{\boldsymbol{\varphi}}^7(\mathbf{v}) = \frac{1}{2} m_I v^2 + E_I. \tag{1.92}$$

We notice that entries of $\underline{\boldsymbol{\varphi}}^4$, $\underline{\boldsymbol{\varphi}}^5$, $\underline{\boldsymbol{\varphi}}^6$ and $\underline{\boldsymbol{\varphi}}^7$ are exactly momentum and total energy defined in (1.58). Instead the quantity $m_3\,\underline{\boldsymbol{\varphi}}^1 + (m_4 - m_2)\,\underline{\boldsymbol{\varphi}}^2 + m_2\,\underline{\boldsymbol{\varphi}}^3$ gives the mass, that is the first quantity of (1.58). Moreover $\underline{\boldsymbol{\varphi}}^1 + \underline{\boldsymbol{\varphi}}^3$ is the total number of molecules involved in the model.

1.3 Macroscopic quantities

Results exposed in the previous sections provide tools to understand the behavior of the mixture at a mesoscopic level, associating each component to its distribution function f_I. Our aim is to move now to a microscopic description of the model, for this reason we introduce the classical macroscopic fields relative to each component C_I, $1 \le I \le L$, that are number densities

$$n_I = \int_{\mathbb{R}^3} f_I d\mathbf{v}, \tag{1.93}$$

mean drift velocities

$$\mathbf{u}_I = \frac{1}{n_I} \int_{\mathbb{R}^3} \mathbf{v} f_I d\mathbf{v}, \tag{1.94}$$

and temperatures

$$T_I = \frac{m_I}{3 n_I} \int_{\mathbb{R}^3} |\mathbf{v} - \mathbf{u}_I|^2 f_I d\mathbf{v}. \tag{1.95}$$

Then we may consider the same quantities relative to each gas species G^s, $1 \le s \le 4$,

$$n^s = \sum_{I=L^{s-1}+1}^{L^s} n_I, \qquad \mathbf{u}^s = \frac{1}{n^s} \sum_{I=L^{s-1}+1}^{L^s} n_I \mathbf{u}_I,$$

$$T^s = \frac{1}{n^s} \left[\sum_{I=L^{s-1}+1}^{L^s} n_I T_I + \frac{1}{3} \sum_{I=L^{s-1}+1}^{L^s} m_I \left(|\mathbf{u}_I|^2 - |\mathbf{u}^s|^2 \right) \right]. \tag{1.96}$$

At last, we define the quantities that globally characterize the gas mixtures. We have total number density, mass density and mass velocity

$$n = \sum_{s=1}^{4} n^s, \quad \rho = \sum_{s=1}^{4} m^s n^s, \quad \mathbf{u} = \frac{1}{\rho} \sum_{s=1}^{4} m^s n^s \mathbf{u}^s, \tag{1.97}$$

while temperature is

$$T = \frac{1}{n} \left[\sum_{s=1}^{4} n^s T^s + \frac{1}{3} \sum_{s=1}^{4} m^s n^s \left(|\mathbf{u}^s|^2 - |\mathbf{u}|^2 \right) \right]. \tag{1.98}$$

We also define excitation energy density

$$E = \sum_{s=1}^{4} \sum_{I=L^{s-1}+1}^{L^s} E_I n_I \tag{1.99}$$

and the total internal energy density

$$\mathcal{E} = \frac{3}{2}nT + E. \tag{1.100}$$

To describe completely the macroscopic features of the mixture, we also need the pressure tensor

$$\mathbf{P} = \sum_{I=1}^{L} m_I \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}) \otimes (\mathbf{v} - \mathbf{u}) f_I d\mathbf{v}, \tag{1.101}$$

from which we recover the viscous stress $\mathbf{p} = \mathbf{P} - \frac{1}{3}\mathbb{I}tr\mathbf{P}$, and the thermal heat flux

$$\mathbf{q} = \frac{1}{2}\sum_{I=1}^{L} m_I \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})^2 (\mathbf{v} - \mathbf{u}) f_I d\mathbf{v}. \tag{1.102}$$

With those quantities at hand, we are able to derive macroscopic conservation equations. From Boltzmann equations (1.15), we take a test vector function $\underline{\varphi}(\mathbf{v})$ and multiplying each equation of (1.15) by φ_I, integrating over velocities and summing over all the components we have

$$\sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I \frac{\partial f_I}{\partial t} d\mathbf{v} + \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I d\mathbf{v} = \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I \mathbf{v} \bar{Q}_I[\underline{\mathbf{f}}] d\mathbf{v} = \mathcal{C}[\underline{\varphi}]. \tag{1.103}$$

Choosing now, as test functions, the seven collision invariants defined in the previous section, $\underline{\varphi}^1, \dots, \underline{\varphi}^7$, since for each one we have $C[\underline{\varphi}^q] = 0$, $q = 1, \dots, 7$, it is a matter of simple calculations to derive the conservation laws. We firstly have the conservation of the total number densities for the couple of species $G^1 + G^3$, indeed, taking the collision invariant $\underline{\varphi}^1$ in (1.103) and expliciting the left-hand side as

$$\begin{aligned}
&\sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^1 \frac{\partial f_I}{\partial t} d\mathbf{v} + \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^1 \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I d\mathbf{v} \\
&\quad = \frac{\partial}{\partial t}\left(\sum_{I=1}^{L^1} \int_{\mathbb{R}^3} f_I d\mathbf{v} + \sum_{I=L^2+1}^{L^3} \int_{\mathbb{R}^3} f_I d\mathbf{v} \right) + \sum_{l=1}^{3} \frac{\partial}{\partial x_l}\left(\sum_{I=1}^{L^1} \int_{\mathbb{R}^3} v_l f_I d\mathbf{v} + \sum_{I=L^2+1}^{L^3} \int_{\mathbb{R}^3} v_l f_I d\mathbf{v} \right),
\end{aligned}$$

we are able to write the equation

$$\frac{\partial}{\partial t}(n^1 + n^3) + \nabla_{\mathbf{x}} \cdot (n^1 u^1 + n^3 u^3) = 0. \tag{1.104}$$

Picking the other two invariants $\underline{\varphi}^2$ and $\underline{\varphi}^3$ we analogously get conservation of the total number densities for the couples $G^1 + G^4$ and $G^2 + G^4$:

$$\frac{\partial}{\partial t}(n^1 + n^4) + \nabla_{\mathbf{x}} \cdot (n^1 u^1 + n^4 u^4) = 0, \tag{1.105}$$

$$\frac{\partial}{\partial t}(n^2 + n^4) + \nabla_{\mathbf{x}} \cdot (n^2 u^2 + n^4 u^4) = 0. \tag{1.106}$$

Considering the invariant $\underline{\varphi}^4$, instead, we obtain

$$\begin{aligned}
&\sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^4 \frac{\partial f_I}{\partial t} d\mathbf{v} + \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^4 \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I d\mathbf{v} = \frac{\partial}{\partial t} \sum_{I=1}^{L} \int_{\mathbb{R}^3} m_I v_1 f_I d\mathbf{v} + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \sum_{I=1}^{L} \int_{\mathbb{R}^3} m_I v_1 v_l f_I d\mathbf{v} \\
&\quad = \frac{\partial}{\partial t} \sum_{I=1}^{L} \int_{\mathbb{R}^3} m_I v_1 f_I d\mathbf{v} + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \sum_{I=1}^{L} \left(\int_{\mathbb{R}^3} m_I (v_1 - u_1)(v_l - u_l) f_I d\mathbf{v} + \int_{\mathbb{R}^3} m_I u_1 u_l f_I d\mathbf{v} \right) \\
&\quad = \frac{\partial}{\partial t}(\rho u_1) + \nabla_{\mathbf{x}} \cdot (\rho u_1 \mathbf{u}) + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \sum_{I=1}^{L} \int_{\mathbb{R}^3} m_I (v_1 - u_1)(v_l - u_l) f_I d\mathbf{v} = 0. \qquad (1.107)
\end{aligned}$$

Repeating calculations for the invariants $\underline{\boldsymbol{\varphi}}^5$ and $\underline{\boldsymbol{\varphi}}^6$ we get two expressions analogous to the previous one, thus we are allowed to write the equation for the momentum as follows

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \nabla_{\mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = \mathbf{0}. \tag{1.108}$$

Finally, we take into account the last invariant $\underline{\boldsymbol{\varphi}}^7$ and calculate

$$\begin{aligned}
&\sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^7 \frac{\partial f_I}{\partial t} d\mathbf{v} + \sum_{I=1}^{L} \int_{\mathbb{R}^3} \varphi_I^7 \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I d\mathbf{v} \\
&\quad = \frac{\partial}{\partial t} \sum_{I=1}^{L} \int_{\mathbb{R}^3} \left(\frac{1}{2} m_I v^2 + E_I \right) f_I d\mathbf{v} + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \sum_{I=1}^{L} \int_{\mathbb{R}^3} \left(\frac{1}{2} m_I v^2 + E_I \right) v_l f_I d\mathbf{v} \\
&\quad = \frac{\partial}{\partial t} \sum_{I=1}^{L} \int_{\mathbb{R}^3} \left[\frac{1}{2} m_I \left(|\mathbf{v} - \mathbf{u}|^2 + |\mathbf{u}|^2 \right) + E_I \right] f_I d\mathbf{v} \\
&\quad + \sum_{l=1}^{3} \frac{\partial}{\partial x_l} \sum_{I=1}^{L} \int_{\mathbb{R}^3} \left[\frac{1}{2} m_I \left(|\mathbf{v} - \mathbf{u}|^2 (v_l - u_l) + |\mathbf{u}|^2 u_l + |\mathbf{v} - \mathbf{u}|^2 u_l \right. \right. \\
&\quad \left. \left. + 2\mathbf{u} \cdot (\mathbf{v} - \mathbf{u})(v_l - u_l) \right) + E_I v_l \right] f_I d\mathbf{v},
\end{aligned} \tag{1.109}$$

that provides the equation for the conservation of total energy

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho \mathbf{u}^2 + \mathcal{E} \right) + \nabla_{\mathbf{x}} \cdot \left[\left(\frac{1}{2} \rho \mathbf{u}^2 + \mathcal{E} \right) \mathbf{u} + \mathbf{P} \cdot \mathbf{u} + \mathbf{q} \right] = 0. \tag{1.110}$$

Collecting equations (1.104) - (1.106), (1.108) and (1.110) we obtain a non-closed system of seven balance equations that governs the behavior of macroscopic observables.

Different strategies may be adopted in order to close the hydrodynamic system (1.104) - (1.106), (1.108) and (1.110) and study the behavior of macroscopic fields in certain physical conditions. We introduce them briefly in order to provide few notions that will be useful later on in this chapter. First of all we recall the definition of mean free path, λ, as the mean distance covered by a particle between a collision and another one. In terms of order of magnitude it holds the following relation

$$\lambda \sim \frac{1}{\bar{n} \bar{\sigma}_{TOT}}, \tag{1.111}$$

being $\bar{n}$ and $\bar{\sigma}_{TOT}$ typical values for density and total cross section, respectively, for the model considered. Let now $\mathfrak{L}$ be a macroscopic typical length for the gas, the Knudsen number is defined as

$$K_n = \frac{\lambda}{\mathfrak{L}}. \tag{1.112}$$

When we are in a spatial scale of observation for which $K_n << 1$, the dynamics is governed by collisions and the gas is seen as a macroscopic continuum. Thus, passing to the hydrodynamic limit of kinetic equations in which $K_n \to 0$, quantities involved in the description of the model actually pass from microscopic to macroscopic ones. If we consider now a generic Boltzmann equation for a distribution f

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f = Q[f], \tag{1.113}$$

and we rescale it introducing the macroscopic time τ and a typical value for molecular velocity ξ and adimensionalizing variables and quantities

$$\tilde{\mathbf{x}} = \frac{x}{\mathfrak{L}}, \quad \tilde{\mathbf{v}} = \frac{\mathbf{v}}{\xi}, \quad t = \frac{t}{\tau}, \quad \tilde{n} = \frac{n}{\bar{n}}, \quad \tilde{\sigma} = \frac{\sigma}{\bar{\sigma}_{TOT}}, \tag{1.114}$$

in the hypothesis in which for the Strouhal number, defined as,

$$Sh = \frac{\mathfrak{L}/\tau}{\xi}, \tag{1.115}$$

we have $Sh \sim 1$, we obtain a rescaled Boltzmann equation that reads as

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f = \frac{1}{Kn} Q[f]. \tag{1.116}$$

At this point, if the Knudsen number is assumed to be a small parameter ϵ, a resolution method for the Boltzmann equation proposed by Hilbert [66, 67] is based on expressing the distribution f as a series

$$f = \sum_{n=0}^{\infty} \epsilon^n f_n, \tag{1.117}$$

and inserting this ansatz into in the Boltzmann equation. Arresting the Hilbert expansion at step 0 and calculating the usual moments (total density, momentum, total energy), is possible to derive the known Euler closed equations for the macroscopic quantities n, $\mathbf{u}$, and T, containing fist order spatial and temporal derivatives. Another possible way of obtaining a closed system for macroscopic quantities is the so called Chapman-Enskog expansion [38, 40, 49]. In this case we still have an expansion for f, but the main moments are obtained only by the first term of the expansion, f_0, while the other terms are suppose to not contribute to the macroscopic observables (corresponding to collision invariants). In this way, truncating the expansion at order 1 the classical Navier-Stokes equations are recovered, with viscosity and conductivity coefficients explicit in terms of microscopic quantities of the gas (as mass and collision frequencies). Also in this case we have a closed system of differential equations for n, $\mathbf{u}$, and T, but also second order spatial derivatives appear for mean velocity and temperature. This kind of closures, presented here for a single Boltzmann equation, have been properly extended in case of more complex gas dynamics. The main issue in these cases is the role played by inelastic or chemical collisions. In particular, in [15], hydrodynamic limit is performed in two separate cases. In the first one the elastic scattering is considered to be the dominant process, for which the relevant relaxation time is much shorter than all the other processes. In another one, instead, all mechanical collisions (elastic and inelastic) play a dominant role, while the time scale for chemical reactions is longer. In both cases, for the resulting systems of Boltzmann equations is possible to perform a Hilbert or Chapman-Enskog type expansion [6, 89] and get Euler or Navier-Stokes macroscopic equations.

1.4 Boltzmann entropy inequality

We define

$$\mathcal{W}[\underline{\mathbf{f}}] = \sum_{I=1}^{L} \int_{\mathbb{R}^3} \log\left(\frac{f_I}{m_I^3}\right) \bar{Q}_I[\underline{\mathbf{f}}] d\mathbf{v}, \tag{1.118}$$

a functional of the form (1.45), with test function $\varphi_I = \log\left(\frac{f_I}{m_I^3}\right)$ The result we are going to present is a generalization in this context of the classical Boltzmann inequality, also known as Boltzmann Lemma.

Theorem 1.4.1. *The functional* $\mathcal{W}$ *defined in* (1.118) *is negative semidefinite, namely* $\mathcal{W}[\underline{\mathbf{f}}] \leq 0$ *for any* $\underline{\mathbf{f}}$ *and, in particular,* $\mathcal{W}[\underline{\mathbf{f}}] = 0$ *if and only if*

$$\frac{f_H}{m_H^3}(\mathbf{v}')\,\frac{f_K}{m_K^3}(\mathbf{w}') = \frac{f_I}{m_I^3}(\mathbf{v})\,\frac{f_J}{m_J^3}(\mathbf{w}), \quad \forall\,(\mathbf{v}.\mathbf{w},\hat{\mathbf{\Omega}}') \in \mathbb{R}^3 \times \mathbb{R}^3 \times S^2, \quad \forall\,(I,J,H,K) \in D^G. \tag{1.119}$$

Proof. Since we can consider the functional $\mathcal{W}[\underline{\mathbf{f}}]$ as a particular case of (1.45) with $\varphi_I = \log\left(\frac{f_I}{m_I^3}\right)$, we can use formulation (1.55) to write

$$\begin{aligned}\mathcal{W}[\underline{\mathbf{f}}] = &-\frac{1}{4}\sum_{(I,J,H,K)\in D^G}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\int_{S^2}\mathbf{H}\left(g^2-\delta_{IJ}^{HK}\right)g\sigma_{IJ}^{HK}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\\ &\times\log\left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3\frac{f_H(\mathbf{v}')f_K(\mathbf{w}')}{f_I(\mathbf{v})f_J(\mathbf{w})}\right]\left[\left(\frac{\mu_{IJ}}{\mu_{HK}}\right)^3\frac{f_H(\mathbf{v}')f_K(\mathbf{w}')}{f_I(\mathbf{v})f_J(\mathbf{w})}-1\right]f_I(\mathbf{v})f_J(\mathbf{w})d\mathbf{v}d\mathbf{w}d\hat{\mathbf{\Omega}}'.\end{aligned} \tag{1.120}$$

Being the function $(x-1)\log x$ nonnegative and vanishing it only for $x = 1$, we can conclude that for each term in the sum on the right-hand side of (1.120) the argument of the integral is nonnegative and it is zero if and only if the relation (1.119) holds for any quadruplet of indices. ☐

The result expressed in Theorem 1.4.1 is a generalization of the so-called "detailed balance principle". We now provide the following definition

Definition 1.4.2. *A vector of distributions* $\underline{\mathbf{f}}$ *is a collision equilibrium if it satisfies*

$$\bar{Q}_I[\underline{\mathbf{f}}] = 0, \quad \forall\,\mathbf{v} \in \mathbb{R}^3, \quad \forall\,I = 1,\dots,L, \tag{1.121}$$

with $\bar{Q}_I$ *the collision operator given in* (1.44).

Theorem 1.4.3. *A vector* $\underline{\mathbf{f}}$ *is a collision equilibrium if and only if it satisfies the condition* (1.119).

Proof. Let $\underline{\mathbf{f}}$ be a collision equilibrium, from (1.118) is clear that $W[\underline{\mathbf{f}}] = 0$ and thanks to Thoerem 1.4.1 we can state that $\underline{\mathbf{f}}$ satisfies (1.119). On the other hand, if $\underline{\mathbf{f}}$ is a distribution vector fulfilling (1.119), from expression (1.26) we have that the integrand is zero and this holds for any (I,J,H,K) in D^G, consequently equation (1.121) is satisfied and $\underline{\mathbf{f}}$ is a collision equilibrium. ☐

An immediate consequence of this result is that a distribution vector $\underline{\mathbf{f}}$ is a collision equilibrium if and only if $W[\underline{\mathbf{f}}] = 0$ and it implies that the net production of each gas component is null not only once that the sum over all the collisions is calculated, but for every single encounter we have the collision term vanishing. At this point, we are able to provide a more detailed and exhaustive characterization of collision equilibria for our system.

Theorem 1.4.4. *Collision equilibria constitute a class of distribution vectors* $\underline{\mathbf{f}}^M$ *such that*

$${f_I}^M(\mathbf{v}) = n_I M_I\left(\mathbf{v}; u, \frac{T}{m_I}\right), \quad 1 \leq I \leq L, \tag{1.122}$$

with $M_I\left(\mathbf{v};\mathbf{u},\frac{T}{m_I}\right)$ *being the classical Maxwellians*

$$M_I\left(\mathbf{v};\mathbf{u},\frac{T}{m_I}\right)=\left(\frac{m_I}{2\pi T}\right)^{\frac{3}{2}}\exp\left[-\frac{m_I}{2T}|\mathbf{v}-\mathbf{u}|^2\right]. \tag{1.123}$$

Furthermore, the relation between number density of each component n_I *and the density of the species* n^s *it belongs to is given by*

$$n_I=\frac{n^s}{\mathcal{Z}^s(T)}\exp\left(-\frac{E_I-E^s}{T}\right),\qquad \textit{for any } I,s \textit{ such that } L^{s-1}<I\leq L^s, \tag{1.124}$$

with the partition function $\mathcal{Z}^s(T)$

$$\mathcal{Z}^s(T)=\sum_{K=L^{s-1}+1}^{L^s}\exp\left(-\frac{E_K-E^s}{T}\right), \tag{1.125}$$

and the quantity E^s *corresponding to* $E_{L^{s-1}+1}$ *for all* $s=1,2,3,4$*. In addition, the number densities of the species involved in the reaction are bound together by the mass action law*

$$\frac{n^1n^2}{n^3n^4}=\left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}}\frac{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}{\mathcal{Z}^3(T)\mathcal{Z}^4(T)}\exp\left(\frac{\Delta E}{T}\right). \tag{1.126}$$

Proof. Let $\underline{\mathbf{f}}$ be a collision equilibrium, which, from Theorem 1.4.3 implies

$$\log\left(\frac{f_I}{m_I^3}\right)(\mathbf{v})+\log\left(\frac{f_J}{m_J^3}\right)(\mathbf{w})=\log\left(\frac{f_H}{m_H^3}\right)(\mathbf{v}')+\log\left(\frac{f_K}{m_K^3}\right)(\mathbf{w}'),$$

$$\forall(\mathbf{v}.\mathbf{w},\hat{\mathbf{\Omega}}')\in\mathbb{R}^3\times\mathbb{R}^3\times S^2,\quad \forall(I,J,H,K)\in D^G. \tag{1.127}$$

Recalling definition (1.56), this implies that the vector $\underline{\boldsymbol{\psi}}(\mathbf{v})$ such that $\psi_I(\mathbf{v})=\log(f_I(\mathbf{v}))$ is a collision invariant. Thus, from Theorem 1.2.2 there exist an L-dimensional vector $\underline{\mathbf{a}}$, a three-dimensional vector $\mathbf{b}$ and a real constant c such that

$$\psi_I(\mathbf{v})=\log\left(\frac{f_I(\mathbf{v})}{m_I^3}\right)=a_I+m_I\mathbf{b}\cdot\mathbf{v}+c\frac{1}{2}m_Iv^2,\quad 1\leq I\leq L, \tag{1.128}$$

with $\underline{\mathbf{a}}$ and c satisfying relations (1.60) and (1.61). It means that

$$\frac{f_I(\mathbf{v})}{m_I^3}=\exp\left(a_I+m_I\mathbf{b}\cdot\mathbf{v}+c\frac{1}{2}m_Iv^2\right). \tag{1.129}$$

The first thing we observe is that the parameter c cannot be positive, otherwise we would lose the summability of functions f_I with respect to $\mathbf{v}$. Defining the quantities

$$\gamma_I=m_I^3\exp\left(a_I-\frac{m_I|\mathbf{b}|^2}{2c}\right), \tag{1.130}$$

we rewrite equilibria as follows

$$f_I(\mathbf{v})=\gamma_I\exp\left[\frac{1}{2}m_Ic\left(\mathbf{v}+\frac{\mathbf{b}}{c}\right)^2\right]. \tag{1.131}$$

We now analyze how the parameters γ_I, $\mathbf{b}$ and c are related to the macroscopic observables of the mixture. For each component C_I the number density of distribution (1.131) is provided by

$$n_I = \gamma_I \int_{\mathbb{R}^3} \exp\left[\frac{1}{2} m_I c \left(\mathbf{v} + \frac{\mathbf{b}}{c}\right)^2\right] d\mathbf{v}. \tag{1.132}$$

After a suitable change of variables and using polar coordinates (ρ, θ, ϕ) with $d\mathbf{v} = \rho^2 \sin\theta d\theta d\phi$ the integral above becomes

$$n_I = \gamma_I 2\pi \left(\frac{-2}{m_I c}\right)^{\frac{3}{2}} \int_0^{+\infty} e^{-\rho^2} d\mathbf{v} = -\gamma_I \pi \Gamma\left(\frac{1}{2}\right)\left(\frac{2}{m_I c}\right)^{\frac{3}{2}} = \gamma_I \left(-\frac{2\pi}{m_I c}\right)^{\frac{3}{2}}, \tag{1.133}$$

where the last result is obtained using the Euler gamma function $\Gamma(\cdot)$ (see Appendix A). Successively, considering mean velocity of each component we have

$$\mathbf{u}_I = \frac{1}{n_I}\gamma_I \int_{\mathbb{R}^3} \mathbf{v} \exp\left[\frac{1}{2} m_I c \left(\mathbf{v} + \frac{\mathbf{b}}{c}\right)^2\right] d\mathbf{v}, \tag{1.134}$$

that, again through a change of variables is

$$\mathbf{u}_I = \frac{1}{n_I}\gamma_I \int_{\mathbb{R}^3} \left(\boldsymbol{\xi} - \frac{\mathbf{b}}{c}\right) \exp\left[\frac{1}{2} m_I c (\boldsymbol{\xi})^2\right] d\mathbf{v} = -\frac{1}{n_I}\frac{\mathbf{b}}{c}\gamma_I \int_{\mathbb{R}^3} \exp\left[\frac{1}{2} m_I c (\boldsymbol{\xi})^2\right] d\mathbf{v} = -\frac{\mathbf{b}}{c}. \tag{1.135}$$

At last, taking into account the macroscopic temperature we obtain

$$T_I = \frac{m_I}{3n_I}\gamma_I \int_{\mathbb{R}^3} |\mathbf{v} - \mathbf{u}_I|^2 \exp\left[\frac{1}{2} m_I c \left(\mathbf{v} + \frac{\mathbf{b}}{c}\right)^2\right] d\mathbf{v}, \tag{1.136}$$

turning into, again thanks to a change of variables,

$$\begin{aligned} T_I &= \frac{m_I}{3n_I}\gamma_I 4\pi \left(\frac{-2}{m_I c}\right)^{\frac{5}{2}} \int_0^{+\infty} \rho^4 e^{-\rho^2} d\mathbf{v} = \frac{m_I}{3n_I}\gamma_I 2\pi \frac{3}{4}\sqrt{\pi}\left(\frac{-2}{m_I c}\right)^{\frac{5}{2}} \\ &= \frac{1}{n_I}\gamma_I \left(-\frac{2\pi}{m_I c}\right)^{\frac{3}{2}} \frac{1}{c} = -\frac{1}{c}. \end{aligned} \tag{1.137}$$

From (1.135) and (1.137) we conclude that, if the distribution vector $\underline{\mathbf{f}}$ is a collision equilibrium all the components C_I share the same mean velocity $\mathbf{u}_I = \mathbf{u}$ and temperature $T_I = T$. Thus, collecting (1.133), (1.135) and (1.137) we have parameters γ_I, $\mathbf{b}$ and c in terms of macroscopic quantities of the mixture:

$$\gamma_I = n_I \left(\frac{m_I}{2\pi T}\right)^{\frac{3}{2}}, \quad \mathbf{b} = T\mathbf{u}, \quad c = -\frac{1}{T}. \tag{1.138}$$

Finally we can thus write the collision equilibria as vectors of Maxwellian distributions of the form

$${f_I}^M(\mathbf{v}) = n_I \left(\frac{m_I}{2\pi T}\right)^{\frac{3}{2}} \exp\left[-\frac{m_I}{2T}|\mathbf{v} - \mathbf{u}|^2\right], \quad 1 \le I \le L. \tag{1.139}$$

Moreover, considering (1.130) we can write, for any I, J such that $L^{s-1} < I, J \le L^s$, for some $1 \le s \le 4$

$$n_I = \exp\left(a_I + \frac{m_I|\mathbf{u}|^2}{2T}\right)(2\pi T m_I)^{\frac{3}{2}}, \quad n_J = \exp\left(a_J + \frac{m_J|\mathbf{u}|^2}{2T}\right)(2\pi T m_J)^{\frac{3}{2}} \tag{1.140}$$

But, since in this case $m_I = m_J$, from relations (1.60) we get

$$n_J = \exp\left(a_I - \frac{E_J - E_I}{T} + \frac{m_I|\mathbf{u}|^2}{2T}\right)(2\pi T m_I)^{\frac{3}{2}} = n_I \exp\left(-\frac{E_J - E_I}{T}\right). \tag{1.141}$$

At this point, we have,

$$n^s = \sum_{I=L^{s-1}+1}^{L^s} n_I = n_{L^{s-1}+1} \sum_{I=L^{s-1}+1}^{L^s} \exp\left(-\frac{E_I - E_{L^{s-1}+1}}{T}\right), \tag{1.142}$$

from which, for any component C_J belonging to the species s, calling E^s the first energy level of such species, namely $E^s = E_{L^{s-1}+1}$,

$$n_J = n_{L^{s-1}+1} \exp\left(-\frac{E_J - E^s}{T}\right) = n^s \frac{\exp\left(-\frac{E_J - E^s}{T}\right)}{\displaystyle\sum_{I=L^{s-1}+1}^{L^s} \exp\left(-\frac{E_I - E^s}{T}\right)}. \tag{1.143}$$

In particular, for each $s = 1, 2, 3, 4$, if we define the partition function

$$\mathcal{Z}^s(T) \overset{\text{def}}{=} \sum_{K=L^{s-1}+1}^{L^s} \exp\left(-\frac{E_K - E^s}{T}\right), \tag{1.144}$$

we can write

$$n_{L^{s-1}+1} = n^s \frac{1}{\mathcal{Z}^s(T)}, \tag{1.145}$$

and, using again (1.130), we have

$$n^s = n_{L^{s-1}+1} \frac{1}{\mathcal{Z}^s(T)} = \exp\left(a_{L^{s-1}+1} + \frac{m^s|\mathbf{u}|^2}{2T}\right)(2\pi T m^s)^{\frac{3}{2}}\, \mathcal{Z}^s(T). \tag{1.146}$$

We can thus derive the expression

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}{\mathcal{Z}^3(T)\mathcal{Z}^4(T)} \exp\left(a_1 + a_{L^1+1} - a_{L^2+1} - a_{L^3+1}\right), \tag{1.147}$$

which, by virtue of (1.61), becomes

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}{\mathcal{Z}^3(T)\mathcal{Z}^4(T)} \exp\left(\frac{\Delta E}{T}\right), \tag{1.148}$$

that represents the mass action law for the chemical reaction (1.1). ☐

At this point we consider the space homogeneous version of the Boltzmann problem for our model (1.15)

$$\frac{\partial f_I}{\partial t} = \bar{Q}_I[\underline{\mathbf{f}}], \quad 1 \le I \le L. \tag{1.149}$$

The complete case with spatial gradients and boundary conditions is fully discussed in [36]. Theorem 1.4.4 provides a class of stationary states depending on 7 free parameters. We want now to give results ensuring the fact that, given an initial configuration $\underline{\mathbf{f}}^0$, it is possible to individuate a unique asymptotically stable equilibrium state $\underline{\mathbf{f}}^M$.

As concerns the existence of such an equilibrium, from equations (1.104) - (1.106), (1.108) and (1.110) in space homogeneous conditions we have that the quantities

$$n^1+n^3, \quad n^1+n^4, \quad n^2+n^4, \quad \rho\mathbf{u}, \quad \frac{3}{2}nT+E \tag{1.150}$$

are kept constant during the evolution. This means that the admissible equilibria are those Maxwellians $\underline{\mathbf{f}}^M$ provided by Theorem 1.4.4 characterized by the same conserved macroscopic quantities.

Theorem 1.4.5. *Fixed an initial state characterized by the distributions vector* $\underline{\mathbf{f}}^0$ *for the system* (1.149)*, it is possible to individuate a unique vector of Maxwellian distributions characterized by the same macroscopic observables of* $\underline{\mathbf{f}}^0$ *that are conserved during the evolution.*

Proof. Let $\underline{\mathbf{f}}^0$ be an initial configuration and let n_0^s, $s=1,2,3,4$, $\mathbf{u}^0$, T^0 the initial number densities of each species, the initial global mean velocity and the initial global temperature, respectively. First of all we observe that we can choose a proper reference frame in such a way that $\mathbf{u}^0=\mathbf{0}$. Our aim is to individuate a Maxwellian configuration $\underline{\mathbf{f}}^M$ with

$$f_I{}^M(\mathbf{v}) = n_I^M M_I\left(\mathbf{v};\mathbf{u}^M,\frac{T^M}{m_I}\right), \quad 1\le I\le L, \tag{1.151}$$

with number densities of components n_I^M satisfying

$$n_I^M = \frac{n_M^s}{\mathcal{Z}^s(T^M)}\exp\left(-\frac{E_I-E^s}{T^M}\right), \qquad \text{for any } I,s \text{ such that } L^{s-1}<I\le L^s, \tag{1.152}$$

and number densities of gas species n_M^s satisfying

$$\frac{n_M^1 n_M^2}{n_M^3 n_M^4} = \left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}}\frac{\mathcal{Z}^1(T^M)\mathcal{Z}^2(T^M)}{\mathcal{Z}^3(T^M)\mathcal{Z}^4(T^M)}\exp\left(\frac{\Delta E}{T^M}\right). \tag{1.153}$$

Conservation of quantities (1.150) implies

$$n_M^1-n_0^1 = n_M^2-n_0^2 = -(n_M^3-n_0^3) = -(n_M^4-n_0^4), \tag{1.154}$$

$$n_M = \sum_{s=1}^4 n_M^s = \sum_{s=1}^4 n_0^s = n_0, \tag{1.155}$$

$$\mathbf{u}^M = \frac{\rho^0}{\rho^M}\mathbf{u}^0 = \mathbf{0}, \tag{1.156}$$

$$\frac{3}{2}n^0T^M + \sum_{s=1}^4 \frac{n_M^s}{\mathcal{Z}^s(T^M)}\sum_{I=L^{s-1}+1}^{L^s} E_I\exp\left(-\frac{E_I-E^s}{T^M}\right) = \frac{3}{2}n^0T^0+E^0. \tag{1.157}$$

The fact that we have $\mathbf{u}=\mathbf{0}$ for any $t>0$ reduces the dimension of the subspace of collision equilibria from 7 to 4, leaving us with a system with the 5 unknowns n_M^s, T^M to be determined in order to individuate the desired Maxwellian. We introduce functions

$$\mathcal{W}^s(T) \stackrel{\text{def}}{=} \frac{\displaystyle\sum_{I=L^{s-1}+1}^{L^s} E_I\exp\left(-\frac{E_I-E^s}{T}\right)}{\mathcal{Z}^s(T)}, \tag{1.158}$$

for any $1 \leq s \leq 4$ and we rewrite (1.157) as

$$\frac{3}{2}n^0 T^M + \sum_{s=1}^{4} (n_M^s - n_0^s)\, \mathcal{W}^s(T^M) + \sum_{s=1}^{4} n_0^s \mathcal{W}^s(T^M) = \frac{3}{2}n^0 T^0 + E^0, \tag{1.159}$$

that, using (1.154), becomes

$$\frac{3}{2}n^0 T^M + \left(n_M^1 - n_0^1\right) \sum_{s=1}^{4} \lambda^s \mathcal{W}^s(T^M) + \sum_{s=1}^{4} n_0^s \mathcal{W}^s(T^M) = \frac{3}{2}n^0 T^0 + E^0. \tag{1.160}$$

This allows us to express each one of equilibrium densities in terms of the equilibrium temperature:

$$n_M^s = n_0^s + \lambda^s \mathcal{X}(T^M), \quad s = 1, \ldots, 4, \tag{1.161}$$

with $\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = 1$ and the function

$$\mathcal{X}(T) \overset{\mathsf{def}}{=} \frac{\mathcal{V}(T)}{\mathcal{Y}(T)}, \tag{1.162}$$

being

$$\mathcal{V}(T) \overset{\mathsf{def}}{=} \frac{3}{2}n^0 T + \sum_{s=1}^{4} n_0^s \mathcal{W}^s(T) - \frac{3}{2}n^0 T^0 - E^0, \tag{1.163}$$

$$\mathcal{Y}(T) \overset{\mathsf{def}}{=} -\sum_{s=1}^{4} \lambda^s \mathcal{W}^s(T). \tag{1.164}$$

The fact that number densities are positive quantities has as consequence that, in virtue of (1.161), the equilibrium temperature should belong to the admissible set

$$A \overset{\mathsf{def}}{=} \left\{T > 0 : \max(-n_0^1, -n_0^2) \leq \mathcal{X}(T) \leq \min(n_0^3, n_0^4)\right\}. \tag{1.165}$$

From mass action law (1.153), now, we can use the expression for number densities obtained above to get the following transcendental equation

$$\mathcal{L}(T^M) = \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}}, \tag{1.166}$$

taking the function $\mathcal{L}$ as follows

$$\mathcal{L}(T) = \mathcal{L}_1(T) \cdot \mathcal{L}_2(T) \cdot \mathcal{L}_3(T),$$

$$\mathcal{L}_1(T) \overset{\mathsf{def}}{=} \frac{\left[n_0^1 + \mathcal{X}(T)\right]\left[n_0^2 + \mathcal{X}(T)\right]}{\left[n_0^3 - \mathcal{X}(T)\right]\left[n_0^4 - \mathcal{X}(T)\right]}, \quad \mathcal{L}_2(T) = \frac{\mathcal{Z}^3(T)\mathcal{Z}^4(T)}{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}, \quad \mathcal{L}_3(T) = \exp\left(-\frac{\Delta E}{T}\right). \tag{1.167}$$

Now we give proof of the following claims:

- **C1** On any interval $I = (T^1, T^2) \subseteq A$ in which the function $\mathcal{Y}(T)$ given in (1.164) is strictly positive (negative), then the function $\mathcal{X}(T)$ given in (1.162) is strictly monotonically decreasing (increasing) in I.
- **C2** On any interval $I = (T^1, T^2) \subseteq A$ the sign of $\mathcal{Y}(T)$ given does not change.

C3 The set A given in (1.165) is a connected set of $\mathbb{R}^+$.

C4 The function $\mathcal{Y}(T)$ defined in (1.164) is strictly monotone in the set A, ranging from 0 to $+\infty$.

Let us start with the demonstration of the first claim. **C1**-*proof* Computing explicitly the derivative of function $\mathcal{X}$ we have

$$\mathcal{X}'(T) = \frac{\mathcal{V}'(T)}{\mathcal{Y}(T)} - \mathcal{X}(T)\frac{\mathcal{Y}'(T)}{\mathcal{Y}(T)}. \tag{1.168}$$

Being

$$(\mathcal{W}^s)'(T) = \frac{\displaystyle\sum_{I=L^{s-1}+1}^{L^s} \sum_{J=L^{s-1}+1}^{L^s} \frac{1}{T^2}\left(E_I^2 - E_I E_J\right)\exp\left(-\frac{E_I + E_J - 2E^s}{T}\right)}{(\mathcal{Z}^s(T))^2}, \tag{1.169}$$

that, if we exchange indices $I \leftrightarrow J$ is equal to

$$(\mathcal{W}^s)'(T) = \frac{\displaystyle\sum_{I=L^{s-1}+1}^{L^s} \sum_{J=L^{s-1}+1}^{L^s} \frac{1}{2T^2}\left(E_I - E_J\right)^2\exp\left(-\frac{E_I + E_J - 2E^s}{T}\right)}{(\mathcal{Z}^s(T))^2} \geq 0, \tag{1.170}$$

for all s=1,. . . ,4. We have

$$\mathcal{V}'(T) = \frac{3}{2}n^0 + \sum_{s=1}^{4} n_0^s (\mathcal{W}^s)'(T) > 0, \tag{1.171}$$

and

$$\mathcal{Y}'(T) = -\sum_{s=1}^{4} \lambda^s (\mathcal{W}^s)'(T). \tag{1.172}$$

This allows us to write

$$\mathcal{X}'(T) = \frac{1}{\mathcal{Y}(T)}\left\{\frac{3}{2}n_0 + \sum_{s=1}^{4}\left[n_0^s + \lambda^s \mathcal{X}(T)\right](\mathcal{W}^s)'(T)\right\}. \tag{1.173}$$

Observing that the terms in square brackets in (1.173) are strictly positive for any T belonging to the admissible set A, we can conclude that on every interval $(T^1, T^2) \subseteq A$ in which the function $\mathcal{Y}$ is strictly positive (negative), the function $\mathcal{X}$ is strictly monotonically increasing (decreasing).

C2-*proof* Now we prove that the function $\mathcal{Y}$ does actually not change its sign on every interval $(T^1, T^2) \subseteq A$. We first make the following considerations about the function $\mathcal{V}$. Since, as already observed, we have $\mathcal{V}'(T) > 0$ and computing

$$\begin{aligned}\lim_{T\to 0^+} \mathcal{V}(T) &= \lim_{T\to 0^+} \frac{3}{2}n^0 T + \sum_{s=1}^{4} n_0^s \left[\frac{E^s + \displaystyle\sum_{I=L^{s-1}+2}^{L^s} E_I \exp\left(-\frac{E_I - E^s}{T}\right)}{1 + \displaystyle\sum_{I=L^{s-1}+2}^{L^s} \exp\left(-\frac{E_I - E^s}{T}\right)}\right] - \frac{3}{2}n^0 T^0 - E^0 \\ &= \sum_{s=1}^{4} \sum_{I=L^{s-1}+1}^{L^s} (E^s - E_I) n_I^0 < 0;\end{aligned} \tag{1.174}$$

and the negativity of the result comes from the fact that the amount of energy of each level is increasing with the index I within each species, recalling the definition of the excitation energy density (1.99). Moreover it is simply verified that

$$\lim_{T\to+\infty} \mathcal{V}(T) = +\infty. \tag{1.175}$$

This means that the function $\mathcal{V}$ admits a unique positive root $T = T^{\#}$, which obviously belongs to the admissible set A. Now we consider again function $\mathcal{Y}$. We note that

$$\lim_{T\to 0^+} \mathcal{Y}(T) = \Delta E, \qquad \lim_{T\to+\infty} \mathcal{Y}(T) = \sum_{s=1}^{4} \frac{1}{4}\lambda^s \sum_{I=L^{s-1}+1}^{L^s} E_I, \tag{1.176}$$

and the sign of $\mathcal{Y}'(T)$ changes, from (1.172), accordingly to internal energy levels. This means that $\mathcal{Y}$ may have a positive root T^*. Supposing that such a root exists and $T^* \neq T^{\#}$, this would imply

$$\lim_{T\to T^*} \mathcal{X}(T) = \pm\infty, \tag{1.177}$$

getting a neighborhood of T^* not contained in A. Thus we can conclude that on every subinterval (T^1, T^2) of A the function $\mathcal{Y}$ keeps the same sign. Instead, if it happens that $\mathcal{Y}(T^{\#}) = 0$, we have that $T^M = T^{\#}$ is a trivial solution of (1.160). This means that, from (1.154) and (1.153) we obtain a second order algebraic equation in the unknown n_M^1

$$\frac{n_M^1 \left[n_0^2 + (n_M^1 - n_0^1)\right]}{\left[n_0^3 - (n_M^1 - n_0^1)\right]\left[n_0^4 - (n_M^1 - n_0^1)\right]} = \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(T^{\#})\mathcal{Z}^2(T^{\#})}{\mathcal{Z}^3(T^{\#})\mathcal{Z}^4(T^{\#})} \exp\left(\frac{\Delta E}{T^{\#}}\right), \tag{1.178}$$

and we can directly recover a Maxwellian state $(n_M^1, n_M^2, n_M^3, n_M^4, T^M)$.

C3-*proof* We verify now that the set A defined in (1.165) is a connected set of $\mathbb{R}^+$. To prove this, we consider a connected component of A, namely an interval (T_a, T_b). We distinguish two cases. If $T_a \neq 0$, being the function $\mathcal{X}$ continuous and strictly monotonically increasing or decreasing on (T_a, T_b), it assumes all the possible values between $\max(-n_0^1, -n_0^2)$ and $\min(n_0^3, n_0^4)$. If $T_a = 0$, since $\lim_{T\to 0^+} \mathcal{Y}(T) = \Delta E$ and the sign of $\mathcal{Y}$ does not change on (T_a, T_b), supposing $\Delta E > 0$, we have that $\mathcal{X}$ is strictly monotonically increasing on (T_a, T_b), going from $\lim_{T\to 0^+} \mathcal{X}(T) < 0$ to $\min(n_0^3, n_0^4)$ (the symmetric result is obtained if $\Delta E < 0$). In both cases, the function $\mathcal{X}$ has a root in (T_a, T_b), but as already observed, it has only one possible root. It follows that (T_a, T_b) is the only connected component of A, thus A is a connected interval (T_{min}, T_{max}).

C4-*proof* All these results are crucial for the analysis of the behavior of function $\mathcal{L}$ given in (1.167). We compute its derivative with respect to T. It holds

$$\begin{aligned}\mathcal{L}_1'(T) = &\mathcal{X}'(T)\left(n_0^3 - \mathcal{X}(T)\right)^{-2}\left(n_0^4 - \mathcal{X}(T)\right)^{-2}\\ &\times \left[\left(n_0^1 + \mathcal{X}(T)\right) + \left(n_0^2 + \mathcal{X}(T)\right)\right]\left(n_0^3 - \mathcal{X}(T)\right)\left(n_0^4 - \mathcal{X}(T)\right)\\ &\times \left[\left(n_0^3 - \mathcal{X}(T)\right) + \left(n_0^4 - \mathcal{X}(T)\right)\right]\left(n_0^1 + \mathcal{X}(T)\right)\left(n_0^2 + \mathcal{X}(T)\right),\end{aligned} \tag{1.179}$$

that can be cast as

$$\mathcal{L}_1'(T) = \mathcal{L}_1(T)\mathcal{X}'(T)\sum_{s=1}^{4}\left[n_0^s + \lambda^s \mathcal{X}(T)\right]^{-1}. \tag{1.180}$$

Analogously we obtain

$$\mathcal{L}_2'(T) = -\mathcal{L}_2(T)\frac{1}{T^2}\sum_{s=1}^{4}\lambda^s\frac{1}{\mathcal{Z}^s(T)}\sum_{I=L^{s-1}+1}^{L^s}(E_I - E^s)\exp\left(-\frac{E_I - E^s}{T}\right). \tag{1.181}$$

Moreover

$$\mathcal{L}_3'(T) = \mathcal{L}_3(T)\frac{\Delta E}{T^2}. \tag{1.182}$$

Thus, collecting the results we have

$$\begin{aligned}\mathcal{L}'(T) = \mathcal{L}(T)\Bigg\{&\mathcal{X}'(T)\sum_{s=1}^{4}\left[n_0^s + \lambda^s\mathcal{X}(T)\right]^{-1} \\ &-\frac{1}{T^2}\sum_{s=1}^{4}\frac{\lambda^s}{\mathcal{Z}^s(T)}\sum_{I=L^{s-1}+1}^{L^s}(E_I - E^s)\exp\left(-\frac{E_I - E^s}{T}\right) + \frac{\Delta E}{T^2}\Bigg\},\end{aligned} \tag{1.183}$$

that can be expressed, using function $\mathcal{Y}$ defined in (1.164), as

$$\mathcal{L}'(T) = \mathcal{L}(T)\left\{\mathcal{X}'(T)\sum_{s=1}^{4}\left[n_0^s + \lambda^s\mathcal{X}(T)\right]^{-1} + \frac{1}{T^2}\mathcal{Y}(T)\right\}. \tag{1.184}$$

We have that, on the whole admissible set A, $\mathcal{L}(T) > 0$ while $\mathcal{X}'(T)$ and $\mathcal{Y}(T)$ have the same sign. Thus $\mathcal{L}$ is monotonically increasing or decreasing on A. Moreover, when $\mathcal{X}(T) \to \max(-n_0^1, -n_0^2)$ it holds $\mathcal{L}(T) \to 0$, while when $\mathcal{X}(T) \to \min(n_0^3, n_0^4)$ it is $\mathcal{L}(T) \to +\infty$. Also if $T_{min} = 0$ we have, if $\Delta E > 0$, $\lim_{T\to 0}\mathcal{L}(T) = 0$ and $\lim_{T\to T_{max}}\mathcal{L}(T) = +\infty$, the opposite if $\Delta E < 0$. In this way we can conclude that there exists a unique admissible value T^M for which the transcendental equation (1.166) is satisfied. This provides the equilibrium temperature and, from (1.161) together with (1.145), the equilibrium densities for each component, allowing us to find the Maxwellian state $\underline{\mathbf{f}}^M$ as the theorem states. □

Just for illustrative purposes, we consider a real bimolecular reversible reaction involving hydrogen H_2 (with mass 2.02 g/mol), iodine I_2 (253.8 g/mol) and hydrogen iodide HI (127.91 g/mol)

$$H_2 + I_2 \leftrightarrows HI + HI, \tag{1.185}$$

and we build a numerical model inspired by it in order to recover from initial fixed data the Maxwellian configuration. So we take four gas species G^i, $i = 1, ..., 4$, and we set masses in such a way that mass ratios are the ones involved in the reaction:

$$m^1 = 0.1, \quad m^2 = 12.8, \quad m^3 = m^4 = 6.45. \tag{1.186}$$

We underline the fact that in this case two of the four species coincide, thus they will be endowed with the same internal structure and initial data. Specifically, we take as configuration for internal energy levels the following

$$\begin{gathered}E_1^1 = 6.5, \quad E_2^1 = 7.5, \quad E_1^2 = 7, \quad E_2^2 = 8, \quad E_3^2 = 8.5, \\ E_1^3 = 6, \quad E_2^3 = 7, \quad E_1^4 = 6, \quad E_2^4 = 7.\end{gathered} \tag{1.187}$$

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2	C_1^3	C_2^3	C_1^4	C_2^4
n_0	9	5	6	4	11	10	8	10	8
T_0	2	4	1	2.5	2	6	1.5	6	1.5

Table 1.1

Initial data for number concentrations and temperatures are given in Table 1.1, while, as already said, we suppose that the mean velocity is null (for simplicity we assume vanishing mean velocity for each component).

In Figure 1.1 we report the behavior of all the functions involved in the calculations to get the Maxwellian state. In panel (a) we plot the number densities of each species in function of the temperature T as given in (1.161), this allows us to individuate the admissible set given by the interval $(T_{min}, T_{max}) = (2.86, 3.38)$ (indicated by the two dotted vertical lines) in which all the quantities are positive. In panel (b), instead, it is possible to verify that both the functions $\mathcal{X}'$ and $\mathcal{Y}$ (dash-dotted line) keep the same sign on the admissible set and that $\mathcal{X}$ (solid line) has a unique root in it. In panel (c), instead, is given the function $\mathcal{L}$ and a magnification of the plot is in panel (d). Here is reported also the horizontal line

$$y = \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}}, \tag{1.188}$$

and it is possible to find its intersection with the graph of $\mathcal{L}$, in such a way we find the solution of the transcendental equation (1.166) and obtain the equilibrium temperature $T^M = 3.37$ (vertical solid line). This value allows also to find the equilibrium densities of each species given by the intersection of the vertical solid line in panel (a) with the other lines, getting

$$n_M^1 = 0.61, \quad n_M^2 = 7.61, \quad n_M^3 = n_M^4 = 31.39. \tag{1.189}$$

1.5 Stability of equilibria: The *H*-theorem

We have proved the existence of an equilibrium state preserving the macroscopic quantities during all the evolution, and now we inquire about the stability and the uniqueness of such a state in space homogeneous conditions. For the stability we are able to provide an extension of the classical Boltzmann H-Theorem [27]. Then, the physical entropy functional $\mathcal{H}$ is defined as follows

$$\mathcal{H}[\underline{\mathbf{f}}] = \sum_{I=1}^{L} \int_{\mathbb{R}^3} \Phi_I(f_I)\, d\mathbf{v}, \tag{1.190}$$

with

$$\Phi_I(x) = x \log\left(\frac{x}{(m_I)^3}\right), \quad i = 1, \ldots, L, \tag{1.191}$$

and we exploit the fact that $\mathcal{H}$ is a Lyapunov functional for our problem in order to state that the Maxwellian configuration previously found is an asymptotically stable equilibrium. We have, indeed, the following result.

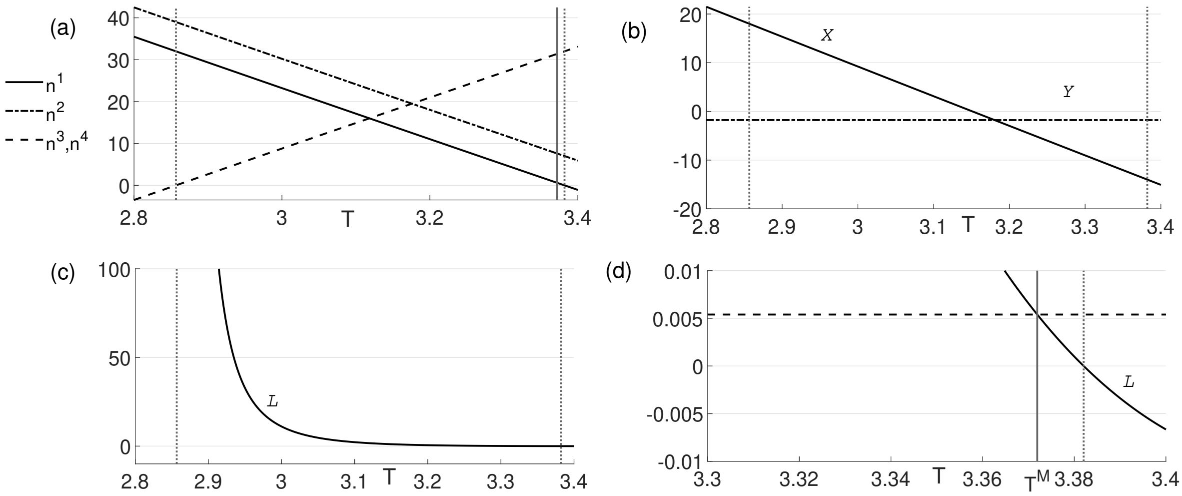

Figure 1.1: Behavior of different quantities in terms of the positive temperature T for a mixture of four reacting gases involved in a reaction inspired by (1.185), considering masses as in (1.186), energy levels as in (1.187) and initial values for number density and temperature as in Table 1.1. Panel (a): number densities of each species as given in (1.161), panel (b): functions $\mathcal{X}$ and $\mathcal{Y}$ defined in (1.162) and (1.164), respectively, panels (c)-(d): function $\mathcal{L}$ defined in (1.167).

Theorem 1.5.1 (H-Theorem). [1] *Given an initial configuration $\underline{\mathbf{f}}^0$, let $\underline{\mathbf{f}}^M$ be the corresponding Maxwellian stationary point individuated by Theorem* (1.4.5)*, then the functional $\mathcal{H}$ defined in* (1.190) *is a strict Lyapunov functional for the problem* (1.15) *in space homogeneous conditions. In particular, it holds:*

i. Being $\dot{\mathcal{H}}[\underline{\mathbf{f}}]$ the time derivative of $\mathcal{H}$ evaluated in the distribution vector $\underline{\mathbf{f}}$ starting from $\underline{\mathbf{f}}^0$, $\dot{\mathcal{H}} \leq 0$ for any $t \geq 0$ and $\dot{\mathcal{H}} = 0$ only for $\underline{\mathbf{f}} = \underline{\mathbf{f}}^M$, where $\underline{\mathbf{f}}^M$ is an equilibrium state compatible with the initial state f^0.

ii. $\mathcal{H}[\underline{\mathbf{f}}^*] > \mathcal{H}[\underline{\mathbf{f}}^M]$ for any other possible configuration $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$.

Proof. It is easy to verify that, in space homogeneous conditions, if $\underline{\mathbf{f}}$ is a solution of (1.15), we have

$$\dot{\mathcal{H}}[\underline{\mathbf{f}}] = \sum_{I=1}^{L} \int_{\mathbb{R}^3} \log\left(\frac{f_I}{m_I^3}\right) \bar{Q}_I[\underline{\mathbf{f}}]d\mathbf{v} + \sum_{I=1}^{L} \int_{\mathbb{R}^3} \bar{Q}_I[\underline{\mathbf{f}}]d\mathbf{v} = \mathcal{W}[\underline{\mathbf{f}}], \tag{1.192}$$

with $\bar{W}$ the functional (1.118) since the vector $\varphi_I = 1$, $1 \leq I \leq L$, is trivially a collision invariant. Thus from the formulation of $\bar{W}$ given in (1.120) and Theorem 1.4.3, we get the nonpositivity of $\dot{\mathcal{H}}$ and the fact that it is null only at $\underline{\mathbf{f}} = \underline{\mathbf{f}}^M$. To prove that $\mathcal{H}[\underline{\mathbf{f}}^*] - \mathcal{H}[\underline{\mathbf{f}}^M] > 0$ for any $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$ in a neighborhood of $\underline{\mathbf{f}}^M$, we rewrite the functional (1.190) as follows

$$\mathcal{H}[\underline{\mathbf{f}}] = \int_{\mathbb{R}^3} \mathfrak{H}[\underline{\mathbf{f}}]\, d\mathbf{v}, \quad \mathfrak{H}[\underline{\mathbf{f}}] = \sum_{I=1}^{L} \Phi_I(f_I). \tag{1.193}$$

---

[1] In his original work, Boltzmann used the letter E to indicate the entropy function, but in 1890 Burbury used the letter H [31] and in 1896 Boltzmann adopted the same notation [28]. This change aroused the curiosity of many scholars, including Sidney Chapman, who suggested that actually the letter H stands for the capital Greek letter *eta*, that corresponds to the Latin letter e [39].

We also express the total energy density as

$$\mathcal{E}[\underline{\mathbf{f}}] = \int_{\mathbb{R}^3} \mathfrak{E}[\underline{\mathbf{f}}]\, d\mathbf{v}, \quad \mathfrak{E}[\underline{\mathbf{f}}] = \sum_{I=1}^{L} \left(\frac{1}{2} m_I |\mathbf{v}-\mathbf{u}|^2 + E_I \right) f_I. \tag{1.194}$$

We compute

$$\left.\frac{\partial \mathfrak{H}}{\partial f_I}\right|_{\underline{\mathbf{f}}^M} = \log n_I^M - \frac{3}{2}\log m_I - \log\big(2\pi T^M\big) - \frac{m_I}{2\,T^M}|\mathbf{v}-\mathbf{u}|^2 + 1 \tag{1.195}$$

$$= -\frac{1}{T^M}\left.\frac{\partial \mathfrak{E}}{\partial f_I}\right|_{\underline{\mathbf{f}}^M} + \frac{E^s}{T^M} + \log\frac{n_M^s}{\mathcal{Z}^s(T^M)} - \frac{3}{2}\log m_I - \log\big(2\pi T^M\big) + 1. \tag{1.196}$$

having used the relation (1.152) to express n_I^M in terms of n_M^s with I, s such that $L^{s-1} < I \leq L^s$. We pick now another density configuration $\underline{\mathbf{f}}^*$, for which number densities are

$$n_I^* = \int_{\mathbb{R}^3} f_I^* d\mathbf{v}, \quad i = 1, \ldots, L. \tag{1.197}$$

Now we calculate

$$\begin{aligned}
&\sum_{I=1}^{L}\int_{\mathbb{R}^3}\left.\frac{\partial \mathfrak{H}}{\partial f_I}\right|_{\underline{\mathbf{f}}^M}\big(f_I^* - f_I^M\big)\, d\mathbf{v} \\
&= -\frac{1}{T^M}\sum_{I=1}^{L}\int_{\mathbb{R}^3}\left.\frac{\partial \mathfrak{E}}{\partial f_I}\right|_{\underline{\mathbf{f}}^M}\big(f_I^* - f_I^M\big)\, d\mathbf{v} \\
&\quad + \sum_{I=1}^{L}\left[\left(\frac{E^s}{T^M} + \log\frac{n_M^s}{\mathcal{Z}^s(T^M)} - \frac{3}{2}\log m_I - \log\big(2\pi T^M\big) + 1\right)\big({n_I}^* - n_I^M\big)\right].
\end{aligned} \tag{1.198}$$

From conservation of the combinations of species densities $n^1 + n^3$, $n^1 + n^4$ and $n^2 + n^4$ we have

$$n_M^1 - n_*^1 = n_M^2 - n_*^2 = -(n_M^3 - n_*^3) = -(n_M^4 - n_*^4), \tag{1.199}$$

thus second term on the right hand side of (1.198) reduces to

$$\left[-\log\left(\frac{n_M^1 n_M^2}{n_M^3 n_M^4}\right) + \frac{\Delta E}{T} + \frac{3}{2}\log\left(\frac{m^1 m^2}{m^3 m^4}\right) + \log\left(\frac{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}{\mathcal{Z}^3(T)\mathcal{Z}^4(T)}\right)\right](n_1^M - n_*^1). \tag{1.200}$$

In addition, being $\mathfrak{E}$ an homogeneous function of order 1 in the variables f_I, we can see that

$$\mathcal{E}[\underline{\mathbf{f}}\,] = \sum_{I=1}^{L}\int_{\mathbb{R}^3} f_I \frac{\partial \mathfrak{E}}{\partial f_I} d\mathbf{v}. \tag{1.201}$$

From the conservation of total energy $\mathcal{E}$, we have that $\mathcal{E}[\underline{\mathbf{f}}^{\,*}] = \mathcal{E}[\underline{\mathbf{f}}_{\,M}]$, consequently

$$\sum_{I=1}^{L}\int_{\mathbb{R}^3}\left.\frac{\partial \mathfrak{E}}{\partial f_I}\right|_{\underline{\mathbf{f}}^M}\big(f_I^* - f_I^M\big)\, d\mathbf{v} = 0. \tag{1.202}$$

But with (1.193) at hand, (1.198) turns into

$$\sum_{i=1}^{L}\int_{\mathbb{R}^3}(\Phi_I)'(f_I^M)\,\big(f_I^* - f_I^M\big)\, d\mathbf{v} = 0. \tag{1.203}$$

We take now $\Phi_I^{\mathcal{T}}$ that is first-order Taylor polynomial of functions Φ_I relevant to f_I^M , i. e.

$$\Phi_I^{\mathcal{T}}(f_I) = \Phi_I(f_I^M) + (\Phi_I)'(f_I^M)\left(f_I - f_I^M\right). \tag{1.204}$$

Expression (1.203) leads to

$$\mathcal{H}[\underline{\mathbf{f}}^*] - \mathcal{H}[\underline{\mathbf{f}}^M] = \sum_{I=1}^{L} \int_{\mathbb{R}^3} [\Phi_I(f_I^*) - \Phi_I(f_I^M)]d\mathbf{v} = \sum_{I=1}^{L} \int_{\mathbb{R}^3} [\Phi_I(f_I^*) - \Phi_I^{\mathcal{T}}(f_I^*)]d\mathbf{v}. \tag{1.205}$$

At this point, we exploit the fact that Φ_I are strictly convex functions in their domain. A direct consequence is that each integral in the last term of (1.205) has nonnegative argument, in particular it is positive on a set with nonzero measure and null only in the case $f_I^* = f_I^M$ for all I. We can thus conclude that it holds $\mathcal{H}[\underline{\mathbf{f}}] - \mathcal{H}[\underline{\mathbf{f}}^M] \geq 0$ for any $\underline{\mathbf{f}}$, and the equality sign is provided if and only if $\underline{\mathbf{f}} = \underline{\mathbf{f}}^M$. □

The just proved result provides the stability of the Maxwellian equilibrium. Its uniqueness is a direct consequence of Theorem 1.5.1. Indeed, supposing the existence of another equilibrium $\underline{\mathbf{f}}^{M_1}$, with $\underline{\mathbf{f}}^{M_1} \neq \underline{\mathbf{f}}^M$, performing the same calculations of the previous proof, we would obtain that also $\mathcal{H}[\underline{\mathbf{f}}^{M_1}]$ is a minimum, but then $\mathcal{H}[\underline{\mathbf{f}}^{M_1}] < \mathcal{H}[\underline{\mathbf{f}}^M]$ and this is a contradiction. So we can conclude with the last result

Theorem 1.5.2. *Given an initial configuration* $\underline{\mathbf{f}}^0$ *for the problem* (1.15) *in space homogeneous conditions, the Maxwellian configuration* $\underline{\mathbf{f}}^M$ *individuated by Theorem* (1.4.5) *is the unique equilibrium for the system and it is asymptotically stable.*

2 A BGK model for mixtures of monatomic and polyatomic gases

In this chapter, we present a BGK-type kinetic model for a mixture of monatomic and polyatomic gas species. The need for this type of model comes from the fact that such mixtures can be found in most of physical environments. For example, in the upper atmosphere of the Earth is possible to find molecular Oxygen (O_2) and molecular Nitrogen (N_2), which are both diatomic. Anyway, because of chemical dissociation and recombination reactions, these two elements are present in atomic state O and N as well, along with diatomic Nitrogen Monoxide (NO).

The classical way in which kinetic theory represents polyatomic molecules consists in modelling the non-translational degrees of freedom by means of a suitable internal energy variable, discrete or continuous. If the energy variable is discrete, the single species is considered as composed by a certain number (the same as the number of levels) of components, each one corresponding to a particular energy level [58]. On the other hand, monatomic molecules lack non-translational degrees of freedom and thus are considered to have only one possible internal energy level. The same approach is used in [11], where for the distribution function of each component is built up a kinetic equation with a single BGK-type collision operator, as already proposed in [16, 61]. In the cited cases, all the species involved are supposed to have the same number of internal energy levels. Our scope is to extend such models to a mixture of gas species having different numbers of internal energy levels, and thus to consider the possibility of having both polyatomic and monoatomic species in a mixture.

In more detail, the chapter is structured as follows. In Section 2.1 we introduce the notations identifying the various components and their distributions. We avoid the notation used in the previous chapter using a single index I for all the components, in order to stress the fact that we are considering a mixture of both monatomic and polyatomic gases. Indeed, we shall use a single-index notation for monatomic species and a double-index notation for polyatomic components. This choice makes additional technicalities appear in the definitions of actual and auxiliary macroscopic fields, as well as in the proofs of the consistency of the model. Afterwards we define macroscopic fields of single species and of the global mixture, we discuss all types of collisions involving monatomic or polyatomic particles and corresponding collision equilibria. Then, Section 2.2 is devoted to the construction of a consistent BGK model for mixtures of monatomic and polyatomic gases, with the auxiliary parameters uniquely determined in terms of the actual number densities, mean velocities and temperatures of each monatomic species and each component of polyatomic ones. In particular, while for the auxiliary number densities and mean velocity is possible to find an explicit expression, the individuation of the auxiliary temperature involves the solution of a transcendental equation for which the well-posedness in not trivial in this frame. Also in the proof of the H-theorem in space homogeneous conditions the lack of symmetry in some kinds of collisions has to be carefully taken into account. In Section 2.3 we derive, from our BGK model, macroscopic evolution equations for densities, velocities and temperatures of all gas components. We then perform some numerical tests in order to analyze the behavior in time and the trend to equilibrium of each quantity in space homogeneous conditions for varying parameters. Two possible gas mixtures are considered, one of a monatomic and a polyatomic species, and one of two polyatomic species having a different number of energy levels; in both cases mass ratios will be varied making sure that the model represents real molecules. Some concluding remarks and perspectives are finally summarized in Section 2.4. The content of this chapter is included in the publication [20].

2.1 Statement of the problem and kinetic approach

We consider a mixture of various monatomic and polyatomic gases. More precisely, we assume to deal with A monatomic and B polyatomic species. As in any kinetic approach, each monatomic gas G^i, $i = 1, \dots, A$, is described by means of a distribution function $f^i(t, \mathbf{x}, \mathbf{v})$, depending on time t, position $\mathbf{x}$, and molecular velocity $\mathbf{v}$. As concerns polyatomic species G^i with $i = A+1, \dots, A+B$, similarly to the Boltzmann description proposed in [58] and considered in Chapter 1, the non–translational degrees of freedom are modeled by means of a discrete internal energy variable, and each polyatomic gas is endowed with a structure of a proper number L^i of discrete energy levels. Thus, analogously to [11,58], each gas G^i with index $i = A+1, \dots, A+B$ is represented as a mixture of L^i monatomic components C^i_j, each one characterized by a different energy level; the superscript i corresponds to the gas which the component belongs to, while the subscript j identifies the energy level. The distribution function of the component C^i_j is denoted by

$$f^i_j(t, \mathbf{x}, \mathbf{v}), \qquad i = A+1, \dots, A+B, \qquad j = 1, \dots, L^i. \tag{2.1}$$

The energy level of the component C^i_j is then consistently denoted by E^i_j, and in the frame of the same gas G^i the energy levels are assumed (without loss of generality) increasing with respect to the subindex j, namely $E^i_j < E^i_k$ for any $j, k = 1, \dots, L^i$ with $j < k$. The fact that we keep two indices i, j to indicate components of the polyatomic gases and their energies allows us to identify immediately the species and the component we are referring to.

All particles of the gas G^i are obviously characterized by the same mass m^i. Number density, mass velocity, and kinetic temperature of monatomic species G^i, $i = 1, \dots, A$, are provided, respectively, by

$$n^i = \int_{\mathbb{R}^3} f^i(\mathbf{v})\, d\mathbf{v}, \qquad \mathbf{u}^i = \frac{1}{n^i} \int_{\mathbb{R}^3} \mathbf{v}\, f^i(\mathbf{v})\, d\mathbf{v}, \qquad T^i = \frac{m^i}{3\, n^i} \int_{\mathbb{R}^3} |\mathbf{v} - \mathbf{u}^i|^2 f^i(\mathbf{v})\, d\mathbf{v}. \tag{2.2}$$

We find also convenient to define for each monatomic species the pressure tensor and the heat flux

$$\mathbf{P}^i = m^i \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}^i) \otimes (\mathbf{v} - \mathbf{u}^i)\, f^i(\mathbf{v})\, d\mathbf{v}, \quad \mathbf{q}^i = \frac{m^i}{2} \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}^i)\, |\mathbf{v} - \mathbf{u}^i|^2\, f^i(\mathbf{v})\, d\mathbf{v}. \tag{2.3}$$

For polyatomic species G^i, $i = A+1, \dots, A+B$, such macroscopic fields are given by suitable combinations of moments of distributions of single components C^i_j as

$$n^i = \sum_{j=1}^{L^i} n^i_j, \qquad \mathbf{u}^i = \frac{1}{n^i} \sum_{j=1}^{L^i} n^i_j\, \mathbf{u}^i_j, \qquad n^i\, T^i = \sum_{j=1}^{L^i} n^i_j\, T^i_j + \frac{1}{3}\, m^i \sum_{j=1}^{L^i} n^i_j \Big(|\mathbf{u}^i_j|^2 - |\mathbf{u}^i|^2 \Big), \tag{2.4}$$

where

$$n^i_j = \int_{\mathbb{R}^3} f^i_j(\mathbf{v})\, d\mathbf{v}\,, \qquad \mathbf{u}^i_j = \frac{1}{n^i_j}\int_{\mathbb{R}^3} \mathbf{v}\, f^i_j(\mathbf{v})\, d\mathbf{v}\,, \qquad T^i_j = \frac{m^i}{3\, n^i_j}\int_{\mathbb{R}^3} |\mathbf{v}-\mathbf{u}^i_j|^2 f^i_j(\mathbf{v})\, d\mathbf{v}\,. \tag{2.5}$$

In addition,

$$\mathbf{P}^i_j = m^i \int_{\mathbb{R}^3} (\mathbf{v}-\mathbf{u}^i_j)\otimes(\mathbf{v}-\mathbf{u}^i_j)\, f^i_j(\mathbf{v})\, d\mathbf{v}\,, \quad \mathbf{q}^i_j = \frac{m^i}{2}\int_{\mathbb{R}^3} (\mathbf{v}-\mathbf{u}^i_j)\, |\mathbf{v}-\mathbf{u}^i_j|^2\, f^i_j(\mathbf{v})\, d\mathbf{v}\,. \tag{2.6}$$

For polyatomic species we can define the excitation energy density as follows

$$E = \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} E^i_j n^i_j. \tag{2.7}$$

The total number density n and mass density ρ of the mixture, as well as the global mean velocity $\mathbf{u}$ and temperature T, are defined as

$$\begin{gathered} n = \sum_{i=1}^{A+B} n^i\,, \qquad \rho = \sum_{i=1}^{A+B} m^i\, n^i\,, \\ \mathbf{u} = \frac{1}{\rho}\sum_{i=1}^{A+B} m^i\, n^i\, \mathbf{u}^i\,, \qquad T = \frac{1}{n}\left[\sum_{i=1}^{A+B} n^i\, T^i + \frac{1}{3}\sum_{i=1}^{A+B} m^i\, n^i\left(|\mathbf{u}^i|^2 - |\mathbf{u}|^2\right)\right]. \end{gathered} \tag{2.8}$$

We introduce also the total internal energy density as

$$\mathcal{E} = \frac{3}{2} nT + E. \tag{2.9}$$

As usual in kinetic theory, molecules interact only through binary instantaneous collisions, that lead to a change in their velocity. Besides classical binary elastic collisions, in the present mixture even suitable inelastic encounters may occur, implying changes of the internal energies of the colliding (polyatomic) particles. More precisely, pairs of particles belonging to monatomic gases G^i, $i = 1, \dots, A$, may give rise only to elastic collisions

$$G^i + G^h \longrightarrow G^i + G^h\,, \qquad\qquad 1 \le i, h \le A\,, \tag{2.10}$$

preserving global momentum and kinetic energy:

$$\begin{aligned} & m^i\, \mathbf{v} + m^h\, \mathbf{w} = m^i\, \mathbf{v}' + m^h\, \mathbf{w}'\,, \\ & \frac{1}{2} m^i\, |\mathbf{v}|^2 + \frac{1}{2} m^h\, |\mathbf{w}|^2 = \frac{1}{2} m^i\, |\mathbf{v}'|^2 + \frac{1}{2} m^h\, |\mathbf{w}'|^2\,, \end{aligned} \tag{2.11}$$

still denoting by $(\mathbf{v}, \mathbf{w})$ the molecular velocities of the ingoing particles, and by $(\mathbf{v}', \mathbf{w}')$ the corresponding post–collision velocities. On the other hand, pairs of polyatomic particles may give rise to elastic collisions (with conservations analogous to (2.11)) or to inelastic scattering in which at least one particle passes from one component to another of the same gas:

$$C^i_j + C^h_k \longrightarrow C^i_l + C^h_m\,, \quad A+1 \le i, h \le A+B\,, \quad 1 \le j, l \le L^i\,, \quad 1 \le k, m \le L^h\,. \tag{2.12}$$

In these collisions one has preservation of global momentum (which is the same as before) and of total (kinetic and internal) energy:

$$\frac{1}{2}\, m^i\, |\mathbf{v}|^2 + E^i_j + \frac{1}{2}\, m^h\, |\mathbf{w}|^2 + E^h_k = \frac{1}{2}\, m^i\, |\mathbf{v}'|^2 + E^i_l + \frac{1}{2}\, m^h\, |\mathbf{w}'|^2 + E^h_m\,. \tag{2.13}$$

Analogous inelastic encounters may involve a monatomic and a polyatomic particle as

$$G^i + C^h_j \longrightarrow G^i + C^h_k\,, \quad 1 \le i \le A \quad A+1 \le h \le A+B\,, \quad 1 \le j,k \le L^h\,, \tag{2.14}$$

and conservation of total energy in this case reads as

$$\frac{1}{2}\, m^i\, |\mathbf{v}|^2 + \frac{1}{2}\, m^h\, |\mathbf{w}|^2 + E^h_j = \frac{1}{2}\, m^i\, |\mathbf{v}'|^2 + \frac{1}{2}\, m^h\, |\mathbf{w}'|^2 + E^h_k\,. \tag{2.15}$$

Is only a matter of change of notation proving that, also in this case of inert mixture, collision equilibria are provided by Maxwellian distributions in which all species share the same mean velocity $\mathbf{u}$ and the same temperature T, similarly to what is done in [36, 40] and repeated in Chapter 1. In particular, denoting by $M^i(\mathbf{v};\mathbf{u},T/m^i)$ the Maxwellian

$$M^i\left(\mathbf{v};\mathbf{u},\frac{T}{m^i}\right) = \left(\frac{m^i}{2\,\pi\,T}\right)^{3/2} \exp\left(-\frac{m^i}{2\,T}\,|\mathbf{v}-\mathbf{u}|^2\right), \tag{2.16}$$

the equilibrium state for monatomic gases reads as

$$f^i_M(\mathbf{v}) = n^i\, M^i\left(\mathbf{v};\mathbf{u},\frac{T}{m^i}\right), \qquad\qquad i = 1,\dots,A\,; \tag{2.17}$$

analogously, equilibrium distributions for polyatomic components may be cast as

$$f^i_{jM}(\mathbf{v}) = n^i_j\, M^i\left(\mathbf{v};\mathbf{u},\frac{T}{m^i}\right), \qquad i = A+1,\dots,A+B\,, \quad j = 1,\dots,L^i\,, \tag{2.18}$$

where, as proven in [58] and Chapter 1, number densities of single components n^i_j and the total number density n^i of the gas G^i they belong to are related by the following relation depending on the internal energy levels:

$$n^i_j = n^i\,\frac{\exp\left(-\frac{E^i_j - E^i_1}{T}\right)}{\mathcal{Z}^i(T)}, \tag{2.19}$$

with functions

$$\mathcal{Z}^i(T) = \sum_{k=1}^{L^i} \exp\left(-\frac{E^i_k - E^i_1}{T}\right). \tag{2.20}$$

We have of course $\sum_{j=1}^{L^i} n^i_j = n^i$, and the ratio appearing in (2.19) represents the fraction of particles of the gas G^i belonging to the component C^i_j in any equilibrium state. Notice that, in our frame with increasing energy levels, such fractions are decreasing with respect to the index j, namely in any equilibrium configuration $n^i_1 > n^i_2 > \cdots > n^i_{L^i}$ (the bigger fraction of particles has the lowest energy E^i_1).

This system of particles has $A+B+4$ independent collision invariants, corresponding to preservation of $A+B$ species number densities n^i, of the three components of global momentum $\mathbf{u}$, and of total energy (kinetic plus internal). In the next section we will build up a BGK model for our mixture able to reproduce correct equilibria and collision invariants.

2.2 BGK relaxation model

We generalize here the BGK model proposed in [11] to the present frame of a mixture of gases with a different number of internal energy levels. We suppose that the kinetic equation for each distribution function f^i (with $i = 1, \ldots, A$) and f^i_j (with $i = A+1, \ldots, A+B$ and $j = 1, \ldots, L^i$) has a collision operator constituted by a unique relaxation term, given by a suitable collision frequency multiplied by the difference between the distribution itself and a Maxwellian–type attractor to be properly determined. This idea was originally proposed in [1] for inert mixtures of monatomic gases, and it allows to build up consistent BGK models that, besides Maxwellian equilibria and correct conservation laws, guarantee positivity of distribution functions and species temperatures.

The BGK equations for monatomic gases G^i, with $i = 1, \ldots, A$, read as

$$\frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i = \nu^i (\mathcal{M}^i - f^i) \,, \tag{2.21}$$

while for each polyatomic species G^i, with $i = A+1, \ldots, A+B$, we have a set of L^i kinetic equations, one for each component C^i_j:

$$\frac{\partial f^i_j}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i_j = \nu^i_j (\mathcal{M}^i_j - f^i_j) \,, \qquad j = 1, \ldots, L^i \,. \tag{2.22}$$

In this way, (2.21) and (2.22) constitute a set of $A + L^{A+1} + \cdots + L^{A+B}$ BGK equations, where ν^i and ν^i_j are macroscopic collision frequencies (independent of molecular velocity $\mathbf{v}$, but possibly dependent on macroscopic fields), while $\mathcal{M}^i$ and $\mathcal{M}^i_j$ are Maxwellian attractors:

$$\mathcal{M}^i(\mathbf{v}) = \tilde{n}^i \left(\frac{m^i}{2\,\pi\,\tilde{T}} \right)^{3/2} \exp\left[-\frac{m^i}{2\,\tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right] \,, \qquad i = 1, \ldots, A, \tag{2.23}$$

$$\mathcal{M}^i_j(\mathbf{v}) = \tilde{n}^i_j \left(\frac{m^i}{2\,\pi\,\tilde{T}} \right)^{3/2} \exp\left[-\frac{m^i}{2\tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right] \,, \qquad \begin{array}{l} i = A+1, \ldots, A+B, \\ j = 1, \ldots, L^i, \end{array} \tag{2.24}$$

depending on auxiliary parameters $\tilde{n}^i$ $(i = 1, \ldots, A)$, $\tilde{n}^i_j$ $(i = A+1, \ldots, A+B,\ j = 1, \ldots, L^i)$, $\tilde{\mathbf{u}}$, $\tilde{T}$, to be suitably determined in terms of the actual macroscopic fields. For any polyatomic gas G^i, $i = A+1, \ldots, A+B$, fictitious densities $\tilde{n}^i_j$ are taken bound together as

$$\tilde{n}^i_j = \tilde{n}^i \, \frac{\exp\left(-\frac{E^i_j - E^i_1}{\tilde{T}} \right)}{\mathcal{Z}^i(\tilde{T})} \,. \tag{2.25}$$

In this way, collision equilibria of the BGK model (2.21)–(2.22) are correctly provided by Maxwellian distributions sharing a common velocity and a common temperature, with number densities of components of polyatomic species related to the total density of the gas by the expected relation (2.19).

The attractors are thus defined in terms of the $A + B + 4$ auxiliary disposable parameters $\tilde{n}^i$, $\tilde{\mathbf{u}}$, $\tilde{T}$ which, analogously to the procedure outlined in [1, 11], may be determined in such a way that the BGK model (2.21)–(2.22) preserves the correct $A + B + 4$ collision invariants. Indeed, these requirements yield the equations for preservation of

- number densities of monatomic species

$$\nu^i \int_{\mathbb{R}^3} (\mathcal{M}^i - f^i) d\mathbf{v} = 0 \qquad i = 1, \ldots, A, \tag{2.26}$$

- number densities of polyatomic species

$$\sum_{j=1}^{L^i} \nu_j^i \int_{\mathbb{R}^3} (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = 0 \qquad i = A+1, \dots, A+B, \tag{2.27}$$

- global momentum

$$\sum_{i=1}^{A} \nu^i \, m^i \int_{\mathbb{R}^3} \mathbf{v} \, (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i \, m^i \int_{\mathbb{R}^3} \mathbf{v} \, (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = \mathbf{0}, \tag{2.28}$$

- total energy

$$\sum_{i=1}^{A} \frac{1}{2} \nu^i \, m^i \int_{\mathbb{R}^3} |\mathbf{v}|^2 \, (\mathcal{M}^i - f^i) d\mathbf{v} + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i \int_{\mathbb{R}^3} \left(\frac{1}{2} m^i |\mathbf{v}|^2 + E_j^i \right) (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = 0. \tag{2.29}$$

We prove now that system (2.26)–(2.29) determines uniquely the $A + B + 4$ unknowns $\tilde{n}^i$, $\tilde{\mathbf{u}}$, $\tilde{T}$, for any choice of masses m^i, collision frequencies ν^i, ν_j^i, and internal energies E_j^i of polyatomic components. Constraint (2.26) immediately provides

$$\tilde{n}^i = n^i \,, \qquad i = 1, \dots, A \,, \tag{2.30}$$

consistently with the fact that number densities of monatomic species do not change through binary collisions. On the other hand, as concerns densities of polyatomic gas components, condition (2.27) provides

$$\sum_{h=1}^{L^i} \nu_h^i \, \tilde{n}_h^i = \sum_{j=1}^{L^i} \nu_j^i \, n_j^i \,, \qquad i = A+1, \dots, A+B \,, \tag{2.31}$$

that recalling (2.25) yields

$$\tilde{n}^i = \frac{\left(\displaystyle\sum_{j=1}^{L^i} \nu_j^i \, n_j^i \right) \mathcal{Z}^i(\tilde{T})}{\displaystyle\sum_{h=1}^{L^i} \nu_h^i \exp\left(- \frac{E_h^i - E_1^i}{\tilde{T}} \right)}, \qquad i = A+1, \dots, A+B \,, \tag{2.32}$$

and

$$\tilde{n}_j^i = \frac{\left(\displaystyle\sum_{j=1}^{L^i} \nu_j^i \, n_j^i \right) \exp\left(- \frac{E_j^i - E_1^i}{\tilde{T}} \right)}{\displaystyle\sum_{h=1}^{L^i} \nu_h^i \exp\left(- \frac{E_h^i - E_1^i}{\tilde{T}} \right)} \,, \qquad \begin{array}{c} i = A+1, \dots, A+B \,, \\ j = 1, \dots, L^i. \end{array} \tag{2.33}$$

These formulas determine uniquely the auxiliary number densities of polyatomic components in terms of actual number densities n_j^i, internal energies E_j^i, and auxiliary temperature $\tilde{T}$, that has to be determined too.

Constraint (2.28), related to momentum conservation, yields

$$\sum_{i=1}^{A} \nu^i\, m^i\, n^i\, (\tilde{\mathbf{u}} - \mathbf{u}^i) + \sum_{i=A+1}^{A+B} \left(\sum_{h=1}^{L^i} \nu_h^i\, m^i\, \tilde{n}_h^i \tilde{\mathbf{u}} - \sum_{j=1}^{L^i} \nu_j^i\, m^i\, n_j^i \mathbf{u}_j^i \right) = \mathbf{0}\,, \tag{2.34}$$

that owing to (2.31) provides

$$\tilde{\mathbf{u}} = \frac{\displaystyle\sum_{i=1}^{A} \nu^i\, m^i\, n^i\, \mathbf{u}^i + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i\, m^i\, n_j^i\, \mathbf{u}_j^i}{\displaystyle\sum_{i=1}^{A} \nu^i\, m^i\, n^i + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i\, m^i\, n_j^i}, \tag{2.35}$$

hence $\tilde{\mathbf{u}}$ is an explicit combination of actual number densities and mass velocities of single gas components.

Finally, constraint (2.29) for temperature conservation is more complicated. Using the trivial relations

$$|\mathbf{v} - \tilde{\mathbf{u}}|^2 = |\mathbf{v}|^2 + |\tilde{\mathbf{u}}|^2 - 2\,\mathbf{v} \cdot \tilde{\mathbf{u}}, \tag{2.36}$$

$$|\mathbf{v} - \mathbf{u}^i|^2 = |\mathbf{v}|^2 + |\mathbf{u}^i|^2 - 2\,\mathbf{v} \cdot \mathbf{u}^i, \tag{2.37}$$

$$|\mathbf{v} - \mathbf{u}_j^i|^2 = |\mathbf{v}|^2 + |\mathbf{u}_j^i|^2 - 2\,\mathbf{v} \cdot \mathbf{u}_j^i, \tag{2.38}$$

we integrate (2.29), and recalling the definitions of global temperature in (2.2) and (2.5) we obtain

$$\begin{aligned} &\sum_{i=1}^{A} \nu^i \left\{ \frac{3}{2}\, \tilde{n}^i\, \tilde{T} - \frac{3}{2}\, n^i\, T^i - \frac{1}{2}\, m^i \tilde{n}^i\, |\tilde{\mathbf{u}}|^2 - n^i\, |\mathbf{u}^i|^2 \right\} \\ &+ \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^1} \nu_j^i \left\{ \left[\frac{3}{2}\, \tilde{n}_j^i\, \tilde{T} - \frac{3}{2}\, n_j^i\, T_j^i \right] - \frac{1}{2}\, m^i \left[\tilde{n}_j^i\, |\tilde{\mathbf{u}}|^2 - n_j^i\, |\mathbf{u}_j^i|^2 \right] + E_j^i\, \left[\tilde{n}_j^i - n_j^i \right] \right\} = 0. \end{aligned} \tag{2.39}$$

From the expressions of auxiliary densities in terms of actual ones and auxiliary temperature (2.30), (2.31) and (2.33) we get a transcendental equation for $\tilde{T}$ of the form

$$\mathcal{F}(\tilde{T}) = \Lambda\,, \tag{2.40}$$

where $\mathcal{F}(\tilde{T})$ in (2.40), after some trivial algebra takes the form

$$\mathcal{F}(\tilde{T}) \overset{\mathsf{def}}{=} \left(\sum_{i=1}^{A} \nu^i\, n^i \right) \frac{3}{2}\, \tilde{T} + \sum_{i=A+1}^{A+B} \left(\sum_{j=1}^{L^i} \nu_j^i\, n_j^i \right) \left[\frac{3}{2}\, \tilde{T} + \frac{\displaystyle\sum_{k=1}^{L^i} \nu_k^i\, E_k^i \exp\left(- \frac{E_k^i - E_1^i}{\tilde{T}} \right)}{\displaystyle\sum_{h=1}^{L^i} \nu_h^i \exp\left(- \frac{E_h^i - E_1^i}{\tilde{T}} \right)} \right], \tag{2.41}$$

and the right hand side Λ contains several addends explicit in terms of actual densities, velocities, and energies:

$$\begin{aligned} \Lambda \overset{\mathsf{def}}{=} \frac{1}{2} &\left(\sum_{i=1}^{A} m^i\, \nu^i\, n^i\, \left(|\mathbf{u}^i|^2 - |\tilde{\mathbf{u}}|^2 \right) + \sum_{i=A+1}^{A+B} m^i \sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, \left(|\mathbf{u}_j^i|^2 - |\tilde{\mathbf{u}}|^2 \right) \right) \\ &+ \frac{3}{2} \left(\sum_{i=1}^{A} \nu^i\, n^i\, T^i + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, T_j^i \right) + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu_j^i\, E_j^i\, n_j^i\,. \end{aligned} \tag{2.42}$$

Even in the case with a different number of energy levels for each gas, it can be proved that the terms on the right hand side in (2.42) involving mass velocities are non-negative. Indeed, the expression of the auxiliary velocity $\tilde{\mathbf{u}}$ given in (2.35) provides

$$\sum_{i=1}^{A} m^i\,\nu^i\,n^i\,|\mathbf{u}^i|^2 - \left(\sum_{i=1}^{A} m^i\,\nu^i\,n^i + \sum_{i=A+1}^{A+B} m^i \sum_{j=1}^{L^i} \nu^i_j\,n^i_j\right) |\tilde{\mathbf{u}}|^2 + \sum_{i=A+1}^{A+B} m^i \sum_{j=1}^{L^i} \nu^i_j\,n^i_j\,|\mathbf{u}^i_j|^2 =$$

$$= \left[\sum_{i=1}^{A} \nu^i\,m^i\,n^i + \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i} \nu^i_j\,m^i\,n^i_j\right]^{-1} \left\{\sum_{i,h=1}^{A} m^i\,m^h\,\nu^i\,\nu^h\,n^i\,n^h\,\Big(|\mathbf{u}^i|^2 - \mathbf{u}^i\cdot\mathbf{u}^h\Big)\right.$$

$$+ \sum_{i,h=A+1}^{A+B}\sum_{j=1}^{L^i}\sum_{k=1}^{L^h} m^i\,m^h\,\nu^i_j\,\nu^h_k\,n^i_j\,n^h_k\,\Big(|\mathbf{u}^i_j|^2 - \mathbf{u}^i_j\cdot\mathbf{u}^h_k\Big)$$

$$\left. + \sum_{i=1}^{A}\sum_{h=A+1}^{A+B}\sum_{k=1}^{L^h} m^i\,m^h\,\nu^i\,\nu^h_k\,n^i\,n^h_k\Big(|\mathbf{u}^i|^2 + |\mathbf{u}^h_k|^2 - 2\,\mathbf{u}^i\cdot\mathbf{u}^h_k\Big)\right\}, \tag{2.43}$$

and the content of the curly brackets, by suitable exchanges of indices into each term separately, becomes

$$\frac{1}{2}\sum_{i,h=1}^{A} m^i\,m^h\,\nu^i\,\nu^h\,n^i\,n^h|\mathbf{u}^i - \mathbf{u}^h|^2 + \frac{1}{2}\sum_{i,h=A+1}^{A+B}\sum_{j=1}^{L^i}\sum_{k=1}^{L^h} m^i\,m^h\,\nu^i_j\,\nu^h_k\,n^i_j\,n^h_k\,|\mathbf{u}^i_j - \mathbf{u}^h_k|^2$$

$$+ \sum_{i=1}^{A}\sum_{h=A+1}^{A+B}\sum_{k=1}^{L^h} m^i\,m^h\,\nu^i\,\nu^h_k\,n^i\,n^h_k|\mathbf{u}^i - \mathbf{u}^h_k|^2, \tag{2.44}$$

providing thus the desired positivity result. Consequently, the whole quantity Λ is such that

$$\Lambda \geq \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i} \nu^i_j\,E^i_j\,n^i_j \geq \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i} \nu^i_j\,n^i_j\,E^i_1, \tag{2.45}$$

recalling that $\min_{1\leq j\leq L^i} E^i_j = E^i_1$. Moreover, setting $\mathcal{G}^i(\tilde{T})$ each term in square brackets appearing in (2.41), i.e.

$$\begin{aligned} \mathcal{G}^i(\tilde{T}) &= \frac{3}{2}\tilde{T} + \frac{\displaystyle\sum_{k=1}^{L^i} \nu^i_k\,E^i_k \exp\left(-\,\frac{E^i_k - E^i_1}{\tilde{T}}\right)}{\displaystyle\sum_{h=1}^{L^i} \nu^i_h \exp\left(-\,\frac{E^i_h - E^i_1}{\tilde{T}}\right)} \\ &= \frac{3}{2}\tilde{T} + \frac{\displaystyle\nu^i_1\,E^i_1 + \sum_{k=2}^{L^i} \nu^i_k\,E^i_k \exp\left(-\,\frac{E^i_k - E^i_1}{\tilde{T}}\right)}{\displaystyle\nu^i_1 + \sum_{h=2}^{L^i} \nu^i_h\,\exp\left(-\,\frac{E^i_h - E^i_1}{\tilde{T}}\right)}, \end{aligned} \tag{2.46}$$

we immediately note that $\mathcal{G}^i(\tilde{T}) \geq E_1^i$ for any $\tilde{T} \geq 0$, and moreover we have the strict positivity of

$$(\mathcal{G}^i)'(\tilde{T}) \\ = \frac{3}{2} + \sum_{h,k=1}^{L^i} \nu_k^i \, \nu_h^i \, \frac{\left(E_k^i - E_h^i\right)^2}{2(\tilde{T})^2} \, \exp\left(-\frac{E_k^i + E_h^i - 2\,E_1^i}{\tilde{T}}\right) \left[\sum_{h=1}^{L^i} \nu_h^i \exp\left(-\frac{E_h^i - E_1^i}{\tilde{T}}\right)\right]^{-2} . \tag{2.47}$$

Consequently, the function $\mathcal{F}(\tilde{T})$ is strictly monotonically increasing, and for positive auxiliary temperature $\tilde{T}$ it varies from

$$\lim_{\tilde{T} \to 0} \mathcal{F}(\tilde{T}) = \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} E_1^i \nu_j^i \, n_j^i \tag{2.48}$$

to

$$\lim_{\tilde{T} \to +\infty} \mathcal{F}(\tilde{T}) = +\infty. \tag{2.49}$$

It follows that, keeping inequality (2.45) in mind, the transcendental equation $\mathcal{F}(\tilde{T}) = \Lambda$ admits a unique solution for any value of masses, energies, collision frequencies, and species densities, velocities and temperatures.

This allows to conclude that all auxiliary parameters of this BGK model are uniquely determined in terms of the actual macroscopic fields: number densities coincide with the actual ones for monatomic species and are provided by relations (2.32) for polyatomic species; mass velocity $\tilde{\mathbf{u}}$ is given in (2.35), while temperature $\tilde{T}$, needed also in the construction of auxiliary number densities, is deduced as the unique solution of the transcendental equation (2.40).

2.2.1 *H* - theorem in space homogeneous conditions

As already noticed, equilibrium states correspond to distribution functions coinciding with Maxwellian attractors: $f^i = \mathcal{M}^i$ for $i = 1, \dots, A$, and $f_j^i = \mathcal{M}_j^i$ for $i = A+1, \dots, A+B$ and $j = 1, \dots, L^i$, therefore

$$\mathbf{u}^i = \tilde{\mathbf{u}} = \mathbf{u}\,, \qquad T^i = \tilde{T} = T, \qquad i = 1, \dots, A, \tag{2.50}$$

$$\mathbf{u}_j^i = \tilde{\mathbf{u}} = \mathbf{u}\,, \qquad T_j^i = \tilde{T} = T, \qquad i = A+1, \dots, A+B, \qquad j = 1, \dots, L^i, \tag{2.51}$$

and number densities of polyatomic components n_j^i are related to global density of the corresponding gas n^i and to temperature T by the relation (2.25), providing thus the correct equilibrium Maxwellian configurations (2.17) and (2.18), with the constraint (2.19).

We can also prove the asymptotic stability of such equilibria. Indeed, in space homogeneous conditions, we set $\underline{\mathbf{f}} = (f^1, \dots, f^A, f_1^{A+1}, \dots, f_{L^{A+B}}^{A+B})$, and define the physical entropy as

$$\mathcal{H}[\underline{\mathbf{f}}] = \sum_{i=1}^{A} \int_{\mathbb{R}^3} f^i \, \log\!\left(\frac{f^i}{(m^i)^3}\right) d\mathbf{v} + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \int_{\mathbb{R}^3} f_j^i \, \log\!\left(\frac{f_j^i}{(m^i)^3}\right) d\mathbf{v}, \tag{2.52}$$

thus setting $\underline{\mathbf{f}}^M = (\mathcal{M}^1, \dots, \mathcal{M}^A, \mathcal{M}_1^{A+1}, \dots, \mathcal{M}_{L^{A+B}}^{A+B})$ we have the following classical result.

Theorem 2.2.1. *The entropy functional* (2.52) *is a Lyapunov functional for the BGK model* (2.23) - (2.24)*. More precisely, once the initial state* $\underline{\mathbf{f}}_0$ *is fixed, denoting by* $\underline{\mathbf{f}}^M$ *the corresponding (unique)* *stationary point we have* $\mathcal{H}[\underline{\mathbf{f}}^*\,] > \mathcal{H}[\underline{\mathbf{f}}^M]$ *for any* $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$*, and* $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ *for any* $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$ *while* $\dot{\mathcal{H}}[\underline{\mathbf{f}}^M] = 0$*.*

Proof. The fact that, if conservation of global densities, momentum and energy holds, the $\mathcal{H}$–functional (2.52) takes its minimum value exactly at the equilibrium Maxwellian state has already been shown in Chapter 1, and it is possible to repeat all the same procedure adjusting to the present notation, that would be even simpler since we have directly conservation of total number density for each species. As concerns the entropy inequality, being the time derivative of the entropy, by (2.21)-(2.22) in space homogeneous conditions,

$$\begin{aligned}\dot{\mathcal{H}}[\underline{\mathbf{f}}] &= \sum_{i=1}^{A}\int_{\mathbb{R}^3}\frac{\partial f^i}{\partial t}\,\log\!\left(\frac{f^i}{(m^i)^3}\right)d\mathbf{v} + \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\int_{\mathbb{R}^3}\frac{\partial f^i_j}{\partial t}\,\log\!\left(\frac{f^i_j}{(m^i)^3}\right)d\mathbf{v}\\ &= \sum_{i=1}^{A}\nu^i\int_{\mathbb{R}^3}\left(\mathcal{M}^i - f^i\right)\,\log\!\left(\frac{f^i}{(m^i)^3}\right)d\mathbf{v} + \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\nu^i_j\int_{\mathbb{R}^3}\left(\mathcal{M}^i_j - f^i_j\right)\,\log\!\left(\frac{f^i_j}{(m^i)^3}\right)d\mathbf{v},\end{aligned} \tag{2.53}$$

we have to prove that $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ for all $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$. To this aim, at first we can check that

$$\sum_{i=1}^{A}\nu^i\int_{\mathbb{R}^3}\left(\mathcal{M}^i - f^{i*}\right)\,\log\!\left(\frac{\mathcal{M}^i}{(m^i)^3}\right)d\mathbf{v} + \sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\nu^i_j\int_{\mathbb{R}^3}\left(\mathcal{M}^i_j - f^{i*}_j\right)\,\log\!\left(\frac{\mathcal{M}^i_j}{(m^i)^3}\right)d\mathbf{v} = 0\,. \tag{2.54}$$

The proof of (2.54) is more involved than the one for a mixture of polyatomic gases only, with the same number of energy levels (see [11]). At first we explicitly compute the logarithm of Maxwellian attractors, leading to

$$\begin{aligned}&\sum_{i=1}^{A}\nu^i\int_{\mathbb{R}^3}\left(\mathcal{M}^i - f^{i*}\right)\left[\log\tilde{n}^i - \frac{3}{2}\,\log\!\left(m^i\right) - \frac{3}{2}\,\log\!\left(2\pi\tilde{T}\right)\right]d\mathbf{v}\\ &\quad+\sum_{i=1}^{A}\nu^i\int_{\mathbb{R}^3}\left(\mathcal{M}^i - f^{i*}\right)\left[-\frac{m^i}{2\tilde{T}}\left(|\mathbf{v}|^2 - 2\tilde{\mathbf{u}}\cdot\mathbf{v} + |\tilde{\mathbf{u}}|^2\right)\right]d\mathbf{v}\\ &\quad+\sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\nu^i_j\int_{\mathbb{R}^3}\left(\mathcal{M}^i_j - f^{i*}_j\right)\left[\log\tilde{n}^i_j - \frac{3}{2}\,\log\!\left(m^i\right) - \frac{3}{2}\,\log\!\left(2\pi\tilde{T}\right)\right]d\mathbf{v}\\ &\quad+\sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\nu^i_j\int_{\mathbb{R}^3}\left(\mathcal{M}^i_j - f^{i*}_j\right)\left[-\frac{m^i}{2\tilde{T}}\left(|\mathbf{v}|^2 - 2\tilde{\mathbf{u}}\cdot\mathbf{v} + |\tilde{\mathbf{u}}|^2\right)\right]d\mathbf{v}\,.\end{aligned} \tag{2.55}$$

Then, owing to conservations of momentum and total energy, we note that the contribution due to monatomic species vanishes, while the one due to polyatomic components simplifies to

$$\sum_{i=A+1}^{A+B}\sum_{j=1}^{L^i}\nu^i_j\left(\tilde{n}^i_j - {n^i_j}^*\right)\left[\log\tilde{n}^i_j + \frac{E^i_j}{\tilde{T}}\right], \tag{2.56}$$

that also vanishes since, bearing in mind (2.25) and (2.32), the term

$$\log\tilde{n}^i_j + \frac{E^i_j}{\tilde{T}} = \frac{E^i_1}{\tilde{T}} + \log\left(\sum_{h=1}^{L^i}\nu^i_h\,{n^i_h}^*\right) - \log\left(\sum_{h=1}^{L^i}\nu^i_h\exp\left(-\,\frac{E^i_h - E^i_1}{\tilde{T}}\right)\right) \tag{2.57}$$

does not depend on the subindex j and the equality (2.31) holds for any index i. Then, by subtracting (2.54) from (2.53) we easily get that for any $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$

$$\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] = -\int_{\mathbb{R}^3} \left[\sum_{i=1}^{A} \nu^i (f^{i*} - \mathcal{M}^i) \log\left(\frac{f^{i*}}{\mathcal{M}^i}\right) + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} \nu^i_j (f^{i*}_j - \mathcal{M}^i_j) \log\left(\frac{f^{i*}_j}{\mathcal{M}^i_j}\right) \right] d\mathbf{v} \tag{2.58}$$

and the inequality $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ holds owing to usual convexity arguments applied to the function $x\log(x)$. $\square$

2.3 Macroscopic equations

In this section, starting from our BGK model (2.21)–(2.22), we derive evolution equations for the main macroscopic fields useful in physical applications, namely for species number densities, mass velocities and temperatures of monatomic species (n^i, $\mathbf{u}^i$, T^i, for $i = 1, \dots, A$) and all components of polyatomic gases (n^i_j, $\mathbf{u}^i_j$, T^i_j, for $i = A+1, \dots, A+B$, and $j = 1, \dots, L^i$). As illustrated at the beginning of Section 2.1, such macroscopic quantities may be obtained as suitable moments of distribution functions, therefore their balance equations are recovered (following the same procedure used in the preliminaries for the Boltzmann case) by multiplying the BGK equations by suitable weight functions $\varphi^i(\mathbf{v})$, $\varphi^i_j(\mathbf{v})$, obtaining

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} \varphi^i(\mathbf{v})\, f^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v}\, \varphi^i(\mathbf{v})\, f^i(\mathbf{v})\, d\mathbf{v} = \nu^i \int_{\mathbb{R}^3} \varphi^i(\mathbf{v}) \big(\mathcal{M}^i(\mathbf{v}) - f^i(\mathbf{v})\big)\, d\mathbf{v}\,, \tag{2.59}$$

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} \varphi^i_j(\mathbf{v})\, f^i_j(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v}\, \varphi^i_j(\mathbf{v})\, f^i_j(\mathbf{v})\, d\mathbf{v} = \nu^i_j \int_{\mathbb{R}^3} \varphi^i_j(\mathbf{v}) \big(\mathcal{M}^i_j(\mathbf{v}) - f^i_j(\mathbf{v})\big)\, d\mathbf{v}\,, \tag{2.60}$$

for monatomic or polyatomic components, respectively. More precisely, equations for number densities correspond to the option $\varphi^i(\mathbf{v}) = \varphi^i_j(\mathbf{v}) = 1$ for all components, equations for mean velocities are provided by $\varphi^i(\mathbf{v}) = \varphi^i_j(\mathbf{v}) = \mathbf{v}$, while equations for temperatures involve the computation of the second order moments with $\varphi^i(\mathbf{v}) = \varphi^i_j(\mathbf{v}) = |\mathbf{v}|^2$. The streaming terms of such equations (obtained performing integrals on the left-hand side of (2.59) - (2.60)) are of course the classical ones [36] and we briefly report here results adjusting them to the present notation.

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} f^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v}\, f^i(\mathbf{v})\, d\mathbf{v} = \frac{\partial n^i}{\partial t} + \nabla_{\mathbf{x}} \cdot (n^i\, \mathbf{u}^i), \tag{2.61}$$

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v})\, f^i(\mathbf{v})\, d\mathbf{v} = \frac{\partial (n^i \mathbf{u}^i)}{\partial t} + \nabla_{\mathbf{x}} \cdot (n^i\, (\mathbf{u}^i \otimes \mathbf{u}^i)) + \frac{1}{m^i} \nabla_{\mathbf{x}} \cdot \mathbf{P}^i, \tag{2.62}$$

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\mathbb{R}^3} |\mathbf{v}|^2 f^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (|\mathbf{v}|^2 \mathbf{v})\, f^i(\mathbf{v})\, d\mathbf{v} = {} & \frac{3}{m^i} \frac{\partial (n^i T^i)}{\partial t} + \frac{\partial (|\mathbf{u}^i|^2 n^i)}{\partial t} \\ & + \frac{2}{m^i} \nabla_{\mathbf{x}} \cdot (\mathbf{u}^i \cdot \mathbf{P}^i + \mathbf{q}^i), \end{aligned} \tag{2.63}$$

for $i = 1, \dots, A$, and

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_j^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v}\, f_j^i(\mathbf{v})\, d\mathbf{v} = \frac{\partial n_j^i}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_j^i\, \mathbf{u}_j^i), \tag{2.64}$$

$$\frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_j^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v})\, f_j^i(\mathbf{v})\, d\mathbf{v} = \frac{\partial (n_j^i \mathbf{u}_j^i)}{\partial t} + \nabla_{\mathbf{x}} \cdot (n_j^i\, (\mathbf{u}_j^i \otimes \mathbf{u}_j^i)) + \frac{1}{m^i} \nabla \cdot \mathbf{P}_j^i, \tag{2.65}$$

$$\begin{aligned} \frac{\partial}{\partial t} \int_{\mathbb{R}^3} |\mathbf{v}|^2 f_j^i(\mathbf{v})\, d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (|\mathbf{v}|^2 \mathbf{v})\, f_j^i(\mathbf{v})\, d\mathbf{v} = {} & \frac{3}{m^i} \frac{\partial (n_j^i T_j^i)}{\partial t} + \frac{\partial (|\mathbf{u}_j^i|^2 n_j^i)}{\partial t} \\ & + \frac{2}{m^i} \nabla_{\mathbf{x}} \cdot (\mathbf{u}_j^i \cdot \mathbf{P}_j^i + \mathbf{q}_j^i), \end{aligned} \tag{2.66}$$

for $i = A+1, \dots, A+B, j = 1, \dots, L^i$, being $\mathbf{P}^i$, $\mathbf{q}^i$, $\mathbf{P}_j^i$, $\mathbf{q}_j^i$ the pressure tensors and heat fluxes for monatomic species and polyatomic components introduced in (2.3) and (2.6), respectively.

Now we focus the attention on the scattering contributions, i.e. integrals on the right-hand side of (2.59) - (2.60). In the equations for number densities we have

$$\int_{\mathbb{R}^3} \big(\mathcal{M}^i(\mathbf{v}) - f^i(\mathbf{v})\big)\, d\mathbf{v} = 0\,, \quad i = 1, \dots, A\,, \tag{2.67}$$

consistently with the fact that particles of monatomic gases do not change during the evolution, while

$$\int_{\mathbb{R}^3} \big(\mathcal{M}_j^i(\mathbf{v}) - f_j^i(\mathbf{v})\big)\, d\mathbf{v} = \tilde{n}_j^i - n_j^i\,, \quad i = A+1, \dots, A+B, \quad j = 1, \dots, L^i \tag{2.68}$$

for polyatomic components. Momentum exchange rates read as

$$\int_{\mathbb{R}^3} \mathbf{v}\, \big(\mathcal{M}^i(\mathbf{v}) - f^i(\mathbf{v})\big)\, d\mathbf{v} = n^i\, (\tilde{\mathbf{u}} - \mathbf{u}^i)\,, \quad i = 1, \dots, A\,, \tag{2.69}$$

and

$$\int_{\mathbb{R}^3} \mathbf{v}\, \big(\mathcal{M}_j^i(\mathbf{v}) - f_j^i(\mathbf{v})\big)\, d\mathbf{v} = \tilde{n}_j^i\, \tilde{\mathbf{u}} - n_j^i\, \mathbf{u}_j^i\,, \quad i = A+1, \dots, A+B, \quad j = 1, \dots, L^i. \tag{2.70}$$

Analogous results hold for the second order moments:

$$\int_{\mathbb{R}^3} |\mathbf{v}|^2\, \big(\mathcal{M}^i(\mathbf{v}) - f^i(\mathbf{v})\big)\, d\mathbf{v} = \frac{3\, n^i}{m^i}\, (\tilde{T} - T^i) + n^i (|\tilde{\mathbf{u}}|^2 - |\mathbf{u}^i|^2)\,, \quad i = 1, \dots, A\,, \tag{2.71}$$

and

$$\begin{gathered} \int_{\mathbb{R}^3} |\mathbf{v}|^2\, \big(\mathcal{M}_j^i(\mathbf{v}) - f_j^i(\mathbf{v})\big)\, d\mathbf{v} = \frac{3}{m^i}\, (\tilde{n}_j^i\, \tilde{T} - n_j^i\, T_j^i) + \tilde{n}_j^i\, |\tilde{\mathbf{u}}|^2 - n_j^i\, |\mathbf{u}_j^i|^2\,, \\ i = A+1, \dots, A+B, \qquad j = 1, \dots, L^i. \end{gathered} \tag{2.72}$$

With these results at hand, some simple algebra allows to write down four independent equations for the main fields of each component. For the monatomic gases ($i = 1, \dots, A$) macroscopic equations may be cast as

$$\begin{cases} \dfrac{\partial n^i}{\partial t} + \nabla_{\mathbf{x}} \cdot (n^i\, \mathbf{u}^i) = 0\,, \\ n^i \left(\dfrac{\partial \mathbf{u}^i}{\partial t} + \mathbf{u}^i \cdot \nabla_{\mathbf{x}} \mathbf{u}^i \right) + \dfrac{1}{m^i}\, \nabla_{\mathbf{x}} \cdot \mathbf{P}^i = \nu^i\, n^i (\tilde{\mathbf{u}} - \mathbf{u}^i)\,, \\ \dfrac{3}{2}\, n^i \left(\dfrac{\partial T^i}{\partial t} + \mathbf{u}^i \cdot \nabla_{\mathbf{x}} T^i \right) + \mathbf{P}^i : \nabla_{\mathbf{x}} \mathbf{u}^i + \nabla_{\mathbf{x}} \cdot \mathbf{q}^i = \\ \qquad\qquad = \nu^i\, n^i \left[\dfrac{3}{2}\, (\tilde{T} - T^i) + \dfrac{1}{2}\, m^i\, |\tilde{\mathbf{u}} - \mathbf{u}^i|^2 \right], \end{cases} \tag{2.73}$$

while for the components of the polyatomic species ($i = A+1, \dots, A+B$, $j = 1, \dots, L^i$) one has

$$\begin{cases} \dfrac{\partial n^i_j}{\partial t} + \nabla_{\mathbf{x}} \cdot (n^i_j\, \mathbf{u}^i_j) = \nu^i_j (\tilde{n}^i_j - n^i_j)\,, \\ n^i_j \left(\dfrac{\partial \mathbf{u}^i_j}{\partial t} + \mathbf{u}^i_j \cdot \nabla_{\mathbf{x}} \mathbf{u}^i_j \right) + \dfrac{1}{m^i}\, \nabla_{\mathbf{x}} \cdot \mathbf{P}^i_j = \nu^i_j\, \tilde{n}^i_j (\tilde{\mathbf{u}} - \mathbf{u}^i_j)\,, \\ \dfrac{3}{2}\, n^i_j \left(\dfrac{\partial T^i_j}{\partial t} + \mathbf{u}^i_j \cdot \nabla_{\mathbf{x}} T^i_j \right) + \mathbf{P}^i_j : \nabla_{\mathbf{x}} \mathbf{u}^i_j + \nabla_{\mathbf{x}} \cdot \mathbf{q}^i_j = \\ \qquad\qquad = \nu^i_j\, \tilde{n}^i_j \left[\dfrac{3}{2}\, (\tilde{T} - T^i_j) + \dfrac{1}{2}\, m^i\, |\tilde{\mathbf{u}} - \mathbf{u}^i_j|^2 \right]. \end{cases} \tag{2.74}$$

2.3.1 Numerical simulations

We report now some numerical simulations of the macroscopic equations in space homogeneous conditions just for illustrative purposes, in order to check and comment on the trend towards equilibria of the main macroscopic fields, for varying parameters. The space homogeneous version of evolution equations (2.73)–(2.74) reads as

$$\begin{cases} \dfrac{\partial n^i}{\partial t} = 0\,, & i = 1, \dots, A, \\ \dfrac{\partial n^i_j}{\partial t} = \nu^i_j (\tilde{n}^i_j - n^i_j)\,, & \begin{array}{l} i = A+1, \dots, A+B, \\ j = 1, \dots, L^i, \end{array} \\ \dfrac{\partial \mathbf{u}^i}{\partial t} = \nu^i (\tilde{\mathbf{u}} - \mathbf{u}^i)\,, & i = 1, \dots, A, \\ \dfrac{\partial \mathbf{u}^i_j}{\partial t} = \nu^i_j\, \dfrac{\tilde{n}^i_j}{n^i_j} (\tilde{\mathbf{u}} - \mathbf{u}^i_j)\,, & \begin{array}{l} i = A+1, \dots, A+B, \\ j = 1, \dots, L^i, \end{array} \\ \dfrac{\partial T^i}{\partial t} = \nu^i \left(\tilde{T} - T^i + \dfrac{1}{3}\, m^i\, |\tilde{\mathbf{u}} - \mathbf{u}^i|^2 \right), & i = 1, \dots, A, \\ \dfrac{\partial T^i_j}{\partial t} = \nu^i_j\, \dfrac{\tilde{n}^i_j}{n^i_j} \left(\tilde{T} - T^i_j + \dfrac{1}{3}\, m^i\, |\tilde{\mathbf{u}} - \mathbf{u}^i_j|^2 \right), & \begin{array}{l} i = A+1, \dots, A+B, \\ j = 1, \dots, L^i, \end{array} \end{cases} \tag{2.75}$$

where $\tilde{n}^i_j$ is provided by (2.25) and (2.32), $\tilde{\mathbf{u}}$ is explicitly given in (2.35), and $\tilde{T}$ may be obtained as the unique solution of the transcendental equation (2.40). Equations (2.75) constitute thus a closed system of $4(A + L^{A+1} + \cdots + L^{A+B})$ equations, having as unknowns densities, velocities and temperatures of monatomic gases and of all components of polyatomic species. Once the initial state $(n^i)_0$, $(n^i_j)_0$, $(\mathbf{u}^i)_0$, $(\mathbf{u}^i_j)_0$, $(T^i)_0$, $(T^i_j)_0$ is assigned, the corresponding equilibrium configuration is unique and may be determined (analogously to the procedure used to relate auxiliary parameters with the actual ones) bearing in mind the conservations of densities n^i of monatomic gases, total densities $\sum_{j=1}^{L^i} n^i_j$ of polyatomic gases, global velocity $\mathbf{u}$ and total energy $\frac{3}{2}T + \sum_{i=A+1}^{A+B} \sum_{j=1}^{L^i} E^i_j\, n^i_j$.

We will show here results relevant to two different test cases: at first, a mixture of a monatomic and a polyatomic gas, and then a mixture of two polyatomic gases. In both cases, for masses of gas species, internal energy levels and initial values for number density, mean velocity and temperature of each component, we set dimensionless quantities. The system (2.75) is simulated by means of MATLAB routines for ordinary differential equations, based on the implementation of the explicit Runge–Kutta method proposed in [26]. At each time step, a bisection method is used to solve the transcendental equation (2.40) for the auxiliary temperature.

Test 1 - Mixture of one monatomic and one polyatomic gas

In the first test case, we consider a monatomic gas G^1 and a polyatomic species G^2, that is assumed to be divided into three different components C^2_1, C^2_2, C^2_3, each one endowed with its internal energy:

$$E^2_1 = 5, \quad E^2_2 = 6, \quad E^2_3 = 9. \tag{2.76}$$

From now on, in place of number densities we will consider the components concentrations

$$c^i = n^i \left[\sum_{h=1}^{A} n^h + \sum_{h=A+1}^{A+B} \sum_{k=1}^{L^h} n^h_k \right]^{-1}, \qquad c^i_j = n^i_j \left[\sum_{h=1}^{A} n^h + \sum_{h=A+1}^{A+B} \sum_{k=1}^{L^h} n^h_k \right]^{-1}, \tag{2.77}$$

and also velocities and temperatures will be suitably normalized. Initial data for number concentrations, velocities and temperatures are given in Table 2.1.

	G^1	C^2_1	C^2_2	C^2_3
c_0	0.32	0.26	0.19	0.22
u_0	0.3	0	0.1	0.4
T_0	2	4	1	2.5

Table 2.1

Collision frequencies, instead, are taken as in [11], where they have been estimated imposing that average loss terms of Boltzmann equations equal the BGK ones. For the monatomic gas, collision frequency turns out to be a linear combination of number densities provided by

$$\nu^1 = \frac{1}{20} \left(n^1 + \sum_{j=1,2,3} n^2_j \right). \tag{2.78}$$

The result for the polyatomic components is more complicated, since one has to separate the exothermic transitions, where the post–collision internal energy is less than the pre–collision value, from the endothermic transitions, where the internal energy increases through the collision. Setting for $j = 1, 2, 3$

$$\mathcal{D}^{ex}{}^2_j = \{k, l, m = 1, 2, 3 \quad : \quad E^2_l + E^2_m - E^2_j - E^2_k \leq 0\}, \tag{2.79}$$

$$\mathcal{D}^{en}{}^2_j = \{k, l, m = 1, 2, 3 \quad : \quad E^2_l + E^2_m - E^2_j - E^2_k > 0\}, \tag{2.80}$$

we finally take

$$\nu^2_j = \frac{1}{20} n^1 + \sum_{k,l,m,\in \mathcal{D}^{ex}{}^2_j} \nu^{l,m}_{k,j} n^2_k + \sum_{k,l,m,\in \mathcal{D}^{en}{}^2_j} \nu^{l,m}_{k,j} n^2_k \exp\left(\frac{E^2_j + E^2_k - E^2_l - E^2_m}{T}\right), \tag{2.81}$$

with $\nu^{l,m}_{k,j} = \dfrac{k+j}{20(l+m)}$.

We want to investigate the behavior of the mixture when the masses of the two considered gas species are relevantly different. For this reason we shall take as reference case the one where the mass ratio can be approximated by one. This case can occur in a realistic framework taking as monatomic gas Argon Ar (39.95 g/mol) and as polyatomic Fluorine Gas F_2 (37.99 g/mol). Then, with masses $m^1 = 1.05$, $m^2 = 1$, equilibrium values for concentrations c^1_M, c^2_{jM}, global mean velocity u_M and temperature T_M are reported in Table 2.2.

	G^1	C^2_1	C^2_2	C^2_3
c_M	0.32	0.35	0.24	0.08
u_M	0.21	0.21	0.21	0.21
T_M	2.79	2.79	2.79	2.79

Table 2.2

The dynamics in time of species concentrations c^1 and c^2_j, normalized velocities $\bar{u}^1 = u^1/u_M$ and $\bar{u}^2_j = u^2_j/u_M$, normalized temperatures $\bar{T}^1 = T^1/T_M$ and $\bar{T}^2_j = T^2_j/T_M$ are computed numerically and showed in Figure 2.1.

Of course the concentration of the monatomic gas G^1 remains constant, while the equilibrium densities of the components of G^2 are decreasing with respect to their subindex, consistently with the equilibrium condition (2.25). Velocities and temperatures show a monotone trend to the corresponding equilibrium value.

Now we consider the case when the mass of the polyatomic species is much bigger than the mass of the monatomic one. More precisely, we take $m^1 = 1$ and $m^2 = 64.97$; this ratio between masses can be obtained with Helium He (4 g/mol) and Iodine Heptafluoride IF_7 (259.89 g/mol). Equilibrium values for concentrations in this case are shown in Table 2.3, as well as the equilibrium velocity and temperature normalized with respect to the equilibrium values of the reference case: $\bar{u}_M = u_M/0.21$, $\bar{T}_M = T_M/2.79$.

Finally, we assume the monatomic gas to have mass significantly bigger than the polyatomic one. For example, considering Radon Rn (222 g/mo) and molecular Hydrogen H_2 (2.02 g/mol), we have a ratio that will be numerically represented choosing $m^1 = 111$ and $m^2 = 1$. Normalized equilibrium values obtained in this case are the ones in Table 2.4.

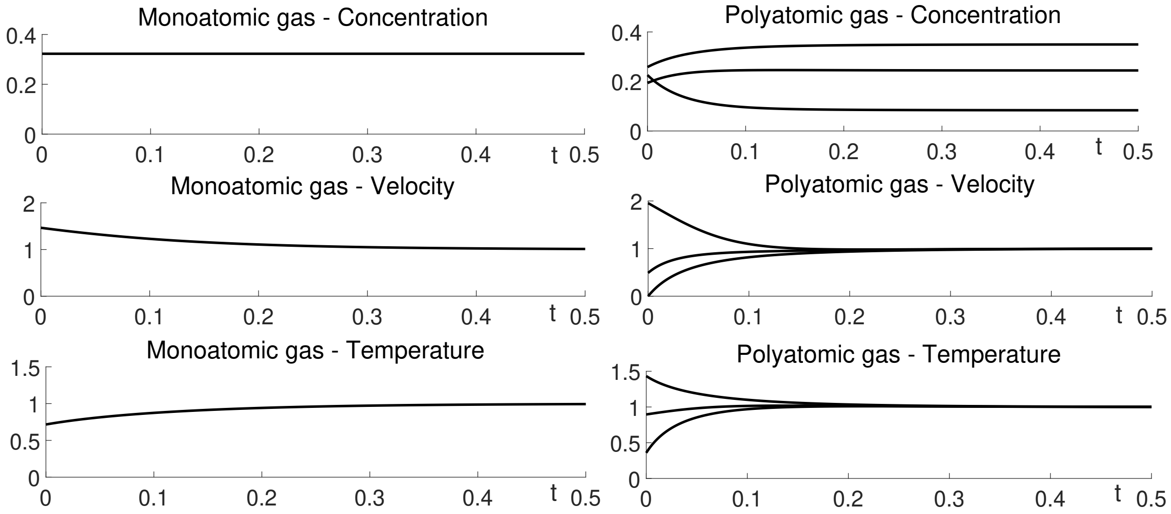

Figure 2.1: Test 1, concentrations, normalized velocities and temperatures for a mixture of a monatomic and a polyatomic gas with energy levels as in (2.76) and initial values as in Table 2.1, considering masses $(m^1, m^2) = (1.05, 1)$.

	G^1	C_1^2	C_2^2	C_3^2
c_M	0.32	0.34	0.24	0.09
$\bar{u}_M$	0.76	0.76	0.76	0.76
$\bar{T}_M$	1.14	1.14	1.14	1.14

Table 2.3

	G^1	C_1^2	C_2^2	C_3^2
c_M	0.32	0.35	0.24	0.08
$\bar{u}_M$	1.38	1.38	1.38	1.38
$\bar{T}_M$	1	1	1	1

Table 2.4

We observe that the equilibrium velocity depends only on mass ratio, and it is slightly increasing versus the ratio m^1/m^2. Number densities and temperature at equilibrium, instead, depend mainly on the polyatomic gas mass value: when it is small, values are approximately the same for any choice for the mass of the monatomic gas, while, when it is bigger, the equilibrium temperature is a bit higher and densities values are slightly closer to each other. Numerical results for these other two mixtures are reported in Figure 2.2.

We notice that in these examples with the gases having disparate masses, velocities and temperatures of the three components of the polyatomic gas (dashed line) tend to assume at first a common value and after they still evolve together until they reach the prescribed equilibrium. This separation between light and heavy particles, with the two species reaching at first a local Maxwellian equilib-

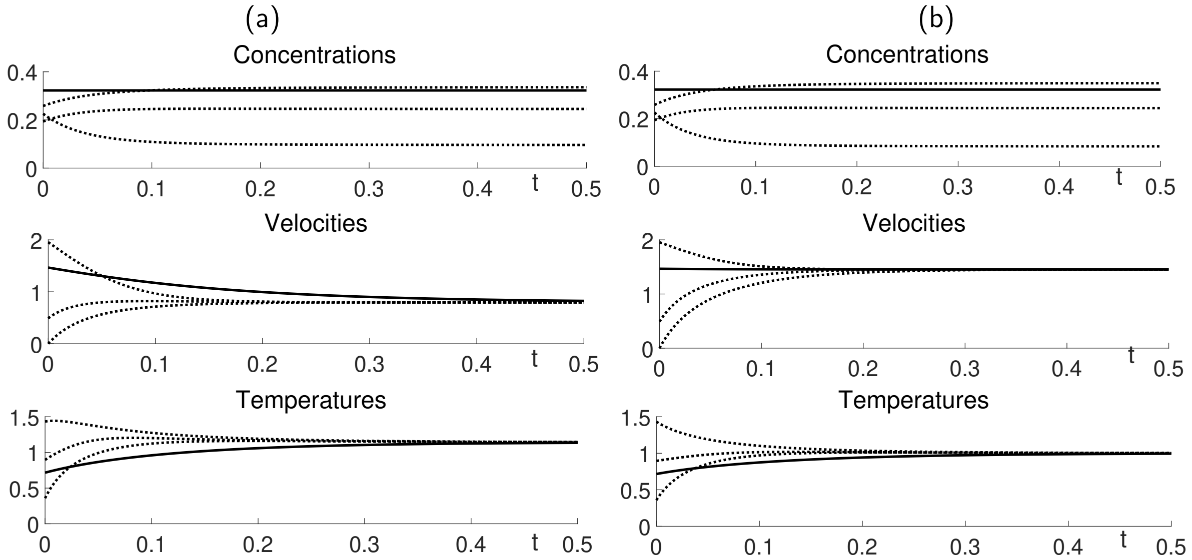

Figure 2.2: Test 1, concentrations, normalized velocities and temperatures for a mixture of a monatomic (solid line) and a polyatomic (dotted line) gas with energy levels as in (2.76) and initial values as in Table 2.1, considering masses $(m^1, m^2) = (1, 64.97)$ (panel (a)) and $(m^1, m^2) = (111, 1)$ (panel (b)).

rium and converging then to the global steady state, is in agreement with several physical problems discussed in the pertinent literature [17, 68, 84]. Moreover, in the case with the mass of the polyatomic molecules much higher than the one of the monatomic particles, temperatures of polyatomic components show a slight overshooting, namely a non monotone trend to the equilibrium.

Test 2 - Mixture of two polyatomic gases having similar masses

We consider now a mixture of two polyatomic gas species, G^1 and G^2. We suppose that the first one has two possible internal energy levels and that the second one has three of them. In this way, the mixture is composed by five different components, namely C_1^1, C_2^1, C_1^2, C_2^2, C_3^2. As before, we set collision frequencies defining the sets, for $i = 1, 2$ and $j = 1, 2, 3$ (for a simpler notation, we shall indicate three energy levels for the first gas too, imposing for the third energy value $E_3^1 = 0$)

$$\mathcal{D}^{ex}{}_j^i = \Big\{h = 1, 2, \quad k, l, m = 1, 2, 3 \quad : \quad E_l^i + E_m^h - E_j^i - E_k^h \leq 0\Big\}, \tag{2.82}$$

$$\mathcal{D}^{en}{}_j^i = \Big\{h = 1, 2, \quad k, l, m = 1, 2, 3 \quad : \quad E_l^i + E_m^h - E_j^i - E_k^h > 0\Big\}, \tag{2.83}$$

and choosing

$$\nu_j^i = \sum_{h,k,l,m, \in \mathcal{D}^{ex}{}_j^i} \nu_{k,j}^{l,m} n_k^h + \sum_{k,l,m, \in \mathcal{D}^{en}{}_j^i} \nu_{k,j}^{l,m} n_k^h \exp\left(\frac{E_j^i + E_k^h - E_l^i - E_m^h}{T}\right), \tag{2.84}$$

with $\nu_{k,j}^{l,m} = \dfrac{k + j}{20(l + m)}$.

At first, we show the case of gas species having similar masses and we let values of energy levels vary. This case can be represented by taking as gas species Nitrous Oxide N_2O (44 g/mol) and

Ozone O_3 (48 g/mol). For numerical simulation we take $m^1 = 1$, $m^2 = 1.09$ and initial data for concentrations, velocities and temperatures those reported in Table 2.5.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2
c_0	0.25	0.22	0.2	0.15	0.175
u_0	0.3	0.2	0	0.1	0.4
T_0	2	3.5	4	1	2.5

Table 2.5

We set as reference case internal energy levels

$$E_1^1 = 2, \quad E_2^1 = 4, \quad E_1^2 = 5, \quad E_2^2 = 6, \quad E_3^2 = 9, \tag{2.85}$$

obtaining as equilibrium values for concentrations, mean velocity and temperature the ones reported in Table 2.6.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2
c_M	0.31	0.16	0.26	0.19	0.07
u_M	0.20	0.20	0.20	0.20	0.20
T_M	3.02	3.02	3.02	3.02	3.02

Table 2.6

The evolution of macroscopic quantities in this case is presented in Figure 2.3.

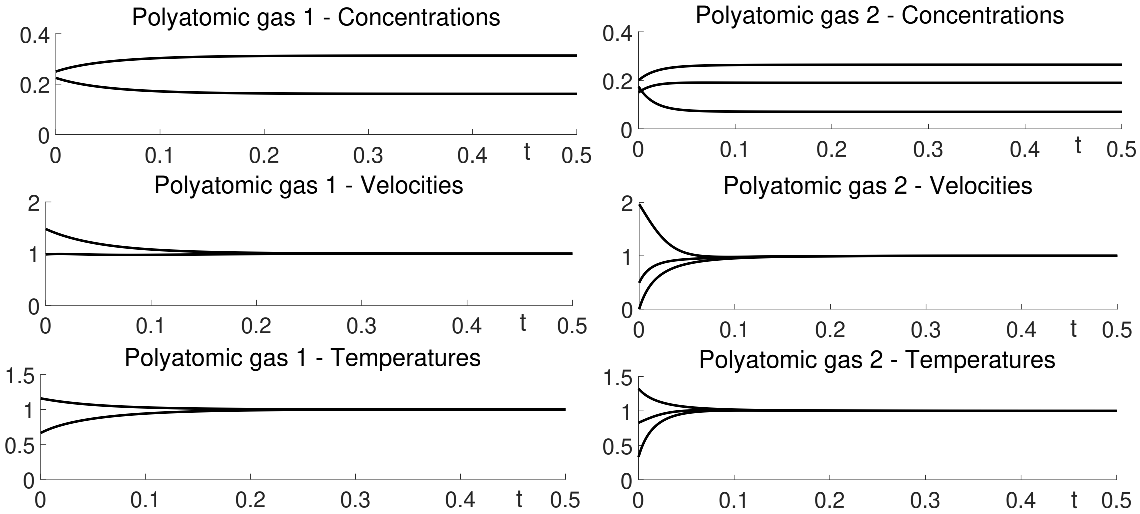

Figure 2.3: Test 2, concentrations, normalized velocities and temperatures for a mixture of two polyatomic gases with energy levels as in (2.85) and initial values as in Table 2.5, considering masses $(m^1, m^2) = (1, 1.09)$.

We want to show evolution of global quantities considering different values for internal energy levels.

First, with respect to energies in the reference case (2.85), we increase each amount of internal energy

$$E_1^1 = 38, \quad E_2^1 = 40, \quad E_1^2 = 35, \quad E_2^2 = 36, \quad E_3^2 = 39, \tag{2.86}$$

then we increase only energy levels of the second gas

$$E_1^1 = 2, \quad E_2^1 = 4, \quad E_1^2 = 35, \quad E_2^2 = 36, \quad E_3^2 = 39. \tag{2.87}$$

In both cases we obtain equilibrium values that are not significantly different from the reference ones.

As third case, we only increase the gap between the lower and the higher energy level for each species,

$$E_1^1 = 4, \quad E_2^1 = 40, \quad E_1^2 = 5, \quad E_2^2 = 18, \quad E_3^2 = 39, \tag{2.88}$$

obtaining the normalized steady values c_M^i, c_{jM}^i, $\bar{u}_M = u_M/0.20$, $\bar{T}_M = T_M/3.02$ reported in Table 2.7.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2
c_M	0.45	0.02	0.38	0.12	0.02
$\bar{u}_M$	1	1	1	1	1
$\bar{T}_M$	3.77	3.77	3.77	3.77	3.77

Table 2.7

Numerical results for the evolution of concentrations, normalized velocities and temperatures corresponding to the options (2.86), (2.87), (2.88) are shown in Figure 2.4.

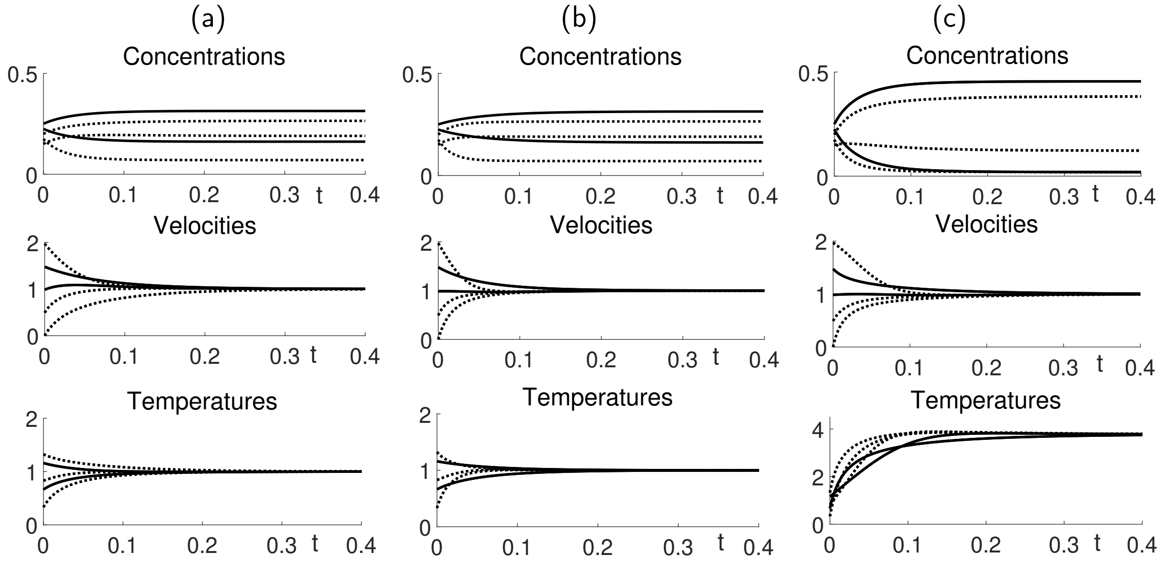

Figure 2.4: Test 2, concentrations, normalized velocities and temperatures for a mixture of a two component (solid line) and a three component (dotted line) polyatomic gas with initial values as in Table 2.5, considering masses $(m^1, m^2) = (1, 1.09)$ and taking energy levels as in (2.86) (panel (a)), (2.87) (panel (b)) and (2.88) (panel (c)).

We point out that when there is a bigger gap between energy values as in (2.88), there is also a bigger gap between concentrations of components corresponding to the highest and to the lowest energy levels. Moreover, a high gap between internal energies causes a considerably higher value for the final temperature (see panel (c)), since it is strongly affected by all the differences $E^i_j - E^i_1$.

We may also observe that, when there is a quite big difference between the total amount of internal energy of the two species, as in (2.87) (panel (b)), the one with higher internal energy levels reaches the equilibrium faster.

At this point, we investigate the case in which one of the two polyatomic gases has a higher total density. We set as initial values for concentrations the ones reported in Table 2.8.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
c_0	0.47	0.43	0.04	0.03	0.03

Table 2.8

Then we keep initial values for velocities and temperatures the same of the reference case (Table 2.5) and energy levels as in (2.85). Normalized equilibrium values c^i_M, c^i_{jM}, $\bar{u}_M = u_M/0.20$, $\bar{T}_M = T_M/3.02$ are listed in Table 2.9.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
c_M	0.60	0.30	0.05	0.04	0.01
$\bar{u}_M$	1.20	1.20	1.20	1.20	1.20
$\bar{T}_M$	0.97	0.97	0.97	0.97	0.97

Table 2.9

Normalized final values for mean velocity and temperature in this case are very close to the ones obtained considering only the first gas (that would be $\bar{u}_M = 1.25$ and $\bar{T}_M = 0.96$). Time behavior of velocities and temperatures are compared with the reference case in Figure 2.5.

We can observe that the presence of a higher concentration of the first gas species leads it to a faster reaching of equilibrium state. Indeed, the species with very high concentration plays the role of a background medium (for instance, the atmosphere), in which a rarefied gas (for instance, a pollutant powder) is diffusing. It has been proved that in this low density limit the particles dynamics may be modelled by a linear Boltzmann equation [116], and the equilibrium velocity and temperature coincide with the corresponding background values [36].

Test 3 - Mixture of two polyatomic gases having different masses

As final test, we show the case of two polyatomic gases having different masses. Keeping in mind a real case of Hydrogen H_2 (2 g/mol) and Arsine AsH_3 (77.95 g/mol), we take as masses $m^1 = 1$ and $m^2 = 38.97$. We consider three different scenarios changing initial velocities of the components. Firstly we take initial values as in Table 2.5 and energy levels as in (2.85), obtaining equilibrium values reported in Table 2.10.

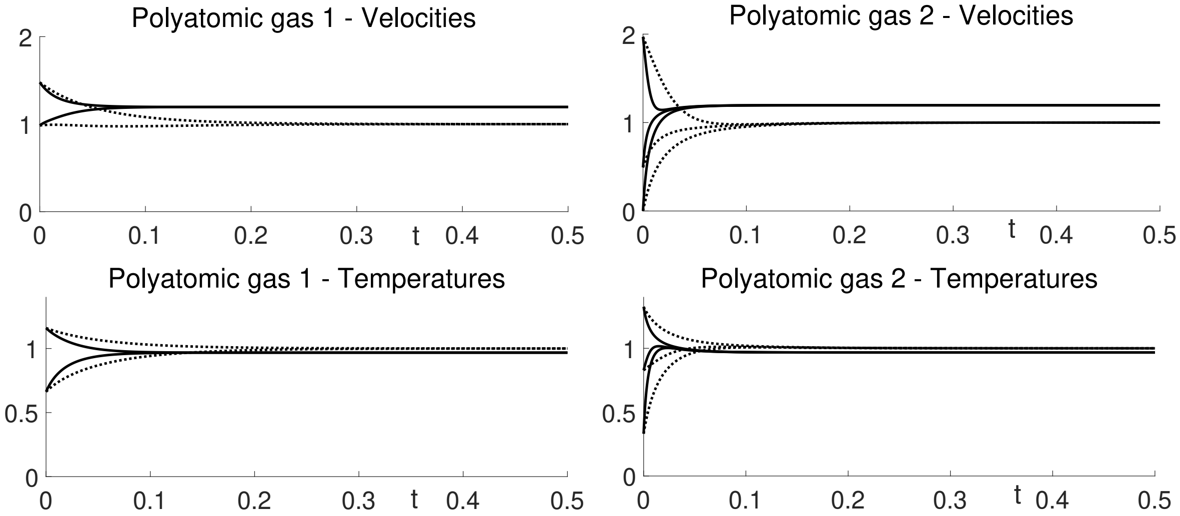

Figure 2.5: Test 2, normalized velocities and temperatures for a mixture of two polyatomic gases with energy levels as in (2.85) and initial values for velocities and temperatures as in Table 2.5, considering masses $(m^1, m^2) = (1, 1.09)$ and taking initial values for concentrations as in Table 2.8 (solid line) and Table 2.5 (dotted line).

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2
c_M	0.31	0.16	0.26	0.20	0.07
u_M	0.16	0.16	0.16	0.16	0.16
T_M	3.20	3.20	3.20	3.20	3.20

Table 2.10

Time behavior of normalized global quantities in this case is shown in Figure 2.6.

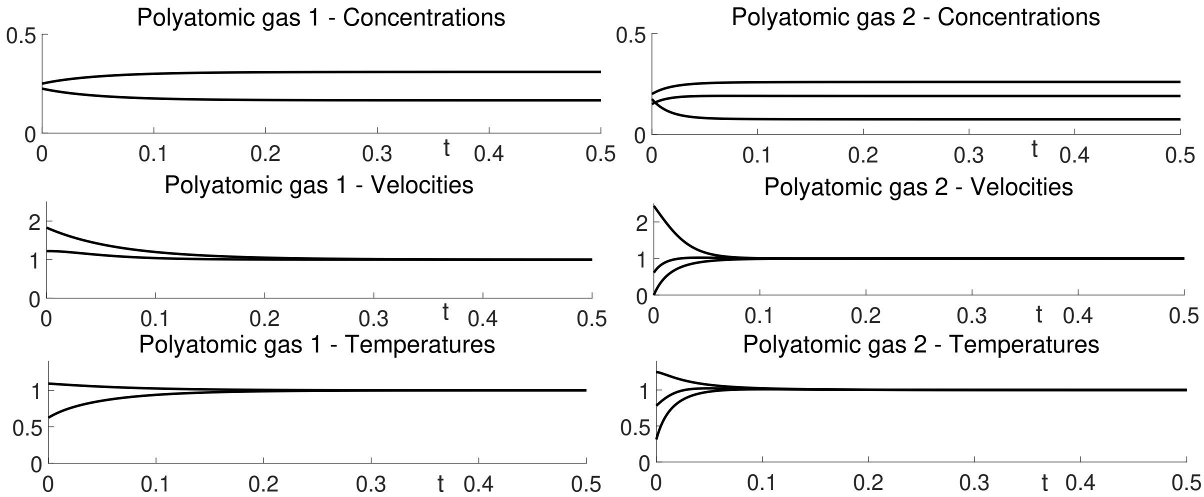

Figure 2.6: Test 3, concentrations, normalized velocities and temperatures for a mixture of two polyatomic gases with energy levels as in (2.85) and initial values as in Table 2.5, considering masses $(m^1, m^2) = (1, 38.97)$.

Then we increase initial velocities of components of the gas having smaller mass as reported in Table 2.11 and we get the normalized equilibrium values c^i_M, c^i_{jM}, $\bar{u}_M = u_M/0.16$, $\bar{T}_M = T_M/3.20$ reported in Table 2.12.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
u_0	10	20	0	0.1	0.4

Table 2.11

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
c_M	0.24	0.23	0.18	0.17	0.16
$\bar{u}_M$	3.06	3.06	3.06	3.06	3.06
$\bar{T}_M$	12.40	12.40	12.40	12.40	12.40

Table 2.12

Finally, we increase initial velocities of components of the gas having bigger mass setting the values as in Table 2.13 and we obtain that normalized equilibrium values are those in Table 2.14.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
u_0	0.3	0.2	10	30	40

Table 2.13

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3
c_M	0.24	0.24	0.17	0.17	0.17
$\bar{u}_M$	157.06	157.06	157.06	157.06	157.06
$\bar{T}_M$	388.81	388.81	388.81	388.81	388.81

Table 2.14

The behavior of the mixture taken into account is depicted in Figure 2.7.

As regards densities, when the initial velocities of components are higher, final equilibrium values are closer to each other. The final value of mean velocity is clearly higher when initial values are higher, but its order of magnitude strongly depends on the mean velocity of the gas having bigger mass; moreover, the trend to equilibrium for the heavy particles is much faster than for the light ones. At last, even equilibrium temperature increases significantly as initial velocities of various levels (especially the ones of heavy molecules) are higher; the temperatures trend to the steady value turns out to be monotone for components of the gas with low velocities, while an evident overshooting appears in the first stage of the evolution of the faster components. The overshooting phenomenon in temperatures evolution has been observed in several experiments both in space homogeneous conditions [33] and in

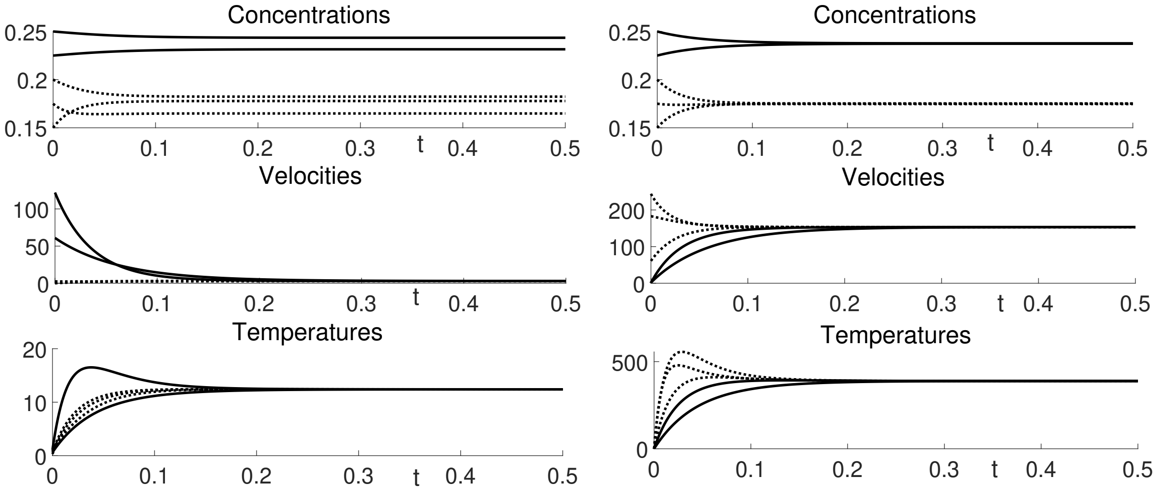

Figure 2.7: Test 3, concentrations, normalized velocities and temperatures for a mixture of a two component (solid line) and a three component (dotted line) polyatomic gas with energy levels as in (2.85) and initial values for number densities and temperatures as in Table 2.5 considering masses $(m^1, m^2) = (1, 38.97)$ and taking initial values for velocities as in Table 2.11 (first panel) and Table 2.13 (second panel).

space dependent situations, such as shock wave formation and combustion problems [48,69,85]. Even the dependence of equilibrium values on the initial data is consistent with the physical expectations: see for instance the discussions in [42, 43] about mixtures with high velocities or large temperature differences between interacting species.

2.4 Conclusions

We have proposed a kinetic BGK model for a mixture of monatomic and polyatomic gases, whose non-translational degrees of freedom are modeled by means of a suitable set of discrete energy levels. This model generalizes the one presented in [11], where all species were assumed polyatomic and with the same number of energy levels. Of course the present frame is much more technical to deal with, since the nature of each interacting particle must be identified by a pair of indices, one denoting the gas that it belongs to and the other referring to the particle energy level. This pair of indices is needed also to denote distribution functions and main macroscopic fields relevant to the various components of a polyatomic gas, as described in the previous sections. We stress again the fact that, with a view to a lighter notation, the pair of indices could be substituted by a single one, as done in Chapter 1, and all the calculations could be performed analogously. However, for our purposes, we kept a separated formulation to treat monatomic and polyatomic species. We have then proved that even for general mixtures the parameters appearing in the Maxwellian attractors of the BGK operators are uniquely determined in terms of the actual fields of the various species by imposing that the kinetic equations of relaxation type preserve the correct collision invariants of the original Boltzmann equations. Even the classical H-theorem still holds. Finally, we have performed some numerical simulations of evolution equations for species densities, velocities and temperatures corresponding to our BGK model. We have considered a mixture constituted by a monatomic and a polyatomic gas, and another mixture composed by two polyatomic species having different number of energy levels. Several tests have been performed for both mixtures, varying the mass ratio, the internal energies, and also the initial values of number densities or mean velocities. In various cases we have noticed that when one gas is very different from the other (for instance much heavier, or denser), the two species spend a different amount of time to reach the equilibrium state. In such situations with species showing disparate values, also overshooting of velocities or temperatures may appear. The characteristic relaxation time for a BGK model depends of course on collision frequencies that, at least for interaction of Maxwell molecule time, could be set in according with experimental data following the method outlined in [17]. Anyway, our qualitative dependence of the hydrodynamic time scale on the macroscopic data and the different species relaxation speed in case of disparate masses are in agreement with the results of [64,70]. Such trends and in particular the separation of the species for very high mass ratios should be discussed also in space-dependent problems, such as shock-wave formation and evaporation-condensation phenomena between parallel plates [105]. In addition, more sophisticated kinetic models for polyatomic particles are highly desirable, where the internal energy is separated into two different components, the vibrational and the rotational ones; since it is well known that the gap between two subsequent discrete levels is much lower for rotational energy than for vibrational energy [65], a possible way of modeling could approximate the rotational part by means of a continuous variable, keeping the vibrational part discrete. A corresponding Boltzmann or BGK description should then mix together in a consistent way the discrete levels approach, introduced in [58] and used also in this work, and the Borgnakke–Larsen procedure involving a continuous internal energy, used for instance in kinetic models [46] and [19].

In the following chapter, we extend the present type of BGK models to frames in which some of the species are subject also to chemical reactions, as already discussed in [11] for a very simple case of only four species (all polyatomic with the same number of internal energies) subject to a bimolecular and reversible chemical reaction. The main additional difficulty with respect to the inert case will be the relations of Arrhenius type (mass action laws) which in any chemical equilibrium configuration must relate temperature with number densities of the reacting species; indeed these are additional transcendental equations to be managed in the construction of auxiliary parameters in the Maxwellian attractors.

3 Kinetic BGK models for reacting mixtures of polyatomic gases

The main purpose of this chapter is to extend results obtained in the previous one for inert gas mixture to a chemically reactive framework. More precisely, we suppose that gas particles of the mixture may undergo, besides elastic and inelastic mechanical scattering, also bimolecular and reversible chemical interactions, involving mass transfer during the collision.

Concerning Boltzmann description of reacting mixtures of particles several works are available [46, 58] and have been summarized and extended to a more general frame in Chapter 1. The treatment of such models involving integro-differential equations can be quite cumbersome due to energy thresholds appearing in the collision operators for endothermic chemical encounters. For this reason, a BGK-type description of these types of mixtures can be helpful. In literature we can find generalizations of the original model proposed in [1]. Such extensions have been performed in different ways, of course facing different emerging technicalities, such as more complicated expressions for auxiliary parameters affecting Maxwellian attractors [16], or the need of simplifying assumptions in the reactive contributions [61].

As already outlined previously, in view of physical applications, for instance the investigation of gas flows in the atmosphere, polyatomic gases should be included in the kinetic description. To this aim, in [11] a BGK-type approximation of a mixture of four chemically interacting gas species has been proposed. Anyway, such work follows the line of [58] and each gas species is endowed with the same number of (discrete) energy levels. The physical need of considering both monatomic and polyatomic species makes desirable an extension of this model to a mixture in which the number of energy levels is different for each gas, analogously to Chapter 2.

In detail, in Section 3.1 of this chapter we firstly consider a mixture of four gas species, G^i, $i = 1, \dots, 4$, whose particles, besides elastic collisions and inelastic transitions from one internal energy level to another, are subject also to the reversible chemical reaction $G^1 + G^2 \leftrightarrows G^3 + G^4$, where a pair of reacting particles of species (G^1, G^2) provides, as products, a pair belonging to (G^3, G^4), or vice versa. The additional difficulties with respect to the inert frame are essentially due to two reasons. At first, single number densities are no more preserved during the evolution; consequently, auxiliary number densities are related in a non–trivial way to species masses and concentrations, to global (auxiliary) temperature and to the chemical energy gap. Then, the mass action law of chemistry that characterizes chemical collision equilibrium, and that is assumed to be valid also for auxiliary parameters, constitutes an additional transcendental equation to be combined to the energy conservation requirement (that is a transcendental law by itself) in order to prove well–posedness of auxiliary number densities and temperature. Mass action law also takes part in the proof of the H-theorem in space homogeneous conditions, that ensures the consistency of the model. Then, in Section 3.2 some numerical simulations, inspired by real bimolecular reactions, of trends to equilibrium of main macroscopic fields in space homogeneous conditions are shown and commented on.

In Section 3.3 we extend the model to a mixture in which there are eight gas species, G^i, with $i = 1, \dots, 8$, that are subject to two reversible chemical reactions

$$G^1 + G^2 \leftrightarrows G^3 + G^4, \tag{3.1}$$

$$G^5 + G^6 \leftrightarrows G^7 + G^8. \tag{3.2}$$

In this case a second mass action law appears and this means that another transcendental equation has to be solved in order to get the proper auxiliary number densities and temperature. Nevertheless, the fact that the two reactions are indeed disjoint allows to reduce the number of unknowns and to recover them as in the case of only four gases, as well as to prove the H-theorem in this case. Also in this frame numerical simulations for the time behavior of macroscopic fields are performed in Section 3.4 and compared to the first case. Finally, Section 3.5 contains some concluding remarks. The first model presented in this chapter is contained in [21], while the second one is contained in [23].

3.1 Statement of the problem for a mixture of four reacting gases and discussion of the relative BGK relaxation model

We take into account a mixture of four polyatomic gas species, G^i, $i = 1, \dots, 4$. The reversible chemical reaction in which the four gas species are involved is

$$G^1 + G^2 \leftrightarrows G^3 + G^4. \tag{3.3}$$

Using the same notation of the previous chapter, each gas species G^i will be characterized by a mass m^i and a certain number L^i of discrete energy levels. Thus, it will be seen as a mixture of components C^i_j, $j = 1, \dots, L^i$, each one corresponding to a different energy level, denoted by E^i_j. In the frame of the same gas G^i the energy levels are assumed (without loss of generality) to be increasing with respect to the subindex j, namely $E^i_j < E^i_k$ for any $j, k = 1, \dots, L^i$ with $j < k$. As concerns masses, according to the conservation law, they have to satisfy the relation $m^1 + m^2 = m^3 + m^4$.

The distribution function of the component C^i_j is denoted by

$$f^i_j(t, \mathbf{x}, \mathbf{v}), \quad i = 1, \dots, 4, \quad j = 1, \dots, L^i. \tag{3.4}$$

We now consider possible interactions between particles, that will be, as usual, only binary instantaneous collisions. We may have, besides classical elastic collisions, also inelastic encounters in which particles may change their internal energy, but also their nature, according to chemical reaction (3.3). We write those generic chemical encounters as follows

$$C^i_j + C^h_k \to C^l_m + C^n_p, \qquad \begin{array}{l} (i,h) \neq (l,n), \\ (i,h), (l,n) \in \{(1,2),(3,4)\}, \end{array} \qquad \begin{array}{l} 1 \le j \le L^i \\ 1 \le k \le L^h \\ 1 \le m \le L^l \\ 1 \le p \le L^n, \end{array} \tag{3.5}$$

and they are endothermic if $E^l_m + E^n_p - E^i_j - E^h_k \ge 0$ or exothermic if $E^l_m + E^n_p - E^i_j - E^h_k < 0$.

Denoting with $(\mathbf{v},\mathbf{w})$ the molecular velocities of the ingoing particles and with $(\mathbf{v}',\mathbf{w}')$ the corresponding post-collision velocities, we have preservation of mass, global momentum and total energy:

$$\begin{aligned}
& m^i + m^h = m^l + m^n \,, \\
& m^i\,\mathbf{v} + m^h\,\mathbf{w} = m^l\,\mathbf{v}' + m^n\,\mathbf{w}' \,, \\
& \frac{1}{2}\,m^i\,|\mathbf{v}|^2 + E^i_j + \frac{1}{2}\,m^h\,|\mathbf{w}|^2 + E^h_k = \frac{1}{2}\,m^l\,|\mathbf{v}'|^2 + E^l_m + \frac{1}{2}\,m^n\,|\mathbf{w}'|^2 + E^n_p \,.
\end{aligned} \tag{3.6}$$

Again we will take into account the major moments of each component C^i_j, that are number densities n^i_j, drift velocity $\mathbf{u}^i_j$ and kinetic temperature T^i_j (for their explicit expressions we address the reader to the previous chapter). Clearly, the total density of each gas species, given by

$$n^i = \sum_{j=1}^{L^i} n^i_j, \quad i = 1,\ldots,4, \tag{3.7}$$

is not constant in time, but thanks in the reaction (3.3) we have that three suitable combinations of them, for instance n^1+n^3, n^1+n^4, n^2+n^4, are conserved, as well as global momentum and total energy of the mixture.

Using the current notation, results from the preliminary part apply directly to this case, in particular equilibria in gas mixtures are provided by Maxwellian distributions in which all species share the same mean velocity $\mathbf{u}$ and the same temperature T. In more detail, for a mixture of polyatomic gases with discrete energies, denoting by $M^i(\mathbf{v};\mathbf{u},T/m^i)$ the Maxwellian

$$M^i\left(\mathbf{v};\mathbf{u},\frac{T}{m^i}\right) = \left(\frac{m^i}{2\,\pi\,T}\right)^{3/2} \exp\left(-\,\frac{m^i}{2T}\,|\mathbf{v}-\mathbf{u}|^2\right), \tag{3.8}$$

the equilibrium state for gas components reads as

$$f^i_{jM}(\mathbf{v}) = n^i_j\,M^i\left(\mathbf{v};\mathbf{u},\frac{T}{m^i}\right), \qquad i=1,\ldots,4, \quad j=1,\ldots,L^i\,, \tag{3.9}$$

where, as proven before, number densities of single components n^i_j are related to the total number density n^i of the gas G^i by the following relation depending on the internal energy levels:

$$n^i_j = n^i\,\frac{\exp\left(-\,\frac{E^i_j-E^i_1}{T}\right)}{\displaystyle\sum_{k=1}^{L^i}\exp\left(-\,\frac{E^i_k-E^i_1}{T}\right)} = n^i\,\frac{\exp\left(-\,\frac{E^i_j-E^i_1}{T}\right)}{\mathcal{Z}^i(T)}. \tag{3.10}$$

In addition, in the present reactive frame, number densities of the four interacting gases must fulfill at equilibrium the mass action law of chemistry representing the chemical equilibrium in a reversible reaction

$$\frac{n^1n^2}{n^3n^4} = \left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(T)\mathcal{Z}^2(T)}{\mathcal{Z}^3(T)\mathcal{Z}^4(T)}\exp\left(\frac{\Delta E}{T}\right), \tag{3.11}$$

with

$$\Delta E = E^3_1 + E^4_1 - E^2_1 - E^1_1. \tag{3.12}$$

Without loss of generality, we suppose that the reaction involving the lower energy levels is endothermic, i.e. $\Delta E > 0$.

3.1.1 BGK model

We propose a BGK model analogous to Chapter 2 by writing a kinetic equation for each component's distribution function f_j^i ($i = 1, \ldots, 4$, $j = 1, \ldots, L^i$) with a collision operator constituted by a unique relaxation term. In this way, we get a set of $L^1 + \ldots + L^4$ BGK equations

$$\frac{\partial f_j^i}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_j^i = \nu_j^i (\mathcal{M}_j^i - f_j^i) \,, \qquad i = 1, \ldots, 4 \qquad j = 1, \ldots, L^i \,, \tag{3.13}$$

where ν_j^i are macroscopic collision frequencies (independent of molecular velocity $\mathbf{v}$, but possibly dependent on macroscopic fields). The distributions $\mathcal{M}_j^i$ are Maxwellian attractors:

$$\mathcal{M}_j^i(\mathbf{v}) = \tilde{n}_j^i \left(\frac{m^i}{2\,\pi\,\tilde{T}} \right)^{3/2} \exp\left[-\frac{m^i}{2\tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right] , \qquad \begin{array}{l} i = 1, \ldots, 4, \\ j = 1, \ldots, L^i, \end{array} \tag{3.14}$$

depending on auxiliary parameters $\tilde{n}_j^i$ ($i = 1, \ldots, 4$, $j = 1, \ldots, L^i$), $\tilde{\mathbf{u}}$, $\tilde{T}$, to be suitably determined in terms of the actual macroscopic fields.

For any gas species G^i, $i = 1, \ldots, 4$, fictitious densities $\tilde{n}_j^i$ are taken bound together as

$$\tilde{n}_j^i = \tilde{n}^i \, \frac{\exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}} \right)}{\mathcal{Z}^i(\tilde{T})} \,, \tag{3.15}$$

and in addition fictitious total densities $\tilde{n}^i$ satisfy the constraint

$$\frac{\tilde{n}^1 \tilde{n}^2}{\tilde{n}^3 \tilde{n}^4} = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(\tilde{T}) \mathcal{Z}^2(\tilde{T})}{\mathcal{Z}^3(\tilde{T}) \mathcal{Z}^4(\tilde{T})} \exp\left(\frac{\Delta E}{\tilde{T}} \right) . \tag{3.16}$$

In this way, collision equilibria of the BGK model (3.13) are correctly provided by Maxwellian distributions sharing a common velocity and a common temperature, with number densities related to the total density of the gas by (3.10) and total densities bound together by (3.11). Our aim is to find auxiliary parameters in terms of the actual ones imposing the preservation of the same (seven) collision invariants of the Boltzmann equations in the BGK model. These correspond to three suitable combinations of gas densities, for instance $n^1 + n^3$, $n^1 + n^4$, $n^2 + n^4$,

$$\sum_{j=1}^{L^1} \nu_j^1 \int_{\mathbb{R}^3} (\mathcal{M}_j^1 - f_j^1) d\mathbf{v} + \sum_{j=3}^{L^3} \nu_j^3 \int_{\mathbb{R}^3} (\mathcal{M}_j^3 - f_j^3) d\mathbf{v} = 0 \tag{3.17}$$

$$\sum_{j=1}^{L^1} \nu_j^1 \int_{\mathbb{R}^3} (\mathcal{M}_j^1 - f_j^1) d\mathbf{v} + \sum_{j=4}^{L^4} \nu_j^4 \int_{\mathbb{R}^3} (\mathcal{M}_j^4 - f_j^4) d\mathbf{v} = 0 \tag{3.18}$$

$$\sum_{j=2}^{L^2} \nu_j^2 \int_{\mathbb{R}^3} (\mathcal{M}_j^2 - f_j^2) d\mathbf{v} + \sum_{j=4}^{L^4} \nu_j^4 \int_{\mathbb{R}^3} (\mathcal{M}_j^4 - f_j^4) d\mathbf{v} = 0, \tag{3.19}$$

global momentum

$$\sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu_j^i \, m^i \int_{\mathbb{R}^3} \mathbf{v} \, (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = \mathbf{0}, \tag{3.20}$$

and total energy

$$\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\int_{\mathbb{R}^3}\left(\frac{1}{2}m^i|\mathbf{v}|^2+E_j^i\right)(\mathcal{M}_j^i-f_j^i)d\mathbf{v}=0. \tag{3.21}$$

Relations (3.17)-(3.19) lead to

$$\sum_{j=1}^{L^i}\nu_j^i(\tilde{n}_j^i-n_j^i)=\lambda^i\sum_{j=1}^{L^1}\nu_j^1(\tilde{n}_j^1-n_j^1), \qquad i=1,\dots,4, \tag{3.22}$$

with

$$\lambda^1=\lambda^2=-\lambda^3=-\lambda^4=1. \tag{3.23}$$

A linear combination of previous equations, together with conservation of mass, gives as results

$$\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\tilde{n}_j^i=\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i n_j^i \tag{3.24}$$

and

$$\sum_{i=1}^{4}m^i\sum_{j=1}^{L^i}\nu_j^i\tilde{n}_j^i=\sum_{i=1}^{4}m^i\sum_{j=1}^{L^i}\nu_j^i n_j^i. \tag{3.25}$$

Expression (3.22) can be written as

$$\sum_{j=1}^{L^i}\nu_j^i\tilde{n}_j^i=\sum_{j=1}^{L^i}\nu_j^i n_j^i+\lambda^i\sum_{j=1}^{L^1}\nu_j^1(\tilde{n}_j^1-n_j^1), \qquad i=1,\dots,4, \tag{3.26}$$

and, from relation (3.15), we have

$$\begin{aligned}\sum_{j=1}^{L^i}\nu_j^i\frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})}&\left[\exp\left(-\frac{E_j^i-E_1^i}{\tilde{T}}\right)\right]\\ &=\sum_{j=1}^{L^i}\nu_j^i n_j^i+\lambda^i\sum_{j=1}^{L^1}\nu_j^1\left(\frac{\tilde{n}^1}{\mathcal{Z}^1(\tilde{T})}\left[\exp\left(-\frac{E_j^1-E_1^1}{\tilde{T}}\right)\right]-n_j^1\right), \quad i=1,\dots,4.\end{aligned} \tag{3.27}$$

This allows us to write three of the auxiliary total densities ($\tilde{n}^2$, $\tilde{n}^3$, $\tilde{n}^4$) as function of the remaining one ($\tilde{n}^1$):

$$\begin{aligned}\frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})}=\left[\sum_{j=1}^{L^i}\nu_j^i\exp\left(-\frac{E_j^i-E_1^i}{\tilde{T}}\right)\right]^{-1}&\left\{\sum_{j=1}^{L^i}\nu_j^i n_j^i-\lambda^i\sum_{j=1}^{L^1}\nu_j^1 n_j^1\right.\\ &\left.+\lambda^i\left[\sum_{j=1}^{L^1}\nu_j^1\exp\left(-\frac{E_j^1-E_1^1}{\tilde{T}}\right)\right]\frac{\tilde{n}^1}{\mathcal{Z}^1(\tilde{T})}\right\},\end{aligned} \tag{3.28}$$

that holds for $i=1,\dots,4$, since for $i=1$ we get a trivial identity.

From momentum conservation (3.20) we get the equation involving auxiliary mean velocity

$$\sum_{i=1}^{4}\left(\sum_{h=1}^{L^i}\nu_h^i\,m^i\,\tilde{n}_h^i\tilde{\mathbf{u}}-\sum_{j=1}^{L^i}\nu_j^i\,m^i\,n_j^i\mathbf{u}_j^i\right)=\mathbf{0}\,, \tag{3.29}$$

that owing to (3.25) provides

$$\tilde{\mathbf{u}} = \frac{\displaystyle\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, m^i\, n_j^i\, \mathbf{u}_j^i}{\displaystyle\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, m^i\, n_j^i}, \tag{3.30}$$

hence $\tilde{\mathbf{u}}$ is an explicit combination of actual number densities and mean velocities of single gas components, analogously to inert mixture case illustrated in the previous chapter.

Total energy conservation (3.21) gives the equation

$$\frac{3}{2}\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i \tilde{T} + \sum_{i=1}^{4}\sum_{j=1}^{L^i} \tilde{n}_j^i \nu_j^i\, E_j^i = \Lambda \tag{3.31}$$

with Λ being a term explicitly depending on actual densities, velocities and energies

$$\Lambda \overset{\mathsf{def}}{=} \frac{1}{2}\left(\sum_{i=1}^{4} m^i \sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, \left(|\mathbf{u}_j^i|^2 - |\tilde{\mathbf{u}}|^2\right)\right) + \frac{3}{2}\left(\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, T_j^i\right) + \sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, E_j^i\, n_j^i\,. \tag{3.32}$$

By inserting expression (3.15) into the left-hand side of (3.31) we get an equation of the form

$$\frac{3}{2}\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i \tilde{T} + \sum_{i=1}^{4} \frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})} \sum_{j=1}^{L^i} \nu_j^i\, E_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right) = \Lambda. \tag{3.33}$$

At this point, we face the main difference with respect to the model without chemical reaction. Instead of a transcendental equation for $\tilde{T}$ having one positive solution and depending only on the actual parameters of the mixture, we have equation (3.33) containing both auxiliary parameters $\tilde{T}$ and $\tilde{n}^1$. Following the procedure applied in [11], we are going to show that those two parameters are uniquely determined, bearing in mind also the fictitious mass action law (3.16). At first, we find it convenient setting

$$Y^i = \frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})} \sum_{j=1}^{L^i} \nu_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right), \tag{3.34}$$

and equation (3.33) thus becomes

$$\frac{3}{2}\sum_{i=1}^{4}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i \tilde{T} + \sum_{i=1}^{4} Y^i\, \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i\, E_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right)}{\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}}\right)} = \Lambda. \tag{3.35}$$

Since from (3.28) we have

$$Y^i = \sum_{j=1}^{L^i} \nu_j^i n_j^i - \lambda^i \sum_{j=1}^{L^1} \nu_j^1 n_j^1 + \lambda^i Y^1, \qquad i = 1, \dots, 4, \tag{3.36}$$

we end up with an equation of the form

$$Y^1 = \sum_{j=1}^{L^1} \nu_j^1 n_j^1 + \mathcal{S}(\tilde{T}), \tag{3.37}$$

where $\mathcal{S}(\tilde{T})$ is written as

$$\mathcal{S}(\tilde{T}) \overset{\text{def}}{=} \frac{\mathcal{N}(\tilde{T})}{\mathcal{D}(\tilde{T})}, \tag{3.38}$$

with the numerator $\mathcal{N}$

$$\mathcal{N}(\tilde{T}) \overset{\text{def}}{=} \Lambda - \sum_{i=1}^{4} \left(\sum_{m=1}^{L^i} \nu_m^i \, n_m^i \right) \left[\frac{3}{2} \tilde{T} + \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i \, E_j^i \exp\left(- \frac{E_j^i - E_1^i}{\tilde{T}} \right)}{\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(- \frac{E_k^i - E_1^i}{\tilde{T}} \right)} \right] \tag{3.39}$$

and the denominator $\mathcal{D}$

$$\mathcal{D}(\tilde{T}) \overset{\text{def}}{=} \sum_{i=1}^{4} \lambda^i \, \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i \, E_j^i \exp\left(- \frac{E_j^i - E_1^i}{\tilde{T}} \right)}{\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(- \frac{E_k^i - E_1^i}{\tilde{T}} \right)} \,. \tag{3.40}$$

We observe that, if we had repeated the previous calculations choosing a different gas species in (3.22) to express the other three ones, we would have obtained analogous expressions for (3.28) leading to

$$Y^i = \sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \mathcal{S}(\tilde{T}), \qquad i = 1, \ldots, 4. \tag{3.41}$$

Putting expressions (3.41) for $i = 1, \ldots, 4$ in the constraint (3.16), we obtain a transcendental equation depending on $\tilde{T}$

$$\mathcal{G}(\tilde{T}) = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{\frac{3}{2}}, \tag{3.42}$$

with

$$\mathcal{G}(\tilde{T}) \overset{\text{def}}{=} \mathcal{G}_1(\tilde{T}) \cdot \mathcal{G}_2(\tilde{T}) \cdot \mathcal{G}_3(\tilde{T}), \tag{3.43}$$

being

$$\mathcal{G}_1(\tilde{T}) \overset{\text{def}}{=} \frac{\left[\displaystyle\sum_{j=1}^{L^1} \nu_j^1 n_j^1 + \mathcal{S}(\tilde{T}) \right] \left[\displaystyle\sum_{j=1}^{L^2} \nu_j^2 n_j^2 + \mathcal{S}(\tilde{T}) \right]}{\left[\displaystyle\sum_{j=1}^{L^3} \nu_j^3 n_j^3 - \mathcal{S}(\tilde{T}) \right] \left[\displaystyle\sum_{j=1}^{L^4} \nu_j^4 n_j^4 - \mathcal{S}(\tilde{T}) \right]}, \tag{3.44}$$

$$\mathcal{G}_2(\tilde{T}) \overset{\text{def}}{=} \frac{\displaystyle\sum_{k=1}^{L^3} \nu_k^3 \exp\left(- \frac{E_k^3 - E_1^3}{\tilde{T}} \right) \sum_{k=1}^{L^4} \nu_k^4 \exp\left(- \frac{E_k^4 - E_1^4}{\tilde{T}} \right)}{\displaystyle\sum_{k=1}^{L^1} \nu_k^1 \exp\left(- \frac{E_k^1 - E_1^1}{\tilde{T}} \right) \sum_{k=1}^{L^2} \nu_k^2 \exp\left(- \frac{E_k^2 - E_1^2}{\tilde{T}} \right)}, \tag{3.45}$$

$$\mathcal{G}_3(\tilde{T}) \overset{\text{def}}{=} \exp\left(- \frac{\Delta E}{\tilde{T}} \right). \tag{3.46}$$

Our aim is now to show that equation (3.42) admits one positive solution in the range in which all the densities n^i are positive. More precisely, referring to the quantities Y^i, we are looking for a solution in the set

$$A = \left\{ \tilde{T} > 0 \, : \, \max \left(-\sum_{j=1}^{L^1} \nu_j^1 n_j^1, -\sum_{j=1}^{L^2} \nu_j^2 n_j^2 \right) < \mathcal{S}(\tilde{T}) < \min \left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3, \sum_{j=1}^{L^4} \nu_j^4 n_j^4 \right) \right\}. \quad (3.47)$$

We will go through the same proof performed in [11], adjusting it to the present frame of polyatomic gases with a different number of internal energy levels. The first result that we point out is the following.

Lemma 3.1.1. *Let $I = (\tilde{T}_1, \tilde{T}_2) \subseteq A$ be any interval in which the function $\mathcal{D}(\tilde{T})$ given in* (3.40) *is strictly negative (positive), then the function $\mathcal{S}(\tilde{T})$ given in* (3.38) *is strictly monotonically increasing (decreasing) in I.*

Proof. From the expression of $\mathcal{S}(\tilde{T})$ we easily get

$$\mathcal{S}'(\tilde{T}) = \frac{\mathcal{N}'(\tilde{T})}{\mathcal{D}(\tilde{T})} - \mathcal{S}(\tilde{T}) \frac{\mathcal{D}'(\tilde{T})}{\mathcal{D}(\tilde{T})}. \quad (3.48)$$

Then we have that

$$\mathcal{D}'(\tilde{T}) = \sum_{i=1}^{4} \lambda^i \frac{\displaystyle\sum_{j=1}^{L^i} \sum_{k=1}^{L^i} \frac{\nu_j^i \nu_k^i}{\tilde{T}^2} \left[\left(E_j^i\right)^2 - E_j^i E_k^i \right] \exp\left(-\frac{E_j^i + E_k^i - 2E_1^i}{\tilde{T}} \right)}{\left[\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}} \right) \right]^2}; \quad (3.49)$$

performing the exchange of indices $j \leftrightarrow k$, equation (3.49) can be written as

$$\mathcal{D}'(\tilde{T}) = \sum_{i=1}^{4} \lambda^i \mathcal{F}^i(\tilde{T}) \quad (3.50)$$

with

$$\mathcal{F}^i(\tilde{T}) \overset{\text{def}}{=} \frac{\displaystyle\sum_{j=1}^{L^i} \sum_{k=1}^{L^i} \frac{\nu_j^i \nu_k^i}{2\tilde{T}^2} \left[E_j^i - E_k^i \right]^2 \exp\left(-\frac{E_j^i + E_k^i - 2E_1^i}{\tilde{T}} \right)}{\left[\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}} \right) \right]^2} \geq 0, \quad i = 1, \ldots, 4. \quad (3.51)$$

Analogously we get

$$\mathcal{N}'(\tilde{T}) = -\sum_{i=1}^{4} \left(\sum_{j=1}^{L^i} \nu_j^i \, n_j^i \right) \left[\frac{3}{2} + \mathcal{F}^i(\tilde{T}) \right] < 0 \,. \quad (3.52)$$

Eventually, from (3.48), the expression for $\mathcal{S}'(\tilde{T})$ is

$$\mathcal{S}'(\tilde{T}) = -\frac{1}{\mathcal{D}(\tilde{T})} \left\{ \sum_{i=1}^{4} \frac{3}{2} \left(\sum_{j=1}^{L^i} \nu_j^i \, n_j^i \right) + \sum_{i=1}^{4} \left[\sum_{j=1}^{L^i} \nu_j^i \, n_j^i + \lambda^i \mathcal{S}(\tilde{T}) \right] \mathcal{F}^i(\tilde{T}) \right\}. \quad (3.53)$$

We notice that the content of the square brackets in (3.53) is strictly positive for $\tilde{T} \in A$ and so the content of the whole curly brackets is positive too, this means that $\mathcal{S}'(\tilde{T})$ and $\mathcal{D}(\tilde{T})$ have opposite sign. $\square$

We focus now on the behavior of the function $\mathcal{S}(\tilde{T})$. For the numerator $\mathcal{N}(\tilde{T})$ we have

Lemma 3.1.2. *The function $\mathcal{N}(\tilde{T})$ has a unique positive root $\tilde{T}^*$.*

Proof. First of all we recall that $\mathcal{N}'(\tilde{T}) < 0$. Moreover we have

$$\begin{aligned}
\lim_{\tilde{T}\to 0^+} \mathcal{N}(\tilde{T}) &= \Lambda - \lim_{\tilde{T}\to 0^+} \sum_{i=1}^{4} \left(\sum_{m=1}^{L^i} \nu^i_m \, n^i_m \right) \left[\frac{3}{2}\tilde{T} + \frac{E^i_1 \nu^i_1 + \displaystyle\sum_{j=2}^{L^i} \nu^i_j \, E^i_j \exp\left(- \frac{E^i_j - E^i_1}{\tilde{T}} \right)}{\nu^i_1 + \displaystyle\sum_{k=2}^{L^i} \nu^i_k \exp\left(- \frac{E^i_k - E^i_1}{\tilde{T}} \right)} \right] \\
&= \Lambda - \sum_{i=1}^{4} \left(\sum_{m=1}^{L^i} \nu^i_m \, n^i_m \right) E^i_1 \\
&= \frac{1}{2} \left(\sum_{i=1}^{4} m^i \sum_{j=1}^{L^i} \nu^i_j \, n^i_j \, \left(|\mathbf{u}^i_j|^2 - |\tilde{\mathbf{u}}|^2 \right) \right) + \frac{3}{2} \left(\sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu^i_j \, n^i_j \, T^i_j \right) \\
&\quad + \sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu^i_j \, n^i_j \, \left(E^i_j - E^i_1 \right) .
\end{aligned} \tag{3.54}$$

As it is shown in Chapter 2, the sum involving mean velocities in (3.54) is non–negative, so the whole limit is strictly positive. In addition it holds

$$\lim_{\tilde{T}\to +\infty} \mathcal{N}(\tilde{T}) = -\infty. \tag{3.55}$$

Thus, $\mathcal{N}(\tilde{T})$ has a unique positive root $\tilde{T}^*$. $\square$

Following the same argument used in [11], we shall omit the situation in which the choice of initial data, internal energies and collision frequencies is such that also $\mathcal{D}(\tilde{T}^*) = 0$. In this case, $\tilde{T} = \tilde{T}^*$ simplifies the function $\mathcal{S}(\tilde{T})$ and we have to deal with a simple algebraic equation for our unknown Y^1.

Now we make some considerations about $\mathcal{D}(\tilde{T})$.

Lemma 3.1.3. *On every interval $\left(\tilde{T}_1, \tilde{T}_2\right) \subseteq A$ the sign of $\mathcal{D}(\tilde{T})$ does not change.*

Proof. Since

$$\lim_{\tilde{T}\to 0} \mathcal{D}(\tilde{T}) = -\Delta E < 0, \qquad \lim_{\tilde{T}\to +\infty} \mathcal{D}(\tilde{T}) = \sum_{i=1}^{4} \lambda^i \frac{\displaystyle\sum_{j=1}^{L^i} \nu^i_j \, E^i_j}{\displaystyle\sum_{j=1}^{L^i} \nu^i_j} \tag{3.56}$$

and the sign of $\mathcal{D}'(\tilde{T})$ given in (3.50) changes in relation to internal energy levels and collision frequencies, $\mathcal{D}(\tilde{T})$ may have a positive root, call it $\tilde{T}^{\#}$, with $\tilde{T}^{\#} \neq \tilde{T}^*$. But in this case we would have

$$\lim_{\tilde{T}\to\tilde{T}^{\#}} \mathcal{S}(\tilde{T}) = \pm\infty \tag{3.57}$$

getting a neighborhood of $\tilde{T}^{\#}$ not contained in A. Thus we can conclude that on every interval $\left(\tilde{T}_1, \tilde{T}_2\right) \subseteq A$ the sign of $\mathcal{D}(\tilde{T})$ does not change. □

Consequently, from Lemma 3.1.1, neither the sign of $\mathcal{S}'(\tilde{T})$ changes. This allows us to prove the following result.

Lemma 3.1.4. *The set A given in* (3.47) *is a connected set of $\mathbb{R}^+$.*

Proof. Let $\left(\tilde{T}_a, \tilde{T}_b\right)$ be a connected component of A. If $\tilde{T}_a \neq 0$ the function $\mathcal{S}(\tilde{T})$ is continuous, strictly monotonically increasing or decreasing on it, hence it assumes all the values between its upper bound that is

$$\min\left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3, \sum_{j=1}^{L^4} \nu_j^4 n_j^4\right) \tag{3.58}$$

and its lower bound that is

$$\max\left(-\sum_{j=1}^{L^1} \nu_j^1 n_j^1, -\sum_{j=1}^{L^2} \nu_j^2 n_j^2\right). \tag{3.59}$$

If $\tilde{T}_a = 0$, since

$$\lim_{\tilde{T}\to 0} \mathcal{D}(\tilde{T}) < 0, \tag{3.60}$$

$S(\tilde{T})$ has to be strictly monotonically increasing on $\left(\tilde{T}_a, \tilde{T}_b\right)$, going from

$$\lim_{\tilde{T}\to 0} \mathcal{S}(\tilde{T}) < 0 \tag{3.61}$$

to

$$\min\left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3, \sum_{j=1}^{L^4} \nu_j^4 n_j^4\right). \tag{3.62}$$

Thus $\mathcal{S}(\tilde{T})$ has a root in $\left(\tilde{T}_a, \tilde{T}_b\right)$, but we know that $\mathcal{S}(\tilde{T})$ has only one positive root, $\tilde{T}^*$. It follows that $\left(\tilde{T}_a, \tilde{T}_b\right)$ is the only connected component of A, i.e. A is a connected set. □

Now we are able to give the final result.

Lemma 3.1.5. *The function $\mathcal{G}(\tilde{T})$ defined in* (3.43) *is strictly monotone in the set A, ranging from 0 to $+\infty$. More precisely, it is increasing if $\mathcal{D}(\tilde{T}) < 0$ and decreasing if $\mathcal{D}(\tilde{T}) > 0$.*

Proof. We compute the derivative of the function $\mathcal{G}(\tilde{T})$. We have

$$\begin{aligned}
\mathcal{G}_1'(\tilde{T}) = {} & \mathcal{S}'(\tilde{T}) \left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3 - \mathcal{S}(\tilde{T})\right)^{-2} \left(\sum_{j=1}^{L^4} \nu_j^4 n_j^4 - \mathcal{S}(\tilde{T})\right)^{-2} \\
& \times \left\{ \left[\left(\sum_{j=1}^{L^1} \nu_j^1 n_j^1 + \mathcal{S}(\tilde{T})\right) + \left(\sum_{j=1}^{L^2} \nu_j^2 n_j^2 + \mathcal{S}(\tilde{T})\right) \right] \left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3 - \mathcal{S}(\tilde{T})\right) \left(\sum_{j=1}^{L^4} \nu_j^4 n_j^4 - \mathcal{S}(\tilde{T})\right) \right. \\
& \left. + \left[\left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3 - \mathcal{S}(\tilde{T})\right) + \left(\sum_{j=1}^{L^4} \nu_j^4 n_j^4 - \mathcal{S}(\tilde{T})\right) \right] \left(\sum_{j=1}^{L^1} \nu_j^1 n_j^1 + \mathcal{S}(\tilde{T})\right) \left(\sum_{j=1}^{L^2} \nu_j^2 n_j^2 + \mathcal{S}(\tilde{T})\right) \right\}
\end{aligned} \tag{3.63}$$

that can be cast as

$$\mathcal{G}_1'(\tilde{T}) = \mathcal{G}_1(\tilde{T}) \sum_{i=1}^{4} \frac{\mathcal{S}'(\tilde{T})}{\displaystyle\sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \mathcal{S}(\tilde{T})}. \tag{3.64}$$

Proceeding in a similar way we have

$$\mathcal{G}_2'(\tilde{T}) = -\mathcal{G}_2(\tilde{T}) \sum_{i=1}^{4} \frac{\lambda^i}{\tilde{T}^2} \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i \left(E_j^i - E_1^i\right) \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right)}{\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}}\right)}, \tag{3.65}$$

and, finally,

$$\mathcal{G}_3'(\tilde{T}) = \mathcal{G}_3(\tilde{T}) \frac{\Delta E}{\tilde{T}^2}. \tag{3.66}$$

In this way we can conclude that

$$\mathcal{G}'(\tilde{T}) = \mathcal{G}(\tilde{T}) \left\{ \sum_{i=1}^{4} \left[\frac{\mathcal{S}'(\tilde{T})}{\displaystyle\sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \mathcal{S}(\tilde{T})} - \frac{\lambda^i}{\tilde{T}^2} \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i \left(E_j^i - E_1^i\right) \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right)}{\displaystyle\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}}\right)} \right] + \frac{\Delta E}{\tilde{T}^2} \right\}, \tag{3.67}$$

that can be written, using function $\mathcal{D}(\tilde{T})$ defined in (3.40), as

$$\mathcal{G}'(\tilde{T}) = \mathcal{G}(\tilde{T}) \left\{ \left[\sum_{i=1}^{4} \frac{\mathcal{S}'(\tilde{T})}{\displaystyle\sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \mathcal{S}(\tilde{T})} \right] - \frac{\mathcal{D}(\tilde{T})}{\tilde{T}^2} \right\}. \tag{3.68}$$

We have that $\mathcal{G}(\tilde{T})$ is positive in the set A that, as we proved in Lemma 3.1.4, is an interval $A = \left(\tilde{T}_{min}, \tilde{T}_{max}\right)$; moreover, thanks to Lemma 3.1.1, $\mathcal{S}'(\tilde{T})$ and $-\mathcal{D}(\tilde{T})$ have the same sign, that does not change in A, and this means that $\mathcal{G}(\tilde{T})$ is strictly monotone. Moreover, recalling the definition of $\mathcal{G}(\tilde{T})$ given in (3.43), when

$$\mathcal{S}(\tilde{T}) \to \min\left(\sum_{j=1}^{L^3} \nu_j^3 n_j^3, \sum_{j=1}^{L^4} \nu_j^4 n_j^4 \right) \tag{3.69}$$

we have

$$\mathcal{G}(\tilde{T}) \to +\infty \tag{3.70}$$

and when

$$\mathcal{S}(\tilde{T}) \to \max\left(-\sum_{j=1}^{L^1} \nu_j^1 n_j^1, -\sum_{j=1}^{L^2} \nu_j^2 n_j^2 \right) \tag{3.71}$$

we have

$$\mathcal{G}(\tilde{T}) \to 0; \tag{3.72}$$

also in the case in which $\tilde{T}_{min} = 0$ it holds $\lim_{\tilde{T}\to 0} \mathcal{G}(\tilde{T}) = 0$, since we are supposing $\Delta E > 0$. We observe here that also for the case $\Delta E < 0$ it is sufficient to take the inverse of both sides of equation (3.16) and modify the equation (3.42) studying the behavior of function $\frac{1}{\mathcal{G}(\tilde{T})}$ in order to get the same result. □

This final result allows us to assert that equation (3.42) has a unique solution, providing thus the auxiliary temperature $\tilde{T}$.

At this point, fictitious densities $\tilde{n}^i_j$ are given by (3.15) and (3.28) together with expression (3.37), hence they are known once $\tilde{T}$ is found, while fictitious mean velocity $\tilde{\mathbf{u}}$ is expressed in (3.30) and this completes the construction of Maxwellian attractors $\mathcal{M}^i_j$ of our BGK model. The equilibrium states correspond to $f^i_j = \mathcal{M}^i_j$ for $i = 1, \dots, 4$ and $j = 1, \dots, L^i$, therefore

$$\mathbf{u}^i_j = \tilde{\mathbf{u}} = \mathbf{u}\,, \qquad T^i_j = \tilde{T} = T, \qquad i = 1, \dots, 4, \qquad j = 1, \dots, L^i, \tag{3.73}$$

and number densities of components n^i_j are related to global density of the corresponding gas n^i by the constraint (3.10), while the densities n^i are bound together by (3.11).

3.1.2 *H*-Theorem for the homogeneous case

We can also prove the asymptotic stability of collision equilibria in this case. Indeed, in space homogeneous conditions, setting $\underline{\mathbf{f}} = (f^1_1, \dots, f^4_{L^4})$, the physical entropy

$$\mathcal{H}[\underline{\mathbf{f}}] = \sum_{i=1}^{4} \sum_{j=1}^{L^i} \int_{\mathbb{R}^3} f^i_j \log\left(\frac{f^i_j}{(m^i)^3}\right) d\mathbf{v} \tag{3.74}$$

is a Lyapunov functional for the present BGK model. Specifically, if $\underline{\mathbf{f}}^M$ denotes the stationary state corresponding to the initial state $\underline{\mathbf{f}}_0$, we have $\mathcal{H}[\underline{\mathbf{f}}] > \mathcal{H}[\underline{\mathbf{f}}^M]$ for any $\underline{\mathbf{f}} \neq \underline{\mathbf{f}}^M$. The proof of this result for the present reactive model is a bit more involved with respect to the inert mixture case since the conservation of species number densities does not hold anymore. Anyway, also in this case the proof is analogous to the one performed in Chapter 2, so we skip details.

We can now prove the entropy inequality $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ for any $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$, while $\dot{\mathcal{H}}[\underline{\mathbf{f}}^M] = 0$.

Let $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}^M$, the time derivative of the H–functional (3.74) reads as

$$\dot{\mathcal{H}}[\underline{\mathbf{f}}] = \sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu^i_j \int_{\mathbb{R}^3} \left(\mathcal{M}^i_j - f^{i*}_j\right) \log\left(\frac{f^{i*}_j}{(m^i)^3}\right) d\mathbf{v}. \tag{3.75}$$

At first we can check that

$$\sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu^i_j \int_{\mathbb{R}^3} \left(\mathcal{M}^i_j - f^{i*}_j\right) \log\left(\frac{\mathcal{M}^i_j}{(m^i)^3}\right) d\mathbf{v} = 0\,. \tag{3.76}$$

Indeed, we explicitly compute the logarithm of Maxwellian attractors, leading to

$$\sum_{i=1}^{4} \sum_{j=1}^{L^i} \nu^i_j \int_{\mathbb{R}^3} \left(\mathcal{M}^i_j - f^{i*}_j\right) \left[\log \tilde{n}^i_j - \frac{3}{2}\log(m^i) - \frac{3}{2}\log\left(2\pi\tilde{T}\right)\right] d\mathbf{v}$$

$$+\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\int_{\mathbb{R}^3}\left(\mathcal{M}_j^i-f_j^{i*}\right)\left[-\frac{m^i}{2\,\tilde{T}}\left(|\mathbf{v}|^2-2\tilde{\mathbf{u}}\cdot\mathbf{v}+|\tilde{\mathbf{u}}|^2\right)\right]d\mathbf{v}\,. \tag{3.77}$$

Then, owing to conservation laws of momentum and total energy, it simplifies to

$$\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\left(\tilde{n}_j^i-n_j^{i*}\right)\left[\log\tilde{n}_j^i+\frac{E_j^i}{\tilde{T}}-\frac{3}{2}\log m^i\right]; \tag{3.78}$$

bearing in mind (3.15), the previous equation becomes

$$\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\left(\tilde{n}_j^i-n_j^{i*}\right)\left[\log\tilde{n}^i+\frac{E_1^i}{\tilde{T}}-\log\left(\mathcal{Z}^i(\tilde{T})\right)-\frac{3}{2}\log m^i\right]. \tag{3.79}$$

Using the relations (3.22), the quantity above can be written as

$$\sum_{j=1}^{L^1}\nu_j^1\left(\tilde{n}_j^1-n_j^{1*}\right)\sum_{i=1}^{4}\lambda^i\left[\log\tilde{n}^i+\frac{E_1^i}{\tilde{T}}-\log\left(\mathcal{Z}^i(\tilde{T})\right)-\frac{3}{2}\log m^i\right]$$

$$=\sum_{j=1}^{L^1}\nu_j^1\left(\tilde{n}_j^1-n_j^{1*}\right)\left\{\log\left[\frac{\tilde{n}^1\tilde{n}^2}{\tilde{n}^3\tilde{n}^4}\left(\frac{m^3m^4}{m^1m^2}\right)^{\frac{3}{2}}\right]-\log\left[\frac{\mathcal{Z}^1(\tilde{T})\mathcal{Z}^2(\tilde{T})}{\mathcal{Z}^3(\tilde{T})\mathcal{Z}^4(\tilde{T})}\exp\left(\frac{\Delta E}{\tilde{T}}\right)\right]\right\}=0 \tag{3.80}$$

due to the mass action law (3.16) for auxiliary parameters. Then, by subtracting (3.76) from (3.75) we easily get that for any $\underline{\mathbf{f}}^*\neq\underline{\mathbf{f}}^M$

$$\dot{\mathcal{H}}[\underline{\mathbf{f}}^*]=-\sum_{i=1}^{4}\sum_{j=1}^{L^i}\nu_j^i\int_{\mathbb{R}^3}\left(f_j^{i*}-\mathcal{M}_j^i\right)\log\left(\frac{f_j^{i*}}{\mathcal{M}_j^i}\right)d\mathbf{v} \tag{3.81}$$

and the inequality $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*]<0$ holds owing to usual convexity arguments.

3.2 Macroscopic equations for mixtures of four reacting gases

Performing the same calculations done in Chapter 2, we are able to derive from BGK model (3.13) the evolution equations for the main macroscopic fields, i.e. number densities, mean velocities and temperatures of all components of the four reacting gases (n_j^i, $\mathbf{u}_j^i$, T_j^i, for $i=1,\ldots,4$ and for $j=1,\ldots,L^i$). We obtain the following system

$$\left\{\begin{aligned}
&\frac{\partial n_j^i}{\partial t}+\nabla_{\mathbf{x}}\cdot(n_j^i\,\mathbf{u}_j^i)=\nu_j^i(\tilde{n}_j^i-n_j^i)\,,\\
&n_j^i\left(\frac{\partial\mathbf{u}_j^i}{\partial t}+\mathbf{u}_j^i\cdot\nabla_{\mathbf{x}}\mathbf{u}_j^i\right)+\frac{1}{m^i}\nabla_{\mathbf{x}}\cdot\mathbf{P}_j^i=\nu_j^i\,\tilde{n}_j^i(\tilde{\mathbf{u}}-\mathbf{u}_j^i)\,,\\
&\frac{3}{2}\,n_j^i\left(\frac{\partial T_j^i}{\partial t}+\mathbf{u}_j^i\cdot\nabla_{\mathbf{x}}T_j^i\right)+\mathbf{P}_j^i:\nabla_{\mathbf{x}}\mathbf{u}_j^i+\nabla_{\mathbf{x}}\cdot\mathbf{q}_j^i\\
&\qquad\qquad=\nu_j^i\,\tilde{n}_j^i\left[\frac{3}{2}\,(\tilde{T}-T_j^i)+\frac{1}{2}\,m^i\,|\tilde{\mathbf{u}}-\mathbf{u}_j^i|^2\right],
\end{aligned}\right. \tag{3.82}$$

where $\mathbf{P}_j^i$ are pressure tensors and $\mathbf{q}_j^i$ heat fluxes for each component defined as

$$\mathbf{P}_j^i=m^i\int_{\mathbb{R}^3}(\mathbf{v}-\mathbf{u}_j^i)\otimes(\mathbf{v}-\mathbf{u}_j^i)\,f_j^i(\mathbf{v})\,d\mathbf{v}\,,\quad\mathbf{q}_j^i=\frac{m^i}{2}\int_{\mathbb{R}^3}(\mathbf{v}-\mathbf{u}_j^i)\,|\mathbf{v}-\mathbf{u}_j^i|^2\,f_j^i(\mathbf{v})\,d\mathbf{v}\,. \tag{3.83}$$

For illustrative purposes we will show some numerical results for two reacting mixtures taking into account the space homogeneous and one–dimensional version of evolution equations (3.82) that reads as

$$\begin{cases} \dfrac{\partial n_j^i}{\partial t} = \nu_j^i (\tilde{n}_j^i - n_j^i)\,, & \begin{array}{l} i = 1, \ldots, 4, \\ j = 1, \ldots, L^i, \end{array} \\[2ex] \dfrac{\partial u_j^i}{\partial t} = \nu_j^i \, \dfrac{\tilde{n}_j^i}{n_j^i} (\tilde{u} - u_j^i)\,, & \begin{array}{l} i = 1, \ldots, 4, \\ j = 1, \ldots, L^i, \end{array} \\[2ex] \dfrac{\partial T_j^i}{\partial t} = \nu_j^i \, \dfrac{\tilde{n}_j^i}{n_j^i} \left(\tilde{T} - T_j^i + \dfrac{1}{3} m^i \, (\tilde{u} - u_j^i)^2 \right), & \begin{array}{l} i = 1, \ldots, 4, \\ j = 1, \ldots, L^i, \end{array} \end{cases} \tag{3.84}$$

where $\tilde{n}_j^i$ is provided by (3.15) and (3.28), $\tilde{u}$ is explicitly given in (3.30), and $\tilde{T}$ may be obtained as the unique solution of the transcendental equation (3.42). Equations (3.84) constitute thus a closed system of $3(L^1 + \ldots + L^4)$ equations, having as unknowns densities, velocities and temperatures of all components of polyatomic species. Once the initial state $(n_j^i)_0$, $(u_j^i)_0$, $(T_j^i)_0$ is assigned, the corresponding equilibrium configuration is unique and may be determined bearing in mind the conservations of three suitable combinations of total densities, global velocity and total energy.

3.2.1 Numerical simulations

Test 1

The first mixture we model is inspired by the reversible reaction involving hydrogen H_2 (with mass 2.02 g/mol), iodine I_2 (253.8 g/mol) and hydrogen iodide HI (127.91 g/mol)

$$H_2 + I_2 \leftrightarrows HI + HI. \tag{3.85}$$

So we take into account four gases G^i, $i = 1, ..., 4$, with mass ratios reproducing the ones of the gases involved in the reaction: $m^1 = 0.1$, $m^2 = 12.8$, $m^3 = m^4 = 6.45$. Notice that in this bimolecular reaction the third and the fourth species coincide, therefore they are characterized by the same internal structure and by the same initial data. We suppose that gas species G^1, $G^3 \equiv G^4$ are endowed with two and G^2 is endowed with three discrete energy levels, respectively. Specifically, we assume the following configuration of internal energy levels

$$\begin{gathered} E_1^1 = 6.5, \quad E_2^1 = 7.5, \quad E_1^2 = 7, \quad E_2^2 = 8, \quad E_3^2 = 8.5, \\ E_1^3 = 6, \quad E_2^3 = 7, \quad E_1^4 = 6, \quad E_2^4 = 7. \end{gathered} \tag{3.86}$$

From now on we will consider concentration c_j^i of each component C_j^i defined as

$$c_j^i = \frac{n_j^i}{\sum_{h=1}^4 \sum_{k=1}^{L^h} n_k^h}\,, \tag{3.87}$$

and also velocities and temperatures will be suitably normalized with respect to the corresponding equilibrium values. Initial data for number concentrations, velocities and temperatures are given in Table 3.1.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3	C^3_1	C^3_2	C^4_1	C^4_2
c_0	0.13	0.07	0.08	0.06	0.15	0.14	0.11	0.14	0.11
u_0	0.3	0	0.1	0.4	0.2	0.6	0.1	0.6	0.1
T_0	2	4	1	2.5	2	6	1.5	6	1.5

Table 3.1

The choice of collision frequencies is done as in [11], setting the sets of indices for $i = 1, \dots, 4$ and $j = 1, \dots, L^i$

$$
{\mathcal{D}^1}^i_j = \left\{ \begin{array}{l} h = 1, \dots, 4, \\ m = 1, \dots, L^i, \\ k, p = 1, \dots, L^h \end{array} \quad : \; E^i_m + E^h_p - E^i_j - E^h_k \, \leq \, 0 \right\}, \tag{3.88}
$$

$$
{\mathcal{D}^2}^i_j = \left\{ \begin{array}{l} h = 1, \dots, 4, \\ m = 1, \dots, L^i, \\ k, p = 1, \dots, L^h \end{array} \quad : \; E^i_m + E^h_p - E^i_j - E^h_k \, > \, 0 \right\}, \tag{3.89}
$$

$$
{\mathcal{D}^3}^i_j = \left\{ h, l, n : \begin{array}{cl} (i,h) \neq (l,n), \; i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(1,2), (3,4), (2,1), (4,3)\}, & p = 1, \dots, L^n \end{array} \; : \; E^l_m + E^n_p - E^i_j - E^h_k \, \leq \, 0 \right\}, \tag{3.90}
$$

$$
{\mathcal{D}^4}^i_j = \left\{ h, l, n : \begin{array}{cl} (i,h) \neq (l,n), \; i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(1,2), (3,4), (2,1), (4,3)\}, & p = 1, \dots, L^n \end{array} \; : \; E^l_m + E^n_p - E^i_j - E^h_k \, > \, 0 \right\}, \tag{3.91}
$$

and taking

$$
\begin{aligned}
\nu^i_j \;=\; & \sum_{h,k,m,p \in {\mathcal{D}^2}^i_j} \nu^{m,p}_{j,k} n^h_k \exp\left(- \frac{E^i_m + E^h_p - E^i_j - E^h_k}{T} \right) + \sum_{h,k,m,p \in {\mathcal{D}^1}^i_j} \nu^{m,p}_{j,k} n^h_k \\
& + \sum_{h,k,l,m,n,p \in {\mathcal{D}^4}^i_j} \nu^{m,p}_{j,k} n^h_k \left(\frac{m^i m^j}{m^l m^n} \right)^{\frac{3}{2}} \exp\left(- \frac{E^l_m + E^n_p - E^i_j - E^h_k}{T} \right) \\
& + \sum_{h,k,l,m,n,p \in {\mathcal{D}^3}^i_j} \nu^{m,p}_{j,k} n^h_k
\end{aligned} \tag{3.92}
$$

with $\nu^{m,p}_{j,k} = \dfrac{k+j}{20(m+p)}$. Equilibrium values for concentrations c^i_{jM} obtained in this setting are reported in Table 3.2 while equilibrium global mean velocity is $u_M = 0.29$ and equilibrium temperature is $T_M = 3.47$.

The evolution in time of species concentrations computed numerically is depicted in Figure 3.1. It is possible to observe that, according to constraint (3.10), for each gas species the component

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2	C_1^3	C_2^3	C_1^4	C_2^4
c_M	0.001	0.001	0.042	0.031	0.027	0.256	0.192	0.256	0.192

Table 3.2

corresponding to a higher energy level will have a lower concentration and vice-versa. Moreover, due to relation (3.11), the concentrations of species G^1 and G^2 are lower, in particular the one of G^1 (that has the lowest mass in the mixture) is the lowest, while concentrations of species G^3 and G^4 are higher. In other words, chemical equilibrium is achieved when species G^1 is almost completely disappeared, so that almost no reactive collision can occur. We also note that trend to equilibrium for concentrations may be non monotone, see for instance c_1^2 and c_2^2.

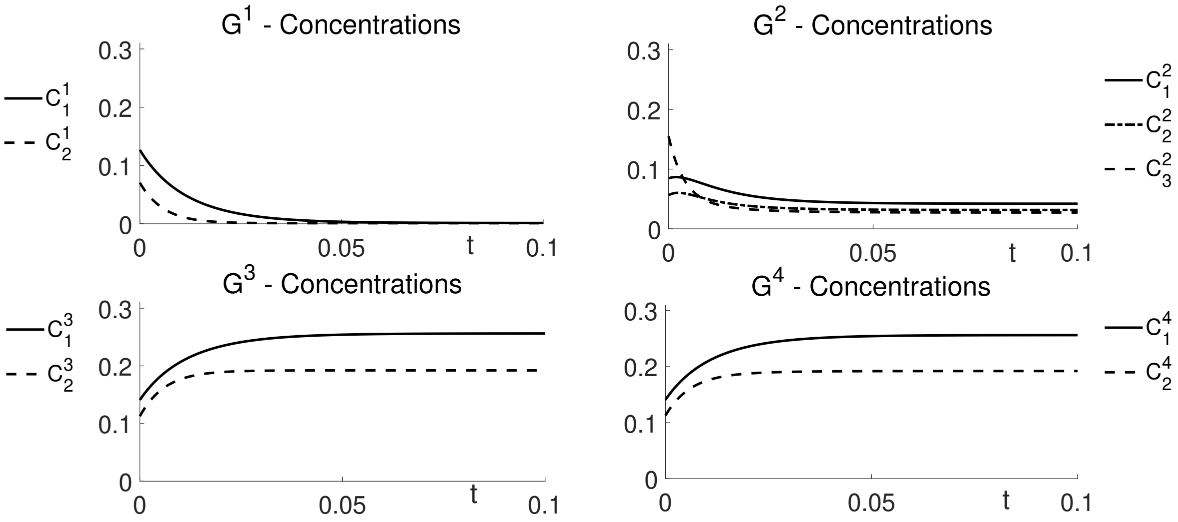

Figure 3.1: Test 1, concentrations for a mixture of four reacting gases with energy levels as in (3.86) and initial values as in Table 3.1, considering masses $(m^1, m^2, m^3, m^4) = (0.1, 12.8, 6.45, 6.45)$.

In Figure 3.2 we report the behavior of normalized velocities $\bar{u}_j^i = u_j^i / u_M$ and normalized temperatures $\bar{T}_j^i = T_j^i / T_M$. We can observe that the species G^1 takes a longer time to reach the equilibrium value for velocity and temperature, its components keep nearly constant values in the first stage of the evolution.

Test 2

The second reacting mixture we take into account for our simulations is the following

$$ClNO_2 + NO \leftrightarrows NO_2 + ClNO, \tag{3.93}$$

where the chloro nitride $ClNO_2$ (81.46 g/mol) reacts with nitric oxide NO (30.01 g/mol) forming nitrosyl chloride $ClNO$ (65,46 g/mol) and nitrogen dioxide NO_2 (46.01 g/mol), and vice-versa in the reverse reaction. As before, we take in our model four gases having mass ratios similar to the ones involved in the real reaction: $m^1 = 1$, $m^2 = 2.72$, $m^3 = 2.18$, $m^4 = 1.53$. We make the assumption that the first gas G^1 is composed by two, the second gas G^2 is composed by four, and the other two

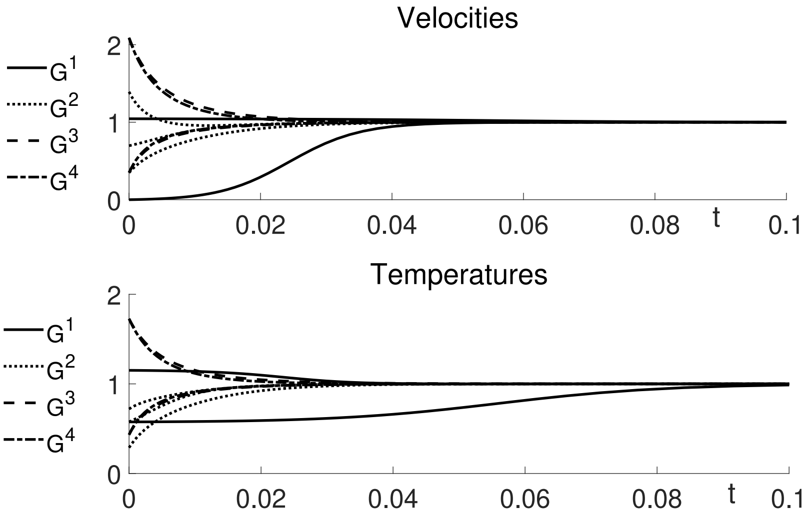

Figure 3.2: Test 1, normalized velocities and temperatures for a mixture of four reacting gases with energy levels as in (3.86) and initial values as in Table 3.1, considering masses $(m^1, m^2, m^3, m^4) = (0.1, 12.8, 6.45, 6.45)$.

gases G^3 and G^4 are composed by three components, respectively. Each component corresponds to a different internal energy level as follows

$$E_1^1 = 6, \quad E_2^1 = 7, \quad E_1^2 = 7, \quad E_2^2 = 8, \quad E_3^2 = 10, \quad E_4^2 = 12,$$

$$E_1^3 = 5.5, \quad E_2^3 = 6, \quad E_3^3 = 7.5, \quad E_1^4 = 4, \quad E_2^4 = 9, \quad E_3^4 = 10. \tag{3.94}$$

We set initial concentrations, velocities and temperatures as reported in the Table 3.3.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2	C_4^2	C_1^3	C_2^3	C_3^3	C_1^4	C_2^4	C_3^4
c_0	0.12	0.09	0.07	0.08	0.11	0.06	0.07	0.05	0.13	0.03	0.08	0.09
u_0	0.3	0	0.1	0.4	0.2	0.6	0.1	0.4	0.5	0.3	0	0.2
T_0	2	4	1	2.5	2	6	1.5	2.5	3	4.5	5	1

Table 3.3

In this case, equilibrium values for equilibrium concentrations of components c_{jM}^i are given in Table 3.4, while equilibrium global mean velocity is $u_M = 0.28$ and temperature is $T_M = 3.59$.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2	C_4^2	C_1^3	C_2^3	C_3^3	C_1^4	C_2^4	C_3^4
c_M	0.09	0.07	0.12	0.08	0.04	0.02	0.13	0.11	0.07	0.2	0.05	0.04

Table 3.4

Numerical results for behavior in time of concentrations for all the components are showed in Figure 3.3. In this case, since there is less difference among masses than in the previous case, final values

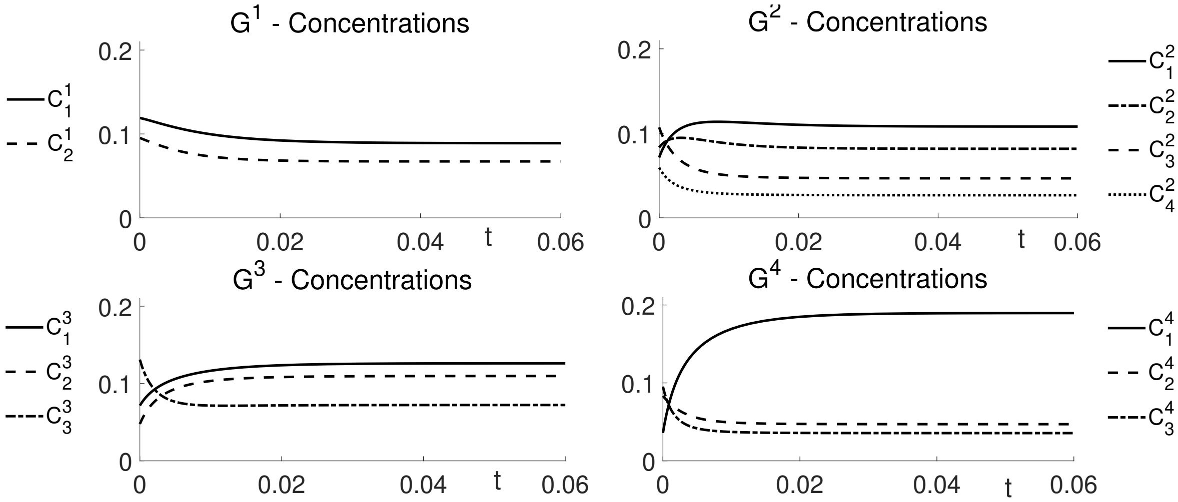

Figure 3.3: Test 2, concentrations for a mixture of four reacting gases with energy levels as in (3.94) and initial values as in Table 3.3, considering masses $(m^1, m^2, m^3, m^4) = (1, 2.72, 2.18, 1.53)$.

of number densities are more similar; we only have a significantly higher concentration of component C_1^4 that corresponds to the lowest energy level.

Trends for normalized mean velocities and temperatures of the species are reported in Figure 3.4 and also in this case we can observe that the lighter gas G^1 takes a longer time to reach the equilibrium value.

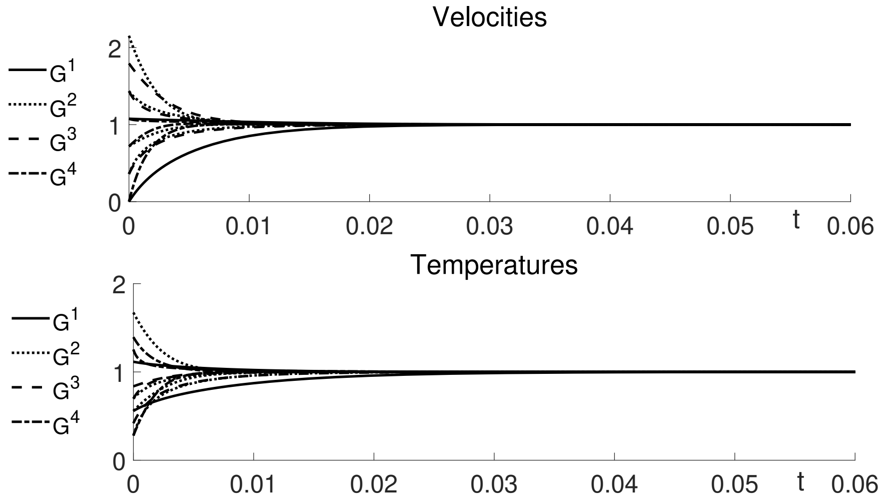

Figure 3.4: Test 2, normalized velocities and temperatures for a mixture of four reacting gases with energy levels as in (3.94) and initial values as in Table 3.3, considering masses $(m^1, m^2, m^3, m^4) = (1, 2.72, 2.18, 1.53)$.

Test 3

At this point, we consider the following physical case

$$O + OH \to O_2 + H. \tag{3.95}$$

This irreversible exothermic reaction between the two radicals atomic Oxygen O (15.99 g/mol) and Hydroxide OH (17.01 g/mol) is known to cause production of molecular Oxygen O_2 (31.99 g/mol) along with Hydrogen H (1.01 g/mol) in the cold core of interstellar clouds [100, 111].

Clearly, since our present model is built up for reversible chemical reactions, it is not possible to implement it to reproduce such physical event. Nevertheless we try to describe a reversible virtual chemical encounter of type (3.3) performing a choice of parameters (energy levels, collision frequencies, initial concentrations, temperatures and velocities) in such a way that inverse reaction becomes highly improbable and the equilibrium state corresponds to a considerable consumption of one of the reactants (its concentration become negligible, as in the equilibrium configuration of the real irreversible process).

Thus we take four gases $G^i, i = 1, \ldots, 4$ having mass ratios analogous to the ones involved in the real reaction, i.e we set $m^1 = 15.83, m^2 = 16.83, m^3 = 31.67, m^4 = 1$. Then we suppose that gas species G^1 and G^4, being monatomic, have only one internal energy level, whereas we assign to both species G^2 and G^3 two energy levels. Fixing values for energies, we assume the energy gap between reactants and products sufficiently large:

$$E^1_1 = 12, \quad E^2_1 = 40.9, \quad E^2_2 = 41, \quad E^3_1 = 0.6, \quad E^3_2 = 0.7, \quad E^4_1 = 0.8. \tag{3.96}$$

We set initial data for number concentrations, velocities and temperatures for the one-dimensional case as reported in Table 3.5. The initial concentration of reactants is higher than the one of products and we take initial temperatures lower than the values adopted in the previous simulations.

	C^1_1	C^2_1	C^2_2	C^3_1	C^3_2	C^4_1
c_0	0.21	0.367	0.42	0.0005	0.001	0.001
u_0	0.1	0.3	0.2	0.4	0.2	0.5
T_0	0.002	0.003	0.004	0.005	0.003	0.006

Table 3.5

For the collision frequencies, we consider for each $i = 1, \ldots, 4$ and $j = 1, \ldots, L^i$ the following

$$\begin{aligned} \nu^i_j \; = & \sum_{h,k,m,p \in \mathcal{D}2^i_j} \nu^{m,p}_{j,k} n^h_k \exp\left(-\frac{E^i_m + E^h_p - E^i_j - E^h_k}{T}\right) + \sum_{h,k,m,p \in \mathcal{D}1^i_j} \nu^{m,p}_{j,k} n^h_k \\ + & \frac{1}{100} \sum_{h,k,l,m,n,p \in \mathcal{D}4^i_j} \nu^{m,p}_{j,k} n^h_k \left(\frac{m^i m^j}{m^l m^n}\right)^{\frac{3}{2}} \exp\left(-\frac{E^l_m + E^n_p - E^i_j - E^h_k}{T}\right) \\ + & \sum_{h,k,l,m,n,p \in \mathcal{D}3^i_j} \nu^{m,p}_{j,k} n^h_k \end{aligned} \tag{3.97}$$

with $\nu^{m,p}_{j,k} = \dfrac{k+j}{20(m+p)}$ and the set of indices $\mathcal{D}1^i_j$, $\mathcal{D}2^i_j$, $\mathcal{D}3^i_j$ and $\mathcal{D}4^i_j$ as defined in (3.88), (3.89), (3.90) and (3.91), respectively. The factor $\frac{1}{100}$ in front of the third addendum in (3.97) represents the fact that inverse endothermic reaction is less frequent than the direct exothermic one.

Equilibrium values obtained for final concentrations of single components c^i_{jM} are reported in Table 3.6 while equilibrium mean velocity and temperature are $u_M = 0.22$ and $T_M = 7.19$, respectively.

	C_1^1	C_1^2	C_2^2	C_1^3	C_2^3	C_1^4
c_M	0.001	0.291	0.287	0.106	0.104	0.21

Table 3.6

We report the behavior in time of concentrations of energy components (Figure 3.5), mean velocities and temperatures (Figure 3.6).

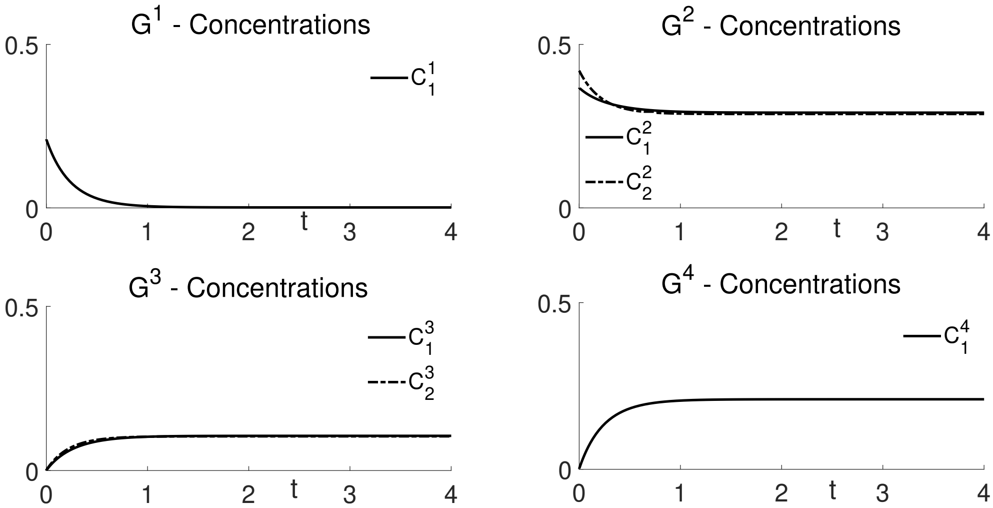

Figure 3.5: Test 3, concentrations for a mixture of four reacting gases with energy levels as in (3.96), initial values for concentrations and velocities as in Table 3.5, considering masses $(m^1, m^2, m^3, m^4) = (15.83, 16.83, 31.67, 1)$.

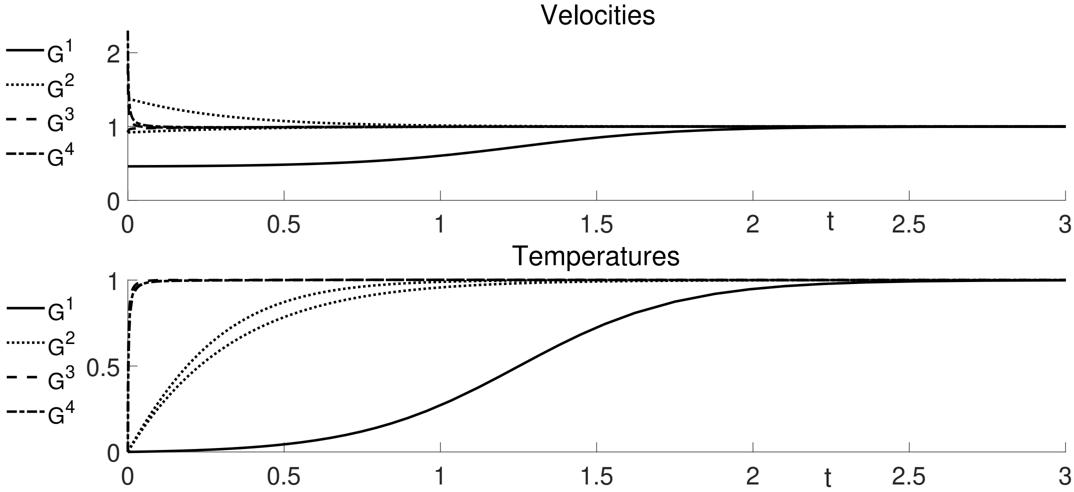

Figure 3.6: Test 3, normalized velocities and temperatures for a mixture of four reacting gases with energy levels as in (3.96), initial values for concentrations and velocities as in Table 3.5, considering masses $(m^1, m^2, m^3, m^4) = (15.83, 16.83, 31.67, 1)$.

We highlight the nearly total disappearance of the monatomic reactant G^1. This means that the equilibrium state of the mixture is similar to the result of an irreversible reaction (the consumed quantity of G^1 and G^2 is approximately the same). Moreover it is worth noticing how the temperature of the mixture is higher than the initial ones, because of the exothermic property of the reaction.

3.3 Statement of the problem for a mixture of eight gases involved in two disjoint chemical reactions and discussion of the relative BGK relaxation model

The following step we would like to take in building BGK models in gas mixtures is to consider a number of gas species greater than four, involved in different chemical reactions. In this case, the equilibrium configuration is governed by a higher number of mass action laws, that lead to a higher number of auxiliary quantities to be determined; in particular we have to find (by means of three transcendental equations) the auxiliary temperature and two of the auxiliary densities. Our intent is to show that, when the reactions are disjoint, i.e. no gas species is involved in more than one reaction, it is possible to write one of the auxiliary densities in terms of the other ones and of the auxiliary temperature. Successively we manage to express everything in terms of the auxiliary temperature and again it can be detected as the unique admissible solution of a transcendental equation.

Thus, we consider a model for a mixture of eight gas species, G^i, $i = 1, , \ldots, , 8$ and we suppose that they are involved in two separate reversible chemical reactions:

$$G^1 + G^2 \leftrightarrows G^3 + G^4, \tag{3.98}$$

$$G^5 + G^6 \leftrightarrows G^7 + G^8. \tag{3.99}$$

Each gas species G^i has its own mass m^i and, due to conservation laws, particle masses satisfy the relations $m^1 + m^2 = m^3 + m^4$ and $m_5 + m_6 = m_7 + m_8$. As before, each gas species can be seen as formed by a certain number L^i of components, C^i_j, $j = 1, \ldots, L^i$, each one corresponding to a discrete internal energy level E^i_j. Even in this case we assume $E^i_j < E^i_k$ for any $1 \le j, k \le L^i$, with $j < k$. Distribution functions for each energy component C^i_j are

$$f^i_j(t, \mathbf{x}, \mathbf{v}), \quad i = 1, \ldots, 8, \quad j = 1, \ldots, L^i. \tag{3.100}$$

Encounters among particles of the mixture are modeled as binary instantaneous collisions and can be generically written as

$$C^i_j + C^h_k \to C^l_m + C^n_p, \quad 1 \le i, h, l, n \le 8, \quad \begin{array}{l} 1 \le j \le L^i \\ 1 \le k \le L^h \\ 1 \le m \le L^l \\ 1 \le p \le L^n. \end{array} \tag{3.101}$$

Those encounters can be elastic if $i = l$, $h = n$, $j = m$, $k = p$, inelastic if $i = l$, $h = n$, $j \neq m$ or $k \neq p$, chemical if $(i, h) \neq (l, n)$ with $(i, h), (l, n) \in \{(1, 2), (3, 4)\}$ or $(i, h), (l, n) \in \{(5, 6), (7, 8)\}$; in the last two cases the collision is endothermic if $E^l_m + E^n_p - E^i_j - E^h_k \ge 0$ or exothermic if $E^l_m + E^n_p - E^i_j - E^h_k < 0$.

Moments of components C^i_j we are interested in are number densities n^i_j, satisfying the relation

$$n^i = \sum_{j=1}^{L^i} n^i_j, \quad i = 1, \ldots, 8, \tag{3.102}$$

drift velocities $\mathbf{u}^i_j$ and kinetic temperature T^i_j. During the kinetic evolution in time of the mixture we have conservation of global quantities that are six combinations of gas species number densities that can be chosen as $n^1 + n^3$, $n^1 + n^4$, $n^2 + n^4$, $n^5 + n^7$, $n^5 + n^8$, $n^6 + n^8$, momentum and total energy.

As usual, at equilibrium the distribution functions of each component will be in the form

$$f^i_{jM}(\mathbf{v}) = n^i_j \, M^i \left(\mathbf{v}; \mathbf{u}, \frac{T}{m^i} \right), \qquad i = 1, \ldots, 8, \quad j = 1, \ldots, L^i \,, \tag{3.103}$$

with

$$M^i \left(\mathbf{v}; \mathbf{u}, \frac{T}{m^i} \right) = \left(\frac{m^i}{2 \pi T} \right)^{3/2} \exp \left(- \frac{m^i}{2 T} \, |\mathbf{v} - \mathbf{u}|^2 \right), \tag{3.104}$$

the Maxwellian containing the common mean velocity $\mathbf{u}$ and temperature T.

The relation at equilibrium between number density of each component n^i_j and the total density n^i is still provided by (3.10). Moreover, we have the two mass action laws of chemistry regulating the ratio between reacting species densities:

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(T) \mathcal{Z}^2(T)}{\mathcal{Z}^3(T) \mathcal{Z}^4(T)} \exp \left(\frac{\Delta E^*}{T} \right), \tag{3.105}$$

$$\frac{n^5 n^6}{n^7 n^8} = \left(\frac{m^5 m^6}{m^7 m^8} \right)^{\frac{3}{2}} \frac{\mathcal{Z}^5(T) \mathcal{Z}^6(T)}{\mathcal{Z}^7(T) \mathcal{Z}^8(T)} \exp \left(\frac{\Delta E^{**}}{T} \right), \tag{3.106}$$

with $\Delta E^* = E^3_1 + E^4_1 - E^2_1 - E^1_1$ and $\Delta E^{**} = E^7_1 + E^8_1 - E^5_1 - E^6_1$.. We shall prove that the choice for the signs of the two quantities is arbitrary and it does not affect the results.

The BGK model we are showing here is analogous to the previous ones, thus we write the set of $L^1 + \ldots + L^8$ kinetic BGK-type equations as

$$\frac{\partial f^i_j}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^i_j = \nu^i_j (\mathcal{M}^i_j - f^i_j) \,, \qquad i = 1, \ldots, 8, \qquad j = 1, \ldots, L^i \,, \tag{3.107}$$

in which the collision operator is a relaxation term, with ν^i_j macroscopic collision frequencies and $\mathcal{M}^i_j$ Maxwellian attractors

$$\mathcal{M}^i_j(\mathbf{v}) = \tilde{n}^i_j \left(\frac{m^i}{2 \pi \tilde{T}} \right)^{3/2} \exp \left[- \frac{m^i}{2 \tilde{T}} |\mathbf{v} - \tilde{\mathbf{u}}|^2 \right], \qquad \begin{array}{l} i = 1, \ldots, 8, \\ j = 1, \ldots, L^i, \end{array} \tag{3.108}$$

depending on auxiliary parameters $\tilde{n}^i_j$ ($i = 1, \ldots, 8$, $j = 1, \ldots, L^i$), $\tilde{\mathbf{u}}$, $\tilde{T}$.

In order to be sure that the BGK model provides correct collision equilibria given by Maxwellian distributions depending on a common mean velocity and temperature, we require that fictitious densities satisfy relations

$$\tilde{n}^i_j = \tilde{n}^i \, \frac{\exp \left(- \frac{E^i_j - E^i_1}{\tilde{T}} \right)}{\mathcal{Z}^i(\tilde{T})} \,, \qquad \begin{array}{l} i = 1, \ldots, 8, \\ j = 1, \ldots, L^i, \end{array} \tag{3.109}$$

and in addition fictitious total densities $\tilde{n}^i$ satisfy the constraints

$$\frac{\tilde{n}^1\tilde{n}^2}{\tilde{n}^3\tilde{n}^4} = \left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^1(\tilde{T})\mathcal{Z}^2(\tilde{T})}{\mathcal{Z}^3(\tilde{T})\mathcal{Z}^4(\tilde{T})} \exp\left(\frac{\Delta E^*}{\tilde{T}}\right), \tag{3.110}$$

$$\frac{\tilde{n}^5\tilde{n}^6}{\tilde{n}^7\tilde{n}^8} = \left(\frac{m^5m^6}{m^7m^8}\right)^{\frac{3}{2}} \frac{\mathcal{Z}^5(\tilde{T})\mathcal{Z}^6(\tilde{T})}{\mathcal{Z}^7(\tilde{T})\mathcal{Z}^8(\tilde{T})} \exp\left(\frac{\Delta E^{**}}{\tilde{T}}\right). \tag{3.111}$$

Our purpose is to show that is possible to express auxiliary parameters in terms of the actual quantities of the mixture. This is achieved imposing that the BGK model preserves the conservation of the same collision invariants of the Boltzmann equations. More specifically, we impose conservation of the six combinations of number densities expressed before that give

$$\sum_{j=1}^{L^h} \nu_j^h \int_{\mathbb{R}^3} (\mathcal{M}_j^h - f_j^h) d\mathbf{v} + \sum_{j=1}^{L^k} \nu_j^k \int_{\mathbb{R}^3} (\mathcal{M}_j^k - f_j^k) d\mathbf{v} = 0, \tag{3.112}$$

with (h,k) varying in the set $\{(1,3),(1,4),(2,4),(5,7),(5,8),(6,8)\}$. Then we have conservation of global momentum

$$\sum_{i=1}^{8}\sum_{j=1}^{L^i} \nu_j^i\, m^i \int_{\mathbb{R}^3} \mathbf{v}\, (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = \mathbf{0}, \tag{3.113}$$

and total energy

$$\sum_{i=1}^{8}\sum_{j=1}^{L^i} \nu_j^i \int_{\mathbb{R}^3} \left(\frac{1}{2}\, m^i |\mathbf{v}|^2 + E_j^i\right) (\mathcal{M}_j^i - f_j^i) d\mathbf{v} = 0. \tag{3.114}$$

Relations (3.112) can be expressed as

$$\sum_{j=1}^{L^i} \nu_j^i \tilde{n}_j^i = \sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \sum_{j=1}^{L^1} \nu_j^1 (\tilde{n}_j^1 - n_j^1), \qquad i = 1,\dots,4, \tag{3.115}$$

$$\sum_{j=1}^{L^i} \nu_j^i \tilde{n}_j^i = \sum_{j=1}^{L^i} \nu_j^i n_j^i + \lambda^i \sum_{j=1}^{L^5} \nu_j^5 (\tilde{n}_j^5 - n_j^5), \qquad i = 5,\dots,8, \tag{3.116}$$

with

$$\lambda^1 = \lambda^2 = -\lambda^3 = -\lambda^4 = \lambda^5 = \lambda^6 = -\lambda^7 = -\lambda^8 = 1. \tag{3.117}$$

Bearing in mind (3.109), from (3.115) and (3.116), we can express total fictitious densities $\tilde{n}^2$, $\tilde{n}^3$, $\tilde{n}^4$ and $\tilde{n}^6$, $\tilde{n}^7$, $\tilde{n}^8$ in terms of $\tilde{n}^1$ and $\tilde{n}^5$, respectively:

$$\begin{aligned}\frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})} = &\left[\sum_{j=1}^{L^i} \nu_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right)\right]^{-1} \left\{\sum_{j=1}^{L^i} \nu_j^i n_j^i - \lambda^i \sum_{j=1}^{L^1} \nu_j^1 n_j^1 \right.\\ &\left. + \lambda^i \left[\sum_{j=1}^{L^1} \nu_j^1 \exp\left(-\frac{E_j^1 - E_1^1}{\tilde{T}}\right)\right] \frac{\tilde{n}^1}{\mathcal{Z}^1(\tilde{T})}\right\}, \quad i = 1,\dots,4,\end{aligned} \tag{3.118}$$

$$\begin{aligned}\frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})} = &\left[\sum_{j=1}^{L^i} \nu_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right)\right]^{-1} \left\{\sum_{j=1}^{L^i} \nu_j^i n_j^i - \lambda^i \sum_{j=1}^{L^5} \nu_j^5 n_j^5 \right.\\ &\left. + \lambda^i \left[\sum_{j=1}^{L^5} \nu_j^5 \exp\left(-\frac{E_j^5 - E_1^5}{\tilde{T}}\right)\right] \frac{\tilde{n}^5}{\mathcal{Z}^5(\tilde{T})}\right\}, \quad i = 5,\dots,8,\end{aligned} \tag{3.119}$$

observing that for $i = 1$ and $i = 5$ we get trivial identities. We rewrite expressions above in a more compact form using functions

$$\mathcal{P}^i \overset{\text{def}}{=} \frac{1}{\mathcal{Z}^i(\tilde{T})} \sum_{j=1}^{L^i} \nu_j^i \exp\left(-\frac{E_j^i - E_1^i}{\tilde{T}}\right), \quad i = 1, \ldots, 8, \tag{3.120}$$

thus relations (3.118)-(3.119) become

$$\tilde{n}^i = \lambda^i \tilde{n}^1 \frac{\mathcal{P}^1(\tilde{T})}{\mathcal{P}^i(\tilde{T})} + \frac{\alpha^i}{\mathcal{P}^i(\tilde{T})}, \qquad i = 1, \ldots, 4, \tag{3.121}$$

$$\tilde{n}^i = \lambda^i \tilde{n}^5 \frac{\mathcal{P}^5(\tilde{T})}{\mathcal{P}^i(\tilde{T})} + \frac{\beta^i}{\mathcal{P}^i(\tilde{T})} \qquad i = 5, \ldots, 8, \tag{3.122}$$

with quantities

$$\alpha^i \overset{\text{def}}{=} \sum_{j=1}^{L^i} \nu_j^i n_j^i - \lambda^i \sum_{j=1}^{L^1} \nu_j^1 n_j^1, \qquad i = 1, \ldots, 4, \tag{3.123}$$

$$\beta^i \overset{\text{def}}{=} \sum_{j=1}^{L^i} \nu_j^i n_j^i - \lambda^i \sum_{j=1}^{L^5} \nu_j^5 n_j^5, \qquad i = 5, \ldots, 8. \tag{3.124}$$

Since in the model we obviously have conservation of total mass, that is expressed as

$$\sum_{i=1}^{8} m^i \sum_{j=1}^{L^i} \nu_j^i \tilde{n}_j^i = \sum_{i=1}^{8} m^i \sum_{j=1}^{L^i} \nu_j^i n_j^i, \tag{3.125}$$

we write conservation of total momentum (3.113) as

$$\sum_{i=1}^{8} \left(\sum_{h=1}^{L^i} \nu_h^i \, m^i \, \tilde{n}_h^i \tilde{\mathbf{u}} - \sum_{j=1}^{L^i} \nu_j^i \, m^i \, n_j^i \mathbf{u}_j^i \right) = \mathbf{0}\,, \tag{3.126}$$

and we use (3.125) to express the auxiliary mean velocity as follows

$$\tilde{\mathbf{u}} = \frac{\displaystyle\sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu_j^i \, m^i \, n_j^i \, \mathbf{u}_j^i}{\displaystyle\sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu_j^i \, m^i \, n_j^i}. \tag{3.127}$$

Conservation of total energy (3.114), instead, leads to

$$\frac{3}{2} \sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu_j^i \, n_j^i \tilde{T} + \sum_{i=1}^{8} \sum_{j=1}^{L^i} \tilde{n}_j^i \nu_j^i \, E_j^i = \Lambda \tag{3.128}$$

and the term Λ containing only actual densities, velocities, temperatures and energies is

$$\Lambda \overset{\text{def}}{=} \frac{1}{2} \left(\sum_{i=1}^{8} m^i \sum_{j=1}^{L^i} \nu_j^i \, n_j^i \, \left(|\mathbf{u}_j^i|^2 - |\tilde{\mathbf{u}}|^2\right) \right) + \frac{3}{2} \left(\sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu_j^i \, n_j^i \, T_j^i \right) + \sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu_j^i \, E_j^i \, n_j^i\,. \tag{3.129}$$

and we have that (3.128) becomes

$$\frac{3}{2}\sum_{i=1}^{8}\sum_{j=1}^{L^i}\nu_j^i\,n_j^i\tilde{T}+\sum_{i=1}^{8}\sum_{j=1}^{L^i}\frac{\tilde{n}^i}{\mathcal{Z}^i(\tilde{T})}\nu_j^i\,E_j^i\exp\left(-\frac{E_j^i-E_1^i}{\tilde{T}}\right)=\Lambda. \tag{3.130}$$

Inserting (3.121) and (3.122) into (3.130), we have the following expression

$$\mathcal{D}(\tilde{T})\left[\tilde{n}^1\mathcal{P}^1(\tilde{T})-\sum_{j=1}^{L^1}\nu_j^1 n_j^1\right]+\mathcal{B}(\tilde{T})\left[\tilde{n}^5\mathcal{P}^5(\tilde{T})-\sum_{j=1}^{L^5}\nu_j^5 n_j^5\right]=\mathcal{N}(\tilde{T}), \tag{3.131}$$

with functions

$$\mathcal{D}(\tilde{T})\overset{\text{def}}{=}\sum_{i=1}^{4}\lambda^i\,\mathcal{E}^i(\tilde{T}),\qquad \mathcal{B}(\tilde{T})\overset{\text{def}}{=}\sum_{i=5}^{8}\lambda^i\,\mathcal{E}^i(\tilde{T}), \tag{3.132}$$

$$\mathcal{N}(\tilde{T})\overset{\text{def}}{=}\Lambda-\sum_{i=1}^{8}\left(\sum_{m=1}^{L^i}\nu_m^i\,n_m^i\right)\left[\frac{3}{2}\tilde{T}+\mathcal{E}^i(\tilde{T})\right], \tag{3.133}$$

being

$$\mathcal{E}^i(\tilde{T})\overset{\text{def}}{=}\frac{\displaystyle\sum_{j=1}^{L^i}\nu_j^i\,E_j^i\exp\left(-\frac{E_j^i-E_1^i}{\tilde{T}}\right)}{\displaystyle\sum_{k=1}^{L^i}\nu_k^i\exp\left(-\frac{E_k^i-E_1^i}{\tilde{T}}\right)}. \tag{3.134}$$

Expression (3.131) gives a relation between the auxiliary densities $\tilde{n}^1$, $\tilde{n}^5$ and $\tilde{T}$, in particular, it allows us to express $\tilde{n}^5$ in terms of $\tilde{n}^1$ and $\tilde{T}$. Showing that these quantities are uniquely determined and that are physically admissible is a much more involved problem, in comparison with the case of only four reacting gases, since we have two remaining free unknowns. Anyway, we can exploit in this case the two fictitious mass action laws (3.110)-(3.111) in order to construct a system of two equations.

By inserting the expressions (3.121) in (3.110) we get a first transcendental equation

$$\mathcal{G}^*(\tilde{T},\tilde{n}^1)=\left(\frac{m^1m^2}{m^3m^4}\right)^{\frac{3}{2}}, \tag{3.135}$$

with

$$\mathcal{G}^*(\tilde{T},\tilde{n}^1)\overset{\text{def}}{=}\mathcal{G}_1(\tilde{n}^1)\cdot\mathcal{G}_2(\tilde{T})\cdot\mathcal{G}_3(\tilde{T}), \tag{3.136}$$

being

$$\mathcal{G}_1(\tilde{T},\tilde{n}^1)\overset{\text{def}}{=}\frac{\tilde{n}^1\left[\tilde{n}^1+\dfrac{\alpha^2}{\mathcal{P}^1(\tilde{T})}\right]}{\left[-\tilde{n}^1+\dfrac{\alpha^3}{\mathcal{P}^1(\tilde{T})}\right]\left[-\tilde{n}^1+\dfrac{\alpha^4}{\mathcal{P}^1(\tilde{T})}\right]}, \tag{3.137}$$

$$\mathcal{G}_2(\tilde{T})\overset{\text{def}}{=}\frac{\displaystyle\sum_{k=1}^{L^3}\nu_k^3\exp\left(-\frac{E_k^3-E_1^3}{\tilde{T}}\right)\sum_{k=1}^{L^4}\nu_k^4\exp\left(-\frac{E_k^4-E_1^4}{\tilde{T}}\right)}{\displaystyle\sum_{k=1}^{L^1}\nu_k^1\exp\left(-\frac{E_k^1-E_1^1}{\tilde{T}}\right)\sum_{k=1}^{L^2}\nu_k^2\exp\left(-\frac{E_k^2-E_1^2}{\tilde{T}}\right)}, \tag{3.138}$$

$$\mathcal{G}_3(\tilde{T}) \overset{\text{def}}{=} \exp\left(-\frac{\Delta E^*}{\tilde{T}}\right). \tag{3.139}$$

We want now to show that there exists a unique pair of values $(\tilde{T},\ \tilde{n}^1)$ for which $\tilde{n}^5$ is uniquely determined accordingly to the two mass action laws and in addition all the densities $\tilde{n}^i$ are positive.

First of all we consider equation (3.135) and define the set of admissible densities $\tilde{n}^1$ as

$$A_1 = \left\{\tilde{n}^1 > 0\ :\ \max\left(0, -\frac{\alpha^2}{\mathcal{P}^1(\tilde{T})}\right) < \tilde{n}^1 < \min\left(\frac{\alpha^3}{\mathcal{P}^1(\tilde{T})}, \frac{\alpha^4}{\mathcal{P}^1(\tilde{T})}\right),\ \forall\ \tilde{T} > 0\right\}. \tag{3.140}$$

Now we rewrite equation (3.135) as follows

$$L^*(\tilde{T}, \tilde{n}^1) = 0, \tag{3.141}$$

with

$$L^*(\tilde{T}, \tilde{n}^1) \overset{\text{def}}{=} \mathcal{G}_1(\tilde{T}, \tilde{n}^1) - M(\tilde{T}), \quad M(\tilde{T}) \overset{\text{def}}{=} \Big[\mathcal{G}_2(\tilde{T}) \cdot \mathcal{G}_3(\tilde{T})\Big]^{-1} \cdot \left(\frac{m^1 m^2}{m^3 m^4}\right)^{\frac{3}{2}}, \tag{3.142}$$

being $\mathcal{G}_1$, $\mathcal{G}_2$, $\mathcal{G}_3$ defined in (3.136), (3.138), (3.139), respectively. We can state the following result.

Lemma 3.3.1. *For any value $\bar{T} > 0$ there exists a unique positive value $\bar{n}^1$ in the admissible set A_1 such that (3.141) is satisfied. Moreover there exists an open interval I with $\bar{T} \in I$ and a unique function $\tilde{n}^1(\tilde{T}) : I \to (0, +\infty)$ such that $\tilde{n}^1(\bar{T}) = \bar{n}^1$ and $L^*(\tilde{T}, \tilde{n}^1(\tilde{T})) = 0$ for any $\tilde{T} \in I$. Moreover $\tilde{n}^1(\tilde{T})$ is differentiable on I and it is possible to write explicitly its derivative with respect to $\tilde{T}$.*

Proof. We compute

$$\frac{\partial \mathcal{G}_1}{\partial \tilde{n}^1} = \mathcal{G}_1 \mathcal{P}^1(\tilde{T}) \left[\frac{1}{\mathcal{P}^1(\tilde{T})\tilde{n}^1} + \frac{1}{\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^2} + \frac{1}{-\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^3} + \frac{1}{-\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^4}\right], \tag{3.143}$$

and we observe that $\dfrac{\partial \mathcal{G}_1}{\partial \tilde{n}^1}$ is strictly positive in the admissible set A_1. It follows that for any fixed value $\bar{T} > 0$ the function $\mathcal{G}_1$ is strictly monotonically increasing with respect to $\tilde{n}^1$ in A_1 and it ranges between

$$\lim_{\tilde{n}^1 \to \max\left(0, -\frac{\alpha^2}{\mathcal{P}^1(\bar{T})}\right)} \mathcal{G}_1 = 0 \tag{3.144}$$

and

$$\lim_{\tilde{n}^1 \to \min\left(\frac{\alpha^3}{\mathcal{P}^1(\bar{T})}, \frac{\alpha^4}{\mathcal{P}^1(\bar{T})}\right)} \mathcal{G}_1 = +\infty. \tag{3.145}$$

Thus, for any positive value $\bar{T}$, there is a unique admissible value $\bar{n}^1$ for which equation (3.141) is satisfied and we are able to express it explicitly in terms of $\bar{T}$:

$$\bar{n}^1 = \tilde{n}^1(\bar{T}) = \frac{-\alpha^2 - M(\bar{T})(\alpha^3 + \alpha^4) + \sqrt{\left[\alpha^2 + M(\bar{T})(\alpha^3 + \alpha^4)\right]^2 + 4\alpha^3\alpha^4 M(\bar{T})(1 - M(\bar{T}))}}{2\left(1 - M(\bar{T})\right)\mathcal{P}^1(\bar{T})}. \tag{3.146}$$

Being $\dfrac{\partial L^*}{\partial \tilde{n}^1} = \dfrac{\partial \mathcal{G}_1}{\partial \tilde{n}^1}$ strictly positive and being $L^*(\tilde{T}, \tilde{n}^1)$ differentiable with respect to $\tilde{T}$ for any $\tilde{T}$, we can apply the implicit function theorem that allows us to write the derivative

$$(\tilde{n}^1)'(\tilde{T}) = -\left(\frac{\partial L^*(\tilde{T}, \tilde{n}^1)}{\partial \tilde{T}}\right)\left(\frac{\partial L^*(\tilde{T}, \tilde{n}^1)}{\partial \tilde{n}^1}\right)^{-1}. \tag{3.147}$$

At this point we compute the derivative of function $L^*(\tilde{T}, \tilde{n}^1)$ with respect to $\tilde{T}$

$$\frac{\partial L^*(\tilde{T}, \tilde{n}^1)}{\partial \tilde{T}} = \frac{\partial \mathcal{G}_1}{\partial \tilde{T}} - M'(\tilde{T}), \tag{3.148}$$

thus, being

$$\frac{\partial \mathcal{G}_1}{\partial \tilde{T}} = \mathcal{G}_1 \tilde{n}^1 (\mathcal{P}^1)'(\tilde{T}) \left[\frac{1}{\mathcal{P}^1(\tilde{T})\tilde{n}^1} + \frac{1}{\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^2} + \frac{1}{-\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^3} + \frac{1}{-\mathcal{P}^1(\tilde{T})\tilde{n}^1 + \alpha^4} \right], \tag{3.149}$$

we get

$$(\tilde{n}^1)'(\tilde{T}) = -\frac{\tilde{n}^1(\tilde{T})(\mathcal{P}^1)'(\tilde{T})}{\mathcal{P}^1(\tilde{T})} + M'(\tilde{T}) \left(\frac{\partial \mathcal{G}_1}{\partial \tilde{n}^1} \right)^{-1}, \tag{3.150}$$

with, repeating calculations analogous to those performed in Section 3.1,

$$M'(\tilde{T}) = \left[\mathcal{G}_2(\tilde{T}) \cdot \mathcal{G}_3(\tilde{T}) \right]^{-1} \cdot \left(\frac{m^1 m^2}{m^3 m^4} \right)^{\frac{3}{2}} \cdot \frac{\mathcal{D}(\tilde{T})}{\tilde{T}^2}. \tag{3.151}$$

□

Now we adopt the notation

$$Y^i(\tilde{T}, \tilde{n}^i) \stackrel{\text{def}}{=} \tilde{n}^i \mathcal{P}^i(\tilde{T}), \quad i = 5, \ldots, 8, \tag{3.152}$$

and, combining (3.122) and (3.131) we express quantities $Y^5, \ldots, Y^8$ in terms of Y^1 and $\tilde{T}$

$$Y^i = \lambda^i \left\{ \frac{\mathcal{N}(\tilde{T})}{\mathcal{B}(\tilde{T})} + \frac{\mathcal{D}(\tilde{T})}{\mathcal{B}(\tilde{T})} \left[\sum_{j=1}^{L^1} \nu_j^1 n_j^1 - Y^1 \right] \right\} + \sum_{j=1}^{L^i} \nu_j^i n_j^i, \quad i = 5, \ldots, 8. \tag{3.153}$$

In addition, thanks to the results obtained in the previous lemma, quantities (3.153) can be actually written in terms of the variable $\tilde{T}$ only; indeed, it is sufficient to insert in the relations above the quantity $Y^1(\tilde{T}) \stackrel{\text{def}}{=} \tilde{n}^1(\tilde{T})\mathcal{P}^1(\tilde{T})$, with $\tilde{n}^1(\tilde{T}\ )$ given by expression (3.146), defining

$$\mathcal{S}(\tilde{T}) \stackrel{\text{def}}{=} \frac{\mathcal{N}(\tilde{T})}{\mathcal{B}(\tilde{T})} + \frac{\mathcal{D}(\tilde{T})}{\mathcal{B}(\tilde{T})} \left[\sum_{j=1}^{L^1} \nu_j^1 n_j^1 - Y^1(\tilde{T}) \right], \tag{3.154}$$

and getting

$$Y^i(\tilde{T}) = \lambda^i \mathcal{S}(\tilde{T}) + \sum_{j=1}^{L^i} \nu_j^i n_j^i, \quad i = 5, \ldots, 8. \tag{3.155}$$

Inserting such quantities into (3.111) we have a second transcendental equation in $\tilde{T}$

$$\mathcal{G}^{**}(\tilde{T}) = \left(\frac{m^5 m^6}{m^7 m^8} \right)^{\frac{3}{2}}, \tag{3.156}$$

with

$$\mathcal{G}^{**}(\tilde{T}) \stackrel{\text{def}}{=} \mathcal{G}_4(\tilde{T}) \cdot \mathcal{G}_5(\tilde{T}) \cdot \mathcal{G}_6(\tilde{T}), \tag{3.157}$$

being

$$\mathcal{G}_4(\tilde{T}) \overset{\text{def}}{=} \frac{\left[\sum_{j=1}^{L^5} \nu_j^5 n_j^5 + \mathcal{S}(\tilde{T})\right] \left[\sum_{j=1}^{L^6} \nu_j^6 n_j^6 + \mathcal{S}(\tilde{T})\right]}{\left[\sum_{j=1}^{L^7} \nu_j^7 n_j^7 - \mathcal{S}(\tilde{T})\right] \left[\sum_{j=1}^{L^8} \nu_j^8 n_j^8 - \mathcal{S}(\tilde{T})\right]}, \tag{3.158}$$

$$\mathcal{G}_5(\tilde{T}) \overset{\text{def}}{=} \frac{\sum_{k=1}^{L^7} \nu_k^7 \exp\left(-\frac{E_k^7 - E_1^7}{\tilde{T}}\right) \sum_{k=1}^{L^8} \nu_k^8 \exp\left(-\frac{E_k^8 - E_1^8}{\tilde{T}}\right)}{\sum_{k=1}^{L^5} \nu_k^5 \exp\left(-\frac{E_k^5 - E_1^5}{\tilde{T}}\right) \sum_{k=1}^{L^6} \nu_k^6 \exp\left(-\frac{E_k^6 - E_1^6}{\tilde{T}}\right)}, \tag{3.159}$$

$$\mathcal{G}_6(\tilde{T}) \overset{\text{def}}{=} \exp\left(-\frac{\Delta E^{**}}{\tilde{T}}\right). \tag{3.160}$$

We show that is possible to find a unique solution of (3.156) in terms of the actual parameters of the mixture. Firstly, we define the admissible set for the temperature

$$A_2 = \left\{ \tilde{T} > 0 \,:\, \max\left(-\sum_{j=1}^{L^5} \nu_j^5 n_j^5, -\sum_{j=1}^{L^6} \nu_j^6 n_j^6\right) < \mathcal{S}(\tilde{T}) < \min\left(\sum_{j=1}^{L^7} \nu_j^7 n_j^7, \sum_{j=1}^{L^8} \nu_j^8 n_j^8\right)\right\}. \tag{3.161}$$

Then, we extend results obtained in Section 3.2 to this case.

Lemma 3.3.2. *Let $I = (\tilde{T}_1, \tilde{T}_2) \subseteq A_2$ be any interval in which the function $\mathcal{B}(\tilde{T})$ given in* (3.132) *is strictly negative (positive), then the function $\mathcal{S}(\tilde{T})$ is strictly monotonically increasing (decreasing) in I with respect to $\tilde{T}$.*

Proof. Recalling expressions (3.133) and (3.132), we define

$$\hat{\mathcal{N}}(\tilde{T}) \overset{\text{def}}{=} \mathcal{N}(\tilde{T}) + \mathcal{D}(\tilde{T}) \left[\sum_{j=1}^{L^1} \nu_j^1 n_j^1 - Y^1(\tilde{T})\right]. \tag{3.162}$$

Thus we write $\mathcal{S}(\tilde{T})$ as

$$\mathcal{S}(\tilde{T}) = \frac{\hat{\mathcal{N}}(\tilde{T})}{\mathcal{B}(\tilde{T})}, \tag{3.163}$$

and its derivative with respect to $\tilde{T}$ can be written as

$$\mathcal{S}'(\tilde{T}) = \frac{\hat{\mathcal{N}}'(\tilde{T})}{\mathcal{B}(\tilde{T})} - \mathcal{S}(\tilde{T}) \frac{\mathcal{B}'(\tilde{T})}{\mathcal{B}(\tilde{T})}. \tag{3.164}$$

Defining functions

$$\mathcal{F}^i(\tilde{T}) \overset{\text{def}}{=} \frac{\sum_{j=1}^{L^i} \sum_{k=1}^{L^i} \frac{\nu_j^i \nu_k^i}{2\tilde{T}^2} \left[E_j^i - E_k^i\right]^2 \exp\left(-\frac{E_j^i + E_k^i - 2E_1^i}{\tilde{T}}\right)}{\left[\sum_{k=1}^{L^i} \nu_k^i \exp\left(-\frac{E_k^i - E_1^i}{\tilde{T}}\right)\right]^2} \geq 0, \quad i = 1, \ldots, 8, \tag{3.165}$$

we are able to write

$$\mathcal{D}'(\tilde{T}) = \sum_{i=1}^{4} \lambda^i \mathcal{F}^i(\tilde{T}), \qquad \mathcal{B}'(\tilde{T}) = \sum_{i=5}^{8} \lambda^i \mathcal{F}^i(\tilde{T}), \tag{3.166}$$

getting

$$\begin{aligned} \hat{\mathcal{N}}'(\tilde{T}) = & -\frac{3}{2}\sum_{i=1}^{8}\left(\sum_{j=1}^{L^i}\nu_j^i\, n_j^i\right) - \sum_{i=5}^{8}\left(\sum_{j=1}^{L^i}\nu_j^i\, n_j^i\right)\mathcal{F}^i(\tilde{T}) \\ & -\sum_{i=1}^{4}\left[\sum_{j=1}^{L^i}\nu_j^i\, n_j^i + \lambda^i\left(Y^1(\tilde{T}) - \sum_{j=1}^{L^1}\nu_j^1 n_j^1\right)\right]\mathcal{F}^i(\tilde{T}) - \mathcal{D}(\tilde{T})(Y^1)'(\tilde{T}) \end{aligned} \tag{3.167}$$

which, since the quantity $Y^1(\tilde{T})$ belongs to A_1, is negative. Thus we get

$$\begin{aligned} \mathcal{S}'(\tilde{T}) = & -\frac{1}{\mathcal{B}(\tilde{T})}\left\{\frac{3}{2}\sum_{i=1}^{8}\left(\sum_{j=1}^{L^i}\nu_j^i\, n_j^i\right) + \sum_{i=5}^{8}\left[\sum_{j=1}^{L^i}\nu_j^i\, n_j^i + \lambda^i\mathcal{S}(\tilde{T})\right]\mathcal{F}^i(\tilde{T})\right. \\ & \left. +\sum_{i=1}^{4}\left[\sum_{j=1}^{L^i}\nu_j^i\, n_j^i + \lambda^i\left(Y^1(\tilde{T}) - \sum_{j=1}^{L^1}\nu_j^1 n_j^1\right)\right]\mathcal{F}^i(\tilde{T}) + \mathcal{D}(\tilde{T})(Y^1)'(\tilde{T})\right\}. \end{aligned} \tag{3.168}$$

Underlying the fact that we are taking $\tilde{T}$ in the admissible set A_2 and since by results of Lemma 3.3.1 we have

$$(Y^1)'(\tilde{T}) = (\tilde{n}^1)'(\tilde{T})\mathcal{P}^1(\tilde{T}) + \tilde{n}^1(\tilde{T})(\mathcal{P}^1)'(\tilde{T}) = M'(\tilde{T})\left(\frac{\partial \mathcal{G}_1}{\partial \tilde{n}^1}\right)^{-1}, \tag{3.169}$$

with $M'(\tilde{T})$ expressed in (3.151) that, being the functions $\mathcal{G}_2$ and $\mathcal{G}_3$ positive, has the same sign of $\mathcal{D}(\tilde{T})$. We can then conclude that the term in the whole curly brackets of (3.168) is positive and thus the signs of $\mathcal{S}'(\tilde{T})$ and $\mathcal{B}(\tilde{T})$ are opposite. □

We prove another result concerning the behavior of $\mathcal{S}$.

Lemma 3.3.3. *The function $\mathcal{S}(\tilde{T})$ admits a unique positive value T^* such that $\mathcal{S}(\tilde{T}) = 0$.*

Proof. Since

$$\mathcal{S}(\tilde{T}) = \frac{\hat{\mathcal{N}}(\tilde{T})}{\mathcal{B}(\tilde{T})}, \tag{3.170}$$

keeping in mind the the expression of $\hat{\mathcal{N}}(\tilde{T})$ defined in (3.162), we show that the function vanishes for a unique value of $\tilde{T}$. We are discussing the result depending on the sign of the quantity ΔE^*. If $\Delta E^* < 0$, recalling the definition of function $M(\tilde{T})$ given in (3.142), we have $\lim_{\tilde{T}\to 0^+} M(\tilde{T}) = 0$, and from expression (3.146) we have

$$Y^1(\tilde{T}) = \frac{-\alpha^2 - M(\tilde{T})(\alpha^3+\alpha^4) + \sqrt{\left[\alpha^2 + M(\tilde{T})(\alpha^3+\alpha^4)\right]^2 + 4\alpha^3\alpha^4 M(\tilde{T})(1-M(\tilde{T}))}}{2\left(1 - M(\tilde{T})\right)}. \tag{3.171}$$

So we can write

$$\lim_{\tilde{T}\to 0^+} Y^1(\tilde{T}) = 0. \tag{3.172}$$

If, instead, $\Delta E^* > 0$, the limit for $\tilde{T} \to 0^+$ of $M(\tilde{T})$ is $+\infty$, so the computation of the limit of $Y^1(\tilde{T})$ is not straightforward. In fact we get (rationalizing (3.171))

$$\begin{aligned}
&\lim_{\tilde{T}\to 0^+} Y^1(\tilde{T}) \\
&= \lim_{\tilde{T}\to 0^+} \frac{2\alpha^3\alpha^4\, M(\tilde{T})}{\alpha^2 + M(\tilde{T})\,(\alpha^3+\alpha^4) + \sqrt{(\alpha^2)^2 + M(\tilde{T})^2\,(\alpha^3-\alpha^4)^2 + M(\tilde{T})\,(2\alpha^2\,[\alpha^3+\alpha^4) + 4\alpha^3\alpha^4]}} \\
&= \lim_{\tilde{T}\to 0^+} \frac{2\alpha^3\alpha^4}{\frac{\alpha^2}{M(\tilde{T})} + (\alpha^3+\alpha^4) + \sqrt{\frac{(\alpha^2)^2}{M(\tilde{T})^2} + (\alpha^3-\alpha^4)^2 + \frac{\alpha^2(\alpha^3+\alpha^4)+4\alpha^3\alpha^4}{M(\tilde{T})}}} \\
&= \frac{2\alpha^3\alpha^4}{\alpha^3+\alpha^4+|\alpha^3-\alpha^4|} = \alpha^K, \qquad (3.173)
\end{aligned}$$

with $K = 4$ if $\alpha^3 > \alpha^4$ or $K = 3$ if $\alpha^4 > \alpha^3$, the effective value does not affect the result. At this point we can state that, keeping in mind the expressions for quantities α^i given in (3.123),

$$\lim_{\tilde{T}\to 0^+} \mathcal{D}(\tilde{T}) \left[\sum_{j=1}^{L^1} \nu_j^1 n_j^1 - Y^1(\tilde{T})\right] = \begin{cases} -\Delta E^* \displaystyle\sum_{j=1}^{L^1} \nu_j^1 n_j^1 & \text{if } \Delta E^* < 0 \\ \Delta E^* \displaystyle\sum_{j=1}^{L^K} \nu_j^K n_j^K & \text{if } \Delta E^* > 0, \end{cases} \qquad (3.174)$$

that is, in both cases, a positive quantity. Computing the limit of $\mathcal{N}(\tilde{T})$

$$\begin{aligned}
\lim_{\tilde{T}\to 0^+} \mathcal{N}(\tilde{T}) =& \frac{1}{2}\left(\sum_{i=1}^{8} m^i \sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, \left(|\mathbf{u}_j^i|^2 - |\tilde{\mathbf{u}}|^2\right)\right) + \frac{3}{2}\left(\sum_{i=1}^{8}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, T_j^i\right) \\
&+ \sum_{i=1}^{8}\sum_{j=1}^{L^i} \nu_j^i\, n_j^i\, \left(E_j^i - E_1^i\right) > 0, \qquad (3.175)
\end{aligned}$$

we can state that the function $\hat{\mathcal{N}}(\tilde{T})$ tends to a positive value as $\tilde{T} \to 0^+$. On the other hand

$$\lim_{\tilde{T}\to +\infty} \hat{\mathcal{N}}(\tilde{T}) = -\infty. \qquad (3.176)$$

Recalling now that $\hat{\mathcal{N}}'(\tilde{T}) < 0$, and being the function $\hat{\mathcal{N}}(\tilde{T})$ continuous, it is null in only one $\tilde{T} = T^*$. $\square$

Now we have the following result.

Lemma 3.3.4. *On every interval* $\left(\tilde{T}_1, \tilde{T}_2\right) \subseteq A_2$ *the sign of* $\mathcal{B}(\tilde{T})$ *does not change.*

Proof. Being the limit

$$\lim_{\tilde{T}\to 0} \mathcal{B}(\tilde{T}) = -\Delta E^{**}, \qquad \lim_{\tilde{T}\to +\infty} \mathcal{B}(\tilde{T}) = \sum_{i=5}^{8} \lambda^i \frac{\displaystyle\sum_{j=1}^{L^i} \nu_j^i\, E_j^i}{\displaystyle\sum_{j=1}^{L^i} \nu_j^i}, \qquad (3.177)$$

and since the derivative of $\mathcal{B}(\tilde{T})$ expressed in (3.166) may change sign in relation to internal energy levels and collision frequencies, it could exist a positive value $T^{\#}$ root of $\mathcal{B}(\tilde{T})$. We shall suppose that the choice of initial data, internal energies and collision frequencies is such that $T^{\#} \neq T^*$, since in this case we would have only algebraic equations. We suppose that $T^{\#}$ belongs to an interval $\left(\tilde{T}_1, \tilde{T}_2\right) \subseteq A_2$, but we would have also

$$\lim_{\tilde{T} \to \tilde{T}^{\#}} \mathcal{S}(\tilde{T}) = \pm\infty \tag{3.178}$$

getting a neighborhood of $\tilde{T}^{\#}$ not contained in A_2. Thus $\mathcal{B}(\tilde{T})$ does not vanish on any interval $\left(\tilde{T}_1, \tilde{T}_2\right)$ of A_2. □

Now, let $\left(\tilde{T}_a, \tilde{T}_b\right)$ be a connected component of A. The previous result has as a consequence the fact that on $\left(\tilde{T}_a, \tilde{T}_b\right)$ the sign of $\mathcal{S}'(\tilde{T})$ does not change. This means that $\mathcal{S}(\tilde{T})$ varies monotonically from the minimum to the maximum value that it can assume in A_2, which have different sign. Consequently it has a root in $\left(\tilde{T}_1, \tilde{T}_2\right)$. Also in the case in which $\tilde{T}_a = 0$, since $\lim_{\tilde{T} \to 0} \mathcal{B}(\tilde{T}) < 0$, $\mathcal{S}(\tilde{T})$ is monotonically increasing from $\lim_{\tilde{T} \to 0} \mathcal{S}(\tilde{T}) < 0$ to its upper bound that is positive, having a root as well. Since in Lemma 3.3.3 we proved that $\mathcal{S}(\tilde{T})$ has a unique positive root, it follows that $\left(\tilde{T}_a, \tilde{T}_b\right)$ is the only connected component of A_2, then the set A_2 is connected. This fact allows us to study the properties of the function $\mathcal{G}^*(\tilde{T}, Y^5)$ defined in (3.136), in particular we have the following statement.

Lemma 3.3.5. *There exists a unique value* $\bar{T} \in A_2$ *such that*

$$L^{**}(\bar{T}) \overset{def}{=} \mathcal{G}^{**}(\bar{T}) - \left(\frac{m^5 m^6}{m^7 m^8}\right)^{\frac{3}{2}} = 0. \tag{3.179}$$

Proof. We compute the derivative with respect to $\tilde{T}$ of the function $L^{**}(\tilde{T})$. Repeating the same calculations performed in Section 3.1 we have

$$\frac{dL^{**}(\tilde{T})}{d\tilde{T}} = L^{**}(\tilde{T}) \left\{ \mathcal{S}'(\tilde{T}) \left[\sum_{i=5}^{8} \left(\sum_{j=1}^{L^i} \nu^i_j n^i_j + \lambda^i \mathcal{S}(\tilde{T}) \right)^{-1} \right] - \frac{1}{\tilde{T}^2} \mathcal{B}(\tilde{T}) \right\}. \tag{3.180}$$

The term in square brackets is positive in A_2 and, as proved in Lemma 3.3.2, $(\mathcal{S})'(\tilde{T})$ and $-\mathcal{B}(\tilde{T})$ have the same sign. It follows that $L^{**}(\tilde{T})$ is strictly monotonically increasing or decreasing in A_2, that is an interval of type $\left(\tilde{T}_{min}, \tilde{T}_{max}\right)$. In particular, when $\tilde{T} \to \tilde{T}_{min}$, $L^{**}(\tilde{T}) \to -\left(\frac{m^5 m^6}{m^7 m^8}\right)^{\frac{3}{2}}$ and when $\tilde{T} \to \tilde{T}_{max}$, $L^{**}(\tilde{T}) \to +\infty$, or vice versa. This holds also in the case $\tilde{T}_{min} = 0$ if we have $\Delta E^{**} > 0$; if, instead, $\Delta E^{**} < 0$, it is needed to take the inverse in both sides of equation (3.156) and repeat all the calculations defining $L^{**}(\bar{T})$ as $\left[G^{**}(\bar{T})\right]^{-1} - \left(\frac{m^7 m^8}{m^5 m^6}\right)^{\frac{3}{2}}$. Thus, we can find a value $\bar{T}$ for which $L^{**}(\bar{T}) = 0$. □

This result provides the existence and uniqueness of a solution of an admissible auxiliary temperature $\tilde{T}$ that can be expressed in terms of actual parameters of the mixture. By inserting it in (3.146) we get the admissible quantity Y^1 then from (3.121) and (3.153) we obtain the remaining Y^i, $i = 2, \ldots, 8$. This allows us to reconstruct the Maxwellian attractors $\mathcal{M}^i_j$ given in (3.108) and those attractors provide the equilibrium states of the distribution functions for $i = 1, \ldots, 8$ and $j = 1, \ldots, L^i$. In particular, equilibrium mean velocities, temperatures, and number densities of each component will be exactly the auxiliary parameters individuated previously:

$$\mathbf{u}^i_j = \tilde{\mathbf{u}} = \mathbf{u}\,, \qquad T^i_j = \tilde{T} = T, \qquad n^i_j = \tilde{n}^i_j, \qquad i = 1, \ldots, 8, \qquad j = 1, \ldots, L^i, \tag{3.181}$$

with global density of each gas n^i related to the number densities of its components by the usual constraint

$$n^i_j = n^i \, \frac{\exp\left(-\frac{E^i_j - E^i_1}{\tilde{T}}\right)}{\mathcal{Z}^i(\tilde{T})}\,, \tag{3.182}$$

and all the densities n^i of the the two quadruples involved in the two reactions are bound together by (3.105) and (3.106), respectively. We are able to prove that, in space homogeneous conditions, these equilibria are asymptotically stable. Indeed, we set the densities vector $\underline{\mathbf{f}} = (f^1_1, \ldots, f^8_{L^8})$ and we define the physical entropy as

$$\mathcal{H}[\underline{\mathbf{f}}] = \sum_{i=1}^{8} \sum_{j=1}^{L^i} \int_{\mathbb{R}^3} f^i_j \log(f^i_j)\, d\mathbf{v}. \tag{3.183}$$

Then we have the classical result already shown in analogous or more general settings.

Theorem 3.3.6. *Let* $\underline{\mathbf{f}}_0$ *be an initial state for the problem* (3.107) *in space homogeneous conditions and let* $\underline{\mathbf{f}}_{\mathcal{M}}$ *be the corresponding stationary state. Then for the functional* $\mathcal{H}$ *defined in* (3.183) *we have* $\mathcal{H}[\underline{\mathbf{f}}^*] > \mathcal{H}[\underline{\mathbf{f}}_{\mathcal{M}}]$ *and* $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ *for any* $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}_{\mathcal{M}}$*, while* $\dot{\mathcal{H}}[\underline{\mathbf{f}}_{\mathcal{M}}] = 0$. *It follows that the functional* $\mathcal{H}$ *defined in* (3.183) *is a Lyapunov functional for the BGK model and* $\underline{\mathbf{f}}_{\mathcal{M}}$ *is the unique stable equilibrium.*

Proof. The proof of this result is analogous to the one performed in Section 3.2 for the four gases case. The main differences are that, when showing the minimality of the Maxwellian configuration, computing the quantity

$$\sum_{i=1}^{8} \sum_{j=1}^{L^i} \int_{\mathbb{R}^3} \left.\frac{\partial \mathfrak{H}}{\partial f^i_j}\right|_{\underline{\mathbf{f}}^M} \left(f^{i*}_j - \mathcal{M}^i_j\right) d\mathbf{v} \tag{3.184}$$

with

$$\mathfrak{H}[\mathbf{f}] = \sum_{i=1}^{8} \sum_{j=1}^{L^i} f^i_j \log\left(\frac{f^i_j}{(m^i)^3}\right) \tag{3.185}$$

and $f^{i^*}_j$ any other configuration, we have to take into account the fact that for number densities in the Maxwellian state n^i and for those in the other state n^{i^*} we have

$$n^1 - n^{1^*} = n^2 - n^{2^*} = -(n^3 - n^{3^*}) = -(n^4 - n^{4^*}), \tag{3.186}$$

$$n^5 - n^{5^*} = n^6 - n^{6^*} = -(n^7 - n^{7^*}) = -(n^8 - n^{8^*}). \tag{3.187}$$

Moreover, in the calculations, we have to take into account both the mass action laws. Similarly, the two laws apply when we show that $\dot{\mathcal{H}}[\underline{\mathbf{f}}^*] < 0$ for any $\underline{\mathbf{f}}^* \neq \underline{\mathbf{f}}_{\mathcal{M}}$ and $\dot{\mathcal{H}}[\underline{\mathbf{f}}_{\mathcal{M}}] = 0$, in particular we use them to state that

$$\sum_{i=1}^{8} \sum_{j=1}^{L^i} \nu^i_j \int_{\mathbb{R}^3} \left(\mathcal{M}^i_j - f^{i*}_j\right) \log\left(\frac{\mathcal{M}^i_j}{(m^i)^3}\right) d\mathbf{v} = 0\,. \tag{3.188}$$

□

3.4 Macroscopic equations for mixtures of eight gases involved in two disjoint chemical reactions

We derive from the BGK model (3.107) evolution equations for main macroscopic fields (number densities, mean velocities, temperatures) for each component of the gas species of the mixture, performing the same calculations reported in the previous sections; we restrict also in this case to the space homogeneous conditions in one space dimension, obtaining the following system

$$\begin{cases} \dfrac{\partial n_j^i}{\partial t} = \nu_j^i (\tilde{n}_j^i - n_j^i)\,, & \begin{array}{l} i = 1, \ldots, 8, \\ j = 1, \ldots, L^i, \end{array} \\ \dfrac{\partial u_j^i}{\partial t} = \nu_j^i \, \dfrac{\tilde{n}_j^i}{n_j^i} (\tilde{u} - u_j^i)\,, & \begin{array}{l} i = 1, \ldots, 8, \\ j = 1, \ldots, L^i, \end{array} \\ \dfrac{\partial T_j^i}{\partial t} = \nu_j^i \, \dfrac{\tilde{n}_j^i}{n_j^i} \left(\tilde{T} - T_j^i + \dfrac{1}{3} \, m^i \, (\tilde{u} - u_j^i)^2 \right), & \begin{array}{l} i = 1, \ldots, 8, \\ j = 1, \ldots, L^i. \end{array} \end{cases} \tag{3.189}$$

Auxiliary quantities are given in terms of the actual ones, more specifically, $\tilde{u}$ is explicitly given in (3.127), $\tilde{n}_j^i$ is provided by (3.109) and (3.118)-(3.119), once that the temperature $\tilde{T}$ is found as solution of the system of two transcendental equations given by (3.135)-(3.156) and the quantity $\tilde{n}^5$ can be obtained from (3.131). The evolution of the $3(L^1 + \ldots + L^8)$ equations of (3.189) provides the trend towards a unique equilibrium configuration that is uniquely determined once that initial quantities $(n_j^i)_0$, $(u_j^i)_0$, $(T_j^i)_0$ are assigned.

3.4.1 Numerical simulations

For simulations, we take into account the two reversible reactions taken as model in Section 3.2, that were considered as two separate mixtures, and we take them now as a mixture of eight interacting gas species. The two reactions are one involving hydrogen H_2 (with mass 2.02 g/mol), iodine I_2 (253.8 g/mol) and hydrogen iodide HI (127.91 g/mol)

$$H_2 + I_2 \leftrightharpoons HI + HI, \tag{3.190}$$

and another one having as reactants chloro nitride $ClNO_2$ (81.46 g/mol) and nitric oxide NO (30.01 g/mol) forming nitrosyl chloride $ClNO$ (65,46 g/mol) and nitrogen dioxide NO_2 (46.01 g/mol)

$$ClNO_2 + NO \leftrightharpoons NO_2 + ClNO. \tag{3.191}$$

Thus, we set up eight gas species that have mass ratios reproducing gases involved in reactions (3.190) - (3.191). In particular, we suppose that species G^3 and G^4 coincide, so they shall share not only the same mass but also the same internal structure and initial data. Masses of gas species involved in our model will then be

$$\begin{gathered} m^1 = 0.1, \quad m^2 = 12.8, \quad m^3 = m^4 = 6.45, \\ m^5 = 4.03, \quad m^6 = 1.49, \quad m^7 = 2.28, \quad m^8 = 3.24. \end{gathered} \tag{3.192}$$

For the internal energy structure of species involved, instead, we suppose each gas composed by energy components with corresponding energy values for each species as follows

$$\begin{aligned}
&G^1 = C_1^1 \cup C_2^1, && E_1^1 = 6.5, \quad E_2^1 = 7.5,\\
&G^2 = C_1^2 \cup C_2^2 \cup C_3^2, && E_1^2 = 7, \quad E_2^2 = 8, \quad E_3^2 = 8.5,\\
&G^3 = C_1^3 \cup C_2^3, && E_1^3 = 6, \quad E_2^3 = 7,\\
&G^4 = C_1^4 \cup C_2^4, && E_1^4 = 6, \quad E_2^4 = 7,\\
&G^5 = C_1^5 \cup C_2^5, && E_1^5 = 6, \quad E_2^5 = 7,\\
&G^6 = C_1^6 \cup C_2^6 \cup C_3^6 \cup C_4^6, && E_1^6 = 7, \quad E_2^6 = 8, \quad E_3^6 = 10, \quad E_4^6 = 12,\\
&G^7 = C_1^7 \cup C_2^7 \cup C_3^7, && E_1^7 = 5.5, \quad E_2^7 = 6, \quad E_3^7 = 7.5,\\
&G^8 = C_1^8 \cup C_2^8 \cup C_3^8, && E_1^8 = 4, \quad E_2^8 = 9, \quad E_3^8 = 10.
\end{aligned} \tag{3.193}$$

Quantities considered in our simulations will be components concentrations given by

$$c_j^i = \frac{n_j^i}{\sum_{h=1}^{8} \sum_{k=1}^{L^h} n_k^h}, \tag{3.194}$$

along with velocities and temperatures, both normalized with respect to the corresponding equilibrium values. We set now initial data for concentrations, velocities and temperatures as reported in Table 3.7 and Table 3.8.

	C_1^1	C_2^1	C_1^2	C_2^2	C_3^2	C_1^3	C_2^3	C_1^4	C_2^4
c_0	0.06	0.03	0.04	0.02	0.07	0.06	0.05	0.06	0.05
u_0	0.3	0	0.1	0.4	0.2	0.6	0.1	0.6	0.1
T_0	2	4	1	2.5	2	6	1.5	6	1.5

Table 3.7

	C_1^5	C_2^5	C_1^6	C_2^6	C_3^6	C_4^6	C_1^7	C_2^7	C_3^7	C_1^8	C_2^8	C_3^8
c_0	0.06	0.05	0.04	0.04	0.06	0.03	0.04	0.02	0.07	0.06	0.04	0.05
u_0	0.3	0	0.1	0.4	0.2	0.6	0.1	0.4	0.5	0.3	0	0.2
T_0	2	4	1	2.5	2	6	1.5	2.5	3	4.5	5	1

Table 3.8

As regards collision frequencies, we define the sets of indices as done in Sections 3.1 and 3.2, taking for $i = 1, \dots, 8$ and $j = 1, \dots, L^i$

$$\mathcal{D}^{1}{}_j^i = \left\{ \begin{array}{l} h = 1, \dots, 8, \\ m = 1, \dots, L^i, \\ k, p = 1, \dots, L^h \end{array} \; : E_m^i + E_p^h - E_j^i - E_k^h \le 0 \right\}, \tag{3.195}$$

$$\mathcal{D}^{2}{}^{i}_{j} = \left\{ \begin{array}{ll} h = 1, \dots, 8, & \\ m = 1, \dots, L^i, & : E^i_m + E^h_p - E^i_j - E^h_k > 0 \\ k, p = 1, \dots, L^h & \end{array} \right\}, \tag{3.196}$$

$$\mathcal{D}^{3}{}^{i}_{j} = \left\{ h, l, n : \begin{array}{cl} i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(1,2), (3,4), (2,1), (4,3)\}, & p = 1, \dots, L^n \end{array} : E^l_m + E^n_p - E^i_j - E^h_k \leq 0 \right\}, \tag{3.197}$$

$$\mathcal{D}^{4}{}^{i}_{j} = \left\{ h, l, n : \begin{array}{cl} i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(1,2), (3,4), (2,1), (4,3)\}, & p = 1, \dots, L^n \end{array} : E^l_m + E^n_p - E^i_j - E^h_k > 0 \right\}, \tag{3.198}$$

$$\mathcal{D}^{5}{}^{i}_{j} = \left\{ h, l, n : \begin{array}{cl} i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(5,6), (7,8), (6,5), (8,7)\}, & p = 1, \dots, L^n \end{array} : E^l_m + E^n_p - E^i_j - E^h_k \leq 0 \right\}, \tag{3.199}$$

$$\mathcal{D}^{6}{}^{i}_{j} = \left\{ h, l, n : \begin{array}{cl} i \neq n, & k = 1, \dots, L^h, \\ (i,h), (l,n) & m = 1, \dots, L^l, \\ \in \{(5,6), (7,8), (6,5), (8,7)\}, & p = 1, \dots, L^n \end{array} : E^l_m + E^n_p - E^i_j - E^h_k > 0 \right\}, \tag{3.200}$$

and taking

$$\nu^i_j = \sum_{h,k,m,p \in \mathcal{D}^{2}{}^{i}_{j}} \nu^{m,p}_{j,k} n^h_k \exp\left(- \frac{E^i_m + E^h_p - E^i_j - E^h_k}{T} \right) + \sum_{h,k,m,p \in \mathcal{D}^{1}{}^{i}_{j}} \nu^{m,p}_{j,k} n^h_k \tag{3.201}$$

$$+ \sum_{h,k,l,m,n,p \in \mathcal{D}^{4}{}^{i}_{j} \cup \mathcal{D}^{6}{}^{i}_{j}} \nu^{m,p}_{j,k} n^h_k \left(\frac{m^i m^j}{m^l m^n} \right)^{\frac{3}{2}} \exp\left(- \frac{E^l_m + E^n_p - E^i_j - E^h_k}{T} \right) \tag{3.202}$$

$$+ \sum_{h,k,l,m,n,p \in \mathcal{D}^{3}{}^{i}_{j} \cup \mathcal{D}^{5}{}^{i}_{j}} \nu^{m,p}_{j,k} n^h_k \tag{3.203}$$

with $\nu^{m,p}_{j,k} = \dfrac{k+j}{20(m+p)}$. Results obtained show final concentrations of single components and of gas species set as reported in Table 3.9, Table 3.10 and Table 3.11.

	C^1_1	C^1_2	C^2_1	C^2_2	C^2_3	C^3_1	C^3_2	C^4_1	C^4_2
c_M	0.002	0.002	0.02	0.015	0.013	0.111	0.084	0.111	0.084

Table 3.9

In particular, we have that ratios between reactants and products of the two reactions are

$$\frac{\gamma^1_M + \gamma^2_M}{\gamma^3_M + \gamma^4_M} = 0.13, \qquad \frac{\gamma^5_M + \gamma^6_M}{\gamma^7_M + \gamma^8_M} = 0.54. \tag{3.204}$$

	C^5_1	C^5_2	C^6_1	C^6_2	C^6_3	C^6_4
c_M	0.044	0.033	0.055	0.041	0.023	0.013
	C^7_1	C^7_2	C^7_3	C^8_1	C^8_2	C^8_3
c_M	0.068	0.059	0.039	0.129	0.031	0.024

Table 3.10

	G^1	G^2	G^3	G^4	G^5	G^6	G^7	G^8
γ_M	0.004	0.047	0.195	0.195	0.077	0.133	0.165	0.227

Table 3.11

Compared with results in Section 3.2 for the two reactions taken separately, for which we recall that ratios between reactants and products were 0.033 for reaction (3.190) and 0.7 for reaction (3.191), we can observe that the equilibrium is different. In particular, for reaction (3.190) we have a higher final presence of reactants, instead for reaction (3.191) reactants are slightly more reduced, with consequent higher increasing of products. Final values for mean velocity and temperature are, instead, $\mathbf{u}_M = 0.27$ and $T_M = 3.54$. These values are not very different from the ones obtained in the two simulations for the separate reactions. The behavior in time of components concentrations, normalized mean velocities $\bar{u}^i_j = u^i_j/u_M$ and normalized temperatures $\bar{T}^i_j = T^i_j/T_M$ in space homogeneous conditions is depicted in Figures 3.7 and 3.8.

3.5 Conclusions

We have generalized the BGK model proposed in Chapter 2 to mixtures of polyatomic gases undergoing bimolecular and reversible chemical reactions. The additional difficulties with respect to the inert frame are essentially due to two reasons. At first, single number densities are no more preserved during the evolution, since particles involved in a reactive collision change their nature; consequently, proper auxiliary number densities affect the Maxwellian attractors of the BGK collision operators, and they are related in a non–trivial way to species masses and concentrations, to global (auxiliary) temperature and to the chemical energy gap. Then, the mass action laws of chemistry that characterize chemical collision equilibrium, and that are assumed to be valid also for auxiliary parameters, constitute additional transcendental equations to be combined to the energy conservation requirement (that is a transcendental law by itself) in order to prove well–posedness of auxiliary number densities and temperature.

In particular, as first model, we have considered a gas mixture of four species undergoing a chemical reaction. In this case from the conservation of total mass, we found that all auxiliary densities can be expressed in terms of only one of them and of the auxiliary temperature. Moreover, from conservation of total energy, the former can be expressed as function of the latter. Finally, from the mass action law related to the reaction, we obtained a transcendental equation for the auxiliary temperature and we proved that it has a unique positive solution in the admissible set, i.e. the set for which all the auxiliary

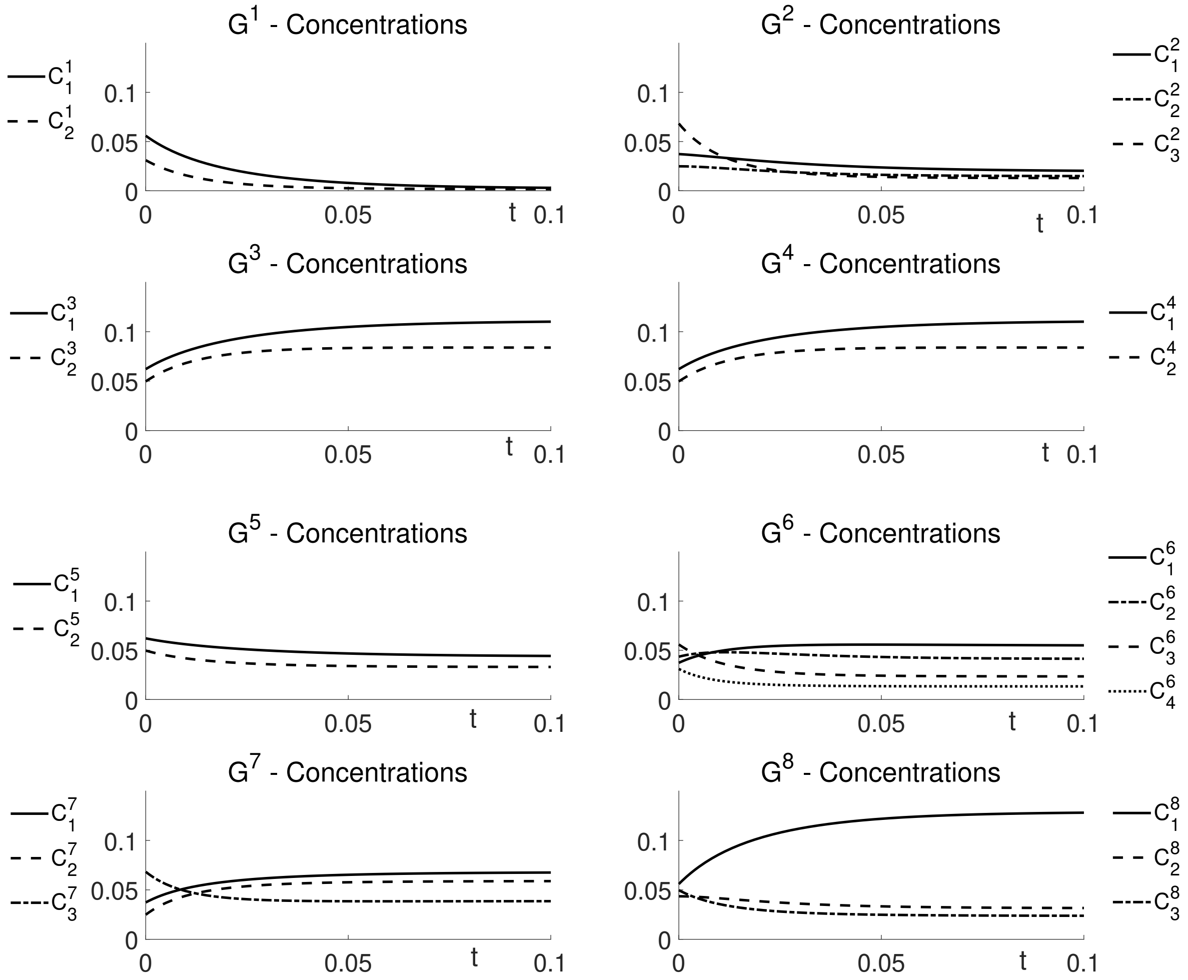

Figure 3.7: Concentrations for a mixture of eight reacting gases with energy levels as in (3.193), initial values for concentrations, velocities and temperatures as in Tables 3.7 and 3.8, considering masses reported in 3.192.

densities are positive. We have also performed some numerical simulations of evolution equations for species concentrations, velocities and temperatures corresponding to this BGK model. Firstly, we have considered two different mixtures, with particle mass ratios corresponding to real cases, namely to the ones of two real bimolecular and reversible chemical reactions. The trend to equilibrium turns out to be much slower for the species much lighter than the others, and this is in agreement with the separation of species with disparate masses observed in several physical problems [68]. As last test, we have taken into account a real case of bimolecular but irreversible reaction. Aware of the fact that our model is based on reversible reactions (for irreversible ones the mass action law used would not be applicable) we have performed numerical simulations taking mass ratios similar to the real ones and then adjusting parameters to have a consistent consumption of one of the reactant in favor of a major final quantity of products. Results obtained show that we have such an outcome taking a quite high energy gap between reactants and products, low initial temperatures values and setting collision frequencies in order to make the inverse endothermic reaction less probable.

The second model for which we have made a BGK-type based study is a mixture of eight gas

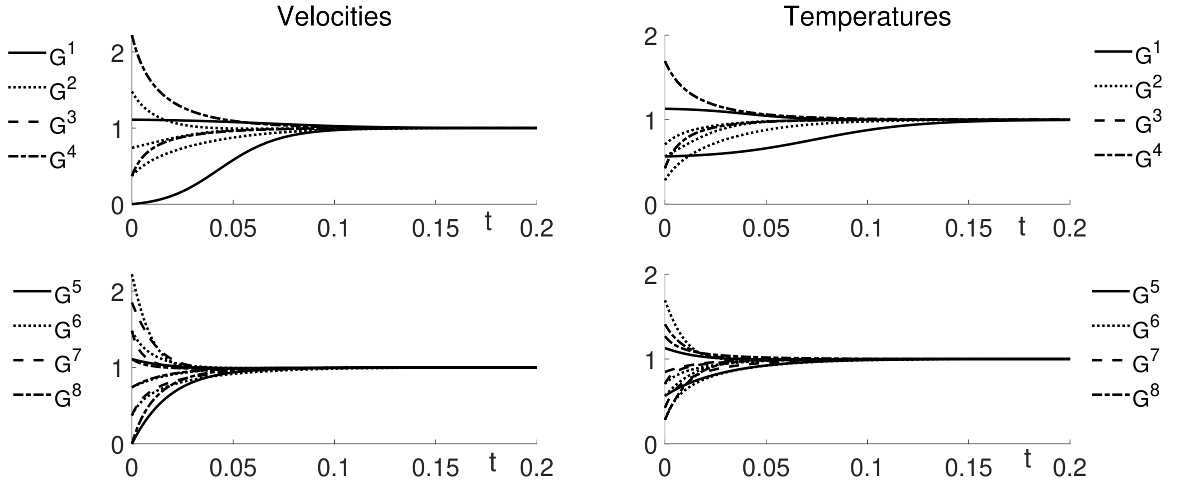

Figure 3.8: Normalized velocities and temperatures for a mixture of eight reacting gases with energy levels as in (3.193), initial values for concentrations, velocities and temperatures as in Tables 3.7 and 3.8, considering masses reported in 3.192.

species involved in two separate chemical reactions. For this framework, the expression of auxiliary quantities in terms of actual parameters is much more technical. From conservation of total mass, we have that species involved in the first reaction can be expressed in terms of the auxiliary temperature and one of the four densities involved, the same for the second reaction. Thus we have three auxiliary unknowns. Applying conservation of total energy, we have obtained a relation involving the three quantities, and this yields that one of the two densities can be written in terms of the other one and the temperature. Using the first mass action law, we have shown that is possible to express the remaining density as function of the temperature, which is finally the only admissible solution of a transcendental equation coming from the second mass action law. The demonstration of existence of such solution is more involved, especially in the first part. Here, in fact, in the computation of various limits the sign of the energy gap related to the first reaction plays an important role and we had to distinguish two possible cases. Also for this second mixture we have performed numerical simulations for macroscopic quantities. Considering the two reversible reactions taken as separated models in the four-species case, we have taken them together, observing different equilibrium ratios between reactants and products for both.

We finally point out how it would be interesting to test our BGK model and corresponding macroscopic equations also in space dependent problems, as for instance the shock wave structure, comparing our results with the ones obtained for inert mixtures in the frame of extended thermodynamics [85], or from kinetic systems for reactive monatomic gases [18] or for a single polyatomic gas [73, 96].

4 Derivation of reaction-diffusion equations from kinetic models for gas mixtures

In the previous part of the thesis, we have derived, from BGK models, equations for the macroscopic quantities. As known, the whole system describing the behavior in space and time of observables is not closed. Through proper scaling procedures is possible to derive the classical Euler or Navier-Stokes equations for gaseous flows, see e.g. [15]. Another possible strategy leading to closed macroscopic systems, adopted in [12], is to obtain, starting from the kinetic description of Boltzmann type for a mixture of four reacting gas species, reaction-diffusion equations for the number densities of reactants. The utility of such an asymptotic closure is confirmed by the fact that a wide range of phenomena can be described by means of reaction-diffusion systems in mathematical biology, with particular reference to the epidemiology (diffusion of infectious diseases) [86, 91, 92, 120], in ecology [34], in the physics of hot plasmas [121], and of course in chemistry [76]. Mathematical aspects of these systems have been extensively investigated, see for instance [62, 95, 119].

Starting from the features of gas mixtures considered so far, we want to apply the strategy of [12] to a mixture where monoatomic and polyatomic gases interact, not only elastically, both also chemically and non-elastically. In more detail, this chapter is organized as follows. In Section 4.1 we present the physical setting we are considering: a binary mixture composed by a polyatomic (diatomic, having two discrete internal energy levels) and a monatomic gas, diffusing in a gaseous background (typically, the atmosphere) composed by three much denser monoatomic gas species. We write the kinetic Boltzmann equations for the two components of the polyatomic species and the monatomic one, with explicit collision operators for elastic collisions, two possible inelastic transitions and two reversible chemical encounters. We perform a time scaling in which the dominant process is assumed to be the elastic scattering with the host medium, while we present three different scalings for the various chemical reactions. In the first one we assume that all elastic encounters with the background occur with the same frequency, and that all chemical and inelastic collisions occur at a much slower (common) scale. In the second, we suppose that monatomic species collides with the background more frequently, while in the third one we also take one of the chemical reactions occurring at a faster time scale. Section 4.2 is devoted to the diffusive asymptotic limit from the kinetic level, in the first hydrodynamic regime, leading to a closed set of three reaction–diffusion equations for species number densities. Then, in Section 4.3 the second regime is explored, obtaining a system of two reaction–diffusion equations and a third equation with only a reactive term. The last modification in the regime is considered in Section 4.4, in which we obtain a reduced set of only two macroscopic equations similar to the classical Brusselator system. Finally, Section 4.5 contains some concluding remarks. This chapter is an extension of results proposed in author's post-print [22].

4.1 Physical setting and Boltzmann equations

We consider a mixture of two rarefied gases diffusing in a background medium: one species Y is supposed to have two possible energy levels, E_1 and E_2, thus, according to the way of modeling proposed in [56, 58] and considered throughout the other chapters of this work, it can be decomposed into two different components, Y_1 and Y_2; the other gas Z is monatomic and has only one energy level, E_Z. Particle masses of these gases are denoted by m_Y and m_Z, respectively.

The host medium, which from the physical point of view could be seen as the atmosphere, is a gaseous mixture and is much denser than the considered species Y_1, Y_2, Z. Specifically, in this model the background is provided by a mixture of three gas species A, B and C, with different particle masses m_A, m_B, m_C. Also these background species are supposed to have only one possible energy level, expressed by E_A, E_B, E_C, respectively. Their distributions are supposed to be fixed Maxwellians, with constant number densities n_A, n_B, n_C, temperature equal to one and zero mean velocity:

$$f_J(\mathbf{v}) = n_J M_J(\mathbf{v}) \qquad M_J(\mathbf{v}) = n_J \left(\frac{m_J}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{m_J|\mathbf{v}|^2}{2}\right) \qquad J = A, B, C. \tag{4.1}$$

We shall write and investigate (in different asymptotic limits) kinetic Boltzmann equations for the evolution of distribution functions of species Y_1, Y_2, Z, denoted by f_1, f_2, f_Z, respectively. Besides on molecular velocity $\mathbf{v}$, they depend also on time t and on the space variable $\mathbf{x}$. Particles, in addition to elastic collisions with the background medium and among themselves, are assumed subject to the following inelastic transitions or chemical reactions

$$A + Y_1 \to A + Y_2, \tag{4.2}$$

$$Z + Y_2 \to Z + Y_1, \tag{4.3}$$

$$B + Y_1 \leftrightarrows A + C, \tag{4.4}$$

$$Y_1 + Y_1 \leftrightarrows Z + B. \tag{4.5}$$

The interactions (4.2) and (4.3) are inelastic transitions where particles of species Y, colliding with the background (in (4.2)) or with the other species Z (in (4.3)), pass from one energy state to the other, namely a particle of the component Y_1 transforms itself into a particle of the component Y_2 or vice versa. The collisions (4.4) and (4.5) represent bimolecular and reversible chemical reactions: (4.4) describes creation or disappearance of a particle of species Y_1 through interactions with the background medium; in (4.5) a pair of particles Y_1 produces a particle Z and a background particle or the other way round. From the physical point of view, the reactions (4.2)–(4.5) represent a simple set of bimolecular interactions (that can be easily modelled by Boltzmann operators) allowing to recover, in a suitable hydrodynamic limit that will be detailed afterwards, the well known Brusselator system [98]. External production of particles is provided by chemical interactions with the fixed background, and passages from one component to another (with the same mass) occur through inelastic transitions.

The kinetic Boltzmann equations for distributions $f_I(t, \mathbf{x}, \mathbf{v})$, with $I = 1, 2, Z$, may be cast as

$$\frac{\partial f_I}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_I = \sum_{J=A,B,C} Q^I_{EL}(f_I, n_J M_J) + \sum_{K=1,2,Z} Q^I_{EL}(f_I, f_K) + Q^I_{IN}(\underline{\mathbf{f}}) + Q^I_{CH}(\underline{\mathbf{f}}) \,. \tag{4.6}$$

Here $Q^I_{EL}(f_I, n_J M_J)$ denotes the collision operator for the elastic scattering between the considered species I and one background species $J = A, B, C$. Then, the operator $Q^I_{EL}(f_I, f_K)$ describes the elastic collisions between particles of the species I and particles of only one other species $K = 1, 2, Z$, including of course the case $K = I$. Finally, the operator $Q^I_{IN}(\underline{\mathbf{f}})$ takes into account the effects on species I due to inelastic transitions (4.2), (4.3), and $Q^I_{CH}(\underline{\mathbf{f}})$ the effects due to the chemical reactions (4.4), (4.5); here $\underline{\mathbf{f}}$ denotes the whole set of distributions, the precise dependencies will be specified here below.

We shall write explicitly the collision operators that govern the dynamics, adapting the generic operators derived in section 1.1 of Chapter 1, which are written for generic encounters, to each particular collision (4.2)–(4.5). For this reason, we shall use the same notation for all quantities and functions involved in calculations. For convenience, we report the operator for a generic encounter between four components, C_I, C_J, C_H, C_K,

$$C_I + C_J \leftrightarrows C_H + C_K, \tag{4.7}$$

that is (for component C_I)

$$\begin{aligned} &Q_I[f_I, f_J, f_H, f_K](\mathbf{v}) \\ &\quad = \int_{\mathbb{R}^3} \int_{S^2} \mathrm{H}\left(g^2 - \delta_{IJ}^{HK}\right) g \sigma_{IJ}^{HK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \left[\left(\frac{\mu_{IJ}}{\mu_{HK}} \right)^3 f_H(\mathbf{v}') f_K(\mathbf{w}') - f_I(\mathbf{v}) f_J(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}'. \end{aligned} \tag{4.8}$$

Concerning operators relative to elastic collisions, they come directly from the classical Boltzmann collision model. In this case there is nor internal energy exchange, nor change of particles masses, thus both the Heaviside function and the ratio between reduced masses are identically one. Consequently, elastic operators between a gas component I and a background species J are

$$Q^I_{EL}(f_I, n_J M_J)(\mathbf{v}) = \int_{\mathbb{R}^3 \times S^2} \sigma_{IJ}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \Big[f_I(\mathbf{v}') n_J M_J(\mathbf{w}') - f_I(\mathbf{v}) n_J M_J(\mathbf{w}) \Big] d\mathbf{w} d\hat{\mathbf{\Omega}}' \tag{4.9}$$

for $I = 1, 2, Z$ and $J = A, B, C$, while elastic operators between a gas component I and another component K are

$$Q^I_{EL}(f_I, f_K)(\mathbf{v}) = \int_{\mathbb{R}^3 \times S^2} \sigma_{IK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \Big[f_I(\mathbf{v}') f_K(\mathbf{w}') - f_I(\mathbf{v}) f_K(\mathbf{w}) \Big] d\mathbf{w} d\hat{\mathbf{\Omega}}'. \tag{4.10}$$

In this case we indicate by $\sigma_{IJ}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')$ and $\sigma_{IK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')$ the differential cross sections. Moreover, a Maxwell molecule assumption [87] will be adopted throughout the chapter: the intermolecular forces are supposed to be proportional to the in verse power $\frac{1}{d^5}$, where d is the intermolecular distance. This has as a consequence [36] that

$$\int_{S^2} \sigma_{IJ}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \, d\hat{\mathbf{\Omega}}' \overset{\text{def}}{=} \nu_{IJ}, \qquad \int_{S^2} \sigma_{IK}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \, d\hat{\mathbf{\Omega}}' \overset{\text{def}}{=} \nu_{IK}, \tag{4.11}$$

where ν_{IJ} and ν_{IK} are constant collision frequencies.

As concerns inelastic transitions, we have dissipation or absorption of internal energy during the collision, but particles do not change their nature. Furthermore, we are taking into account only "one-way" transitions, thus we shall take the collision operator in case of irreversible processes, outlined in Chapter 1 as well. Since components Y_1 and Y_2 are involved in both interactions (4.2) and (4.3), their inelastic operators may be split into two parts

$$Q^I_{IN}(\underline{\mathbf{f}}) = Q^I_{IN}(f_1, f_2, n_A M_A) + Q^I_{IN}(f_1, f_2, f_Z)\,, \qquad I = 1, 2. \tag{4.12}$$

Inelastic collision operator for Y_1 related to the collision (4.2) is simply provided by a loss term as

$$Q^1_{IN}(f_1, f_2, n_A M_A)(\mathbf{v}) = -\int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{A2}_{A1}\right) g\sigma^{A2}_{A1}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\, f_1(\mathbf{v}) n_A M_A(\mathbf{w})\, d\mathbf{w} d\hat{\mathbf{\Omega}}'\,. \tag{4.13}$$

On the other hand, collision (4.2) produces a gain term for component Y_2, that may be cast as

$$Q^2_{IN}(f_1, f_2, n_A M_A)(\mathbf{v}) = \int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{A1}_{A2}\right) \frac{(g')^2}{g} \sigma^{A2}_{A1}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') f_1(\mathbf{v}') n_A M_A(\mathbf{w}') d\mathbf{w} d\hat{\mathbf{\Omega}}'. \tag{4.14}$$

Analogous operators are in order for transition (4.3), with a gain term for Y_1 and a loss term for Y_2:

$$Q^1_{IN}(f_1, f_2, f_Z)(\mathbf{v}) = \int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{Z2}_{Z1}\right) \frac{(g')^2}{g} \sigma^{Z1}_{Z2}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\, f_2(\mathbf{v}') f_Z(\mathbf{w}')\, d\mathbf{w} d\hat{\mathbf{\Omega}}'\,, \tag{4.15}$$

$$Q^2_{IN}(f_1, f_2, f_Z)(\mathbf{v}) = -\int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{Z1}_{Z2}\right) g\sigma^{Z1}_{Z2}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\, f_2(\mathbf{v}) f_Z(\mathbf{w})\, d\mathbf{w} d\hat{\mathbf{\Omega}}'. \tag{4.16}$$

The species Z is involved only in the inelastic transition (4.3), and it has both a gain term and a loss term, thus we have

$$\begin{aligned} Q^Z_{IN}(\underline{\mathbf{f}}) = Q^Z_{IN}(f_1, f_2, f_Z)(\mathbf{v}) = \int_{\mathbb{R}^3\times S^2} \Bigg[& \mathbf{H}\left(g^2 - \delta^{Z2}_{Z1}\right) \frac{(g')^2}{g} \sigma^{Z1}_{Z2}(g', \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\, f_2(\mathbf{v}') f_Z(\mathbf{w}') \\ & - \mathbf{H}\left(g^2 - \delta^{Z1}_{Z2}\right) g\sigma^{Z1}_{Z2}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')\, f_2(\mathbf{v}) f_Z(\mathbf{w}) \Bigg] d\mathbf{w} d\hat{\mathbf{\Omega}}'. \end{aligned} \tag{4.17}$$

Boltzmann collision operators relevant to chemical reactions (4.4) and (4.5) are more standard, since bimolecular reversible reactions have been extensively studied in kinetic theory [12, 13, 58] and they can be directly derived from the general operator (4.8). Component Y_1 is involved in both reactions (4.4) and (4.5), therefore the relevant operator is the sum of two terms

$$Q^1_{CH}(\underline{\mathbf{f}}) = Q^1_{CH}(f_1, n_A M_A, n_B M_B, n_C M_C) + Q^1_{CH}(f_1, f_Z, n_B M_B)\,, \tag{4.18}$$

where the first one, taking into account the reaction (4.4), is provided by

$$\begin{aligned} Q^1_{CH}(f_1, n_A M_A, n_B M_B, n_C M_C)(\mathbf{v}) = & \int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{AC}_{B1}\right) \sigma^{AC}_{B1}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') g \\ & \times \left[\left(\frac{m_B m_Y}{m_A m_C}\right)^3 n_C M_C(\mathbf{v}') n_A M_A(\mathbf{w}') - f_1(\mathbf{v}) n_B M_B(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}'\,, \end{aligned} \tag{4.19}$$

and the second one, accounting for the effects of (4.5), reads as

$$\begin{aligned} Q^1_{CH}(f_1, f_Z, n_B M_B)(\mathbf{v}) = & \int_{\mathbb{R}^3\times S^2} \mathbf{H}\left(g^2 - \delta^{ZB}_{11}\right) \sigma^{ZB}_{11}(g, \hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') g \\ & \times \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^3 f_Z(\mathbf{v}') n_B M_B(\mathbf{w}') - f_1(\mathbf{v}) f_1(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}'\,. \end{aligned} \tag{4.20}$$

The other component Y_2 of the polyatomic gas is not involved in reactions (4.4) and (4.5), therefore $Q^2_{CH}(\underline{\mathbf{f}}) = 0$. The monatomic gas Z appears only in reaction (4.5), and we have

$$\begin{aligned} Q^Z_{CH}(\underline{\mathbf{f}}) = Q^Z_{CH}(f_1, f_Z, n_B M_B)(\mathbf{v}) = \int_{\mathbb{R}^3 \times S^2} &\mathrm{H}\left(g^2 - \delta^{11}_{ZB}\right) \sigma^{11}_{ZB}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \\ &\times \left[\left(\frac{m_Z m_B}{m_Y^2} \right)^3 f_1(\mathbf{v}') f_1(\mathbf{w}') - f_Z(\mathbf{v}) n_B M_B(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}' . \end{aligned} \tag{4.21}$$

Even for inelastic transitions (4.2), (4.3) and for the direct reactions in (4.4), (4.5), cross sections will be assumed of Maxwell molecule type as

$$\int_{S^2} \sigma^{HK}_{IJ}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \, d\hat{\mathbf{\Omega}}' \overset{\text{def}}{=} \nu^{HK}_{IJ} , \tag{4.22}$$

with ν^{HK}_{IJ} denoting constant collision frequencies.

4.2 Derivation of a three-component reaction-diffusion system

In this section we derive a reaction–diffusion system for the number densities of the two components Y_1 and Y_2 of the polyatomic gas, and of the monatomic constituent Z as well, in a suitable hydrodynamic limit. To this aim, we rescale the set of Boltzmann equations (4.6) in terms of a small parameter ϵ, standing for the Knudsen number (ratio of the particle mean free path to a macroscopic length, introduced in Chapter 1). We assume different time scales for collisions among particles as follows: the dominant phenomenon is provided by the elastic collisions with the much denser background medium, that are taken of order $1/\epsilon$; binary elastic collisions between particles of the species Y_1, Y_2, Z are less frequent, of order ϵ^p with whatever $p \geq 0$; inelastic and chemical encounters (4.2), (4.3), (4.4) and (4.5) are assumed to be slow processes of order ϵ. Since we are interested also in the effects on species number densities of inelastic or chemical interactions, we take the same $O(\epsilon)$ scaling in front of the temporal derivatives. Thus, the rescaled Boltzmann equations for distribution functions of Y_1, Y_2 and Z read as

$$\begin{aligned} \epsilon \frac{\partial f^\epsilon_1}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^\epsilon_1 = &\ \frac{1}{\epsilon} \sum_{J=A,B,C} Q^1_{EL}(f^\epsilon_1, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q^1_{EL}(f^\epsilon_1, f^\epsilon_I) \\ &+ \epsilon \, Q^1_{IN}(\underline{\mathbf{f}}) + \epsilon \, Q^1_{CH}(\underline{\mathbf{f}}) , \end{aligned} \tag{4.23}$$

$$\epsilon \frac{\partial f^\epsilon_2}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^\epsilon_2 = \frac{1}{\epsilon} \sum_{J=A,B,C} Q^2_{EL}(f^\epsilon_2, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q^2_{EL}(f^\epsilon_2, f^\epsilon_I) + \epsilon \, Q^2_{IN}(\underline{\mathbf{f}}) , \tag{4.24}$$

$$\begin{aligned} \epsilon \frac{\partial f^\epsilon_Z}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f^\epsilon_Z = &\ \frac{1}{\epsilon} \sum_{J=A,B,C} Q^Z_{EL}(f^\epsilon_Z, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q^Z_{EL}(f^\epsilon_Z, f^\epsilon_I) \\ &+ \epsilon \, Q^Z_{IN}(\underline{\mathbf{f}}) + \epsilon \, Q^Z_{CH}(\underline{\mathbf{f}}) . \end{aligned} \tag{4.25}$$

In order to stress the fact that the solution of this system depends on the scaling parameter ϵ, distribution functions are denoted by f^ϵ_I, $I = 1, 2, Z$, and the corresponding number densities will be given by n^ϵ_1, n^ϵ_2, n^ϵ_Z, respectively. We have skipped here the rigorous dimensional analysis leading to the rescaled system (4.23), (4.24), (4.25). A detailed derivation of dimensionless Boltzmann–like or BGK kinetic equations may be found in several references, as for instance [4, 7, 36, 93, 106].

We immediately note that in the kinetic equations (4.23), (4.24) and (4.25) the Boltzmann operators describing collisions with the background play the dominant role, namely

$$\sum_{J=A,B,C} Q^I_{EL}(f^\epsilon_I, n_J M_J) = O(\epsilon), \qquad I = 1,2,Z. \tag{4.26}$$

We show now how distributions f^ϵ_I, for $I = 1,2,Z$, may be seen as perturbations of a collision equilibrium. Since (4.26), we write a first order expansion for each distribution:

$$f^\epsilon_I(t,\mathbf{x},\mathbf{v}) = \tilde{f}^\epsilon_I(t,\mathbf{x},\mathbf{v}) + \epsilon\, \tilde{h}^\epsilon_I(t,\mathbf{x},\mathbf{v})\,, \qquad I = 1,2,Z, \tag{4.27}$$

Consequently, for any subindex I the Boltzmann equation can be written as

$$\mathbf{v}\cdot\nabla_{\mathbf{x}}\tilde{f}^\epsilon_I = \frac{1}{\epsilon}\sum_{J=A,B,C} Q^I_{EL}(\tilde{f}^\epsilon_I, n_J M_J) + \sum_{J=A,B,C} Q^I_{EL}(\tilde{h}^\epsilon_I, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q^J_{EL}(\tilde{f}^\epsilon_I, \tilde{f}^\epsilon_J) + O(\epsilon). \tag{4.28}$$

As first, we immediately get

$$\sum_{J=A,B,C} Q^I_{EL}(\tilde{f}^\epsilon_I, n_J M_J) = 0, \qquad I = 1,2,Z. \tag{4.29}$$

This means that the functions $\tilde{f}^\epsilon_I$ are of Maxwellian type, having mean velocity $\mathbf{0}$ and temperature one as the host medium, namely

$$\tilde{f}^\epsilon_I(t,\mathbf{x},\mathbf{v}) = \tilde{n}^\epsilon_I(t,\mathbf{x}) M_I(\mathbf{v}), \tag{4.30}$$

with

$$M_I(\mathbf{v}) = \left(\frac{m_I}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{m_I|\mathbf{v}|^2}{2}\right). \tag{4.31}$$

From the next order ($O(\epsilon^0)$) of (4.28) we have instead (here we consider the case $p = 0$)

$$\mathbf{v}\cdot\nabla_{\mathbf{x}}\tilde{f}^\epsilon_I - \sum_{I=1,2,Z} Q^J_{EL}(\tilde{f}^\epsilon_I, \tilde{f}^\epsilon_J) = \sum_{J=A,B,C} Q^I_{EL}(\tilde{h}^\epsilon_I, n_J M_J). \tag{4.32}$$

If we define the linear operator:

$$L_I(\cdot) \overset{\text{def}}{=} \sum_{J=A,B,C} Q^I_{EL}(\cdot, n_J M_J), \tag{4.33}$$

it turns out to have the well known mathematical properties of boundedness, self–adjointness, and validity of the Fredholm alternative [12,36] in a suitable L^2 space W, which can be thus decomposed as

$$W = \mathcal{R}(L_I) \oplus \mathcal{K}(L_I), \tag{4.34}$$

being $\mathcal{R}(L_I)$ and $\mathcal{K}(L_I)$ the range and the kernel of L_I, respectively. It means that is possible to uniquely (up to a Maxwellian addendum) determine the functions $\tilde{h}^\epsilon_I$. Summing up, we have

$$f^\epsilon_I(t,\mathbf{x},\mathbf{v}) = \tilde{n}^\epsilon_I(t,\mathbf{x}) M_I(\mathbf{v}) + \epsilon\, \tilde{h}^\epsilon_I(t,\mathbf{x},\mathbf{v}), \qquad I = 1,2,Z. \tag{4.35}$$

Integrating (4.35) in $d\mathbf{v}$ we get, indicating by n_I^ϵ the number density provided by $\int_{\mathbb{R}^3} f_I^\epsilon(\mathbf{v})d\mathbf{v}$,

$$\tilde{n}_I^\epsilon(t,\mathbf{x}) = n_I^\epsilon(t,\mathbf{x}) - \int_{\mathbb{R}^3} \tilde{h}_I^\epsilon(\mathbf{v})d\mathbf{v}, \tag{4.36}$$

and, inserting this expression into (4.35),

$$f_I^\epsilon(t,\mathbf{x},\mathbf{v}) = n_I^\epsilon(t,\mathbf{x})M_I(\mathbf{v}) + \epsilon\, h_I^\epsilon(t,\mathbf{x},\mathbf{v}), \qquad I = 1,2,Z, \tag{4.37}$$

with

$$h_I^\epsilon(t,\mathbf{x},\mathbf{v}) = \tilde{h}_I^\epsilon(\mathbf{v}) - M_I(\mathbf{v})\int_{\mathbb{R}^3} \tilde{h}_I^\epsilon(\mathbf{v})d\mathbf{v}. \tag{4.38}$$

The function h_I^ϵ is of order $O(1)$, fulfilling the constraint

$$\int_{\mathbb{R}^3} h_I^\epsilon(\mathbf{v})\, d\mathbf{v} = 0. \tag{4.39}$$

Therefore, in this hydrodynamic regime, in order to describe the evolution of distribution functions f_I^ϵ at leading order accuracy it is enough to build up consistent evolution equations for number densities n_1^ϵ, n_2^ϵ, n_Z^ϵ.

4.2.1 Equation for the density of the first component

By integrating (4.23) with respect to the kinetic variable $\mathbf{v}$, we get

$$\epsilon\frac{\partial}{\partial t}\int_{\mathbb{R}^3} f_1^\epsilon d\mathbf{v} + \nabla_{\mathbf{x}}\cdot\int_{\mathbb{R}^3} \mathbf{v}f_1^\epsilon d\mathbf{v} = \epsilon\int_{\mathbb{R}^3}\left(Q_{IN}^1\left(\underline{\mathbf{f}}\right) + Q_{CH}^1\left(\underline{\mathbf{f}}\right)\right)d\mathbf{v}, \tag{4.40}$$

since elastic contributions obviously vanish [36] (the nature of particles does not change in elastic collisions):

$$\int_{\mathbb{R}^3} Q_{EL}^1(f_1^\epsilon, n_J M_J)d\mathbf{v} = 0, \quad J = A,B,C, \quad \text{and} \quad \int_{\mathbb{R}^3} Q_{EL}^1(f_1^\epsilon, f_I^\epsilon)d\mathbf{v} = 0, \quad I = 1,2,Z. \tag{4.41}$$

Bearing in mind the expression of the distribution functions provided in (4.37), the equation (4.40) becomes

$$\epsilon\frac{\partial}{\partial t}n_1^\epsilon + \epsilon\,\nabla_{\mathbf{x}}\cdot\int_{\mathbb{R}^3} \mathbf{v}h_1^\epsilon d\mathbf{v} = \epsilon\int_{\mathbb{R}^3}\left(Q_{IN}^1\left(\underline{\mathbf{nM}}\right) + Q_{CH}^1\left(\underline{\mathbf{nM}}\right)\right)d\mathbf{v} + O(\epsilon^2), \tag{4.42}$$

with $\underline{\mathbf{nM}}$ the whole set of Maxwellian distributions $n_I^\epsilon M_I$ $(I = 1,2,Z)$ and $n_J M_J$ $(J = A,B,C)$.

Inelastic and chemical collision contributions may be explicitly computed (for Maxwell molecules interactions) when distributions are accommodated at a Maxwellian shape [13, 56, 58]. Detailed calculations for a general bimolecular and reactive encounter are reported in Appendix A, here we summarize the results relevant to species Y_1. Contributions due to inelastic transitions (4.2) and (4.3) read as

$$\int_{\mathbb{R}^3} Q_{IN}^1(n_1^\epsilon M_1, n_2^\epsilon M_2, n_A M_A)(\mathbf{v})d\mathbf{v} = -\nu_{A1}^{A2}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right)n_A n_1^\epsilon, \tag{4.43}$$

$$\int_{\mathbb{R}^3} Q_{IN}^1(n_1^\epsilon M_1, n_2^\epsilon M_2, n_Z^\epsilon M_Z)(\mathbf{v})d\mathbf{v} = \nu_{Z2}^{Z1}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right)n_Z^\epsilon n_2^\epsilon, \tag{4.44}$$

respectively. As expected, contribution (4.43) is negative, since transitions (4.2) produce a loss of particles Y_1, while term (4.44) is positive, since in encounters (4.3) one gains a particle Y_1. Reactive source terms due to collisions (4.4) and (4.5) are provided, respectively, by

$$\begin{aligned}\int_{\mathbb{R}^3} Q^1_{CH}(n^\epsilon_1 M_1, n_A M_A, n_B M_B, n_C M_C)(\mathbf{v}) d\mathbf{v} =& \nu^{AC}_{B1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{AC}_{B1})\right) \\ & \times \left[\left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{AC}_{B1}\bigr) n_A n_C - n_B n^\epsilon_1 \right], \end{aligned} \tag{4.45}$$

$$\begin{aligned}\int_{\mathbb{R}^3} Q^1_{CH}(n^\epsilon_1 M_1, n^\epsilon_Z M_Z, n_B M_B)(\mathbf{v}) d\mathbf{v} =& \nu^{ZB}_{11} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{ZB}_{11})\right) \\ & \times \left[\left(\frac{m_Y^2}{m_B m_Z}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{ZB}_{11}\bigr) n^\epsilon_Z n_B - (n^\epsilon_1)^2 \right], \end{aligned} \tag{4.46}$$

and they turn out to be a balance between a gain and a loss term, since reactions (4.4) and (4.5) are reversible. In (4.43)–(4.46), symbols ν^{HK}_{IJ} denote collision frequencies defined in (4.22), while Γ is the incomplete Euler gamma function

$$\Gamma(\alpha, y) = \int_y^{+\infty} \tau^{\alpha-1} e^{-\tau} d\tau\,, \tag{4.47}$$

and $\Theta(y) = \max\{y, 0\}$. The presence of these functions is due to the fact that if a reaction is endothermic (namely with a positive internal energy gap $\Delta E^{HK}_{IJ} > 0$), it occurs only if the kinetic energy of the ingoing particles is enough, as already explained in Chapter 1.

By inserting results (4.43)–(4.46) into equation (4.42), we get

$$\begin{aligned} &\frac{\partial}{\partial t} n^\epsilon_1 + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v} \\ &\quad = -\nu^{A2}_{A1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{A2}_{A1})\right) n_A n^\epsilon_1 + \nu^{Z1}_{Z2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{Z1}_{Z2})\right) n^\epsilon_Z n^\epsilon_2 \\ &\qquad + \nu^{AC}_{B1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{AC}_{B1})\right) \left[\left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{AC}_{B1}\bigr) n_A n_C - n_B n^\epsilon_1 \right] \\ &\qquad + \nu^{ZB}_{11} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{ZB}_{11})\right) \left[\left(\frac{m_Y^2}{m_B m_Z}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{ZB}_{11}\bigr) n^\epsilon_Z n_B - (n^\epsilon_1)^2 \right] + O(\epsilon). \end{aligned} \tag{4.48}$$

We would like to express even the integral $\int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v}$ in terms of our unknown macroscopic fields (number densities); to this aim we resort to the momentum equation for species Y_1. More precisely, we multiply (4.23) by the weight function $\mathbf{v}$ and integrate in $d\mathbf{v}$:

$$\begin{aligned} \epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f^\epsilon_1 d\mathbf{v} + & \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f^\epsilon_1 d\mathbf{v} \\ &= \frac{1}{\epsilon} \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q^1_{EL}(f^\epsilon_1, n_J M_J) d\mathbf{v} + \epsilon^p \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q^1_{EL}(f^\epsilon_1, f^\epsilon_I) d\mathbf{v} \\ &\quad + \epsilon \int_{\mathbb{R}^3} \mathbf{v} Q^1_{IN}(\underline{\mathbf{f}})\, d\mathbf{v} + \epsilon \int_{\mathbb{R}^3} \mathbf{v} Q^1_{CH}(\underline{\mathbf{f}})\, d\mathbf{v}. \end{aligned} \tag{4.49}$$

By substituting the expansions (4.37) for $I = 1, 2, Z$, we obtain

$$
\begin{aligned}
\nabla_{\mathbf{x}} \cdot \frac{n_1^\epsilon}{m_Y}\mathbb{I} + \epsilon\, \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) h_1^\epsilon \, d\mathbf{v}
&= \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(h_1^\epsilon, n_J M_J) d\mathbf{v} + \epsilon^{p+1} \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(h_1^\epsilon, n_I^\epsilon M_I) d\mathbf{v} \\
&\quad + \epsilon^{p+1} \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(n_1^\epsilon M_1, h_I^\epsilon) d\mathbf{v} + \epsilon \int_{\mathbb{R}^3} \mathbf{v} \left(Q_{IN}^1\left(\underline{\mathbf{nM}}\right) + Q_{CH}^1\left(\underline{\mathbf{nM}}\right)\right) d\mathbf{v} \\
&\quad + O(\epsilon^2).
\end{aligned}
\tag{4.50}
$$

Here it has been taken into account that, since all Maxwellians share the same zero mean velocity, it clearly holds

$$
\sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(n_1^\epsilon M_1, n_J M_J) d\mathbf{v} = \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(n_1^\epsilon M_1, n_I^\epsilon M_I) d\mathbf{v} = \mathbf{0}, \tag{4.51}
$$

and use has been made also of the trivial results

$$
\int_{\mathbb{R}^3} \mathbf{v}\, n_1^\epsilon M_1 d\mathbf{v} = \mathbf{0}\,, \qquad \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) n_1^\epsilon M_1 d\mathbf{v} = \frac{n_1^\epsilon}{m_Y}\mathbb{I}\,. \tag{4.52}
$$

Neglecting $O(\epsilon)$ terms, (4.50) may be cast as

$$
\nabla_{\mathbf{x}} \cdot \frac{n_1^\epsilon}{m_Y}\mathbb{I} = \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(h_1^\epsilon, n_J M_J) d\mathbf{v} + O(\epsilon)\,. \tag{4.53}
$$

We aim now at computing the elastic contribution on the right hand side of (4.53), bearing in mind that the weak form of the bi-species elastic Boltzmann operator derived in Chapter 1 now reads as

$$
\int_{\mathbb{R}^3} \varphi(\mathbf{v})\, Q_{EL}(f_I, f_J) d\mathbf{v} = \int_{S^2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \Big[\varphi(\mathbf{v}') - \varphi(\mathbf{v})\Big] \sigma_{IJ}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g\, f_I(\mathbf{v})\, f_J(\mathbf{w})\, d\mathbf{v}\, d\mathbf{w}\, d\hat{\mathbf{\Omega}}'\,. \tag{4.54}
$$

In our case we have

$$
\int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^1(h_1^\epsilon, n_J M_J) d\mathbf{v} = \int_{S^2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} (\mathbf{v}' - \mathbf{v})\, \sigma_{1J}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g\, h_1^\epsilon(\mathbf{v}) n_J M_J(\mathbf{w})\, d\mathbf{v}\, d\mathbf{w}\, d\hat{\mathbf{\Omega}}'\,, \tag{4.55}
$$

therefore, recalling relations between pre-collision and post-collision velocities reported in Chapter 1

$$
\mathbf{v}' = \alpha_{IJ}\, \mathbf{v} + \alpha_{JI}\, \mathbf{w} + \alpha_{JI}\, g\, \hat{\mathbf{\Omega}}', \tag{4.56}
$$

being α_{IJ} the mass ratio $\alpha_{IJ} = m_I/(m_I + m_J)$, we have to compute

$$
\int_{S^2} \int_{\mathbb{R}^3 \times \mathbb{R}^3} \sigma_{1J}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \alpha_{JY} (g \hat{\mathbf{\Omega}}' - \mathbf{v} + \mathbf{w})\, h_1^\epsilon(\mathbf{v}) n_J M_J(\mathbf{w})\, d\mathbf{v}\, d\mathbf{w}\, d\hat{\mathbf{\Omega}}'. \tag{4.57}
$$

By parity arguments

$$
\int_{S^2} \sigma_{1J}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') g \hat{\mathbf{\Omega}}' d\hat{\mathbf{\Omega}}' = \mathbf{0}\,. \tag{4.58}
$$

Still adopting the Maxwel molecules hypothesis and taking collision frequencies ν_{IJ} as the integral of cross section multiplied by module of relative velocity, as defined in (4.11), we have to determine

$$
-\nu_{1J} \alpha_{JY} \int_{\mathbb{R}^3} \mathbf{v} h_1^\epsilon(\mathbf{v}) d\mathbf{v} \int_{\mathbb{R}^3} n_J M_J(\mathbf{w}) d\mathbf{w} + \nu_{1J} \alpha_{JY} \int_{\mathbb{R}^3} h_1^\epsilon(\mathbf{v}) d\mathbf{v} \int_{\mathbb{R}^3} \mathbf{w} n_J M_J(\mathbf{w}) d\mathbf{w}; \tag{4.59}
$$

last term obviously vanishes, and in conclusion we get

$$\int_{\mathbb{R}^3} \mathbf{v} Q^1_{EL}(h^\epsilon_1, n_J M_J) d\mathbf{v} = -\nu_{1J} n_J \alpha_{JY} \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1(\mathbf{v}) d\mathbf{v}. \tag{4.60}$$

By inserting this result into (4.53) we obtain

$$\nabla_{\mathbf{x}} \cdot \frac{n^\epsilon_1}{m_Y} \mathbb{I} = -\left(\sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY} \right) \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1(\mathbf{v}) d\mathbf{v} + O(\epsilon). \tag{4.61}$$

In this way we have expressed the sought streaming contribution appearing in (4.48) in terms of masses, collision frequencies and number densities; more precisely, by substituting (4.61) into (4.48), we get the reaction–diffusion equation

$$\begin{aligned} \frac{\partial}{\partial t} n^\epsilon_1 - & \frac{\Delta_{\mathbf{x}}\, n^\epsilon_1}{m_Y \displaystyle\sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \\ & = -\nu^{A2}_{A1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{A2}_{A1})\right) n_A n^\epsilon_1 + \nu^{Z1}_{Z2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{Z1}_{Z2})\right) n^\epsilon_Z n^\epsilon_2 \\ & \quad + \nu^{AC}_{B1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{AC}_{B1})\right) \left[\left(\frac{m_B m_Y}{m_A m_C} \right)^{\frac{3}{2}} \exp(\Delta E^{AC}_{B1}) n_A n_C - n_B n^\epsilon_1 \right] \\ & \quad + \nu^{ZB}_{11} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{ZB}_{11})\right) \left[\left(\frac{m^2_Y}{m_B m_Z} \right)^{\frac{3}{2}} \exp(\Delta E^{ZB}_{11}) n^\epsilon_Z n_B - (n^\epsilon_1)^2 \right] + O(\epsilon). \end{aligned} \tag{4.62}$$

It's important to remark that an evolution equation of this kind could be obtained also without Maxwell molecule assumptions on collision kernels. At first, even for hard potentials or for hard spheres with cutoff, the spectral properties of the linear Boltzmann operator [36] allow to conclude that distributions functions in the present scaling take the form (4.27). Moreover, looking at the detailed computations of inelastic and reactive contributions outlined in Appendix A, we note that their dependence on species number densities may be recovered without any assumption on cross sections σ^{HK}_{IJ} (see formula (A.10)); the Maxwellian potential allows only to explicitly compute the coefficient in front of the classical Arrhenius term, vanishing at chemical equilibrium. The major additional difficulty arising for non–Maxwell collisions concerns the computation of the integral $\int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v}$, since in general it is not directly amenable to the moment of the linear operator $\int_{\mathbb{R}^3} \mathbf{v} Q^1_{EL}(h^\epsilon_1, n_J M_J) d\mathbf{v}$ as in (4.60). By inserting expansions (4.27) into the rescaled Boltzmann equation (4.23), we get that h^ϵ_1 should be a solution to the linear problem

$$\sum_{J=A,B,C} Q^1_{EL}(h^\epsilon_1, n_J M_J)(\mathbf{v}) = \mathbf{v}\, M_1(\mathbf{v}) \cdot \nabla_{\mathbf{x}} n^\epsilon_1 + O(\epsilon). \tag{4.63}$$

It can be proved [12, 45] that the problem $Q^1_{EL}(k_{1J}, n_J M_J)(\mathbf{v}) = \mathbf{v}\, M_1(\mathbf{v})$ has a unique solution that may be cast as $k_{1J}(\mathbf{v}) = -\tilde{k}_{1J}(|\mathbf{v}|)\, \mathbf{v}$, where $\tilde{k}_{1J}(|\mathbf{v}|)$ depends only on the modulus of $\mathbf{v}$. Consequently, the sought perturbation takes the form $h^\epsilon_1 = -\left(\sum_{J=A,B,C} \tilde{k}_{1J}(|\mathbf{v}|)\right) \mathbf{v} \cdot \nabla_{\mathbf{x}} n^\epsilon_1 + O(\epsilon)$, and the streaming term of the macroscopic equation for n^ϵ_1 becomes

$$\nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v} = -\left(\sum_{J=A,B,C} \int_{\mathbb{R}^3} \tilde{k}_{1J}(|\mathbf{v}|) \frac{|\mathbf{v}|^2}{3} d\mathbf{v} \right) \Delta_{\mathbf{x}}\, n^\epsilon_1\,, \tag{4.64}$$

therefore it is again a diffusion operator, but with a non explicit diffusion coefficient. Since the final aim of our work is to investigate the stability properties of reaction–diffusion systems derived from the kinetic level, we consider only the case of Maxwell molecule interactions, in order to have diffusion and reaction coefficients completely explicit in terms of the microscopic parameters of the gas mixture.

4.2.2 Equation for the density of the second component

Now we perform the same procedure in order to obtain an equation for density n_2^ϵ. By integrating (4.24) in $d\mathbf{v}$ we get

$$\epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_2 d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} f_2 d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} Q^2_{IN}\left(\underline{\mathbf{f}}\right) d\mathbf{v}\,, \tag{4.65}$$

since

$$\int_{\mathbb{R}^3} Q^2_{EL}(f_2^\epsilon, n_J M_J) d\mathbf{v} = 0, \quad J = A, B, C \quad \text{and} \quad \int_{\mathbb{R}^3} Q^2_{EL}(f_2^\epsilon, f_I) d\mathbf{v} = 0, \quad I = 1, 2, Z. \tag{4.66}$$

Substituting again for $I = 1, 2, Z$ the asymptotic expansions (4.37) we have

$$\epsilon \frac{\partial}{\partial t} n_2^\epsilon + \epsilon\, \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h_2^\epsilon d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} Q^2_{IN}\left(\underline{\mathbf{nM}}\right) d\mathbf{v} + O(\epsilon^2). \tag{4.67}$$

Inelastic collision contributions may be computed as described in Appendix A, giving

$$\begin{aligned} \frac{\partial}{\partial t} n_2^\epsilon + &\nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h_2^\epsilon d\mathbf{v} \\ &= \nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon - \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) n_Z^\epsilon n_2^\epsilon + O(\epsilon)\,, \end{aligned} \tag{4.68}$$

where the first term appearing on the right side is due to encounters (4.2) and the second one to interactions (4.3). In order to have an explicit expression for the streaming term, similarly to previous subsection we multiply (4.24) by $\mathbf{v}$ and integrate in $d\mathbf{v}$, getting

$$\begin{aligned} \epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_2^\epsilon d\mathbf{v} + &\nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_2 d\mathbf{v} \\ &= \frac{1}{\epsilon} \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q^2_{EL}(f_2^\epsilon, n_J M_J) d\mathbf{v} + \epsilon^p \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q^2_{EL}(f_2^\epsilon, f_I) d\mathbf{v} \\ &\quad + \epsilon \int_{\mathbb{R}^3} \mathbf{v} Q^2_{IN}\left(\underline{\mathbf{f}}\right) d\mathbf{v}. \end{aligned} \tag{4.69}$$

We again substitute, for $I = 1, 2, Z$, the expansions (4.37) for the distribution functions obtaining, as above,

$$\nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) n_2^\epsilon M_2 d\mathbf{v} = \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q^2_{EL}(h_2^\epsilon, n_J M_J) d\mathbf{v} + O(\epsilon), \tag{4.70}$$

since all other elastic contributions vanish to the leading order accuracy. This leads, as for the component Y_1, to

$$\nabla_{\mathbf{x}} \cdot \frac{n_2^\epsilon}{m_Y} \mathbb{I} = -\left[\sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}\right] \int_{\mathbb{R}^3} \mathbf{v} h_2^\epsilon(\mathbf{v}) d\mathbf{v} + O(\epsilon). \tag{4.71}$$

Finally, inserting (4.71) into equation (4.68) we have the reaction–diffusion equation

$$\frac{\partial}{\partial t} n_2^\epsilon - \frac{\Delta_{\mathbf{x}} n_2^\epsilon}{m_Y \sum\limits_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} = \nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon - \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) n_Z^\epsilon n_2^\epsilon + O(\epsilon). \tag{4.72}$$

4.2.3 Equation for the density of the monatomic species

Once again, we start from the rescaled kinetic equation (4.25) and integrate in $d\mathbf{v}$, obtaining

$$\epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} f_Z^\epsilon d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} f_Z^\epsilon d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} \left(Q_{IN}^Z\left(\underline{\mathbf{f}}\right) + Q_{CH}^Z\left(\underline{\mathbf{f}}\right)\right) d\mathbf{v}, \tag{4.73}$$

being

$$\int_{\mathbb{R}^3} Q_{EL}^Z(f_Z^\epsilon, n_J M_J) d\mathbf{v} = 0, \quad J = A, B, C \quad \text{and} \quad \int_{\mathbb{R}^3} Q_{EL}^Z(f_Z^\epsilon, f_I) d\mathbf{v} = 0, \quad I = 1, 2, Z. \tag{4.74}$$

Substituting the asymptotic expansions (4.37) we have

$$\epsilon \frac{\partial}{\partial t} n_Z^\epsilon + \epsilon \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h_Z^\epsilon d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} \left(Q_{IN}^Z\left(\underline{\mathbf{nM}}\right) + Q_{CH}^Z\left(\underline{\mathbf{nM}}\right)\right) d\mathbf{v} + O(\epsilon^2). \tag{4.75}$$

We observe that the contribution given by the inelastic encounter (4.3) is null, since there is no net production of particles of species Z, in fact we have

$$\begin{aligned}\int_{\mathbb{R}^3} Q_{IN}^Z(\underline{\mathbf{nM}})(\mathbf{v}) d\mathbf{v} = &\int_{\mathbb{R}^3\times\mathbb{R}^3\times S^2} \mathtt{H}\left(g^2 - \delta_{Z1}^{Z2}\right) \frac{(g')^2}{g} \sigma_{Z2}^{Z1}(g', \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')\, n_2 M_2(\mathbf{v}') n_Z M_Z(\mathbf{w}') d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}' \\ &- \int_{\mathbb{R}^3\times\mathbb{R}^3\times S^2} \mathtt{H}\left(g^2 - \delta_{Z2}^{Z1}\right) g \sigma_{Z2}^{Z1}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')\, n_2 M_2(\mathbf{v}) n_Z M_Z(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}';\end{aligned} \tag{4.76}$$

using relation (1.37) given in Chapter 1, and noticing that in this case we do not have mass exchange, in the first term on the right-hand side of the integral above it becomes

$$\begin{aligned}\int_{\mathbb{R}^3} Q_{IN}^Z(\underline{\mathbf{nM}})(\mathbf{v}) d\mathbf{v} = &\int_{\mathbb{R}^3\times\mathbb{R}^3\times S^2} \mathtt{H}\left((g')^2 - \delta_{Z2}^{Z1}\right) g'\, \sigma_{Z2}^{Z1}(g', \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')\, n_2 M_2(\mathbf{v}') n_Z M_Z(\mathbf{w}') d\mathbf{v}' d\mathbf{w}' d\hat{\mathbf{\Omega}} \\ &- \int_{\mathbb{R}^3\times\mathbb{R}^3\times S^2} \mathtt{H}\left(g^2 - \delta_{Z2}^{Z1}\right) g \sigma_{Z2}^{Z1}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}')\, n_2 M_2(\mathbf{v}) n_Z M_Z(\mathbf{w}) d\mathbf{v} d\mathbf{w} d\hat{\mathbf{\Omega}}' = 0.\end{aligned} \tag{4.77}$$

We now compute the chemical integral due to the bimolecular and reversible reaction (4.5) and we get

$$\frac{\partial}{\partial t} n_Z^\epsilon + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h_Z^\epsilon d\mathbf{v} = -\nu_{11}^{ZB} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{11}^{ZB})\right) \left[\left(\frac{m_Y^2}{m_B m_Z}\right)^{\frac{3}{2}} \exp(\Delta E_{11}^{ZB}) n_Z^\epsilon n_B - (n_1^\epsilon)^2\right] + O(\epsilon). \tag{4.78}$$

By multiplying (4.25) by $\mathbf{v}$ and integrating in $d\mathbf{v}$ we have

$$\begin{aligned} \epsilon \frac{\partial}{\partial t} \int_{\mathbb{R}^3} \mathbf{v} f_Z^\epsilon d\mathbf{v} + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) f_Z^\epsilon d\mathbf{v} & \\ = \frac{1}{\epsilon} \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^Z (f_Z^\epsilon, n_J M_J) d\mathbf{v} &+ \epsilon^p \sum_{I=1,2,Z} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^Z (f_Z^\epsilon, f_I^\epsilon) d\mathbf{v} \\ &+ \epsilon \int_{\mathbb{R}^3} \mathbf{v} \left(Q_{IN}^Z (\underline{\mathbf{f}}) + Q_{CH}^Z (\underline{\mathbf{f}}) \right) d\mathbf{v} \,, \end{aligned} \tag{4.79}$$

and use of expansions (4.37) now gives

$$\begin{aligned} \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) n_Z^\epsilon M_Z d\mathbf{v} & \\ = \frac{1}{\epsilon} \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^Z (n_Z^\epsilon M_Z, n_J M_J) d\mathbf{v} &+ \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q_{EL}^Z (h_Z^\epsilon, n_J M_J) d\mathbf{v} \\ &+ \epsilon \int_{\mathbb{R}^3} \left(Q_{IN}^Z (\underline{\mathbf{nM}}) + Q_{CH}^Z (\underline{\mathbf{nM}}) \right) d\mathbf{v} + O(\epsilon^2), \end{aligned} \tag{4.80}$$

leading again to the equality

$$\nabla_{\mathbf{x}} \cdot \frac{n_Z^\epsilon}{m_Z} \mathbb{I} = - \left[\sum_{J=A,B,C} \nu_{ZJ} n_J \alpha_{JZ} \right] \int_{\mathbb{R}^3} \mathbf{v} h_Z^\epsilon (\mathbf{v}) d\mathbf{v} + O(\epsilon). \tag{4.81}$$

We have now obtained the third reaction-diffusion equation for the density of species Z

$$\begin{aligned} & \frac{\partial}{\partial t} n_Z^\epsilon - \frac{\Delta_{\mathbf{x}} n_Z^\epsilon}{m_Z \displaystyle\sum_{J=A,B,C} \nu_{ZJ} n_J \alpha_{JZ}} \qquad\qquad\qquad\qquad\qquad\qquad (4.82) \\ & = -\nu_{11}^{ZB} \frac{2}{\sqrt{\pi}} \Gamma \left(\frac{3}{2}, \Theta(\Delta E_{11}^{ZB}) \right) \left[\left(\frac{m_Y^2}{m_B m_Z} \right)^{\frac{3}{2}} \exp\left(\Delta E_{11}^{ZB}\right) n_Z^\epsilon n_B - (n_1^\epsilon)^2 \right] + O(\epsilon). \end{aligned} \tag{4.83}$$

4.2.4 Reaction-diffusion system

By passing to the limit $\epsilon \to 0$ in equations (4.62), (4.72), and (4.83), and denoting by (n_1, n_2, n_Z) the limit of the sequence of density functions $(n_1^\epsilon, n_2^\epsilon, n_Z^\epsilon)$, we have that (n_1, n_2, n_Z) is a solution of the system of reaction–diffusion equations:

$$\begin{aligned} & \frac{\partial}{\partial t} n_1 - \frac{1}{m_Y \displaystyle\sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_1 = \tilde{a} - (\tilde{b} + \tilde{c}) n_1 + \tilde{\eta} n_Z n_2 + \tilde{e} n_Z - \tilde{f} n_1^2 \\ & \frac{\partial}{\partial t} n_2 - \frac{1}{m_Y \displaystyle\sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_2 = \tilde{b} n_1 - \tilde{\eta} n_Z n_2 \\ & \frac{\partial}{\partial t} n_Z - \frac{1}{m_Z \displaystyle\sum_{J=A,B,C} \nu_{ZJ} n_J \alpha_{JZ}} \Delta_{\mathbf{x}} n_Z = \tilde{f} n_1^2 - \tilde{e} n_Z, \end{aligned} \tag{4.84}$$

with

$$\tilde{a} =\nu_{B1}^{AC}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{B1}^{AC})\right)\left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}}\exp(\Delta E_{B1}^{AC})n_A n_C \tag{4.85}$$

$$\tilde{b} =\nu_{A1}^{A2}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{A1}^{A2})\right)n_A \tag{4.86}$$

$$\tilde{c} =\nu_{B1}^{AC}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{B1}^{AC})\right)n_B \tag{4.87}$$

$$\tilde{\eta} =\nu_{Z2}^{Z1}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{Z2}^{Z1})\right) \tag{4.88}$$

$$\tilde{e} =\nu_{11}^{ZB}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{11}^{ZB})\right)\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}}\exp(\Delta E_{11}^{ZB})n_B \tag{4.89}$$

$$\tilde{f} =\nu_{11}^{ZB}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{11}^{ZB})\right). \tag{4.90}$$

Later on in this work, the stability properties of system (4.84) will be investigated in a regular open space domain Ω. If we suppose that the rescaled distribution functions f_I^ϵ, $I = 1, 2, Z$, satisfy the initial conditions

$$f_I^\epsilon(0,\mathbf{x},\mathbf{v}) = f_I^0(\mathbf{x},\mathbf{v}), \quad I = 1, 2, Z, \tag{4.91}$$

and the specular reflection boundary conditions

$$f_I^\epsilon(t,\mathbf{x},\mathbf{v}) = f_I^\epsilon(t,\mathbf{x},R\mathbf{v}) \qquad \forall\, t > 0, \quad \mathbf{x} \in \partial\Omega, \quad \mathbf{v} \in \mathbb{R}^3, \quad I = 1, 2, Z, \tag{4.92}$$

with $R\mathbf{v} = \mathbf{v} - 2(\mathbf{v}\cdot\underline{\hat{\mathbf{n}}})\underline{\hat{\mathbf{n}}}$, being $\underline{\hat{\mathbf{n}}}(\mathbf{x})$ the outward normal vector to $\partial\Omega$ at a point $\mathbf{x}$, then, as proved in [12], by integrating the rescaled kinetic system (4.23)–(4.25) over $(t, \mathbf{x}, \mathbf{v}) \in (0, +\infty) \times \Omega \times \mathbb{R}^3$ and passing to the limit $\epsilon \to 0$, we get exactly the weak form of the reaction–diffusion system (4.84), with initial data

$$n_I(0,\mathbf{x}) = \int_{\mathbb{R}^3} f_I^0(\mathbf{x},\mathbf{v})d\mathbf{v}, \quad I = 1, 2, Z, \tag{4.93}$$

and homogeneous Neumann boundary conditions

$$\underline{\hat{\mathbf{n}}}\cdot\nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0, +\infty) \times \partial\Omega, \quad I = 1, 2, Z. \tag{4.94}$$

Changing the time variable $\tilde{t} = \tilde{c}t$ and defining

$$a = \frac{\tilde{a}}{\tilde{c}}, \qquad b = \frac{\tilde{b}}{\tilde{c}}, \qquad \eta = \frac{\tilde{\eta}}{\tilde{c}}, \qquad e = \frac{\tilde{e}}{\tilde{c}}, \qquad f = \frac{\tilde{f}}{\tilde{c}}, \tag{4.95}$$

$$\begin{gathered} D_1 = \left[\tilde{c}\, m_Y \sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}\right]^{-1}, \qquad D_2 = \left[\tilde{c}\, m_Y \sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}\right]^{-1}, \\ D_Z = \left[\tilde{c}\, m_Z \sum_{J=A,B,C} \nu_{ZJ} n_J \alpha_{JZ}\right]^{-1}, \end{gathered} \tag{4.96}$$

we have that the system (4.84) for n_1, n_2 and n_Z may be rewritten as

$$\begin{aligned} &\frac{\partial n_1}{\partial t} - D_1\Delta_{\mathbf{x}} n_1 = a - (b+1)n_1 + \eta n_Z n_2 + e n_Z - f n_1^2 \\ &\frac{\partial n_2}{\partial t} - D_2\Delta_{\mathbf{x}} n_2 = b n_1 - \eta n_Z n_2 \\ &\frac{\partial n_Z}{\partial t} - D_Z\Delta_{\mathbf{x}} n_Z = f n_1^2 - e n_Z. \end{aligned} \tag{4.97}$$

Diffusion coefficients D_1, D_2, D_Z are essentially due to the very frequent interactions with the host medium; indeed, they depend on collision frequencies of such dominant collisions, on number densities of background species, and on masses of the colliding particles. The terms on the right hand sides are due to inelastic transitions and chemical reactions (4.2)–(4.5). Notice that, besides quadratic contributions due to binary reactions involving a pair of the considered components Y_1, Y_2, Z, there are linear terms caused by non–conservative interactions with background particles, and in the equation for n_1 there appears also a constant source term, taking into account the production of particles Y_1 due to the background only (see the reverse reaction in (4.4)). As we will show in the following, the occurrence of this "external" particle source allows the system to have a unique homogeneous state, independent of initial data. A great advantage of the present derivation from the kinetic level is that diffusion and reaction coefficients are explicitly provided in terms of the microscopic parameters of the colliding system, namely particle masses, collision frequencies and internal energies.

4.3 Derivation of a reaction-diffusion system with a non-diffusive species

In [44] the so-called bimolecular Brusselator model is presented. It is inspired by the idea introduced in [77] of considering an intermediate state in the classical Brusselator chemical environment. This system is composed by three differential equations, two of which of reaction-diffusion type, while the third is an ODE for the time evolution of the species. Aiming to obtain a similar system for our model, we suppose that the species Z has a faster collision rate with the background, more precisely, elastic collisions between gas species Z and A, B, C are of order $\frac{1}{\epsilon^2}$. We keep all the other assumptions made in the previous section, i.e. interactions of species Y_1, Y_2 with the background are of order $1/\epsilon$, all other bi–species elastic collisions are of order ϵ^p, $p \geq 0$, as above, and inelastic encounters (4.2), (4.3) and chemical reactions (4.4),(4.5) are of order ϵ. For the distribution functions of Y_1 and Y_2 we have the same Boltzmann equations given in (4.23) and (4.24), whereas, for the species Z the Boltzmann equation reads as

$$\epsilon \frac{\partial f_Z^\epsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_Z^\epsilon = \frac{1}{\epsilon^2} \sum_{J=A,B,C} Q_{EL}^Z(f_Z^\epsilon, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q_{EL}^Z(f_Z^\epsilon, f_I^\epsilon) + \epsilon \, Q_{IN}^Z(\underline{\mathbf{f}}) + \epsilon \, Q_{CH}^Z(\underline{\mathbf{f}}) \, . \tag{4.98}$$

Also in this case, the dynamics is dominated by collisions with the background, it means that

$$\sum_{J=A,B,C} Q_{EL}^I(f_I^\epsilon, n_J M_J) = O(\epsilon) \quad I = 1, 2, \qquad \sum_{J=A,B,C} Q_{EL}^I(f_I^\epsilon, n_J M_J) = O(\epsilon^2) \quad I = Z. \tag{4.99}$$

thus the perturbed expressions of distributions are now

$$f_I^\epsilon(t, \mathbf{x}, \mathbf{v}) = n_I^\epsilon(t, \mathbf{x}) M_I(\mathbf{v}) + \epsilon \, h_I^\epsilon(t, \mathbf{x}, \mathbf{v}) \, , \qquad I = 1, 2, \tag{4.100}$$

$$f_I^\epsilon(t, \mathbf{x}, \mathbf{v}) = n_I^\epsilon(t, \mathbf{x}) M_I(\mathbf{v}) + \epsilon^2 \, h_I^\epsilon(t, \mathbf{x}, \mathbf{v}) \, , \qquad I = Z, \tag{4.101}$$

with functions h_I^ϵ still fulfilling constraint (4.39).

We observe that, willing to obtain partial differential equations for number densities n_1^ϵ and n_2^ϵ we can repeat the integration procedure of Boltzmann equations performed in the previous section, ending up with the same expressions (4.62) and (4.72). For the density n_Z^ϵ, instead, if we integrate (4.98) in $d\mathbf{v}$ we obtain again (4.73) but, substituting the expressions (4.100) for f_1^ϵ, f_2^ϵ and (4.101) for f_Z^ϵ, we get

$$\epsilon \frac{\partial}{\partial t} n_Z^\epsilon = \epsilon \int_{\mathbb{R}^3} \left(Q_{IN}^Z \left(\underline{\mathbf{nM}} \right) + Q_{CH}^Z \left(\underline{\mathbf{nM}} \right) \right) d\mathbf{v} + O(\epsilon^2), \tag{4.102}$$

that, once computed the integrals, provides

$$\frac{\partial}{\partial t} n_Z^\epsilon = -\nu_{11}^{ZB} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{11}^{ZB}) \right) \left[\left(\frac{m_Y^2}{m_B m_Z} \right)^{\frac{3}{2}} \exp\left(\Delta E_{11}^{ZB}\right) n_Z^\epsilon n_B - (n_1^\epsilon)^2 \right] + O(\epsilon). \tag{4.103}$$

We see that the diffusive term does not appear because of its higher order nature. Collecting equations (4.62), (4.72) and (4.103) and considering again the limit $\epsilon \to 0$, the system for number densities (n_1, n_2, n_Z) is

$$\begin{aligned}
&\frac{\partial}{\partial t} n_1 - \frac{1}{m_Y \sum\limits_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_1 = \tilde{a} - (\tilde{b} + \tilde{c}) n_1 + \tilde{\eta} n_Z n_2 + \tilde{e} n_Z - \tilde{f} n_1^2 \\
&\frac{\partial}{\partial t} n_2 - \frac{1}{m_Y \sum\limits_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_2 = \tilde{b} n_1 - \tilde{\eta} n_Z n_2 \\
&\frac{\partial}{\partial t} n_Z = \tilde{f} n_1^2 - \tilde{e} n_Z,
\end{aligned} \tag{4.104}$$

with coefficients of the equations defined as in (4.85)-(4.90).

Considering again a regular open domain Ω, we can set initial data and boundary conditions for the distribution functions as (4.91) and (4.92) and after the time scaling $\tilde{t} = \tilde{c} t$ we obtain the reaction-diffusion system

$$\begin{aligned}
&\frac{\partial n_1}{\partial t} - D_1 \Delta_{\mathbf{x}} n_1 = a - (b+1) n_1 + \eta n_Z n_2 + e n_Z - f n_1^2 \\
&\frac{\partial n_2}{\partial t} - D_2 \Delta_{\mathbf{x}} n_2 = b n_1 - \eta n_Z n_2 \\
&\frac{\partial n_Z}{\partial t} = f n_1^2 - e n_Z,
\end{aligned} \tag{4.105}$$

with coefficients

$$a = \frac{\tilde{a}}{\tilde{c}}, \qquad b = \frac{\tilde{b}}{\tilde{c}}, \qquad \eta = \frac{\tilde{\eta}}{\tilde{c}}, \qquad e = \frac{\tilde{e}}{\tilde{c}}, \qquad f = \frac{\tilde{f}}{\tilde{c}}, \tag{4.106}$$

$$D_1 = \left[\tilde{c} m_Y \sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY} \right]^{-1}, \qquad D_2 = \left[\tilde{c} m_Y \sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY} \right]^{-1}, \tag{4.107}$$

initial data

$$n_I(0, \mathbf{x}) \text{ on } \Omega, \quad I = 1, 2, Z, \tag{4.108}$$

and homogeneous Neumann boundary conditions

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0, +\infty) \times \partial\Omega, \quad I = 1, 2, Z. \tag{4.109}$$

4.4 Derivation of a reduced two-component reaction-diffusion system

The presence of an intermediate unstable state in the Brusselator–type reaction was introduced in [77], later it has been explored in [44]. More precisely, to obtain the classical two-species Brusselator system, besides being a non diffusive component, the transient state is also considered to be quickly disappearing through proper interactions. In this section we present a derivation from our kinetic model of a closed Brusselator–type system of reaction–diffusion equations for the two components Y_1, Y_2 of the polyatomic gas only. In this hydrodynamic regime, the other gas Z will play the role of the unstable particle state.

We show that it is possible to derive such a reduction assuming, in addition to faster time scales for elastic collisions between the background and the species Z as done in the previous section, also a faster rate for the reaction (4.5) which involves the unstable state Z. In particular, we prove that in the considered scaling the number density n_Z^ϵ is completely determined in terms of the number density n_1^ϵ and other fixed parameters (masses, internal energies, and background density), therefore in order to have a complete description of the evolution of concentrations, it suffices to derive a system of two coupled reaction–diffusion equations for n_1^ϵ, n_2^ϵ.

In the present scaling, elastic scattering with the host medium is still the dominant process: collisions of the two components of the gas Y with the background are taken of order $1/\epsilon$, while scattering between the monatomic gas Z and the background is assumed of order $1/\epsilon^2$. All other elastic collisions are of order ϵ^p, $p \geq 0$, as above. Inelastic encounters (4.2), (4.3) and chemical reaction (4.4) are of order ϵ (slow as above), while the bimolecular reaction (4.5), involving the unstable state Z, is faster, of order 1. This means that a pair of particles Y_1 easily recombines to give rise to a particle Z, and then such particle Z, colliding with the host medium, very quickly dissociates again into a pair (Y_1, Y_1). We use here a separate notation for the chemical collision operator for reactions (4.4) and (4.5), respectively:

$$\begin{aligned} Q_{CH}^{1^*}(\underline{\mathbf{f}}) &= Q_{CH}^{1}(f_1^\epsilon, n_A M_A, n_B M_B, n_C M_C), \\ Q_{CH}^{1^{**}}(\underline{\mathbf{f}}) &= Q_{CH}^{1}(f_1^\epsilon, f_Z^\epsilon, n_B M_B), \\ Q_{CH}^{Z^{**}}(\underline{\mathbf{f}}) &= Q_{CH}^{Z}(f_1^\epsilon, f_Z^\epsilon, n_B M_B). \end{aligned} \tag{4.110}$$

Thus, rescaled Boltzmann equations for Y_1, Y_2 and Z read as:

$$\begin{aligned} \epsilon \frac{\partial f_1^\epsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_1^\epsilon = {} & \frac{1}{\epsilon} \sum_{J=A,B,C} Q_{EL}^{1}(f_1^\epsilon, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q_{EL}^{1}(f_1^\epsilon, f_I^\epsilon) + \epsilon\, Q_{IN}^{1}(\underline{\mathbf{f}}) \\ & + \epsilon\, Q_{CH}^{1^*}(\underline{\mathbf{f}}) + Q_{CH}^{1^{**}}(\underline{\mathbf{f}}), \end{aligned} \tag{4.111}$$

$$\epsilon \frac{\partial f_2^\epsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_2^\epsilon = \frac{1}{\epsilon} \sum_{J=A,B,C} Q_{EL}^{2}(f_2^\epsilon, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q_{EL}^{2}(f_2^\epsilon, f_I^\epsilon) + \epsilon\, Q_{IN}^{2}(\underline{\mathbf{f}}), \tag{4.112}$$

$$\begin{aligned} \epsilon \frac{\partial f_Z^\epsilon}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_Z^\epsilon = {} & \frac{1}{\epsilon} \sum_{J=A,B,C} Q_{EL}^{Z}(f_Z^\epsilon, n_J M_J) + \epsilon^p \sum_{I=1,2,Z} Q_{EL}^{Z}(f_Z^\epsilon, f_I^\epsilon) \\ & + \epsilon\, Q_{IN}^{Z}(\underline{\mathbf{f}}) + Q_{CH}^{Z^{**}}(\underline{\mathbf{f}}). \end{aligned} \tag{4.113}$$

The same dominant role as in the previous section is played by collisions with the background,

$$\sum_{J=A,B,C} Q^I_{EL}(f^\epsilon_I, n_J M_J) = O(\epsilon) \quad I=1,2, \qquad \sum_{J=A,B,C} Q^I_{EL}(f^\epsilon_I, n_J M_J) = O(\epsilon^2) \quad I=Z. \tag{4.114}$$

Consequently, the perturbed expressions of distributions are once again

$$f^\epsilon_I(t,\mathbf{x},\mathbf{v}) = n^\epsilon_I(t,\mathbf{x}) M_I(\mathbf{v}) + \epsilon\, h^\epsilon_I(t,\mathbf{x},\mathbf{v}), \qquad I=1,2, \tag{4.115}$$

$$f^\epsilon_I(t,\mathbf{x},\mathbf{v}) = n^\epsilon_I(t,\mathbf{x}) M_I(\mathbf{v}) + \epsilon^2\, h^\epsilon_I(t,\mathbf{x},\mathbf{v}), \qquad I=Z, \tag{4.116}$$

where assume again constraint (4.39).

4.4.1 Equation for the density of the first component

By integrating the Boltzmann equation (4.111) with respect to the velocity variable $\mathbf{v}$, and substituting the expressions (4.115) and (4.116) for distributions we get, eliminating vanishing terms,

$$\begin{aligned} \epsilon \frac{\partial}{\partial t} n^\epsilon_1 + \epsilon \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v} = \epsilon \int_{\mathbb{R}^3} \left(Q^1_{IN}\left(\underline{\mathbf{nM}}\right) + Q^{1^*}_{CH}\left(\underline{\mathbf{nM}}\right)\right) d\mathbf{v} + \int_{\mathbb{R}^3} Q^{1^{**}}_{CH}\left(\underline{\mathbf{nM}}\right) d\mathbf{v} \\ + \epsilon \int_{\mathbb{R}^3} \tilde{Q}^{1^{**}}_{CH}(h^\epsilon_1, n^\epsilon_1 M_1) d\mathbf{v} + O(\epsilon^2), \end{aligned} \tag{4.117}$$

where $\tilde{Q}^{1^{**}}_{CH}(h^\epsilon_1, n^\epsilon_1 M_1)$ is the first order ($O(\epsilon)$) correction of the dominant chemical term $Q^{1^{**}}_{CH}(\underline{\mathbf{f}})$ given in (4.20), that turns out to be

$$\tilde{Q}^{1^{**}}_{CH}(h^\epsilon_1, n^\epsilon_1 M_1) = -2 \int_{\mathbb{R}^3} \int_{S^2} H\left(g^2 - \delta^{ZB}_{11}\right) \sigma^{ZB}_{11}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') g\, h^\epsilon_1(\mathbf{v}) n^\epsilon_1 M_1(\mathbf{w}) d\mathbf{w} d\hat{\boldsymbol{\Omega}}'. \tag{4.118}$$

We notice that, at the first order, only the correction of the loss term in the the chemical operator remains, since the gain term contains the expansion of f_Z, so that its correction is of order 2, and thus negligible.

Leading order of equation (4.117) provides

$$\int_{\mathbb{R}^3} Q^{1^{**}}_{CH}\left(\underline{\mathbf{nM}}\right) d\mathbf{v} = O(\epsilon), \tag{4.119}$$

which after the explicit computation of collision contribution, following the procedure outlined in Appendix A, becomes

$$\nu^{ZB}_{11} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{ZB}_{11})\right) \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\left(\Delta E^{ZB}_{11}\right) n^\epsilon_Z n_B - (n^\epsilon_1)^2 \right] = O(\epsilon). \tag{4.120}$$

We note that this provides an explicit expression for number density n^ϵ_Z, to the leading order accuracy, as function of n^ϵ_1:

$$n^\epsilon_Z = (n^\epsilon_1)^2 \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\left(\Delta E^{ZB}_{11}\right) n_B \right]^{-1} + O(\epsilon). \tag{4.121}$$

With this result at hand, by writing explicitly next order ($O(\epsilon)$) of equation (4.117) we get

$$\frac{\partial}{\partial t} n^\epsilon_1 + \nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} \mathbf{v} h^\epsilon_1 d\mathbf{v} = \int_{\mathbb{R}^3} \left(Q^1_{IN}\left(\underline{\mathbf{nM}}\right) + Q^{1^*}_{CH}\left(\underline{\mathbf{nM}}\right)\right) d\mathbf{v} + \int_{\mathbb{R}^3} \tilde{Q}^{1^{**}}_{CH}(h^\epsilon_1, n^\epsilon_1 M_1) d\mathbf{v} + O(\epsilon). \tag{4.122}$$

Under a Maxwell molecule assumption for the direct reaction in (4.5), the last integral in (4.122) is explicitly provided by

$$\int_{\mathbb{R}^3} \tilde{Q}^{1**}_{CH}(h_1^\epsilon, n_1^\epsilon M_1)\, d\mathbf{v} = -\,2\,\nu_{11}^{ZB}\, n_1^\epsilon \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \mathtt{H}\left(g^2 - \delta_{11}^{ZB}\right) h_1^\epsilon(\mathbf{v}) M_1(\mathbf{w})\, d\mathbf{v} d\mathbf{w}. \tag{4.123}$$

If we suppose that the quantity $\Delta E_{11}^{ZB} = E_B + E_Z - 2E_1 < 0$, we have $\mathtt{H}\left(g^2 - \delta_{11}^{ZB}\right) \equiv 1$ and thus the whole integral is zero, owing to (4.39). In the opposite case, the contribution cannot be made explicit without further assumptions on the perturbation $h_1^\epsilon(\mathbf{v})$. Anyway, we expect that such contribution would be very small (bearing in mind (4.39)), and therefore negligible in the final macroscopic equation; moreover, we will see in next chapter that the assumption $\Delta E_{11}^{ZB} < 0$ is almost no restrictive in determining the configurations of masses and energy values allowing pattern formation, therefore it may be reasonably adopted.

Also in equation (4.122) we need an expression for $\int_{\mathbb{R}^3} \mathbf{v}\, h_I^\epsilon d\mathbf{v}$ in terms of number densities; we multiply (4.111) by $\mathbf{v}$ and integrate in $d\mathbf{v}$. Substituting again expansions (4.115) and (4.116) and taking only the leading order terms, we obtain

$$\nabla_{\mathbf{x}} \cdot \int_{\mathbb{R}^3} (\mathbf{v} \otimes \mathbf{v}) n_1^\epsilon M_1 d\mathbf{v} = \sum_{J=A,B,C} \int_{\mathbb{R}^3} \mathbf{v} Q^1_{EL}(h_1^\epsilon, n_J M_J) d\mathbf{v} + \int_{\mathbb{R}^3} \mathbf{v} Q^{1**}_{CH}\left(\underline{\mathbf{nM}}\right) d\mathbf{v} + O(\epsilon). \tag{4.124}$$

But for $\Delta E_{11}^{ZB} < 0$ we easily get

$$\int_{\mathbb{R}^3} \mathbf{v} Q^{1**}_{CH}\left(\underline{\mathbf{nM}}\right) d\mathbf{v} = \mathbf{0}\,, \tag{4.125}$$

since it is enough to perform the change of variables $(\mathbf{v}, \mathbf{w}) \to (\mathbf{g}, \mathbf{G})$ expressed in formula (1.10) of the preliminary Chapter and to observe that

$$\int_{\mathbb{R}^3} \mathbf{G} \exp\left(-\, m_Y\, G^2\right) d\mathbf{G} \;=\; \int_{\mathbb{R}^3} \mathbf{g} \exp\left(-\frac{1}{4}\, m_Y\, g^2\right) d\mathbf{g} = \mathbf{0}. \tag{4.126}$$

Thus it holds again the relation

$$\nabla_{\mathbf{x}} \cdot \frac{n_1^\epsilon}{m_Y} \mathbb{I} = -\left(\sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY} \right) \int_{\mathbb{R}^3} \mathbf{v} h_1^\epsilon(\mathbf{v}) d\mathbf{v} + O(\epsilon). \tag{4.127}$$

It is now sufficient to insert this into the equation (4.122) and to compute inelastic and chemical collision integrals in order to obtain the reaction–diffusion equation

$$\begin{aligned} \frac{\partial}{\partial t} n_1^\epsilon - & \frac{\Delta_{\mathbf{x}}\, n_1^\epsilon}{m_Y \sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \\ & = -\nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon + \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) n_Z^\epsilon n_2^\epsilon \\ & \quad + \nu_{B1}^{AC} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) \left[\left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp(\Delta E_{B1}^{AC}) n_A n_C - n_B n_1^\epsilon \right] + O(\epsilon). \end{aligned} \tag{4.128}$$

Substituting on the right hand side the expression (4.121) for the density of the unstable state n_Z^ϵ, it becomes

$$\begin{aligned}\frac{\partial}{\partial t}n_1^\epsilon - &\frac{\Delta_{\mathbf{x}}\, n_1^\epsilon}{m_Y \sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \\ &= -\nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon \qquad (4.129)\\ &+ \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\bigl(\Delta E_{11}^{ZB}\bigr) n_B\right]^{-1} (n_1^\epsilon)^2 n_2^\epsilon \\ &+ \nu_{B1}^{AC} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) \left[\left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp\bigl(\Delta E_{B1}^{AC}\bigr) n_A n_C - n_B n_1^\epsilon\right] + O(\epsilon).\end{aligned} \tag{4.130}$$

4.4.2 Equation for the density of the second component

Being the component Y_2 not involved in reaction (4.5), that is the only one with a modified scaling with respect to previous sections, the derivation of the reaction–diffusion equation for density n_2^ϵ is really analogous to the one performed in Section 4.2, thus we skip details here. With the usual asymptotic procedure we derive the equation

$$\begin{aligned}\frac{\partial}{\partial t}n_2^\epsilon - &\frac{\Delta_{\mathbf{x}} n_2^\epsilon}{m_Y \sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} \\ &= \nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon - \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) n_Z^\epsilon n_2^\epsilon + O(\epsilon).\end{aligned} \tag{4.131}$$

Again we substitute the expression for n_Z^ϵ provided by (4.121), obtaining

$$\begin{aligned}\frac{\partial}{\partial t}n_2^\epsilon - &\frac{\Delta_{\mathbf{x}} n_2^\epsilon}{m_Y \sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} \\ &= \nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A n_1^\epsilon \\ &- \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\bigl(\Delta E_{11}^{ZB}\bigr) n_B\right]^{-1} (n_1^\epsilon)^2 n_2^\epsilon + O(\epsilon).\end{aligned} \tag{4.132}$$

4.4.3 Reaction-diffusion system

We pass to the limit $\epsilon \to 0$ in (4.130) and (4.132) obtaining the following reaction–diffusion system for the unknown number densities n_1, n_2, which denote the limiting values of the sequences n_1^ϵ, n_2^ϵ:

$$\begin{aligned}\frac{\partial n_1}{\partial t} - \frac{1}{m_Y \displaystyle\sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_1 &= \tilde{a} - (\tilde{b} + \tilde{c}) n_1 + \tilde{d} n_1^2 n_2 \\ \frac{\partial n_2}{\partial t} - \frac{1}{m_Y \displaystyle\sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}} \Delta_{\mathbf{x}} n_2 &= \tilde{b} n_1 - \tilde{d} n_1^2 n_2,\end{aligned} \tag{4.133}$$

with

$$\tilde{a} = \nu_{B1}^{AC} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) \left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp\bigl(\Delta E_{B1}^{AC}\bigr) n_A n_C \tag{4.134}$$

$$\tilde{b} = \nu_{A1}^{A2} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) n_A \tag{4.135}$$

$$\tilde{c} = \nu_{B1}^{AC} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) n_B \tag{4.136}$$

$$\tilde{d} = \nu_{Z2}^{Z1} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) \left[\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\bigl(\Delta E_{11}^{ZB}\bigr) n_B\right]^{-1}. \tag{4.137}$$

Notice that coefficients $\tilde{a}$, $\tilde{b}$, $\tilde{c}$ coincide with the ones obtained in the previous section for the system of three equations (see formulas (4.85), (4.86), (4.87)). The coefficient $\tilde{d}$ may be instead recovered from (4.88), (4.89), (4.90) as $\tilde{d} = \tilde{\eta}\,\tilde{f}/\tilde{e}$. Indeed, system (4.133) could also be formally obtained from the macroscopic system (4.84) in a suitable scaling. In order to do this, one has to carefully check the implications at the macroscopic level of the additional assumption $\Delta E_{11}^{ZB} < 0$ introduced in this section. Specifically, this requirement makes the chemical contribution (4.123) vanish, implying that $n_Z^\epsilon = \tilde{f}(n_1^\epsilon)^2/\tilde{e} + O(\epsilon^2)$. For this reason, the right scaling allowing to derive (4.133) from (4.84) consists in putting $1/\epsilon^2$ in front of the right hand side of equation for n_Z^ϵ in (4.84) and in the analogous contribution appearing in the equation for n_1^ϵ. The derivation of a system of type (4.133) as a reduction of a system of three equations may be found also in [44], where one of the species (Z) is assumed non–diffusing and unstable, so that it may be considered accommodated at an equilibrium configuration, with its number density related to the ones of other constituents as in (4.121).

We will investigate Turing instability of system (4.133) in a bounded domain Ω, and to this aim, as already motivated in previous sections, we set an initial datum

$$n_I(0, \mathbf{x}) = \int_{\mathbb{R}^3} f_I^0(\mathbf{x}, \mathbf{v}) d\mathbf{v}, \quad I = 1, 2, \tag{4.138}$$

and we assume Neumann boundary conditions

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0, \infty) \times \partial\Omega, \quad I = 1, 2. \tag{4.139}$$

For convenience, we perform again the change of time variable $\tilde{t} = \tilde{c}t$ and define

$$a = \frac{\tilde{a}}{\tilde{c}}, \qquad b = \frac{\tilde{b}}{\tilde{c}}, \qquad d = \frac{\tilde{d}}{\tilde{c}}, \tag{4.140}$$

$$D_1 = \left[\tilde{c} m_Y \sum_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}\right]^{-1}, \quad D_2 = \left[\tilde{c} m_Y \sum_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}\right]^{-1}; \tag{4.141}$$

in this way, the evolution system for n_1 and n_2 reads as

$$\begin{aligned} &\frac{\partial n_1}{\partial t} - D_1 \Delta_{\mathbf{x}} n_1 = a - (b+1) n_1 + d {n_1}^2 n_2, \\ &\frac{\partial n_2}{\partial t} - D_2 \Delta_{\mathbf{x}} n_2 = b n_1 - d {n_1}^2 n_2. \end{aligned} \tag{4.142}$$

The system (4.142) is similar to the classical Brusselator model, whose stability properties were investigated for the first time in [98] and [77] (the only difference is the presence of our coefficient d instead of 1). In that context, coefficients of the system were expression of the kinetic constants of the individual reaction steps of the auto–catalytic process and of concentrations of constant reactants involved. Here, coefficients of the system play a similar role; indeed, their dependence is on microscopic quantities that, besides masses and energy levels, are collision frequencies (determining the interaction rates between elements of the mixture) and densities of the background species.

4.5 Conclusions

We have derived reaction–diffusion equations from the kinetic level for a mixture of two gas species in a dense background medium in three different hydrodynamic limits. The mixture is assumed composed by a monatomic and a polyatomic gas, this last one having two possible internal energy levels, thus it is considered separated into two different components. Different interactions between particles have been taken into account. In particular, apart from elastic scattering with the background (the dominant process), intra–species or inter–species elastic collisions (both less frequent), also two inelastic transitions and two reversible chemical reactions have been supposed to take place among particles at different time scales. In the first scenario, all inelastic and chemical transitions have been assumed of the same order. This has allowed us to derive from the rescaled Boltzmann equations suitable closed macroscopic equations for the number densities of the monatomic gas and of the two components of the polyatomic one. In the system of reaction–diffusion equations obtained, coefficients of both the diffusive and the reactive part are actually functions of microscopic quantities as particle masses, background densities, collision frequencies and internal energy amounts. We have repeated the same asymptotic procedure in a second case in which the elastic scattering with the background has not the same features for all the species. In particular for the monatomic gas, collisions with the host medium are supposed to be faster, this leads to the fact that the diffusion term for this species vanishes at leading order accuracy. Thus we have derived a system similar to the previous, but with a non-diffusive component. Finally, an additional assumption has been made for the model, i.e. one of the two chemical reactions (the one involving the unstable state, namely the monatomic gas) has been considered faster. In this case, in the derivation of the reaction-diffusion system the number density of the monatomic component can be expressed in terms of the other two concentrations. This has led to a system of only two reaction-diffusion equations, similar to the classical Brusselator, known to exhibit Turing instability for particular choices of the coefficients. In this frame, a natural step is the investigation of Turing instability for our reaction–diffusion systems and its discussion upon the dependence of the coefficients on microscopic quantities. The next chapter will be devoted to such an analysis.

5 Turing instability of reaction-diffusion systems for gas mixtures

As observed, the three reaction-diffusion systems derived in Chapter 4 are somehow related to the classical Brusselator model, used to describe a class of chemical reactions that have as a result the formation of oscillating patterns. The implementation of a specific mathematical model able to reproduce real phenomena in which there is pattern formation was introduced by Alan Turing in his work of 1952 [118]. His aim was to describe the chemistry behind morphogenesis, i.e. the formation of different patterns in natural systems. At the basis of this phenomenon there is a reaction-diffusion system for which a stable homogeneous stationary state turns into spatially non–homogeneous structures in presence of diffusion. This kind of investigation was then applied in various fields in which is possible to observe patterns, as biology, social science, medicine, environmental studies, etc. Consequently, our aim is to apply this analysis to the reaction-diffusion systems obtained and to find proper conditions on parameters of the gas mixture leading to spatial patterns.

In more detail, this chapter is structured as follows. In Section 5.1 we discuss the Turing instability for the reduced system of two equations. In particular, we write conditions on the coefficients of both reactive and diffusive part of the system. Then we express them as functions of the amount of internal energy of components of the mixture, fixing all the other microscopic parameters. We individuate then a range of possible energies for which we have space non-homogeneous equilibria and we validate our results through numerical simulations. In Section 5.2 the discussion is made for the complete system of three reaction-diffusion equations. In this case we are able to find only necessary conditions for the Turing instability, but with the help of numerical simulations we are able to show, also in this case, pattern formation. In Section 5.3, finally, we perform the analysis for the system of three equations with a non-diffusive component; as in the two equations case, here we find explicit conditions on energy levels allowing to observe Turing patterns. Section 5.4 contains some concluding remarks. Part of the results presented in this chapter are contained in [22].

5.1 Turing instability for the reduced two-components system

We consider the last system derived in Chapter 4, that we report here for the convenience of the reader

$$
\begin{aligned}
&\frac{\partial n_1}{\partial t} - D_1 \Delta_{\mathbf{x}} n_1 = a - (b+1) n_1 + d {n_1}^2 n_2, \\
&\frac{\partial n_2}{\partial t} - D_2 \Delta_{\mathbf{x}} n_2 = b n_1 - d {n_1}^2 n_2.
\end{aligned}
\tag{5.1}
$$

Quantities n_1 and n_2 are the number densities for the two energetic components of the species Y that take part in the system of reactions

$$A + Y_1 \to A + Y_2, \tag{5.2}$$

$$Z + Y_2 \to Z + Y_1, \tag{5.3}$$

$$B + Y_1 \leftrightarrows A + C, \tag{5.4}$$

$$Y_1 + Y_1 \leftrightarrows Z + B, \tag{5.5}$$

modeled in the previous chapter. The behavior of these quantities will be studied in a bounded, open, regular spatial domain Ω, having fixed initial data $n_1(0, \mathbf{x}), n_2(0, \mathbf{x})$ and Neumann boundary conditions

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0, \infty) \times \partial\Omega, \quad I = 1, 2. \tag{5.6}$$

Following the procedure outlined in more detail in Appendix B, we first look for conditions on the coefficients a, b, d and on diffusion coefficients D_1, D_2 in order to have Turing instability, then we discuss the fulfillment of such conditions for varying microscopic quantities, energy levels in particular. The first step consists in imposing the stability of a space homogeneous steady state, and to this aim we consider the system in absence of diffusion:

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= a - (b+1) n_1 + d {n_1}^2 n_2 \\ \frac{\partial n_2}{\partial t} &= b n_1 - d {n_1}^2 n_2. \end{aligned} \tag{5.7}$$

We note that this set of ODEs admits a unique stationary state, provided by

$$(\bar{n}_1, \bar{n}_2) = \left(a, \frac{b}{ad} \right). \tag{5.8}$$

Uniqueness of the equilibrium is due to the presence of a source term a, related to chemical interactions with the host medium. Indeed, in self–contained reacting systems, involving for instance four gases undergoing only a bimolecular and reversible chemical reaction, one has that the collision contribution in equations for number densities is provided by an Arrhenius–type law, having a manifold of steady equilibria (of the form $n_1 \, n_2 = K \, n_3 \, n_4$) [12, 104].

In order to study the equilibrium stability in space homogeneous conditions, we linearize the system (5.7) getting

$$\frac{\partial \mathbf{W}}{\partial t} = A \mathbf{W}, \tag{5.9}$$

with $\mathbf{W} = \begin{pmatrix} n_1 - \bar{n}_1 \\ n_2 - \bar{n}_2 \end{pmatrix}$ and $A = \begin{pmatrix} b-1 & a^2 d \\ -b & -a^2 d \end{pmatrix}$. Conditions to have the stability of the stationary state are $tr\, A < 0$ and $det\, A > 0$. Since in our model coefficients of the system are all positive quantities, the determinant is trivially positive, while for the sign of the trace we get the constraint

$$b < 1 + a^2 d. \tag{5.10}$$

The linearized system including diffusive terms in a bounded space domain $\Omega \subset \mathbb{R}^N$ with zero–flux boundary conditions reads as

$$\begin{cases} \dfrac{\partial \mathbf{W}}{\partial t} = D \Delta_{\mathbf{x}} \mathbf{W} + A \mathbf{W} & \text{on } (0, \infty) \times \Omega \\ \hat{\mathbf{n}} \cdot \nabla_{\mathbf{x}} \mathbf{W} = 0 & \text{on } (0, \infty) \times \partial\Omega \end{cases} \tag{5.11}$$

with diffusion matrix $D = \begin{pmatrix} D_1 & 0 \\ 0 & D_2 \end{pmatrix}$.

We look for solutions of this system represented in Fourier series as

$$\mathbf{W}(\mathbf{x},t) = \sum_k \mathbf{W}_k(\mathbf{x},t) = \sum_k c_k e^{\lambda_k t} \tilde{\mathbf{W}}_k(\mathbf{x}) \,, \tag{5.12}$$

with $k \in \mathbb{N}$ and the eigenfunction $\tilde{\mathbf{W}}_k(\mathbf{x})$ denoting a solution of the time–independent problem

$$\begin{cases} \Delta_{\mathbf{x}} \tilde{\mathbf{W}} + k^2 \tilde{\mathbf{W}} = \mathbf{0} & \text{on } (0,\infty) \times \Omega \\ \hat{\mathbf{n}} \cdot \nabla_{\mathbf{x}} \tilde{\mathbf{W}} = 0 & \text{on } (0,\infty) \times \partial\Omega. \end{cases} \tag{5.13}$$

In our numerical simulations we will consider as domain Ω a one-dimensional segment $\Omega = [0, L]$, and solutions of (5.13) in this case are

$$\tilde{\mathbf{W}}_{k_n}(x) = \mathbf{C}_n \cos(k_n\, x) \tag{5.14}$$

with wavenumbers k_n given by

$$k_n = \frac{n\,\pi}{L} \,, \qquad n \in \mathbb{N} \,. \tag{5.15}$$

Going back to (5.11), with the ansatz (5.12), the linear PDE provides

$$\sum_k \lambda_k c_k e^{\lambda_k t} \tilde{\mathbf{W}}_k(\mathbf{x}) = D \sum_k (-k^2) c_k e^{\lambda_k} \tilde{\mathbf{W}}_k(\mathbf{x}) + A \sum_k c_k e^{\lambda_k t} \tilde{\mathbf{W}}_k(\mathbf{x}), \tag{5.16}$$

and this means that, for each k, λ_k is an eigenvalue of the matrix $A - k^2 D$. Imposing $det(A - k^2 D - \lambda_k I) = 0$, we find

$$\lambda_{k1,2} = \frac{1}{2} \left[trA - k^2(D_1 + D_2) \pm \sqrt{[trA - k^2(D_1 + D_2)]^2 - 4h(k^2)} \right] , \tag{5.17}$$

being the function

$$h(k^2) \overset{\text{def}}{=} k^4 D_1 D_2 + k^2 [D_2(1-b) + D_1 a^2 d] + a^2 d. \tag{5.18}$$

Turing instability occurs if there exists at least one wavenumber $\bar{k}$ such that the corresponding solution $\mathbf{W}_{\bar{k}}(\mathbf{x},t)$ has $Re\lambda_{\bar{k}} > 0$. This implies that $h(k^2)$ is needed to attain a negative value for some $k \neq 0$. To this aim, we have to require firstly that

$$D_2(1-b) + D_1 a^2 d < 0. \tag{5.19}$$

If we introduce the quantity $\delta \overset{\text{def}}{=} \frac{D_1}{D_2}$, conditions (5.10) and (5.19) may be recast as

$$\delta < \frac{b-1}{a^2 d} < 1 \,, \tag{5.20}$$

and consequently it must be $\delta < 1$ and $b > 1$. Compared to the classical theory of Turing systems [92, 118], this result states that the component Y_2 of gas species Y corresponding to the energy level E_2 plays the role of "inhibitor", while the component Y_1 plays the role of "activator" in the reaction–diffusion dynamics, being known that Turing patterns may appear only below a critical value for the parameter δ, representing the ratio of the diffusion constants of the activator to the inhibitor. A second condition to be satisfied in order to have $h(k^2) < 0$ is that $h_{min} < 0$, and being

$$h_{min} = -\frac{[D_2(1-b) + D_1 a^2 d]^2 - 4D_1 D_2 a^2 d}{4D_1 D_2}, \tag{5.21}$$

it becomes

$$\delta^2 a^4 d^2 - 2\delta(1+b)a^2 d + (1-b)^2 > 0. \tag{5.22}$$

By solving this algebraic equation with respect to the parameter δ, we get

$$\delta < \frac{(\sqrt{b}-1)^2}{a^2 d} \quad \vee \quad \delta > \frac{(\sqrt{b}+1)^2}{a^2 d}, \tag{5.23}$$

but, bearing in mind (5.20), only the first of the two inequalities above provides admissible values for δ.

In conclusion, necessary conditions to have unstable modes can be summed up as follows

$$\begin{gathered} 0 < \frac{b-1}{a^2 d} < 1, \\ \delta < \frac{(\sqrt{b}-1)^2}{a^2 d}. \end{gathered} \tag{5.24}$$

The range of possible wavenumbers $\bar{k}$ such that $Re\lambda_{\bar{k}} > 0$ is then $k_1 < \bar{k} < k_2$, where k_1^2, k_2^2 are the solutions of the equation $h(k^2) = 0$, reading as

$$k_{1,2}^2 = \frac{b - 1 - \delta a^2 d \pm \sqrt{(1 - b + \delta a^2 d)^2 - 4a^2 d}}{2D_1}. \tag{5.25}$$

We should bear in mind that for finite domains the relevant wavenumbers are discrete (see (5.15) for a one–dimensional problem), therefore Turing instability occurs only if at least one of them belongs to the interval (k_1, k_2).

5.1.1 Analysis with respect to microscopic parameters

We investigate now conditions (5.24) in terms of the parameters of the mixture. Before proceeding in this direction, we introduce some assumptions, especially concerning the fixed parameters of the host medium. Indeed, since the background may be considered as a unique external medium, we may suppose that collision frequencies relevant to elastic scattering of species Y_1 with the background take a unique value, independently of the species A, B, C of the colliding molecule: $\nu_{1A} = \nu_{1B} = \nu_{1C} = \bar{\nu}_1$, and analogously for scattering involving species Y_2 and the background: $\nu_{2A} = \nu_{2B} = \nu_{2C} = \bar{\nu}_2$. Also for background number densities we assume for simplicity $n_A = n_B = n_C = \bar{n}$. We fix particle masses of background species and of gases Y and Z, bearing in mind the obvious conservations of masses prescribed by the encounters considered. We fix also background energies, and for convenience we pick a value for E_1 in such a way that $\Delta E_{B1}^{AC} \leq 0$. This implies $\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) = \frac{\sqrt{\pi}}{2}$, but the presence of a different value would not change the main results of the investigation below.

With these assumptions, the analysis of Turing instability depends only on the difference $E_2 - E_1$ and on E_Z, which has to be chosen such that $\Delta E_{11}^{ZB} \leq 0$, as required by assumptions made in

Chapter 4 for the integral of chemical collision operator (4.123). Reaction coefficients of system (5.1) may be recast as

$$\begin{aligned} a &= \left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{AC}_{B1}\bigr)\bar{n}, \\ b &= \frac{\nu^{A2}_{A1}}{\nu^{AC}_{B1}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{A2}_{A1})\right) \frac{2}{\sqrt{\pi}}, \\ d &= \frac{\nu^{Z1}_{Z2}}{\nu^{AC}_{B1}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{Z1}_{Z2})\right) \left[\frac{\sqrt{\pi}}{2}\left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp\bigl(\Delta E^{ZB}_{11}\bigr)\bar{n}^2\right]^{-1}, \end{aligned} \tag{5.26}$$

while the ratio between diffusion coefficients is simply provided by

$$\delta = \frac{D_1}{D_2} = \frac{\bar{\nu}_2}{\bar{\nu}_1}. \tag{5.27}$$

By defining the following functions

$$\mathcal{G}(E_2 - E_1) \overset{\text{def}}{=} \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{A2}_{A1})\right) - \frac{\nu^{AC}_{B1}}{\nu^{A2}_{A1}} \frac{\sqrt{\pi}}{2} \tag{5.28}$$

$$\mathcal{H}(E_2 - E_1) \overset{\text{def}}{=} \left[\sqrt{\Gamma\left(\frac{3}{2}, \Theta(\Delta E^{A2}_{A1})\right)} - \sqrt{\frac{\nu^{AC}_{B1}}{\nu^{A2}_{A1}} \frac{\sqrt{\pi}}{2}}\right]^2 \tag{5.29}$$

$$\mathcal{N}(E_2 - E_1) \overset{\text{def}}{=} \gamma\, \Gamma\left(\frac{3}{2}, \Theta(\Delta E^{Z1}_{Z2})\right) \tag{5.30}$$

with

$$\gamma = \left(\frac{m_B^3 m_Z}{m_C^2 m_A^2}\right)^{\frac{3}{2}} \exp\Bigl(2(E_A + E_C) - 3E_B\Bigr) \frac{\nu^{Z1}_{Z2}}{\nu^{AC}_{B1}}, \tag{5.31}$$

conditions (5.24) can be written as

$$0 < \frac{\mathcal{G}(E_2 - E_1)}{\mathcal{N}(E_2 - E_1)} e^{E_Z} < 1 \tag{5.32}$$

$$\delta < \frac{\mathcal{H}(E_2 - E_1)}{\mathcal{N}(E_2 - E_1)} e^{E_Z}. \tag{5.33}$$

We observe that $\mathcal{H}(E_2 - E_1) \geq 0$ and $\mathcal{N}(E_2 - E_1) > 0$, thus the first requirement to have Turing instability is

$$\mathcal{G}(E_2 - E_1) > 0. \tag{5.34}$$

This is possible only if the ratio $\frac{\nu^{AC}_{B1}}{\nu^{A2}_{A1}}$ is less than one. More precisely, for $E_2 - E_1 \leq 0$ we have

$$\mathcal{G} \equiv \frac{\sqrt{\pi}}{2}\left(1 - \frac{\nu^{AC}_{B1}}{\nu^{A2}_{A1}}\right), \tag{5.35}$$

while in the range $E_2 - E_1 > 0$ the function $\mathcal{G}$ is decreasing [1] and

$$\lim_{E_2 - E_1 \to +\infty} \mathcal{G} = -\frac{\sqrt{\pi}}{2} \frac{\nu^{AC}_{B1}}{\nu^{A2}_{A1}} < 0. \tag{5.36}$$

---

[1] We recall the definition of upper incomplete Euler gamma function provided in Appendix A, that is $\Gamma(\alpha, \beta) = \int_{\beta}^{+\infty} \tau^{\alpha-1} e^{-\tau} d\tau$, thus its derivative with respect to β is $\frac{\partial \Gamma(\alpha, \beta)}{\partial \beta} = -\beta^{\alpha-1} e^{-\beta}$.

Therefore, if $\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}} < 1$, there exists a unique value E^* such that $\mathcal{G} > 0$ for every $E_2 - E_1 < E^*$ and $\mathcal{G}$ is negative after this threshold.

In this admissible range, conditions (5.32) and (5.33) can be summarized as

$$\delta\,\frac{\mathcal{N}(E_2 - E_1)}{\mathcal{H}(E_2 - E_1)} < e^{E_Z} < \frac{\mathcal{N}(E_2 - E_1)}{\mathcal{G}(E_2 - E_1)}. \tag{5.37}$$

At this point, we notice that there could be admissible values for E_Z only if the inequality

$$\delta\frac{\mathcal{G}(E_2 - E_1)}{\mathcal{H}(E_2 - E_1)} < 1 \tag{5.38}$$

holds. It's easy to check that the function $\delta\frac{\mathcal{G}}{\mathcal{H}}$ is increasing where $\mathcal{G}$ is positive, and its limit for $E_2 - E_1 \to E^*$ is $+\infty$. Since for $E_2 - E_1 \leq 0$ we have

$$\delta\frac{\mathcal{G}}{\mathcal{H}} \equiv \delta\left(1 + \sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\right)\left(1 - \sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\right)^{-1}, \tag{5.39}$$

only if collision frequencies are chosen in such a way that this quantity is less than one we can find a nonnegative value $\overline{E}$ (less than E^*) such that $\delta\frac{\mathcal{G}}{\mathcal{H}} < 1$ for every $E_2 - E_1 < \overline{E}$. Another condition for the existence of values for the energy E_Z fulfilling (5.37) is that the right hand side has to be greater than one (since energy E_Z is positive):

$$\frac{\mathcal{N}(E_2 - E_1)}{\mathcal{G}(E_2 - E_1)} > 1\,. \tag{5.40}$$

But, being the function $\frac{\mathcal{N}}{\mathcal{G}}$ increasing where $\mathcal{G}$ is positive, ranging from zero (for $E_2 - E_1 \to -\infty$) to $+\infty$ (for $E_2 - E_1 \to E^*$), we get that there exists a unique $\widetilde{E}$ such that $\frac{\mathcal{N}}{\mathcal{G}}(\widetilde{E}) = 1$, and $\frac{\mathcal{N}}{\mathcal{G}} > 1$ for $E_2 - E_1 > \widetilde{E}$. Thus, we can conclude that Turing instability may occur only if $\widetilde{E} < \overline{E}$ and we take values for $E_2 - E_1$ in the interval $\left(\widetilde{E}, \overline{E}\right)$. With $E_2 - E_1$ in this range, inequalities (5.37) are fulfilled for E_Z such that

$$\log(\delta) + \log(\mathcal{N}(E_2 - E_1)) - \log(\mathcal{H}(E_2 - E_1)) < E_Z < \log(\mathcal{N}(E_2 - E_1)) - \log(\mathcal{G}(E_2 - E_1))\,. \tag{5.41}$$

As test case, we choose the following set of masses and background energies for the mixture:

$$m_A = 2, \quad m_B = 3.5, \quad m_C = 4, \quad m_Y = 2.5 \quad m_Z = 1.5, \tag{5.42}$$

$$E_A = 4.5, \quad E_B = 3.6, \quad E_C = 4, \tag{5.43}$$

and we fix $E_1 = 7.2$. We remark that masses fulfill conservation laws prescribed by chemical reactions (5.4)–(5.5), namely $m_B + m_Y = m_A + m_C$ and $2\,m_Y = m_Z + m_B$. Collision frequencies are the ones listed below

$$\nu_{A1}^{A2} = 0.004, \quad \nu_{Z2}^{Z1} = 0.3, \quad \nu_{B1}^{AC} = 0.0001, \quad \nu_{11}^{ZB} = 1, \tag{5.44}$$

$$\bar{\nu}_1 = 150, \quad \bar{\nu}_2 = 20, \quad \bar{\nu}_Z = 3000. \tag{5.45}$$

Elastic collisions frequencies $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_Z$ are much higher than the others in order to take into account that scattering with the host medium is the dominant process. We note that, actually, $\bar{\nu}_Z$ disappears from the quantities involved in the discussion, but we find it useful to set it as well, underlining that it is much higher than $\bar{\nu}_1$ and $\bar{\nu}_2$ in order to express the fact that the species Z has more frequent collisions with the background. Concerning the other collision rates, $\nu_{11}^{ZB} = 1$ is the highest recalling the assumption that the chemical reaction (5.5) is faster.

Region of energy parameters allowing Turing instability is the black one in Figure 5.1.

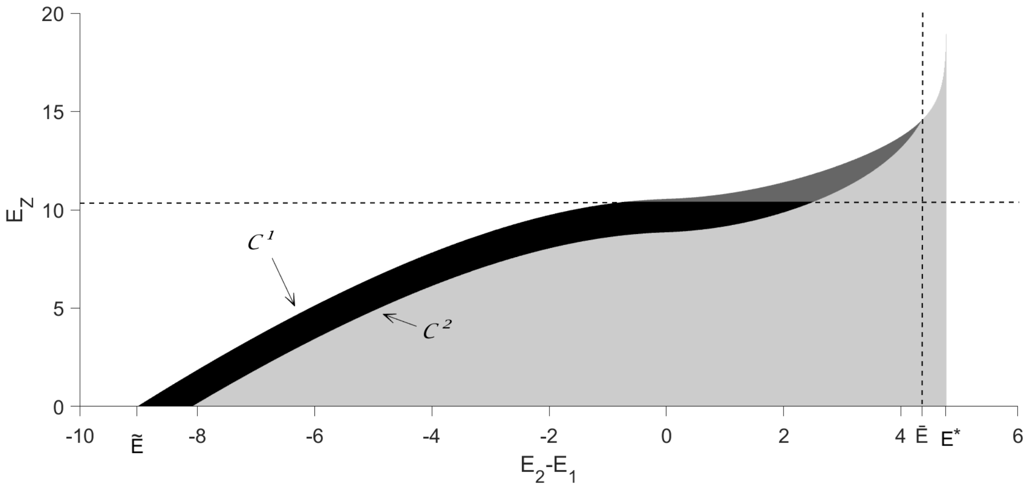

Figure 5.1: Values for E_Z and $E_2 - E_1$ satisfying requirements for Turing instability in system (5.1). Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.44)-(5.45) and $E_1 = 7.2$. The region allowing Turing instability is depicted in black. The meaning of the plotted curves is explained in the text.

The first value that we highlight is $E^* \approx 4.77$, for which $\mathcal{G}(E^*) = 0$. Then we plot the critical curve given by

$$\mathcal{C}^1 : E_Z = \log\left(\mathcal{N}(E_2 - E_1)\right) - \log\left(\mathcal{G}(E_2 - E_1)\right), \tag{5.46}$$

whose intersection with the $E_2 - E_1$ axis is at the point $\widetilde{E} \approx -9.03$. For points $(E_2 - E_1, E_Z)$ in the region under this curve we have linear stability of the stationary state. Moreover, we have the other critical curve

$$\mathcal{C}^2 : E_Z = \log(\delta) + \log\left(\mathcal{N}(E_2 - E_1)\right) - \log\left(\mathcal{H}(E_2 - E_1)\right), \tag{5.47}$$

and the intersection of curves $\mathcal{C}^1$ and $\mathcal{C}^2$ occurs at $\overline{E} \approx 4.36$. For $(E_2 - E_1, E_Z)$ in the region between curves $\mathcal{C}^2$ and $\mathcal{C}^1$, conditions (5.24) for Turing instability hold. We should recall that we have to take $E_Z < 2\,E_1 - E_B = 10.8$ (individuated by the horizontal dashed line), therefore, in conclusion, energy levels for which pattern formation can be expected are the ones in the black area of the picture. It is worth noticing that Turing instability may occur both if $E_2 - E_1$ is positive, namely with the inelastic transition (5.2) endothermic and (5.3) exothermic, and also if $E_2 - E_1$ is negative, thus with (5.2) exothermic and (5.3) endothermic.

5.1.2 Numerical simulations

We perform some numerical simulations for the system (5.1) in a one-dimensional domain $\Omega = [0, L]$, taking values for masses, background energies and collision frequencies as in (5.42), (5.43) and (5.44)-(5.45), and fixing energy of component Y_1 as $E_1 = 7.2$. Initial data are random perturbations of the space homogeneous equilibrium state. We take values for the difference of energy values $E_2 - E_1$ and for E_Z in the region where Turing instability is expected. It is important to remark that pattern formation occurs only if at least a squared wavenumber $k_n^2 = (n\pi/L)^2$ belongs to the interval individuated by the roots (5.25); in our simulations we fix $L = 30$.

Firstly, we choose $E_2 - E_1 = 1$ and take three possible values for E_Z. The results of this case are shown in Figure 5.2.

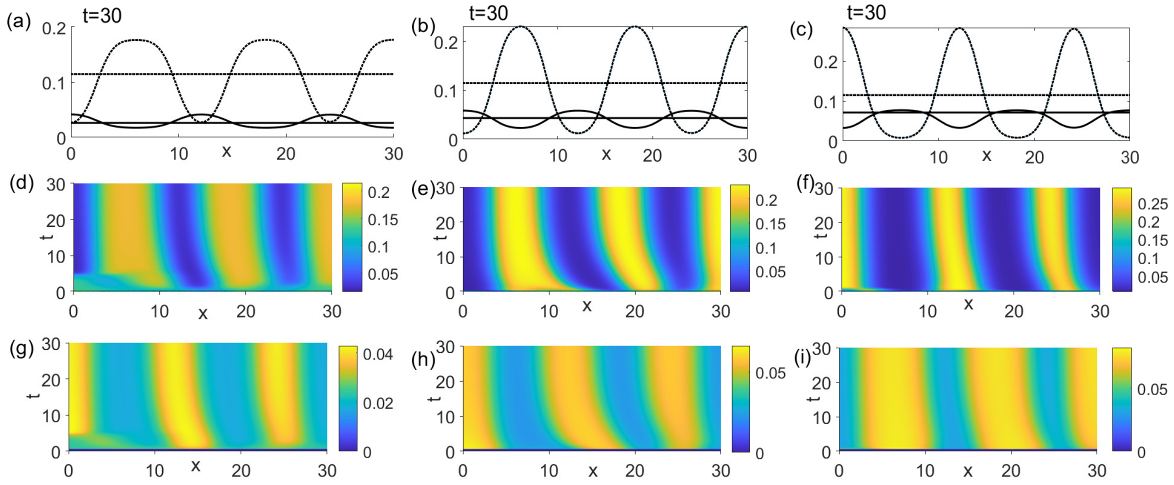

Figure 5.2: Panels (a), (b), (c): Configuration at time $t = 30$ of the densities compared to their equilibrium state $\bar{n}_1$ (dotted line) and $\bar{n}_2$ (solid line) taking $E_2 - E_1 = 1$ and $E_Z = 9.3, 9.8, 10.3$, respectively. Panels (d), (e), (f): behavior of density n_1 in space and time for the energy levels taken above. Panels (g), (h), (i): behavior of density n_2 in space and time. Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.44)-(5.45) and $E_1 = 7.2$.

In the panels (a), (b), (c), we plot the configuration at time $t = 30$ of number densities n_1, n_2, compared with the relevant space homogeneous equilibrium value. We see that the density of the two components is considerably heterogeneous and we notice that the two distributions oscillate around the homogeneous equilibrium values. As E_Z increases, we observe for the quantity n_1 a bigger fluctuation from the equilibrium, giving rise to regions where n_1 is nearly zero alternated to regions with higher density. For n_2, instead, oscillations are not equally sharp and for higher values of E_Z its plot remains mostly under the equilibrium value. In the other plots of Figure 5.2 we show the time and space behavior of number densities (panels (d), (e), (f) for n_1 and panels (g), (h), (i) for n_2): in the trend from the initial data to the oscillating configurations at $t = 30$ one can appreciate the formation of space periodic patterns.

Analogous behaviors appear in different tests, we show here two of them focusing the attention mainly on density n_1, which shows higher oscillations. We fix $E_Z = 10.3$ and we increase $E_2 - E_1$ starting from 1 to a value close to the highest one allowing Turing instability. Results for this case can be observed in Figure 5.3.

We note that for higher values of $E_2 - E_1$, the number of space oscillations for n_1 decreases, but the space amplitude of the peaks increases. Fixing, instead, a negative value for $E_2 - E_1 = -2$, when E_Z is higher we observe that the number of oscillations for n_1 is lower, but peaks are high and narrow, thus the component Y_1 is highly concentrated in few points, as can be observed in Figure

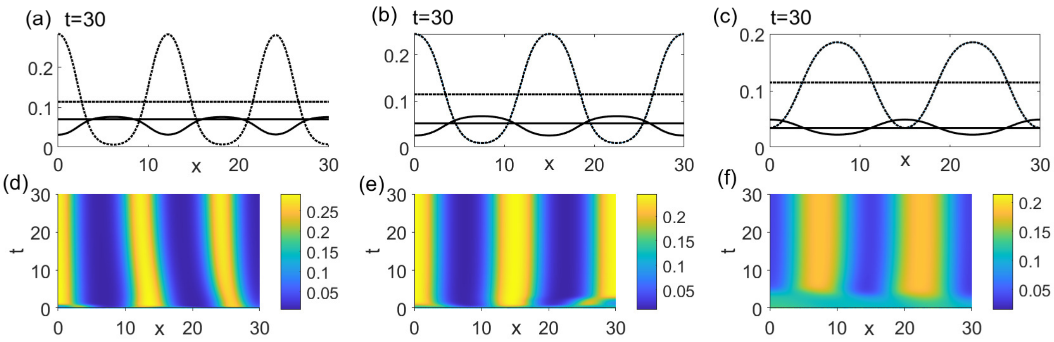

Figure 5.3: Panels (a), (b), (c): Configuration at time $t = 30$ of the densities compared to their equilibrium state $\bar{n}_1$ (dotted line) and $\bar{n}_2$ (solid line) taking $E_Z = 10.3$ and $E_2 - E_1 = 1, 1.6, 2.2$, respectively. Panels (d), (e), (f): behavior of density n_1 in space and time for the energy levels taken above. Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.44)-(5.45) and $E_1 = 7.2$.

5.4.

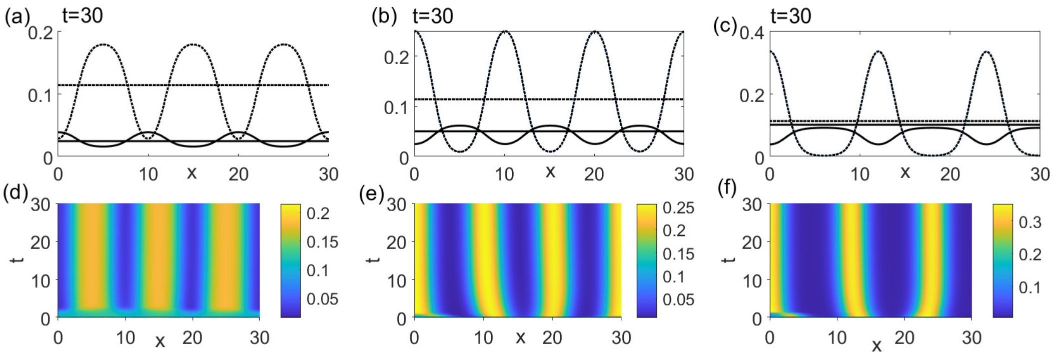

Figure 5.4: Panels (a), (b), (c): Configuration at time $t = 30$ of the densities compared to their equilibrium state $\bar{n}_1$ (dotted line) and $\bar{n}_2$ (solid line) taking $E_2 - E_1 = -2$ and $E_Z = 8.2, 8.9, 9.6$, respectively. Panels (d), (e), (f): behavior of density n_1 in space and time for the energy levels taken above. Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.44)-(5.45) and $E_1 = 7.2$.

5.2 Turing instability for the complete three-components system

This section is devoted to the investigation of stability properties and pattern formation for system obtained in Section 4.2 of the previous chapter. It is a system of three reaction-diffusion equations describing the dynamics of number densities for two energy components of a polyatomic gas species Y and a monatomic species Z. The system turns out to be the following

$$\begin{aligned}
&\frac{\partial n_1}{\partial t} - D_1 \Delta_{\mathbf{x}} n_1 = a - (b+1) n_1 + \eta n_Z n_2 + e n_Z - f n_1^2 \\
&\frac{\partial n_2}{\partial t} - D_2 \Delta_{\mathbf{x}} n_2 = b n_1 - \eta n_Z n_2 \\
&\frac{\partial n_Z}{\partial t} - D_Z \Delta_{\mathbf{x}} n_Z = f n_1^2 - e n_Z .
\end{aligned} \tag{5.48}$$

Also in this case we describe how densities change in a spatial domain Ω once that initial data $n_1(0,\mathbf{x})$, $n_2(0,\mathbf{x})$, $n_Z(0,\mathbf{x})$ and Neumann boundary conditions

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0,\infty) \times \partial\Omega, \quad I = 1,2,Z \tag{5.49}$$

are fixed.

First of all, we look for stationary states for our model in absence of diffusion, given by the system

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= a - (b+1)n_1 + \eta n_Z n_2 + e n_Z - f n_1^2 \\ \frac{\partial n_2}{\partial t} &= b n_1 - \eta n_Z n_2 \\ \frac{\partial n_Z}{\partial t} &= f n_1^2 - e n_Z . \end{aligned} \tag{5.50}$$

By imposing in the system above $\frac{\partial n_1}{\partial t} = \frac{\partial n_2}{\partial t} = \frac{\partial n_Z}{\partial t} = 0$, we get a unique steady state

$$(\bar{n}_1, \bar{n}_2, \bar{n}_Z) = \left(a, \frac{be}{a\eta f}, \frac{fa^2}{e} \right) . \tag{5.51}$$

The state $(\bar{n}_1, \bar{n}_2, \bar{n}_Z)$ is Turing unstable if it is locally stable for the homogeneous system (5.50), but unstable for the system with diffusion (5.48). We linearize at first the system in space homogeneous conditions, writing it in the following form

$$\frac{\partial \mathbf{W}}{\partial t} = B\mathbf{W}, \tag{5.52}$$

with $\mathbf{W} = \begin{pmatrix} n_1 - \bar{n}_1 \\ n_2 - \bar{n}_2 \\ n_Z - \bar{n}_Z \end{pmatrix}$ and

$$B = \begin{pmatrix} -b-1-2af & \dfrac{a^2\eta f}{e} & e\left(\dfrac{b}{af}+1\right) \\ b & -\dfrac{a^2\eta f}{e} & -\dfrac{be}{af} \\ 2af & 0 & -e \end{pmatrix} . \tag{5.53}$$

The stability of the stationary state is achieved if all the eigenvalues of B have negative real part. They are provided by the roots of the characteristic polynomial

$$-\lambda^3 + \lambda^2 trB - \lambda\,\tilde{\Lambda} + detB, \tag{5.54}$$

with

$$trB = -b - 1 - 2af - \frac{a^2\eta f}{e} - e < 0\,, \tag{5.55}$$

$$\tilde{\Lambda} = 2\frac{a^3\eta f^2}{e} + a^2\eta f + \frac{a^2\eta f}{e} - eb + e \tag{5.56}$$

and $detB = -a^2\eta f < 0$. Applying the Routh–Hurwitz criterion [54], all roots have negative real part if the condition

$$\tilde{\Lambda}\, trB < detB \tag{5.57}$$

is satisfied. Of course this is possible only if the term $\tilde{\Lambda}$ is positive; more precisely, since in this case we would have $\tilde{\Lambda}\, trB = detB + \tilde{\Gamma}$ with $\tilde{\Gamma}$ a negative quantity, the condition $\tilde{\Lambda} > 0$, that we rewrite as

$$\left[\frac{2af+1}{e^2} + \frac{1}{e}\right] a^2\eta f > b - 1, \tag{5.58}$$

is also sufficient for the equilibrium stability.

Now we consider the linearized system including diffusive terms in Ω with zero–flux boundary conditions

$$\begin{cases} \dfrac{\partial \mathbf{W}}{\partial t} = D\Delta_{\mathbf{x}}\mathbf{W} + B\mathbf{W} & \text{on } (0,\infty)\times\Omega \\ \\ \hat{\mathbf{n}}\cdot\nabla_{\mathbf{x}}\mathbf{W} = 0 & \text{on } (0,\infty)\times\partial\Omega \end{cases} \tag{5.59}$$

with diffusion matrix

$$D = \begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_Z \end{pmatrix}. \tag{5.60}$$

As in Section 5.1, we look for solutions in the form

$$\mathbf{W}(\mathbf{x},t) = \sum_k \mathbf{W}_k(\mathbf{x},t) = \sum_k c_k e^{\lambda_k t}\tilde{\mathbf{W}}_k(\mathbf{x}), \tag{5.61}$$

with $\tilde{\mathbf{W}}_k(\mathbf{x})$ solution of the time–independent problem. Choosing as domain Ω a one–dimensional segment of length L it can be checked that wavenumbers allowing the existence of a solution to the time–independent problem are again $k_n = \pi\, n/L$, with $n \in \mathbb{N}$. Concerning the global problem (5.59), for each k, the exponent λ_k has to be an eigenvalue of the matrix $B - k^2 D$, hence a root of the characteristic polynomial

$$-\lambda^3 + \lambda^2 tr\left(B - k^2 D\right) - \lambda\,\Lambda + det\left(B - k^2 D\right), \tag{5.62}$$

with $tr\left(B - k^2 D\right) = trB - k^2(D_1 + D_2 + D_Z) < 0$,

$$\begin{aligned} \Lambda = {} & (D_1D_2 + D_1D_Z + D_2D_Z)\,k^4 \\ & + \left(D_2 + 2afD_2 + D_1\frac{a^2\eta f}{e} + 2D_Zaf + D_Zb + D_Z + 2D_1D_Z\frac{a^2\eta f}{e} + D_2e\right)k^2 \\ & + \frac{a^2\eta f}{e} + 2\frac{a^3\eta f^2}{e} + a^2\eta f - eb + e \end{aligned} \tag{5.63}$$

and

$$\begin{aligned} \beta(k^2) \overset{\text{def}}{=} det(B - k^2D) = {} & -D_1D_2D_Zk^6 \\ & - \left(D_1D_Z\frac{a^2\eta f}{e} + 2D_2D_Zaf + eD_1D_2 + bD_2D_Z + D_2D_Z\right)k^4 \\ & - \left(2D_Z\frac{a^3\eta f^2}{e} + D_1a^2\eta f + D_Z\frac{a^2\eta f}{e} - D_2eb + eD_2\right)k^2 - a^2\eta f. \end{aligned} \tag{5.64}$$

Turing instability may occur only if for some k the characteristic polynomial (5.62) has roots with positive real part. Again for the Routh–Hurwitz criterion, this happens if there exists k such that

$$det(B - k^2D) > 0 \tag{5.65}$$

or

$$\Lambda\, tr(B-k^2D) > det(B-k^2D). \tag{5.66}$$

We notice that last five terms of Λ in (5.63) are exactly the quantity $\tilde{\Lambda}$ that we have supposed to be positive in (5.58) for the stability in the homogeneous problem, and consequently we have $\Lambda > 0$. Since we have

$$\Lambda\, tr(B-k^2D) = det(B-k^2D) + \Gamma, \tag{5.67}$$

being Γ a negative quantity, we see that (5.66) can never be satisfied. It means that the matrix $B-k^2D$ has eigenvalues with positive real part only if condition (5.65) holds.

5.2.1 Analysis with respect to microscopic parameters

We aim at finding more specific conditions on the parameters of the system (5.48) allowing Turing instability. As in Subsection 5.1.1, we suppose that collision frequencies for the elastic scattering with the background take a unique value for each species:

$$\nu_{1A} = \nu_{1B} = \nu_{1C} = \bar{\nu}_1, \quad \nu_{2A} = \nu_{2B} = \nu_{2C} = \bar{\nu}_2, \quad \nu_{ZA} = \nu_{ZB} = \nu_{ZC} = \bar{\nu}_Z, \tag{5.68}$$

and also background number densities have the common value $n_A = n_B = n_C = \bar{n}$. We fix energies E_A, E_B, E_C, and E_1 in such a way that $\Delta E_{B1}^{AC} \leq 0$, so that $\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{B1}^{AC})\right) = \frac{\sqrt{\pi}}{2}$. The analysis of conditions allowing pattern formation still depends on the difference $E_2 - E_1$ and on E_Z: we restrict our investigation to E_Z such that $\Delta E_{11}^{ZB} \leq 0$ (just for convenience, in order to be able to compare results with the ones obtained for the two–component system in Section 5.1). Moreover, as usual in kinetic models dealing with energy levels [56, 58], we assume $E_2 > E_1$, then also $\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{Z2}^{Z1})\right) = \frac{\sqrt{\pi}}{2}$. With these assumptions at hand, the parameters appearing in the reaction–diffusion system (5.48) read as

$$\begin{aligned}
a &= \left(\frac{m_B m_Y}{m_A m_C}\right)^{\frac{3}{2}} \exp(\Delta E_{B1}^{AC})\bar{n}, \\
b &= \frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) \frac{2}{\sqrt{\pi}}, \\
\eta &= \frac{\nu_{Z2}^{Z1}}{\nu_{B1}^{AC}} \frac{1}{\bar{n}}, \\
e &= \frac{\nu_{11}^{ZB}}{\nu_{B1}^{AC}} \left(\frac{m_Y^2}{m_Z m_B}\right)^{\frac{3}{2}} \exp(\Delta E_{11}^{ZB}), \\
f &= \frac{\nu_{11}^{ZB}}{\nu_{B1}^{AC}} \frac{1}{\bar{n}},
\end{aligned} \tag{5.69}$$

$$D_1 = \left[\nu_{B1}^{AC} m_Y \bar{n} \bar{\nu}_1 \sum_{J=A,B,C} n_J \alpha_{JY}\right]^{-1}, \quad D_2 = \frac{\bar{\nu}_1}{\bar{\nu}_2} D_1, \quad D_Z = \left[\nu_{B1}^{AC} m_Z \bar{n} \bar{\nu}_Z \sum_{J=A,B,C} n_J \alpha_{JZ}\right]^{-1}. \tag{5.70}$$

Our first purpose is to find suitable values for energies $E_2 - E_1$ and E_Z in order to have condition (5.58) for the linear stability in the space homogeneous problem satisfied. We find convenient rewriting condition (5.58) as

$$(1-b)e^2 + ea^2\eta f + (2af+1)a^2\eta f > 0. \tag{5.71}$$

If $b < 1$ this inequality is obviously fulfilled, while the case $b > 1$ is much more involved. The condition $b > 1$ means

$$\mathcal{L}(E_2 - E_1) \overset{\text{def}}{=} \frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) - 1 > 0; \tag{5.72}$$

the function $\mathcal{L}$ has the same behavior of the function $\mathcal{G}$ introduced in the previous section, thus also in this case there exists a unique value E^* such that $\mathcal{L} > 0$ for every $E_2 - E_1 < E^*$. Notice that in the inequality (5.71) the dependence on E_Z is included only in the parameter e. Therefore, by defining a second function

$$\mathcal{T}(E_2 - E_1) \overset{\text{def}}{=} \frac{\gamma}{2} \left[1 + \sqrt{1 + 4\chi \left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} \frac{2}{\sqrt{\pi}} \Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right) - 1 \right)} \right], \tag{5.73}$$

with γ as in (5.31) and

$$\chi = 2 \left[\left(\frac{m_B m_Y}{m_A m_C} \right)^{\frac{3}{2}} \exp(\Delta E_{B1}^{AC}) \frac{\nu_{Z2}^{Z1}}{\nu_{B1}^{AC}} \right]^{-1} + \left[\left(\frac{m_B m_Y}{m_A m_C} \right)^{3} \exp\left(2\Delta E_{B1}^{AC}\right) \frac{\nu_{Z2}^{Z1} \nu_{11}^{ZB}}{(\nu_{B1}^{AC})^2} \right]^{-1}, \tag{5.74}$$

condition (5.71) leads to the explicit constraint:

$$e^{E_Z} < \frac{\mathcal{T}(E_2 - E_1)}{\mathcal{L}(E_2 - E_1)}. \tag{5.75}$$

Since we are dealing with positive energies, we have $e^{E_Z} > 1$, so we must require that the right hand side of (5.75) is greater than one. But, being $\mathcal{L}' > 0$ and

$$\left(\frac{\mathcal{T}}{\mathcal{L}} \right)' = \frac{\gamma}{2} \left(\frac{-\sqrt{1 + 4\chi\mathcal{L}} - 1 - 2\chi\mathcal{L}}{\mathcal{L}^2 \sqrt{1 + 4\chi\mathcal{L}}} \right) \mathcal{L}', \tag{5.76}$$

the function $\frac{\mathcal{T}}{\mathcal{L}}$ is increasing where $\mathcal{L}$ is positive, and its limit for $E_2 - E_1 \to E^*$ is $+\infty$, while for $E_2 - E_1 = 0$ we have

$$\frac{\mathcal{T}}{\mathcal{L}} \equiv \frac{\gamma \left[1 + \sqrt{1 + 4\chi \left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} - 1 \right)} \right]}{2 \left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} - 1 \right)}. \tag{5.77}$$

Consequently, if masses, background energies and collision frequencies are chosen in such a way that the quantity above is less than one, then there exists a unique $\widetilde{E} < E^*$ for which $\mathcal{T}/\mathcal{L} > 1$ is satisfied for every $E_2 - E_1 > \widetilde{E}$; otherwise, if the same quantity is greater than one, then $\mathcal{T}/\mathcal{L} > 1$ holds for every $E_2 - E_1 > 0$. In conclusion, for $E_2 - E_1 \in (\max\{\widetilde{E}, 0\}, E^*)$, condition (5.71) guaranteeing stability of the steady state of the homogeneous problem is fulfilled for

$$E_Z < \log\left(\mathcal{T}(E_2 - E_1)\right) - \log\left(\mathcal{L}(E_2 - E_1)\right). \tag{5.78}$$

As concerns Turing instability, it has been proved in [107] that it is prevented if all minors of order q of the matrix B given in (5.53) have a determinant with the same sign as $(-1)^q$ (with $1 \leq q \leq 3$, in our three equations system). Consequently, it's easy to check that in our problem a bifurcation leading to Turing instability is possible only when the determinant of the submatrix extracted from B eliminating the second row and second column, given by

$$\begin{pmatrix} -b-1-2af & e\left(\dfrac{b}{af}+1\right) \\ 2af & -e \end{pmatrix}, \tag{5.79}$$

has a negative determinant. This implies the condition $b > 1$, namely $E_2 - E_1 < E^*$, analogously to the result obtained in previous section for the reduced two–component system. In this region, we are able to find a necessary condition on parameters E_Z and $E_2 - E_1$ for Turing instability, recalling that unstable modes are possible only if the determinant of the matrix $B - k^2 D$, given by (5.64), is positive for some k. According to the Descartes rule, the cubic function $\beta(k^2)$ may have two positive roots (and consequently it may assume positive values) only if the coefficient of k^2 in (5.64) is positive, which means

$$(1-b)e^2 + \frac{D_1}{D_2}a^2\eta f e + \frac{D_Z}{D_2}a^2\eta f(2af+1) < 0. \tag{5.80}$$

Keeping in mind (5.58) (that has to be valid for the stability of the homogeneous equilibrium), the above relation implies that at least one of coefficients D_1 and D_Z must be smaller than D_2. Defining the function

$$\mathcal{S}(E_2-E_1) \overset{\mathsf{def}}{=} \frac{\gamma}{2}\frac{D_1}{D_2}\left[1+\sqrt{1+4\frac{D_Z}{D_1}\chi\left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{A1}^{A2})\right)-1\right)}\,\right], \tag{5.81}$$

condition (5.80) becomes

$$e^{E_Z} > \frac{\mathcal{S}(E_2-E_1)}{\mathcal{L}(E_2-E_1)}. \tag{5.82}$$

The behaviour of the ratio $\frac{\mathcal{S}}{\mathcal{L}}$ is analogous to that of $\frac{\mathcal{T}}{\mathcal{L}}$ discussed above. We point out that condition (5.82) is compatible with (5.75) only if

$$\frac{\mathcal{T}(E_2-E_1)}{\mathcal{S}(E_2-E_1)} > 1, \tag{5.83}$$

but this is ensured if we take also $D_1 > D_Z$.

One should also check that the cubic function β assumes a positive value in correspondence of its positive stationary point, but with this analysis we are not provided with any information about the sign of $det(B - k^2 D)$ as function of k. Nevertheless, as proved in [107], a wider range of k for which $det(B - k^2 D) > 0$ can be obtained taking the diffusion coefficients D_1 and D_Z sufficiently smaller than D_2. More precisely, taking $D_1 = \alpha\, D_Z \approx \omega$, with ω small positive quantity, we have

$$det(B - k^2 D) = D_2 e(b-1)k^2 - a^2\eta f - O(\omega). \tag{5.84}$$

In this case, the component Y_2 can be seen as inhibitor and component Y_1 and gas species Z as activators.

Just for illustrative purpose, we report the conditions established in this section in Figure 5.5, choosing as particle masses and background energies the same as in (5.42) and (5.43), fixing $E_1 = 7.2$, taking as collision frequencies for the inelastic and the chemical collisions the ones below

$$\nu_{A1}^{A2} = 0.004, \qquad \nu_{Z2}^{Z1} = 0.3, \qquad \nu_{B1}^{AC} = 0.0001, \qquad \nu_{11}^{ZB} = 0.1, \tag{5.85}$$

and adopting the following choice for collision frequencies with the background

$$\bar{\nu}_1 = 1.5 \times 10^3, \qquad \bar{\nu}_2 = 2, \qquad \bar{\nu}_Z = 3 \times 10^3, \tag{5.86}$$

in order to have diffusion coefficients given in (5.70) such that $D_1 > D_Z$ and $D_1 \ll D_2$. With these data we have again $E^* \approx 4.77$ such that $\mathcal{L}(E^*) = 0$, and Turing instability prevented for $E_2 - E_1 > E^*$. In Figure 5.5 we show the critical curve given by

$$\mathcal{C}^3 : E_Z = \log\left(\mathcal{T}(E_2 - E_1)\right) - \log\left(\mathcal{L}(E_2 - E_1)\right), \tag{5.87}$$

under which we have linear stability of the stationary state, and also the second curve

$$\mathcal{C}^4 : E_Z = \log\left(\mathcal{S}(E_2 - E_1)\right) - \log\left(\mathcal{L}(E_2 - E_1)\right), \tag{5.88}$$

above of which the determinant of the matrix $B - k^2 D$ might have positive roots. We also plot the line $E_Z = 2E_1 - E_B$, below of which the assumption $\Delta E_{11}^{ZB} \leq 0$ is satisfied, and the region where Turing instability might occur is thus the black one.

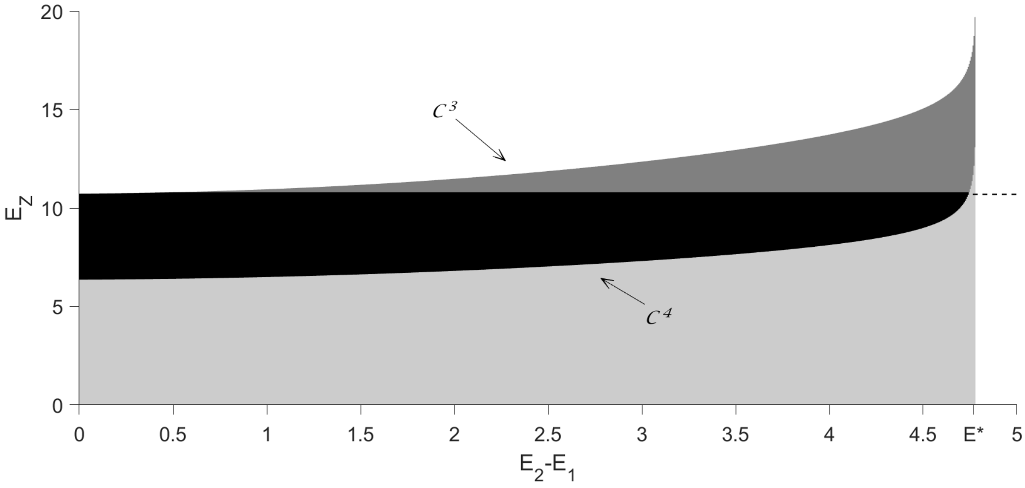

Figure 5.5: Values for E_Z and $E_2 - E_1$ satisfying (5.75) and (5.82). Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.85), (5.86) and $E_1 = 7.2$. The region allowing Turing instability is depicted in black. The meaning of the plotted curves is explained in the text.

We may compute $det(B - k^2 D)$ numerically: in Figure 5.6 we plot it versus k for some values of E_Z and $E_2 - E_1$, and in Table 5.1 we show its maximal value in the right half–plane.

We notice that, for $E_Z = 10$ and $E_2 - E_1 = 2.5$ there is a particularly wide range in which there could exist wavenumbers k leading to unstable modes. For these values we perform a simulation of the behaviour in time and space for functions n_1, n_2, n_Z in a one–dimensional domain of size $L = 0.15$ and we report the result in Figure 5.7. We see that for a time $t = 50$, the component Y_1 and the gas species Z, characterized by a very low diffusion coefficient, turn out to be concentrated in one point of the domain, while we have a low but nearly uniform concentration of component Y_2, due to its much higher diffusion coefficient.

E_Z	$E_2 - E_1$	Max $det(B - k^2 D)$
7.5	1	$1.16{\times}10^6$
10	2.5	5×10^7
6.4	2.5	6.27×10^5
8	3.5	-3.1×10^4

Table 5.1: Maximal values of determinant $det(B - k^2 D)$ as function of k picking some values for E_Z and $E_2 - E_1$ when values for masses are as in (5.42), background energies as in (5.43), frequencies as in (5.85), (5.86) and $E_1 = 7.2$.

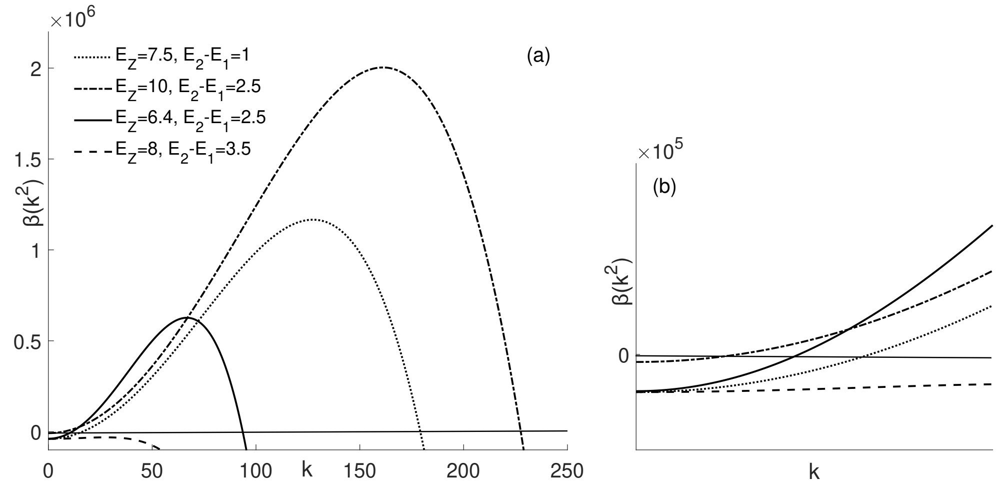

Figure 5.6: Panel (a): Behavior of the quantity in (5.64) as function of wavenumbers k, taking values of E_Z and $E_2 - E_1$ as in Table 5.1 (the graph corresponding to the values $E_Z = 10, E_2 - E_1 = 2.5$ is reduced by a factor 5). Panel (b): Zoom of the area close to $k = 0$ of panel (a).

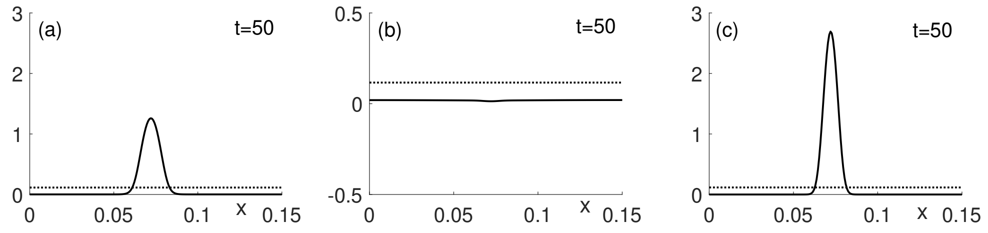

Figure 5.7: Panels (a), (b), (c): Configuration at time $t = 50$ of the densities n_1, n_2 and n_Z (solid lines) compared to their equilibrium state (dotted lines), respectively, taking $E_Z = 10$ and $E_2 - E_1 = 2.5$. Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.85), (5.86) and $E_1 = 7.2$.

5.3 Turing instability for three-components system with a non-diffusive term

Adding a further assumption on different frequency of collisions with the background for the monatomic species Z, in Section 4.3 of the previous chapter we derived a second system of three reaction-diffusion equations in which the diffusion term for species Z disappears at first order accuracy. The resulting system is

$$\begin{aligned} &\frac{\partial n_1}{\partial t} - D_1 \Delta_{\mathbf{x}} n_1 = a - (b+1) n_1 + \eta n_Z n_2 + e n_Z - f n_1^2 \\ &\frac{\partial n_2}{\partial t} - D_2 \Delta_{\mathbf{x}} n_2 = b n_1 - \eta n_Z n_2 \\ &\frac{\partial n_Z}{\partial t} = f n_1^2 - e n_Z . \end{aligned} \tag{5.89}$$

We want to investigate its stability properties again in a spatial domain Ω with initial conditions $n_1(0,\mathbf{x}), n_2(0,\mathbf{x}), n_Z(0,\mathbf{x})$ and with absence of flux at the boundary, i.e.

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} n_I = 0 \quad \text{on} \quad (0,\infty) \times \partial\Omega, \quad I = 1, 2, Z. \tag{5.90}$$

In absence of diffusion, we have the same system as (5.50), that linearized around the equilibrium state has the same matrix B given in (5.53); for this reason, the unique equilibrium state is again the one given in (5.51) and condition for the linear stability is again

$$\left[\frac{2af+1}{e^2} + \frac{1}{e} \right] a^2 \eta f > b - 1. \tag{5.91}$$

If we include the diffusion, instead, we have a system similar to (5.59), but with a different diffusion matrix:

$$\begin{cases} \dfrac{\partial \mathbf{W}}{\partial t} = D_0 \Delta_{\mathbf{x}} \mathbf{W} + B \mathbf{W} & \text{on } (0,\infty) \times \Omega \\ \hat{\mathbf{n}} \cdot \nabla_{\mathbf{x}} \mathbf{W} = 0 & \text{on } (0,\infty) \times \partial\Omega \end{cases} \tag{5.92}$$

$$D_0 = \begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & 0 \end{pmatrix} . \tag{5.93}$$

We still look for a solution of the system of the form

$$\mathbf{W}(\mathbf{x}, t) = \sum_k c_k e^{\lambda_k t} \tilde{\mathbf{W}}_k(\mathbf{x}), \tag{5.94}$$

and wavenumbers, considering again as domain Ω a one-dimensional segment of length L, $k_n = \pi \frac{n}{L}$. Eigenvalues of the matrix $B - k^2 D_0$, λ_k, are now roots of the characteristic polynomial

$$-\lambda^3 + \lambda^2 tr\left(B - k^2 D\right) - \lambda \left[\Xi\right] + det\left(B - k^2 D_0\right), \tag{5.95}$$

with

$$\Xi = \left(D_2 + 2af D_2 + D_1 \frac{a^2 \eta f}{e} + 2 D_1 + D_2 e \right) k^2 + \frac{a^2 \eta f}{e} + 2 \frac{a^3 \eta f^2}{e} + a^2 \eta f - eb + e \tag{5.96}$$

and

$$\rho(k^2) \overset{\text{def}}{=} det(B - k^2 D_0) = -eD_1D_2k^4 - \left(D_1a^2\eta f + D_2eb - eD_2\right)k^2 - a^2\eta f. \tag{5.97}$$

Also in this case, the only condition allowing to have eigenvalues with positive real part is

$$det(B - k^2 D_0) > 0, \tag{5.98}$$

i.e. the function $\rho(k^2)$ should attain a positive value for some $k \neq 0$. It means requiring firstly that

$$D_2(1-b) + D_1a^2\frac{\eta f}{e} < 0, \tag{5.99}$$

that, if we introduce the quantity $\delta \overset{\text{def}}{=} \frac{D_1}{D_2}$, becomes

$$\delta < \frac{(b-1)e}{a^2\eta f} \tag{5.100}$$

which implies conditions $\delta < 1 + \frac{2af+1}{e}$ and $b > 1$. Also in this case, the component Y_2 can be seen as inhibitor and Y_1 as activator. A second condition to be satisfied to have $\rho(k^2) > 0$ is that $\rho_{max} > 0$ and being

$$\rho_{max} = \frac{\left[D_2(1-b) + D_1a^2\frac{\eta f}{e}\right]^2 - 4D_1D_2a^2\frac{\eta f}{e}}{4D_1D_2}, \tag{5.101}$$

it becomes

$$\delta^2a^4\left(\frac{\eta f}{e}\right)^2 - 2\delta(1+b)a^2\frac{\eta f}{e} + (1-b)^2 > 0. \tag{5.102}$$

Solving with respect to the parameter δ, we get as a result

$$\delta < \frac{(\sqrt{b}-1)^2e}{a^2\eta f} \quad \vee \quad \delta > \frac{(\sqrt{b}+1)^2e}{a^2\eta f}. \tag{5.103}$$

But, since (5.100), the only admissible values for δ are given by the first of the two inequalities above. To conclude, necessary conditions to have unstable modes can be summed up as follows

$$\begin{aligned} 0 < \frac{(b-1)e}{a^2\eta f} < 1 + \frac{2af+1}{e} \\ \delta < \frac{(\sqrt{b}-1)^2e}{a^2\eta f}. \end{aligned} \tag{5.104}$$

Turing instability then occurs if at least a wavenumber belongs to the interval (k_1, k_2), with

$$k_{1,2}^2 = \frac{b - 1 - \delta a^2\frac{\eta f}{e} \pm \sqrt{\left(1 - b + \delta a^2\frac{\eta f}{e}\right)^2 - 4a^2\frac{\eta f}{e}}}{2D_1}. \tag{5.105}$$

5.3.1 Analysis with respect to microscopic parameters

Coefficients of system (5.89) are explicitly expressed in (5.69) and (5.70) and, in addition, we have

$$\delta = \frac{\sum\limits_{J=A,B,C} \nu_{2J} n_J \alpha_{JY}}{\sum\limits_{J=A,B,C} \nu_{1J} n_J \alpha_{JY}}. \tag{5.106}$$

Assumptions on the other parameters, i. e. collision frequencies, masses and background energies, are the same as in previous sections, in such a way that the analysis still depends only on the difference $E_2 - E_1$ (as in the previous section we suppose $E_2 - E_1 > 0$) and on E_Z. As already noticed, conditions on parameters for the stability of homogeneous equilibrium are not different from the previous section, that we recall here

$$E_Z < \log\left(\mathcal{T}(E_2 - E_1)\right) - \log\left(\mathcal{L}(E_2 - E_1)\right) , \tag{5.107}$$

with functions $\mathcal{T}$ and $\mathcal{L}$ defined in (5.72) and (5.73), respectively.

For Turing instability analysis, instead, we define the following function

$$\mathcal{H}(E_2 - E_1) \overset{\mathsf{def}}{=} \frac{1}{\gamma}\left[\sqrt{\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right)} - \sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\right]^2 \tag{5.108}$$

with γ as in (5.31). In this way conditions (5.104) can be written as, recalling also (5.107),

$$\frac{\delta}{\mathcal{H}(E_2 - E_1)} < e^{E_Z} < \frac{\mathcal{T}(E_2 - E_1)}{\mathcal{L}(E_2 - E_1)}. \tag{5.109}$$

Also here, there are admissible values for E_Z only if the inequality

$$\delta \frac{\mathcal{L}(E_2 - E_1)}{\mathcal{H}(E_2 - E_1)\mathcal{T}(E_2 - E_1)} < 1 \tag{5.110}$$

holds. We compute the derivative

$$\left(\frac{\mathcal{L}}{\mathcal{H}\mathcal{T}}\right)' \\ = -\frac{\mathcal{L}\mathcal{H}'}{\mathcal{T}\mathcal{H}^2}\left[\sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\left(\sqrt{1 + 4\chi\mathcal{L}} + 1 + 2\chi\mathcal{L}\right) + 4\chi\mathcal{L}\left(\sqrt{\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2}, \Theta(\Delta E_{A1}^{A2})\right)} + \sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\right)\right]. \tag{5.111}$$

Referring to the condition (5.72), we observe that the functions $\mathcal{L}$ and $\mathcal{H}$ have the same sign, and in particular we identify again the value E^* such that $\mathcal{H} > 0$ for every $E_2 - E_1 < E^*$. in addition, we have $\mathcal{H}' > 0$, thus the function $\frac{\mathcal{L}}{\mathcal{H}\mathcal{T}}$ is increasing, with the limit for $E_2 - E_1$ going to E^* being $+\infty$. For $E_2 - E_1 = 0$, instead, we have

$$\delta \frac{\mathcal{L}}{\mathcal{H}\mathcal{T}} \equiv \delta \frac{\left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} - 1\right)}{2\left[1 + \sqrt{1 + 4\chi\left(\frac{\nu_{A1}^{A2}}{\nu_{B1}^{AC}} - 1\right)}\right]\left(1 - \sqrt{\frac{\nu_{B1}^{AC}}{\nu_{A1}^{A2}}}\right)^2}. \tag{5.112}$$

As a consequence, if choice for collision frequencies is made in such a way the quantity above is smaller than one, there exists a nonnegative value $\bar{E}$ such that $\delta \frac{\mathcal{L}}{\mathcal{H}\mathcal{T}} < 1$ for every $0 < E_2 - E_1 < \bar{E}$.

We now take masses and background energies as in (5.42) and (5.43). For collision frequencies, instead, the ones for inelastic and chemical reactions are as in Section 5.2, while collisions frequencies of components Y_1, Y_2 and species Z with the background as in Section 5.1, recalling the fact that they have different orders of magnitude:

$$\nu_{A1}^{A2} = 0.004, \qquad \nu_{Z2}^{Z1} = 0.3, \qquad \nu_{B1}^{AC} = 0.0001, \qquad \nu_{11}^{ZB} = 0.1, \tag{5.113}$$

$$\bar{\nu}_1 = 150, \qquad \bar{\nu}_2 = 20, \qquad \bar{\nu}_Z = 3000. \tag{5.114}$$

Taking $E_1 = 7.2$ in this case as well, we individuate the region of parameters leading to Turing instability reported in Figure 5.8 (black area).

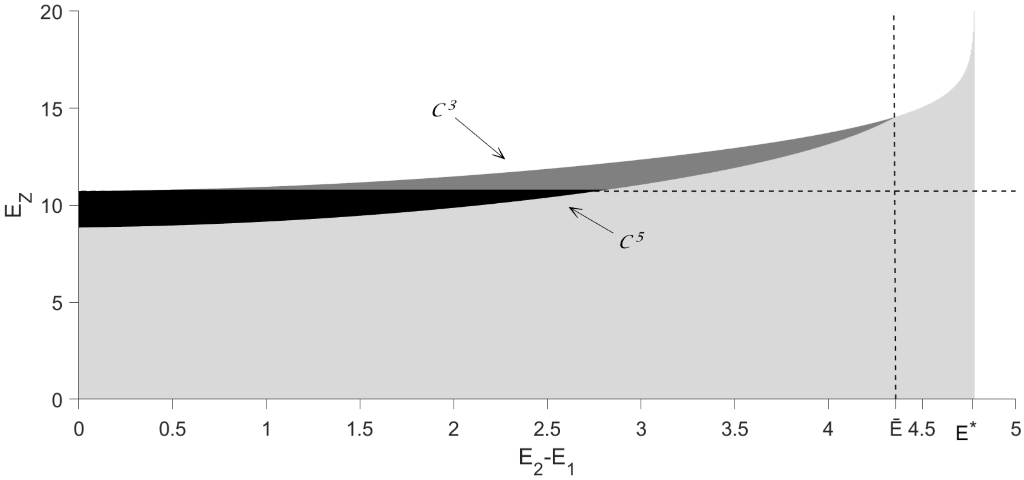

Figure 5.8: Values for E_Z and $E_2 - E_1$ satisfying (5.109). Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.113)- (5.114) and $E_1 = 7.2$.The region allowing Turing instability is depicted in black. The meaning of the plotted curves is explained in the text.

Here we have again the curve $\mathcal{C}^3$ given in (5.87) and the other curve

$$\mathcal{C}^5 : E_Z = \log(\delta) - \log(\mathcal{H}(E_2 - E_1)). \tag{5.115}$$

Their intersection occurs at $\bar{E} \approx 4.36$. We may now perform a comparison between this case and the previous two. The stability region for the steady state of current system is obviously the same of the complete three-equations system (5.48), which in both cases is bigger than the stability region of system (5.1). For the Turing instability, instead, with respect to the case of species Z diffusing, the range of possible values for the difference $E_2 - E_1$ allowing pattern formation is considerably shorter, but, differently from the two-equations case, values close to zero for this quantity can be taken. We also observe that in both the three-equations cases the energy level E_Z must be, in order to have Turing instability, higher than in the reduced case, where very low values are admitted.

We verify the formation of pattern taking $E_Z = 10$ and $E_2 - E_1 = 1$. The behavior in time and space of quantities n_1, n_2, n_Z is reported in Figure 5.9.

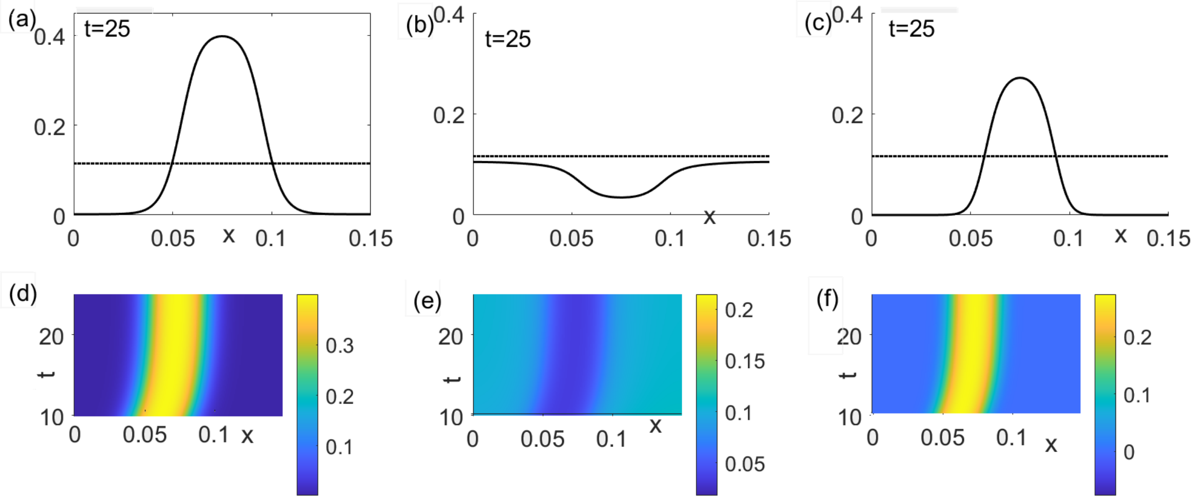

Figure 5.9: Panels (a), (b), (c): Configuration at time $t = 25$ of the densities n_1, n_2, n_Z (solid lines) compared to their equilibrium states (dotted lines) taking $E_2 - E_1 = 1$ and $E_Z = 10$. Panels (d), (e), (f): behavior of densities n_1, n_2, n_Z in space and time for the energy levels taken above. Values for masses as in (5.42), background energies as in (5.43), frequencies as in (5.113)-(5.114) and $E_1 = 7.2$.

5.4 Conclusions

The different reaction-diffusion systems derived in Chapter 4 for a mixture of two gas species (a monatomic and a polyatomic one, the latter having two possible internal energy levels) in a dense background medium considering various hydrodynamic limits have been here analyzed in detail. In particular we have inquired about the possibility of having Turing instability and the consequent formation of spatial patterns for the densities of chemical species involved, setting the discussion upon the dependence of the coefficients on microscopic quantities.

We have started from the two equations system and we have focused our analysis on collision frequencies and energy levels. First of all, we have pointed out that, as in any system showing formation of Turing patterns in which the diffusion coefficient of the inhibitor species has to be bigger than the one of the activator, in our case this means that for component of the polyatomic species corresponding to the higher energy level (playing the role of inhibitor) collision frequencies with the background have to be less than the ones relevant to the the other component corresponding to the lower energy, (acting as activator). We have explicitly individuated a region for values for the internal energy of the monatomic gas and for the difference of the two energy levels of the polyatomic species in order to have spatial oscillations in the equilibrium configuration. We have also verified the appearing of a spatially non–homogeneous solution owing to some numerical simulations, and we have discussed the dependence of the number of oscillations on the choice of the energy levels. As expected, the component with the higher diffusion coefficient shows a more homogeneous profile at equilibrium. Concerning the complete system of three equations, we have been able to derive necessary conditions on microscopic parameters allowing Turing instability but, being the number of parameters involved higher than in the two–component Brusselator–type system, it has not been possible to verify analytically when such conditions really lead to unstable modes. To this aim we have numerically simulated a test case, obtaining as final state a configuration in which the polyatomic component having the lower energy is concentrated in a small region, as well as the monatomic species, while the density of the second component, characterized by a much higher diffusion coefficient, is basically constant in space. For the system of three equations in which only the two components of the polyatomic gas exhibit a diffusion term, at last, the fact that the diffusion matrix contains only two nonzero terms on the diagonal has allowed us to find explicit conditions leading to unstable modes, as in the reduced case. Thus, we have been able to make comparisons between this case and the other ones, and we have also validated results obtained analytically with a numerical simulation.

The derivation performed in these chapters, based on a diffusive asymptotic limit of a system of kinetic equations, has provided reaction–diffusion systems in which the diffusion matrix is diagonal and constant. Actually, in many physical situations the Brusselator–type dynamics is better described if the diffusive part is nonlinear, as for instance in [53], or if there is also a cross diffusion term, as in [50]. In these cases the discussion of Turing instability requires a deeper analysis of parameters appearing in the diffusion part. A possible step forward in our models is to look for a different set of possible interactions among particles of the mixture, and to investigate different hydrodynamic limits of the kinetic equations that may lead to the appearance of nonlinear diffusion or cross diffusion terms, in order to study also their dependence on microscopic quantities.

Concluding remarks and perspectives

The research work presented in this thesis has been aimed at constructing kinetic models and hydrodynamic equations able to reproduce accurately the behavior of real gas mixtures. The main features of physical settings we considered take into account the fact that, in a gaseous flow, gas species may be found in both monoatomic or polyatomic state and they may interact elastically, inelastically or chemically.

We have, first of all, collected the main results of the classical Boltzmann description of a mixture of four polyatomic gases involved in a bimolecular and reversible chemical reaction proposed in [15], extending them to a more general case in which the four gas species may have different numbers of discrete internal energy levels. In this way, also the presence monatomic constituents (having only one internal energy level) is allowed. To this aim, we have introduced a more compact notation for the description of the model.

Aware of the mathematical and computational difficulties of the investigation of the the classical Boltzmann model, in the following chapters of the thesis we have adopted a BGK-type description of a gas mixture, following the research line of [11]. We have built up consistent BGK models for coexisting monatomic and polyatomic species in an inert (Chapter 2) or reacting (Chapter 3) frame. This generalization has allowed us to simulate numerically the behavior of more realistic chemical species. In the inert case we have been able to understand how the possible differences between masses of interacting species may affect the trend towards equilibrium of the macroscopic quantities. For the reacting model, furthermore, we could take inspiration from real bimolecular reactions and we describe the behavior of densities, mean velocities and temperatures. A further development in this research line could involve a more specific description of the internal energy structure of particles, considering separately the rotational and the vibrational energy of each polyatomic species. The macroscopic analysis presented in Chapters 2 and Chapter 3 was performed essentially in space homogeneous conditions; it would be highly desirable to consider also space dependent problems, for example shock wave structure, starting from suitable BGK models.

On the other hand, in this thesis we have approached to the time-space dependent problems for macroscopic quantities following a different line. In fact, in Chapter 4 and Chapter 5, we have performed a derivation of reaction-diffusion equations for the densities of a mixture of a polyatomic and a monatomic species interacting in a gaseous medium, starting from the Boltzmann type description of the model. In this case,our starting point was the paper [12], where an analogous derivation is obtained for a mixture of four reacting species, without considering the internal energy structure of each one. In our work we have considered various hydrodynamic regimes, one of them leading to a reaction-diffusion system analogous to the classical Brusselator system. Our approach allows thus to derive classical chemical systems starting from the kinetic level, with reaction and diffusion coefficients completely explicit in terms of microscopic parameters (masses, collision frequencies, internal energies). In our reaction-diffusion systems, we have investigated the possible occurrence of

Turing instability, namely the formation of periodic non-homogeneous stable solutions. We have been able to find analytic conditions on the microscopic parameters of the mixture allowing or preventing pattern formation, and our results have been confirmed by numerical simulations. The utility of this approach to the study of gas mixtures is that it can be extended to a wide set of possible interactions among particles. An important future research line, already in progress, should be the investigation of different asymptotic limits of the kinetic equations, possibly leading to the appearance of nonlinear diffusion or cross diffusion terms, to be studied also in terms of microscopic quantities.

A Integrals of collision contributions

In Chapter 4 of this thesis a system of reaction-diffusion equations for number densities of components of a particular gas mixture is derived from a system of Boltzmann equations for the distribution functions. In particular, after writing each distribution function as a Maxwellian distribution plus a perturbation term, the derivation is obtained by integrating each Boltzmann equation. Thus, we have to compute the integrals of Boltzmann collision operators involving Maxwellian distributions. We provide here details of such calculations considering a generic bimolecular encounter of type

$$A_1 + A_2 \leftrightarrows A_3 + A_4, \tag{A.1}$$

with each component having a certain mass m_I and internal energy E_I, $I = 1, 2, 3, 4$. We assume that distribution functions are

$$f_I(\mathbf{v}) = n_I M_I(\mathbf{v}) \qquad M_I(\mathbf{v}) = n_I \left(\frac{m_I}{2\pi}\right)^{\frac{3}{2}} \exp\left(-\frac{m_I|\mathbf{v}|^2}{2}\right) \qquad I = 1, 2, 3, 4. \tag{A.2}$$

Keeping in mind the notation used in the preliminary chapter of this work, we write the collision operator for each component, denoting by $\underline{\mathbf{nM}}$ the vector $[n_1M_1, n_2M_2, n_3M_3, n_4M_4]$. The collision operator for A_1 reads as

$$\begin{aligned} Q_1[\underline{\mathbf{nM}}](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} & \mathtt{H}\left(g^2 - \delta_{12}^{34}\right) g\sigma_{12}^{34}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \\ & \times \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 n_3M_3(\mathbf{v}')n_4M_4(\mathbf{w}') - n_1M_1(\mathbf{v})n_2M_2(\mathbf{w})\right] d\mathbf{w}d\hat{\mathbf{\Omega}}', \end{aligned} \tag{A.3}$$

recalling that $\mu_{ij} = \frac{(m_i+m_j)}{m_im_j}$, $\delta_{ij}^{hk} = 2\frac{\Delta E_{ij}^{hk}}{\mu_{ij}}$, with $\Delta E_{ij}^{hk} = E_h + E_k - E_i - E_j$. Here we suppose that $\Delta E_{12}^{34} > 0$. Operators for the remaining A_I can be derived accordingly to the exchange of indices and variables performed in Chapter 1, obtaining

$$\begin{aligned} Q_2[\underline{\mathbf{nM}}](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} & \mathtt{H}\left(g^2 - \delta_{12}^{34}\right) g\sigma_{12}^{34}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \\ & \times \left[\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 n_4M_4(\mathbf{v}')n_3M_3(\mathbf{w}') - n_2M_2(\mathbf{v})n_1M_1(\mathbf{w})\right] d\mathbf{w}d\hat{\mathbf{\Omega}}', \end{aligned} \tag{A.4}$$

$$\begin{aligned} Q_3[\underline{\mathbf{nM}}](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} & \mathtt{H}\left(g^2 - \delta_{34}^{12}\right) g\sigma_{34}^{12}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \\ & \times \left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 n_1M_1(\mathbf{v}')n_2M_2(\mathbf{w}') - n_3M_3(\mathbf{v})n_4M_4(\mathbf{w})\right] d\mathbf{w}d\hat{\mathbf{\Omega}}', \end{aligned} \tag{A.5}$$

$$\begin{aligned} Q_4[\underline{\mathbf{nM}}](\mathbf{v}) = \int_{\mathbb{R}^3}\int_{S^2} & \mathtt{H}\left(g^2 - \delta_{34}^{12}\right) g\sigma_{34}^{12}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \\ & \times \left[\left(\frac{\mu_{34}}{\mu_{12}}\right)^3 n_2M_2(\mathbf{v}')n_1M_1(\mathbf{w}') - n_4M_4(\mathbf{v})n_3M_3(\mathbf{w})\right] d\mathbf{w}d\hat{\mathbf{\Omega}}'. \end{aligned} \tag{A.6}$$

It is worth to observe that in (A.5) and (A.6) the quantity $\mathtt{H}\left(g^2-\delta_{34}^{12}\right)$ could have been omitted since it is identically 1 with hypothesis made on energy gap. We are now interested in calculating explicitly the integral

$$\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}. \tag{A.7}$$

Substituting the expressions for the Maxwellians we have

$$\begin{aligned}\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} \;=\; & \frac{1}{(2\pi)^3}\int_{\mathbb{R}^3\times\mathbb{R}^3}\int_{S^2}\sigma_{12}^{34}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')g\,\mathtt{H}\left(g^2-\delta_{12}^{34}\right)\\ & \times\left[\left(\frac{m_1m_2}{\sqrt{m_3m_4}}\right)^3 n_3n_4\exp\left(-\frac{1}{2}m_3v'^2-\frac{1}{2}m_4w'^2\right)\right.\\ & \left.-\left(m_1m_2\right)^{\frac{3}{2}} n_1n_2\exp\left(-\frac{1}{2}m_1v^2-\frac{1}{2}m_2w^2\right)\right]d\mathbf{w}\,d\mathbf{v}\,d\hat{\mathbf{\Omega}}',\end{aligned} \tag{A.8}$$

and using the conservation of total energy during the collision (A.1) written as

$$\frac{1}{2}m_3v'^2+\frac{1}{2}m_4w'^2=-\Delta E_{12}^{34}+\frac{1}{2}m_1v^2+\frac{1}{2}m_2w^2, \tag{A.9}$$

we have

$$\begin{aligned}\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} \;=\; & \frac{(m_1m_2)^{\frac{3}{2}}}{(2\pi)^3}\left[\left(\frac{m_1m_2}{m_3m_4}\right)^{\frac{3}{2}}\exp\left(\Delta E_{12}^{34}\right)n_3n_4-n_1n_2\right]\int_{S^2}\sigma_{12}^{34}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')g\,d\hat{\mathbf{\Omega}}'\\ & \times\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathtt{H}\left(g^2-\delta_{12}^{34}\right)\exp\left(-\frac{1}{2}m_1v^2-\frac{1}{2}m_2w^2\right)d\mathbf{w}\,d\mathbf{v}.\end{aligned} \tag{A.10}$$

The Maxwell molecules assumption adopted throughout this work still holds here, thus we have constant collision frequency

$$\int_{S^2}\sigma_{12}^{34}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')g\,d\hat{\mathbf{\Omega}}'\overset{\mathsf{def}}{=}\nu_{12}^{34}. \tag{A.11}$$

Moreover, inside the six-folds remaining integral

$$\int_{\mathbb{R}^3\times\mathbb{R}^3}\mathtt{H}\left(g^2-\delta_{12}^{34}\right)\exp\left(-\frac{1}{2}m_1v^2-\frac{1}{2}m_2w^2\right)d\mathbf{w}\,d\mathbf{v} \tag{A.12}$$

by writing

$$\begin{aligned}m_1v^2+m_2w^2 &= \frac{m_1-m_2}{m_1+m_2}(m_1v^2+m_2w^2)+2\frac{m_1m_2}{m_1+m_2}(\mathbf{v}\cdot\mathbf{w})-2\frac{m_1m_2}{m_1+m_2}(\mathbf{v}\cdot\mathbf{w})\\ &= \frac{|m_1\mathbf{v}+m_2\mathbf{w}|^2}{m_1+m_2}+\frac{m_1m_2|\mathbf{v}-\mathbf{w}|^2}{m_1+m_2},\end{aligned} \tag{A.13}$$

we perform the change of variables $(\mathbf{v},\mathbf{w})\to(\mathbf{g},\mathbf{G})$ that we recall here

$$\begin{cases}\mathbf{g}=\mathbf{v}-\mathbf{w}\\ \mathbf{G}=\alpha_{12}\mathbf{v}+\alpha_{21}\mathbf{w},\end{cases} \tag{A.14}$$

being $\alpha_{ij}=\frac{m_i}{m_i+m_j}$, and we obtain

$$\int_{\mathbb{R}^3}\exp\left(-\frac{1}{2}G^2(m_1+m_2)\right)d\mathbf{G}\int_{g^2>\delta_{12}^{34}}\exp\left(-\frac{1}{2}g^2\frac{m_1m_2}{m_1+m_2}\right)d\mathbf{g}. \tag{A.15}$$

Passing to spherical coordinates in both integrals above, we have

$$16\pi^2 \int_0^{+\infty} \exp\left(-\frac{1}{2}\rho_G^2(m_1+m_2)\right)\rho_G^2 d\rho_G \int_{\rho_g^2>\delta_{12}^{34}} \exp\left(-\frac{1}{2}\rho_g^2\frac{m_1m_2}{m_1+m_2}\right)\rho_g^2 d\rho_g. \tag{A.16}$$

Setting

$$y=\sqrt{\frac{1}{2}(m_1+m_2)}\rho_G, \qquad \xi=\frac{1}{2}\frac{m_1m_2}{m_1+m_2}\rho_g^2, \tag{A.17}$$

the integral may be rewritten as

$$\begin{aligned} 16\pi^2\frac{2}{(m_1m_2)^{\frac{3}{2}}}&\int_0^{+\infty}\exp\left(-y^2\right)2y^2dy\int_{\xi>\Delta E_{12}^{34}}\exp\left(-\xi\right)\sqrt{\xi}d\xi \\ &=16\pi^{\frac{5}{2}}\frac{1}{(m_1m_2)^{\frac{3}{2}}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{12}^{34})\right), \end{aligned} \tag{A.18}$$

with $\Gamma(\alpha,\beta)$ the upper incomplete Euler gamma function

$$\Gamma(\alpha,\beta)=\int_\beta^{+\infty}\tau^{\alpha-1}e^{-\tau}d\tau \tag{A.19}$$

and $\Theta(x)=\max\{x,0\}$. Finally we get the result

$$\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = \nu_{12}^{34}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{12}^{34})\right)\left[\left(\frac{m_1m_2}{m_3m_4}\right)^{\frac{3}{2}}\exp\left(\Delta E_{12}^{34}\right)n_3n_4-n_1n_2\right].$$

We want now to calculate integrals for the remaining collision operators (A.4)-(A.6). We notice that, via a change of variables $\mathbf{v}\leftrightarrow\mathbf{w}$, it is easy to check that

$$\int_{\mathbb{R}^3} Q_2[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}=\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}.$$

For the remaining two integrals, being the Jacobian of the transformation involving pre-collisional and post-collisional velocities $(\mathbf{v}',\mathbf{w}',\hat{\mathbf{\Omega}})\to(\mathbf{v},\mathbf{w},\hat{\mathbf{\Omega}}')$ for the reverse reaction in (A.1) equal to

$$\mathbf{H}\left((g')^2-\delta_{12}^{34}\right)\frac{\mu_{12}}{\mu_{34}}\frac{g}{g'}, \tag{A.20}$$

we have, after the change of variables,

$$\begin{aligned} \int_{\mathbb{R}^3} Q_3[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}=\int_{\mathbb{R}^3\times\mathbb{R}^3}&\int_{S^2}\mathbf{H}\left((g')^2-\delta_{34}^{12}\right)\frac{g^2}{g'}\sigma_{34}^{12}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}') \\ &\times\left(\frac{\mu_{34}}{\mu_{12}}\right)^2\Big[n_1M_1(\mathbf{v}')n_2M_2(\mathbf{w}') \\ &-\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 n_3M_3(\mathbf{v})n_4M_4(\mathbf{w})\Big]d\mathbf{v}'d\mathbf{w}'d\hat{\mathbf{\Omega}}, \end{aligned} \tag{A.21}$$

By microreversibility introduced in (1.25) [52, 80] and that now reads as

$$\mu_{34}^2g^2\sigma_{34}^{12}(g,\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}')=\mu_{12}^2(g')^2\sigma_{12}^{34}(g',\hat{\mathbf{\Omega}}\cdot\hat{\mathbf{\Omega}}'), \tag{A.22}$$

the integral above becomes

$$\begin{aligned}\int_{\mathbb{R}^3} Q_3[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} &= \int_{\mathbb{R}^3\times\mathbb{R}^3}\int_{S^2} \mathtt{H}\left((g')^2-\delta_{34}^{12}\right) g'\sigma_{12}^{34}(g',\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')\\ &\quad\times\left[n_1M_1(\mathbf{v}')n_2M_2(\mathbf{w}')-\left(\frac{\mu_{12}}{\mu_{34}}\right)^3 n_3M_3(\mathbf{v})n_4M_4(\mathbf{w})\right]d\mathbf{v}'d\mathbf{w}'d\hat{\boldsymbol{\Omega}}\\ &= -\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}. \end{aligned} \tag{A.23}$$

Exchanging again velocities $\mathbf{v}$ and $\mathbf{w}$ we get

$$\int_{\mathbb{R}^3} Q_4[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = \int_{\mathbb{R}^3} Q_3[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = -\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}. \tag{A.24}$$

Considering, instead, a "one-directional" irreversible collision of type

$$A_1 + A_2 \to A_3 + A_4, \tag{A.25}$$

accordingly to results obtained in the preliminaries, the collision operator for components A_1 has only the loss term, thus its integral is

$$\begin{aligned}\int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} &= -\int_{\mathbb{R}^3\times\mathbb{R}^3}\int_{S^2} \mathtt{H}\left(g^2-\delta_{12}^{34}\right) g\sigma_{12}^{34}(g,\hat{\boldsymbol{\Omega}}\cdot\hat{\boldsymbol{\Omega}}')n_1M_1(\mathbf{v})n_2M_2(\mathbf{w})d\mathbf{w}d\hat{\boldsymbol{\Omega}}'\\ &= -\nu_{12}^{34}\frac{2}{\sqrt{\pi}}\Gamma\left(\frac{3}{2},\Theta(\Delta E_{12}^{34})\right)n_1n_2. \end{aligned} \tag{A.26}$$

Repeating the procedure performed for the reversible case we get to relations for the other integrals

$$\int_{\mathbb{R}^3} Q_2[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = \int_{\mathbb{R}^3} Q_1[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = -\int_{\mathbb{R}^3} Q_3[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v} = -\int_{\mathbb{R}^3} Q_4[\underline{\mathbf{nM}}](\mathbf{v})d\mathbf{v}\,. \tag{A.27}$$

B Turing instability in reaction-diffusion systems

In Chapter 5, the stability properties of three different types of reaction-diffusion systems previously obtained are analyzed through the Turing instability procedure, outlined by Alan Turing in 1952 [118] and applied by Murray in [92] to models describing pattern formation in biology. We report here an overview of the topic.

The starting point is the reaction-diffusion system for a certain number of substances that diffuse, interacting, on a bounded domain. The system reads as

$$\mathbf{u}_t = D\Delta_{\mathbf{x}}\mathbf{u} + \mathbf{F}(\mathbf{u}), \tag{B.1}$$

where $\mathbf{u} = (u_1, \ldots, u_k)$ is the vector whose entries are the uri nknown quantities of the system depending on time and The systems are somehow related to the classical Brusselator model, used to describe a class of chemical reactions that have as a result the formation of patterns. The implementation of a specific mathematical model able to reproduce real phenomena in which there is pattern formation was introduced by Alan Turing in his work of 1952 [118]. His aim was to describe the chemistry behind morphogenesis, i.e. the formation of different patterns in natural systems. The analysis of a generic reacting system with linear diffusion, along with the discussion of its stability properties, leading to an accurate description pattern formation in biology, was provided by Murray in [92] space $u_i = u_i(\mathbf{x}, t)$, D is the diffusion matrix containing diffusion rates and $\mathbf{F}$ is a vector of smooth non-linear functions representing the interaction among quantities. Turing's idea was that steady heterogeneous spatial patterns may be obtained by means of a diffusion-driven instability of the steady state. In other words, the appearance of patterns occurs when the system exhibits the so-called Turing instability: a homogeneous steady state is stable under small perturbation when there is no diffusion, but it becomes unstable if the diffusive part is considered. These stability/instability features can be obtained only if specific necessary and sufficient conditions on the diffusion coefficients and on parameters of the reaction functions are satisfied, and identifying these conditions is the main issue of the Turing analysis.

We shall present here the classical model in which two quantities (in our case are they are number densities of gaseous constituents) u, v are involved, but, as discussed in the last part of this thesis, it can also be generalized to a higher number of components, not without additional technical difficulties. We will also consider only the case in which the matrix D is diagonal. Thus we write the system in the form

$$\begin{aligned} u_t - D_1\Delta_{\mathbf{x}}u &= f(u, v) \\ v_t - D_2\Delta_{\mathbf{x}}v &= g(u, v), \end{aligned} \tag{B.2}$$

with $t \in (0, +\infty)$ and $\mathbf{x} \in \Omega$, being Ω a smooth, bounded and connected set. The functions f and g represent the interaction between u and v, while the matrix $D = \begin{pmatrix} D_1 & 0 \\ 0 & D_2 \end{pmatrix}$ contains the positive diffusion rates of the two chemical species on Ω. The dynamics is all contained in Ω, for this reason we impose zero flux at the closed boundary $\partial\Omega$ of the domain (homogeneous Neumann boundary conditions):

$$\underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} u = 0, \quad \underline{\hat{\mathbf{n}}} \cdot \nabla_{\mathbf{x}} v = 0 \quad \text{on} \quad (0, +\infty) \times \partial\Omega, \tag{B.3}$$

being $\underline{\hat{\mathbf{n}}}$ the unit outward normal to $\partial\Omega$. Once that initial data $u(\mathbf{x}, 0), v(\mathbf{x}, 0)$ are set on Ω, the first step is to individuate a steady state for the space-homogeneous system obtained without considering the diffusion, namely

$$\begin{aligned} u_t &= f(u, v) \\ v_t &= g(u, v). \end{aligned} \tag{B.4}$$

Thus, imposing $f(u, v) = 0$ and $g(u, v) = 0$, we assume the existence of a steady state belonging to the interior of Ω, that we denote by $(\bar{u}, \bar{v})$.

As mentioned before, the diffusion-driven instability occurs when the state is first of all stable in spatial homogeneous conditions, under small perturbations. To this aim, we linearize the system in absence of diffusion around the state $(\bar{u}, \bar{v})$ and we write it in a compact form, getting

$$\mathbf{W}_t = A\mathbf{W}, \tag{B.5}$$

with $\mathbf{W} = \begin{pmatrix} u - \bar{u}, \\ v - \bar{v} \end{pmatrix}$ and the matrix A defined as $A = \begin{pmatrix} f_u & f_v \\ g_u & g_v \end{pmatrix} = \left.\begin{pmatrix} \frac{\partial f}{\partial u} & \frac{\partial f}{\partial v} \\ \frac{\partial g}{\partial u} & \frac{\partial g}{\partial v} \end{pmatrix}\right|_{(\bar{u}, \bar{v})}$.

The stability of the steady state, that now is $\bar{\mathbf{W}} = (0, 0)$, implies that the solution $\mathbf{W}$ of (B.5) is such that $\mathbf{W} \to (0, 0)$ as $t \to 0$ when the initial state is sufficiently close to zero. Being the solution $\mathbf{W}$ with respect to time of the form $e^{\lambda t}$, with λ given by eigenvalues of the matrix A, the asymptotic stability of the steady state is possible only if the eigenvalues have negative real part. Computing the characteristic polynomial of A, which is

$$p(\lambda) = det(A - \lambda I) = \lambda^2 - \lambda trA + detA, \tag{B.6}$$

its roots have negative real part if $trA < 0$ and $detA > 0$, conditions that can be explicitly written as

$$f_u + g_v < 0, \quad f_u g_v - f_v g_u > 0. \tag{B.7}$$

The fulfillment of conditions above depends on the parameters appearing in f and g, upon which is usually set the analysis.

After that conditions on linear stability are set, we consider the complete system with the diffusion, again linearized around the steady state, together with the boundary conditions considered above, that is

$$\begin{cases} \mathbf{W}_t = D\Delta_{\mathbf{x}}\mathbf{W} + A\mathbf{W} & \text{on } (0, \infty) \times \Omega \\ \hat{\mathbf{n}} \cdot \nabla_{\mathbf{x}}\mathbf{W} = 0 & \text{on } (0, \infty) \times \partial\Omega \end{cases} \tag{B.8}$$

The solutions of this system are represented in Fourier series as

$$\mathbf{W}(\mathbf{x}, t) = \sum_k \mathbf{W}_k(\mathbf{x}, t) = \sum_k c_k e^{\lambda_k t} \tilde{\mathbf{W}}_k(\mathbf{x}), \tag{B.9}$$

where $k \in \mathbb{N}$ and each eigenfunction $\tilde{\mathbf{W}}_k(\mathbf{x})$ is a solution of the time–independent problem

$$\begin{cases} \Delta_{\mathbf{x}}\tilde{\mathbf{W}} + k^2\tilde{\mathbf{W}} = \mathbf{0} & \text{on } (0,\infty)\times\Omega \\ \hat{\mathbf{n}}\cdot\nabla_{\mathbf{x}}\tilde{\mathbf{W}} = 0 & \text{on } (0,\infty)\times\partial\Omega. \end{cases} \tag{B.10}$$

Inserting the series (B.9) in the linear PDE of (B.8) we get

$$\sum_k \lambda_k c_k e^{\lambda_k t}\tilde{\mathbf{W}}_k(\mathbf{x}) = D\sum_k(-k^2)c_k e^{\lambda_k}\tilde{\mathbf{W}}_k(\mathbf{x}) + A\sum_k c_k e^{\lambda_k t}\tilde{\mathbf{W}}_k(\mathbf{x}). \tag{B.11}$$

This implies that, for each k,

$$\lambda_k\tilde{\mathbf{W}}_k(\mathbf{x}) = \left[A - k^2D\right]\tilde{\mathbf{W}}_k(\mathbf{x}), \tag{B.12}$$

thus λ_k is an eigenvalue of the matrix $A - k^2D$, whose characteristic polynomial is

$$p_k(\lambda) = det(A - k^2D - \lambda I) = \lambda^2 + \lambda\left[k^2(D_1 + D_2) - (f_u + g_v)\right] + r(k^2), \tag{B.13}$$

with the function

$$r(k^2) \overset{\text{def}}{=} k^4D_1D_2 - k^2[D_1g_v + D_2f_u] + f_ug_v - f_vg_u. \tag{B.14}$$

The instability predicted by Turing analysis is achieved if at least one term $\mathbf{W}_{\bar{k}}(\mathbf{x},t)$ of (B.9) is not vanishing as $t \to +\infty$, it means that there exists at least one wavenumber $\bar{k}$ such that $Re\lambda_{\bar{k}} > 0$. Since, for each k, roots of (B.13) are

$$\lambda_{k1,2} = \frac{1}{2}\left[f_u + g_v - k^2(D_1 + D_2) \pm \sqrt{[f_u + g_v - k^2(D_1 + D_2)]^2 - 4r(k^2)}\right], \tag{B.15}$$

and recalling the negativity of trA required for the linear stability, one eigenvalue $\lambda_{\bar{k}}$ may have positive real part only if the function $r(k^2)$ attains a negative value. To have this, keeping in mind the other constraint $detA > 0$, first of all it must be

$$D_2f_u + D_1g_v > 0. \tag{B.16}$$

Taking (B.7) and (B.16) together, it follows that f_u and g_v must have opposite signs. This means that if $f_u > 0$ it has to be $D_2 > D_1$, the opposite if $f_u < 0$. The discussion of all possible cases along with physical examples can be found in [92], in which the "activator-inhibitor" dynamics is considered to be at the basis of pattern formation.

On the other hand, condition (B.16) is not sufficient to ensure $r(k^2) < 0$ for some values of k, in fact we should also check that $r_{min} < 0$ and, being

$$r_{min} = -\frac{(D_2f_u + D_1g_v)^2}{4D_1D_2} + f_ug_v - f_vg_u, \tag{B.17}$$

it means

$$4D_1D_2(f_ug_v - f_vg_u) - (D_2f_u + D_1g_v)^2 < 0. \tag{B.18}$$

Summing up, if the following conditions are satisfied by parameters of the system

$$\begin{aligned} &trA = f_u + g_v < 0, \\ &detA = f_ug_v - f_vg_u > 0, \\ &D_2f_u + D_1g_v > 0 \\ &4D_1D_2(f_ug_v - f_vg_u) - (D_2f_u + D_1g_v)^2 < 0, \end{aligned} \tag{B.19}$$

is possible to identify a range (k_1^2, k_2^2) of wavenumbers, with k_1^2 and k_2^2 solutions of $r(k^2) = 0$ given by

$$k_{1,2}^2 = \frac{D_1 g_v + D_2 f_u \pm \sqrt{(D_1 g_v + D_2 f_u)^2 - 4 D_1 D_2 (f_u g_v - f_v g_u)}}{2 D_1 D_2}, \tag{B.20}$$

such that for any integer (if there exists) $\bar{k}$ such that $k_1^2 < (\bar{k})^2 < k_2^2$ one has $Re\lambda_{\bar{k}} > 0$, getting an unstable mode $\mathbf{W}_{\bar{k}}$ that leads to formation of patterns.

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