A Kinetic Model for Chemical Reactions without Barriers: Transport Coefficients and Eigenmodes

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Abstract

The kinetic model of the Boltzmann equation proposed in the work [1] for a binary mixture undergoing chemical reactions of symmetric type which occur without activation energy is revisited here, with the aim of investigating in detail the transport properties of the reactive mixture and the influence of the reaction process on the transport coefficients. Accordingly, the non-equilibrium solution of the Boltzmann equation is determined through an expansion in Sonine polynomials up to the first order, using the Chapman-Enskog method, in a chemical regime for which the reaction process is close to its final equilibrium state. The non-equilibrium deviations are explicitly calculated for what concerns the thermal-diffusion ratio and coefficients of shear viscosity, diffusion and thermal conductivity. The theoretical and formal analysis developed in the present paper is complemented with some numerical simulations performed for different concentrations of reactants and products of the reaction as well as for both exothermic and endothermic chemical processes. The results reveal that chemical reactions without energy barrier can induce an appreciable influence on the transport properties of the mixture. Oppositely to the case of reactions with activation energy, the coefficients of shear viscosity and thermal conductivity become larger than those of an inert mixture when the reactions are exothermic. An application of the non-barrier model and its detailed transport picture is included in this paper, in order to investigate the dynamics of the local perturbations on the constituent number densities, and velocity and temperature of the whole mixture, induced by spontaneous internal fluctuations. It is shown that for the longitudinal disturbances there exist two hydrodynamic sound modes, one purely diffusive hydrodynamic mode and one kinetic mode.

1 Introduction

Transport processes in reactive mixtures have become a fundamental subject of theoretical and experimental works, due to significant applications of reactive flows with detailed transport properties in chemical technology, plasma chemistry, combustion, atmosphere physics at high altitudes and several others. In particular, kinetic theory calculations directed to the estimation of transport coefficients for chemically reactive systems have been established by several authors, after the first studies conducted by Prigogine and co-workers in papers [2] and [3]. In fact, over the past few decades, many contributions to the scientific literature of chemically reactive systems have been proposed in order to evaluate the transport coefficients and investigate the non-equilibrium effects induced by the chemical reaction on the gas properties. Among others, some reference works on this field are [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14].

In most papers in the existing literature, the chemical processes are described in terms of reactive cross sections with an activation energy so that the large part of the collisions result in elastic scattering, since only few particles can go beyond the activation energy barrier. Some few works consider reactive cross sections without activation energy, corresponding to chemical interactions of hard sphere type [8],

[16] or corresponding to Maxwellian-type molecules [15]. However, the collision terms in [15] and [16] do not contain any feature which guarantees that each collision contributes exactly once to either elastic or reactive term. Conversely, in paper [8], the authors propose a reactive kinetic model equation where the elastic collision terms have a correction part with the meaning of excluding from the total number of elastic collisions those events that lead to chemical reaction.

In the present work we study the transport properties of a binary gaseous mixture which undergoes a chemical reaction of the type A+A⇌B+B which proceeds without activation energy. The starting point is the kinetic model proposed in [1] and improved in [17]. More precisely, the explicit expressions of the thermal-diffusion ratio and coefficients of shear viscosity, diffusion and thermal conductivity have been obtained from the perturbation solution of the Boltzmann equation, in a chemical regime for which the reaction process is close to its final equilibrium state. A detailed analysis of the transport properties is then performed and a rather complete spectrum of the transport coefficients is shown.

The plan of this paper is as follows. The main aspects of the non-barrier kinetic model are presented in Section 2. The collisional dynamics is detailed and the Boltzmann equation is derived with a new form of the elastic and reactive collision terms. Following the ideas of papers [1] and [17], probability coefficients χ and $(1-\chi)$ are introduced in the reactive and elastic collision terms, respectively, in order to account each binary encounter among identical particles exactly once, either as a reactive or an elastic event. The corresponding macroscopic picture is also described by means of the balance equations for the relevant hydrodynamic fields of the reactive mixture. At last, the Chapman-Enskog method and a first order Sonine polynomial expansion of the distributions functions are used to approximate the non-equilibrium solution of the Boltzmann equation in a chemical regime close to the final stage of the reaction process. In Section 3, the non-equilibrium distribution is used to deduce the constitutive equations for the pressure tensor and heat flux vector of the mixture, and diffusion velocities and chemical reaction rates of the constituents. The explicit expressions of the transport coefficients of shear viscosity, thermal conductivity, thermal-diffusion ratio and diffusion, as well as the detailed expressions of the direct and reverse reaction rates are obtained. The behavior of such kinetic properties is illustrated with several numerical simulations for exothermic and endothermic chemical reactions, as well as for different constituent concentrations. The results obtained in this section are discussed in detail, focusing the effects induced by the chemical reaction on the gas mixture. In Section 4, an application of the non-barrier kinetic model where the transport effects play an important role is studied. The dynamical behavior of small perturbations induced by spontaneous internal fluctuations are investigated, characterizing the existence of two hydrodynamic sound modes, one purely diffusive hydrodynamic mode and one kinetic mode. At last, in Section 5, the results are summarized and some final remarks are stated.

Cartesian notation for tensors and the convention on repeated indices are used throughout the paper. Greek indices denote the constituents of the mixture while Latin indices denote the cartesian coordinates. The velocity vector of a molecule is denoted by $\mathbf{c}_\alpha$ while its components by c_i^α.

2 Basic Theory of the Non-Barrier Kinetic Model

The system we are interested in this work consists of a binary reactive mixture of ideal gases whose constituents, denoted by A and B, undergo a simple reversible chemical reaction of the type $A+A \rightleftharpoons B+B$. The molecules of the constituents have binding (or formation) energies ϵ_A and ϵ_B, but equal masses $m_A = m_B = m$ and equal diameters $\mathsf{d}_A = \mathsf{d}_B = \mathsf{d}$. This kind of reaction can be considered as the first stage of the Lindemann-Hinshelwood mechanism for reactions whose constituents are isomers [18], in particular the transitions of crotonaldehyde and acrolein (s-cisands-transconformers), the reaction CH3NC⇌CH3CN and the transformation cyclopropane $\rightleftharpoons$ propene. Non-equilibrium effects for model reactive systems undergoing symmetric chemical processes have been investigated by several authors. See, for example, papers [11], [19], [20] and [21], just to cite some of them.

The elastic binary collisions are characterized by the conservation laws of momentum and kinetic energy, namely,

$$m\mathbf{c}_\alpha + m\mathbf{c}_\beta = m\mathbf{c}'_\alpha + m\mathbf{c}'_\beta, \qquad \frac{1}{2}mc_\alpha^2 + \frac{1}{2}mc_\beta^2 = \frac{1}{2}mc_\alpha'^2 + \frac{1}{2}mc_\beta'^2, \qquad (\alpha, \beta = A, B), \qquad (1)$$

where $(\boldsymbol{c}_\alpha, \boldsymbol{c}_\beta)$ refer to pre-collisional velocities and $(\boldsymbol{c}'_\alpha, \boldsymbol{c}'_\beta)$ to post-collisional velocities. The relative velocity is denoted by $\boldsymbol{g}_{\beta\alpha} = \boldsymbol{c}_\beta - \boldsymbol{c}_\alpha$ and the energy conservation law implies that $g_{\beta\alpha} = g'_{\beta\alpha}$.

The conservation laws of momentum and total energy (kinetic plus binding energy) for reactive binary collisions read

$$m\boldsymbol{c}_A + m\boldsymbol{c}_{A_1} = m\boldsymbol{c}'_A + m\boldsymbol{c}'_{A_1}, \qquad \frac{1}{2}mc_A^2 + \epsilon_A + \frac{1}{2}mc_{A_1}^2 + \epsilon_A = \frac{1}{2}mc_B^2 + \epsilon_B + \frac{1}{2}mc_{B_1}^2 + \epsilon_B. \qquad (2)$$

In the above equations $(\boldsymbol{c}_A, \boldsymbol{c}_{A_1})$ are the velocities of the reactants, while $(\boldsymbol{c}_B, \boldsymbol{c}_{B_1})$ are the velocities of the products of the reaction. The subindex 1 is used in order to distinguish two identical molecules that participate in the reactive collision. The relative velocities of the reactants and products of the forward reaction are denoted by $\boldsymbol{g}_A = \boldsymbol{c}_{A_1} - \boldsymbol{c}_A$ and $\boldsymbol{g}_B = \boldsymbol{c}_{B_1} - \boldsymbol{c}_B$, respectively, and the conservation law of the total energy in terms of the relative velocities reads: $g_A^2 = g_B^2 + 4Q/m$, where the difference of the binding energies of the products and reactants is identified with the reaction heat $Q = 2(\epsilon_B - \epsilon_A)$. Thus the forward reaction is exothermic when $Q < 0$ and endothermic when $Q > 0$. For ideal gas mixtures whose constituents are at the same temperature T, the chemical potential of the constituent α reads [22]

$$\mu_\alpha = \epsilon_\alpha - kT \left[\frac{3}{2} \ln T - \ln n_\alpha + \mathcal{C} \right], \qquad (3)$$

where n_α is the particle number density of the constituent α, k denotes Boltzmann's constant and $\mathcal{C}$ is a constant, which according to statistical mechanics is given by $\mathcal{C} = 3 \ln(2\pi mk/h^2)/2$ with h denoting Planck's constant.

The affinity $\mathcal{A}$ of a chemical reaction is defined as the difference of the chemical potentials of the reactants and products, i.e.,

$$\mathcal{A} = 2(\mu_A - \mu_B) = -Q + 2kT \ln\left(\frac{n_A}{n_B}\right), \qquad (4)$$

where the last equality follows from (3). At equilibrium the affinity vanishes and the above equation reduces to the law of mass action:

$$Q = 2kT \ln\left(\frac{n_A^{\text{eq}}}{n_B^{\text{eq}}}\right), \qquad (5)$$

where n_B^{eq} and n_A^{eq} refer to the equilibrium values of the particle number densities.

The reactive mixture is characterized in the phase space, spanned by the positions and velocities of the molecules, by the distribution functions $f_\alpha(\boldsymbol{x}, \boldsymbol{c}_\alpha, t)$, $\alpha = A, B$, such that $f_\alpha(\boldsymbol{x}, \boldsymbol{c}_\alpha, t)d\boldsymbol{x}\, d\boldsymbol{c}_\alpha$ gives at time t the number of molecules of constituent α in the volume element $d\boldsymbol{x}\, d\boldsymbol{c}_\alpha$. We adopt the convention on repeated indices, and use Greek subscripts for the constituents of the mixture as well as and Latin subscripts for cartesian components of a vector. The space-time evolution of the distribution functions is governed by the Boltzmann equations

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \sum_{\beta=A}^{B} (1 - \chi \delta_{\alpha\beta}) \int \left[f'_\alpha f'_\beta - f_\alpha f_\beta \right] g_{\beta\alpha}\, \sigma_{\alpha\beta}\, d\Omega\, d\boldsymbol{c}_\beta \qquad (6)$$

$$+ \chi \int \left[f_\gamma f_{\gamma_1} - f_\alpha f_{\alpha_1} \right] \sigma_\alpha^\star\, g_\alpha\, d\Omega^\star\, d\boldsymbol{c}_{\alpha_1}, \qquad \alpha \neq \gamma = A, B.$$

The first expression on the right-hand side of (6) is the elastic collision term, while the second one the reactive collision term. The differentials $d\Omega$, $d\Omega^\star$ are elements of solid angle which characterize the elastic and reactive scattering processes, respectively, and $\delta_{\alpha\beta}$ is the Kronecker symbol. At molecular level, the differential cross sections characterize the types of collisions between the molecules and, in this work, it is assumed that for the elastic encounters the differential cross section is that of rigid spheres of diameter d, i.e., $\sigma_{\alpha\beta} = \mathsf{d}^2/4$. For the inelastic collisions, we investigate chemical reactions of hard-sphere type which proceed without activation energy, so that $\sigma_\alpha^* = \mathsf{d}^2/4$. Other differential cross sections for reactive collisions without activation energy are considered, for example, in Stiller [23] and Brouard [24]. It would

be interesting to underline that, with regard to the line-of-centers reactive cross section, in our model it is not possible to consider the activation energy equal to zero, $\epsilon^\star = 0$, in order to recover the case without activation energy. In fact, this procedure would lead to the wrong fact that the reaction heat would also vanish. Although the reaction heat can be expressed as the difference between the forward and backward activation energies, by definition it is the difference between the binding energies of the reactants and products of the reaction. In our model for a symmetric chemical reaction, the binding energy is the unique characteristic that distinguishes reactants and products, so that it should be positive or negative, but not equal to zero. Moreover, in Eq. (6) the parameter χ, with $0 \leq \chi \leq 1$, is a scalar factor, which represents the probability of a reactive encounter. In the case $\alpha = \beta$, the term $(1 - \chi)$ is a reduced factor for the elastic contributions among identical molecules with the following meaning. According to the considered reaction dynamics, each encounter among identical molecules can result in both a reactive collision or an elastic encounter. However, for hard-sphere type elastic and reactive cross sections, both integrals on the right-hand-side of Eq. (6) extend over all values of the translational energy, so that the contributions associated to each encounter among identical molecules are included in both the reactive and elastic collision integrals $\int [f_\beta f_\beta - f_\alpha f_{\alpha_1}] \sigma_\alpha^\star g_\alpha \, d\Omega^\star \, d\mathbf{c}_{\alpha_1}$ and $\int [f_\alpha' f_\alpha' - f_\alpha f_\alpha] g_{\alpha\alpha} \sigma_{\alpha\alpha} \, d\Omega \, d\mathbf{c}_\alpha$. It seems then reasonable to subtract from the elastic collision integral those events among identical particles which give rise to a reactive encounter. This can be done introducing the probability χ of resulting a reactive encounter from a binary collision among identical molecules and multiplying the corresponding elastic and reactive collision integrals by $(1 - \chi)$ and χ, respectively. In particular, the reduced factor $(1 - \chi)$ avoids a double counting in the sense that each encounter among identical molecules gives only one contribution to Eq. (6), which can be either of elastic or reactive type. This is not the usual procedure in the literature of the Boltzmann equation for chemically reacting mixtures, since the majority of the research papers deal with reactive cross sections with activation energy and introduce a steric factor connecting elastic and reactive interaction diameters. Therefore, reactive collisions occur only for those pairs of molecules with relative translational energy larger than the activation energy, whereas almost elastic collisions occur for low energy levels. In this sense there exists some overlapping for high energies, since each encounter between particles of the same constituent is counted both as an elastic collision and as a reactive interaction.

The macroscopic picture of the reacting mixture is described by the balance equations for the basic fields of the constituent particle number densities n_α, mean velocity v and temperature T of the whole mixture, which are defined in terms of the distribution functions by

$$n_\alpha = \int f_\alpha d\mathbf{c}_\alpha, \qquad v_i = \frac{1}{n} \sum_{\alpha=A}^{B} \int c_i^\alpha f_\alpha d\mathbf{c}_\alpha, \quad T = \frac{1}{3nk} \sum_{\alpha=A}^{B} \int m \xi_\alpha^2 f_\alpha d\mathbf{c}_\alpha, \tag{7}$$

where $n = \sum_{\alpha=A}^{B} n_\alpha$ is the particle number density of the mixture and $\xi_i^\alpha = c_i^\alpha - v_i$ is a peculiar velocity. The balance equations for the fields (7) are obtained from the Boltzmann equation (6) and read [13]

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial x_i}(n_\alpha u_i^\alpha + n_\alpha v_i) = \tau_\alpha, \qquad \alpha = A, B, \tag{8}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(p_{ij} + \varrho v_i v_j) = 0, \tag{9}$$

$$\frac{\partial}{\partial t}\left[\frac{3}{2}nkT + \sum_{\alpha=A}^{B} n_\alpha \epsilon_\alpha + \frac{1}{2}\varrho v^2\right] + \frac{\partial}{\partial x_i}\left[q_i + p_{ij}v_j + \left(\frac{3}{2}nkT + \sum_{\alpha=A}^{B} n_\alpha \epsilon_\alpha + \frac{1}{2}\varrho v^2\right)v_i\right] = 0. \tag{10}$$

Above, u_i^α is the constituent diffusion velocity, p_{ij} and q_i are pressure tensor and heat flux vector of the mixture, defined by

$$u_i^\alpha = \int \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad p_{ij} = \sum_{\alpha=A}^{B} \int m \xi_i^\alpha \xi_j^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad q_i = \sum_{\alpha=A}^{B} \left(\int \frac{m}{2} \xi_\alpha^2 \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha + n_\alpha \epsilon_\alpha u_i^\alpha\right). \tag{11}$$

Furthermore, τ_α is the production rate of particle number density of constituent α whose expression is

given by

$$\tau_\alpha = \chi \int [f_\gamma f_{\gamma 1} - f_\alpha f_{\alpha 1}] \sigma_\alpha^\star g_\alpha \, d\Omega^\star \, d\mathbf{c}_{\alpha 1} \, d\mathbf{c}_\alpha, \qquad \alpha \neq \gamma = A, B. \tag{12}$$

The Chapman-Enskog approach for the determination of non-equilibrium distribution function is described in the text of Chapman-Cowling [25]. Many other authors have followed this method and expanded upon the theory, including the case of reactive systems [2], [3], [4], [5], [6], [7], [9], [10], [11], [13]. The chemical regime of the considered gas mixture is the one of the final stage of the reaction process, when the chemical affinity $\mathcal{A}$ is a small quantity and the relaxation times of both chemical reaction and elastic scattering are of the same order. This fast regime has been first analyzed in [26] by Ludwig and Heil and further investigated by other authors, see e.g. [13], [27], [29], [28]. Accordingly, the collisional integrals that appear on the right side of Boltzmann equation (6) have the same order of magnitude and the χ parameter must be close to $\chi = 0.5$.

It is well known (see [10]) that in the case of slow reactions or very fast reactions, the magnitudes of the elastic Knudsen number $\mathrm{Kn_E}$ and of the reactive Knudsen number $\mathrm{Kn_R}$ are very distinct, namely $\mathrm{Kn_R} \gg \mathrm{Kn_E}$ for slow reactions whereas $\mathrm{Kn_E} \gg \mathrm{Kn_R}$, for very fast reactions. Conversely, in the case of fast reactions, the chemical process is near the chemical equilibrium and the parameters $\mathrm{Kn_E}$ and $\mathrm{Kn_R}$ have comparable order of magnitude. For the chemical regime considered in the present paper, $\mathrm{Kn_R} \approx \mathrm{Kn_E}$ and, at the same time, the relaxation times of both chemical reaction and elastic scattering are smaller than the characteristic time of the flow. Accordingly, the Boltzmann Eq. (6) is rewritten in the form

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = \frac{1}{\theta} \left[\sum_{\beta=A}^{B} (1 - \chi \delta_{\alpha\beta}) \int [f'_\alpha f'_\beta - f_\alpha f_\beta] \, g_{\beta\alpha} \, \sigma_{\alpha\beta} \, d\Omega \, d\mathbf{c}_\beta \right. \tag{13}$$

$$\left. + \chi \int [f_\gamma f_{\gamma 1} - f_\alpha f_{\alpha 1}] \sigma_\alpha^\star g_\alpha \, d\Omega^\star \, d\mathbf{c}_{\alpha 1} \right], \qquad \alpha \neq \gamma = A, B,$$

where θ is a small parameter. The first step of the method consists in expanding the distribution function f_α in a power series around the local equilibrium distribution $f_\alpha^{(0)}$, using the expansion parameter θ, as

$$f_\alpha = f_\alpha^{(0)} \left(1 + \theta \, \Phi_\alpha^{(1)} + \theta^2 \Phi_\alpha^{(2)} + \cdots \right) = f_\alpha^{(0)} + \theta \, f_\alpha^{(1)} + \theta^2 f_\alpha^{(2)} + \cdots \tag{14}$$

The expansion (14) of the distribution function f_α is then substituted in the Boltzmann Eq. (13) and the terms of the same order in θ are grouped, resulting in a hierarchy of equations for the different orders of approximation of f_α. The first integral equation identifies the zero-order distribution function $f_\alpha^{(0)}$ as the Maxwellian distribution f_α^M

$$f_\alpha^{(0)} = f_\alpha^M = n_\alpha^{\mathrm{eq}} \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp \left(-\frac{m\xi_\alpha^2}{2kT} \right), \tag{15}$$

with n_α^{eq} being the equilibrium number densities which are constrained by the mass action law (5).

The second integral equation can be written as (see [13])

$$f^{(0)} \left\{ \left[\frac{\nu_\alpha}{n_\alpha} - \frac{Q}{3n} \left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT} \right) + \frac{\nu_\alpha}{\ell_F^{(0)}} \int f_{\alpha 1}^{(0)} g_\alpha \sigma_\alpha^\star d\Omega_\star d\mathbf{c}_{\alpha 1} \right] \ell_F^{(0)} \frac{\mathcal{A}}{kT} + \xi_i^\alpha \xi_j^\alpha \frac{m}{kT} \frac{\partial v_{\langle i}}{\partial x_{j \rangle}} + \frac{n}{n_\alpha} \xi_i^\alpha d_i^\alpha \right.$$

$$\left. - \xi_i^\alpha \left(\frac{5}{2} - \frac{m\xi_\alpha^2}{2kT} \right) \frac{1}{T} \frac{\partial T}{\partial x_i} \right\} = \sum_{\beta=A}^{B} \int f_\alpha^{(0)} f_\beta^{(0)} (\Phi_\beta'^{(1)} + \Phi_\alpha'^{(1)} - \Phi_\beta^{(1)} - \Phi_\alpha^{(1)}) g_{\beta\alpha} \, \sigma_{\alpha\beta} \, d\Omega \, d\mathbf{c}_\beta$$

$$+ \sum_{\beta=A}^{B} \int f_\alpha^{(0)} f_{\alpha 1}^{(0)} (\Phi_{\gamma 1}'^{(1)} + \Phi_\gamma'^{(1)} - \Phi_{\gamma 1}^{(1)} - \Phi_\gamma^{(1)}) \sigma_\alpha^\star g_\alpha \, d\Omega^\star \, d\mathbf{c}_{\alpha 1}, \tag{16}$$

where the first-order time derivatives of n_α, u and T have been eliminated by using the balance equations of mass density, momentum density and temperature of an Eulerian mixture where the phenomena

of diffusion, heat conduction and viscous are not taken into account. Above, we have introduced the stoichiometric coefficients $\nu_A = -\nu_B = -1$ and the following abbreviations

$$\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) - \frac{1}{3}\frac{\partial v_r}{\partial x_r}\delta_{ij}, \qquad \ell_F^{(0)} = \int f_\alpha^{(0)} f_{\alpha_1}^{(0)} \sigma_A^\star \, g_A \, d\Omega^\star \, d\mathbf{c}_{A_1} d\mathbf{c}_A. \tag{17}$$

Proceeding with the usual steps of the Chapman-Enskog method, the deviations are represented in terms of the first-order Sonine polynomials $\mathcal{S}_m^{(r)}$ in the form

$$\Phi_\alpha^{(1)} = -\sum_{n=0}^{1} \mathsf{a}_n^\alpha \mathcal{S}_{3/2}^{(n)}\left(\mathcal{C}_\alpha^2\right) \xi_i^\alpha \frac{1}{T}\frac{\partial T}{\partial x_i} - \mathsf{b}_0^\alpha \mathcal{S}_{5/2}^{(0)}\left(\mathcal{C}_\alpha^2\right) \xi_{\langle i}^\alpha \xi_{j\rangle}^\alpha \frac{m}{kT}\frac{\partial v_{\langle i}}{\partial x_{j\rangle}} - \sum_{n=0}^{1} \mathsf{d}_n^\alpha \mathcal{S}_{3/2}^{(n)}\left(\mathcal{C}_\alpha^2\right) \xi_i^\alpha d_i^A - \mathsf{e}_1^\alpha \mathcal{S}_{1/2}^{(1)}\left(\mathcal{C}_\alpha^2\right) \frac{\mathcal{A}}{kT}. \tag{18}$$

Above, $\mathcal{C}_\alpha^2 = m\xi_\alpha^2/2kT$ are dimensionless quantities, whereas a_n^α, b_0^α, d_n^α and e_1^α are coefficients which depend on n_α and T and are determined from the Boltzmann equation. For more details on the above representation, one is referred to the work [13]. The traceless part of the gradient of velocity $\partial v_{\langle i}/\partial x_{j\rangle}$, the temperature gradient $\partial T/\partial x_i$, the affinity $\mathcal{A}/kT$ and the generalized diffusion force d_i^A represent the thermodynamic forces. Furthermore, the generalized diffusion force is given by

$$d_i^A = \frac{\partial x_A}{\partial x_i} = -\frac{\partial x_B}{\partial x_i} = -d_i^B, \tag{19}$$

with $x_\alpha = n_\alpha/n$ being the molar fraction of the constituent α.

After some standard but rather cumbersome calculations, the deviations $\Phi_\alpha^{(1)}$ have been explicitly computed. By writing the deviations $\Phi_\alpha^{(1)}$ in terms of the first-order Sonine polynomials as given by Eq. (18), the reactive contribution to the deviation, that is the term which is proportional to affinity, is treated in an equivalent manner to those terms related to the velocity gradient, temperature gradient and generalized diffusion force. The deviations of the distribution function related to the to transport phenomena as well as to the chemical affinity are all considered small and of the same order, since the elastic and reactive collisions are treated with the same relevance. The detailed expression for $\Phi_\alpha^{(1)}$ is here omitted for brevity. It depends on the probability coefficient χ and contains all information about the deviations of the reactive system from the equilibrium state. One is also referred to the work [13] for some details about similar calculations.

By considering additional terms in the expansion (18), the non-equilibrium contributions to the reaction rate and transport coefficients of the mixture would have a greater accuracy. However, these non-equilibrium contributions should not be so relevant in the case of the present mixture, since we assume that the heat of reaction is a small quantity and the parameter χ is about 0.5.

The range of validity of the Chapman-Enskog method used in this paper as well as the convergence of the first-order Sonine expansion (18) are not investigated here. Some relevant studies on this topic can be found, for example, in Refs. [6], [10], [13], [26] and [27]. In particular, in paper [10], the authors have shown that the method can be applied to the case of slow, fast and very fast bimolecular chemical reactions. In the present paper, we consider a very fast bimolecular reaction of symmetric type, and applied the solution technique analyzed in paper [10] for the considered regime.

Our results, obtained with the Chapman-Enskog method for the considered fast chemical regime, together with the first-order Sonine polynomial expansion, give a satisfactory description of the nonequilibrium behavior of the considered reactive system, provided that the probability χ of a reactive collision and the molar fraction x_A of the reactants are considered in the ranges $0.45 \leq \chi \leq 0.55$ and $0.4 \leq x_A \leq 0.6$, respectively.

3 Transport Coefficients

Once the non-equilibrium distribution functions have been determined as described in the Section 2, we can obtain the constitutive equations for the pressure tensor p_{ij} and heat flux vector q_i of the mixture, as well as for the diffusion velocities u_i^α and production rates τ_α of the particle number densities. Hence, we

can analyze the first approximations to the transport coefficients of a binary mixture of reacting gases by considering the non-equilibrium effects due to the presence of chemical processes. We consider a linear theory, so there is no term involving the coupling between different tensorial processes. In particular, the chemical effect arises from the heat of reaction as well as from the parameter χ. The chemical effects analyzed in this paper arise from the considered chemical kinetic parameters, namely from the binding energies (or heat of reaction Q) and from the parameter χ.

3.1 General expressions

The constitutive equations are obtained by inserting the non-equilibrium distribution function (15) together with the deviation (18) into the definitions (11) and (12). The integration of the resulting equations lead to the following constitutive laws.

(i) *Generalized Fick Law:* in the case of a binary mixture there exists only one independent diffusion velocity since $u_i^B = -n_A u_i^A / n_B$ and the generalized Fick law reads

$$u_i^A = -\frac{D_{12}}{x_A}\left[d_i^A + \frac{k_T}{T}\frac{\partial T}{\partial x_i}\right],\tag{20}$$

where the coefficient of diffusion D_{12} and the thermal-diffusion ratio k_T are given by

$$D_{12} = x_A \frac{kT}{m}\mathsf{d}_0^A \quad\text{and}\quad k_T = \frac{\mathsf{a}_0^A}{\mathsf{d}_0^A}.\tag{21}$$

By inspecting (20) we can conclude that the diffusion of the constituents of a mixture is caused by two forces, namely the generalized diffusion force d_i^A and the temperature gradient $\partial T/\partial x_i$.

(ii) *Navier-Stokes Law:* the pressure tensor of the mixture is given by a sum of two contributions, i.e., a hydrostatic pressure and a shear term proportional to the traceless part of the velocity gradient, namely,

$$p_{ij} = p\delta_{ij} - 2\mu\frac{\partial v_{\langle i}}{\partial x_{j\rangle}},\tag{22}$$

where p and μ represent the hydrostatic pressure and the shear viscosity coefficient of the mixture, respectively. Their expressions are given by

$$p = \sum_{\alpha=A}^{B} n_\alpha\, kT \qquad\text{and}\qquad \mu = \sum_{\alpha=A}^{B} n_\alpha\, \mathsf{b}_0^\alpha\, kT.\tag{23}$$

(iii) *Generalized Fourier Law:* the total heat flux of the mixture $(11)_3$ was defined as the sum of two terms, the first one corresponds to partial heat fluxes, while the second one is associated with the transport of the binding energy by diffusion. The generalized Fourier law is also a function of the generalized diffusion force d_i^A and the temperature gradient $\partial T/\partial x_i$ and reads

$$q_i = -\lambda'\frac{\partial T}{\partial x_i} - D'd_i^A,\tag{24}$$

where the coefficients λ' and D' associated with the thermal conductivity and diffusion-thermal effect, respectively, are specified through the relations

$$\lambda' = -\frac{k^2 T}{m}\left[\frac{5}{2}\sum_{\alpha=A}^{B} n_\alpha \mathsf{a}_1^\alpha + \frac{Q}{2kT}n_A\mathsf{a}_0^A\right] \quad\text{and}\quad D' = -\frac{k^2 T^2}{m}\left[\frac{5}{2}\sum_{\alpha=A}^{B} n_\alpha\mathsf{d}_1^\alpha + \frac{Q}{2kT}n_A\mathsf{d}_0^A\right].\tag{25}$$

In order to determine the coefficient of thermal conductivity it is necessary to eliminate from (24) the generalized diffusion force by assuming that there is no diffusion processes. From (20) we get

$$d_i^A = -\frac{k_T}{T}\frac{\partial T}{\partial x_i},\tag{26}$$

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so that the heat flux vector (24) becomes

$$q_i = -\lambda \frac{\partial T}{\partial x_i}, \qquad \text{with} \quad \lambda = -\frac{5}{2}\frac{k^2 T}{m}\left[\sum_{\alpha=A}^{B} n_\alpha \mathsf{a}_1^\alpha - \frac{\mathsf{a}_0^A}{\mathsf{d}_0^A}\sum_{\alpha=A}^{B} n_\alpha \mathsf{d}_1^\alpha\right], \tag{27}$$

λ being the coefficient of thermal conductivity of the mixture.

(iv) *Reaction rate law:* in an inert gas, the number of the molecules of each constituent always remains constant even if the system is in some non-equilibrium state; conversely, in the case of reactive systems, the chemical reaction modifies the number of the molecules of each constituent and there appear production rate densities which are given by the term τ_α on the right hand side of the balance equation (8). For the binary system in study here, we have $\tau_B = -\tau_A$ and a positive production of the A-constituent implies that the B-constituent is being consumed by the reaction. Hence, it is necessary to know the behavior of the production rate of only one constituent, which can be the one of the A-constituent. The production rate of the A-constituent results from the net balance between what is produced by the reverse reaction $A + A \leftarrow B + B$ and what is consumed by the direct reaction $A + A \rightarrow B + B$, which are expressed by the quantities τ_A^{r} and τ_A^{d} defined by

$$\tau_A = \tau_A^{\mathrm{r}} - \tau_A^{\mathrm{d}}, \quad \tau_A^{\mathrm{r}} = \chi \int f_B f_{B_1} g_B \sigma_B^\star \, d\Omega^\star \, d\mathbf{c}_{B_1} d\mathbf{c}_B, \quad \tau_A^{\mathrm{d}} = \chi \int f_A f_{A_1} g_A \sigma_A^\star d\Omega^\star \, d\mathbf{c}_{A_1} d\mathbf{c}_A. \tag{28}$$

In a linearized theory their expressions read

$$\tau_A^{\mathrm{r}} = n_A^2 \kappa^{(0)}\left[1 - (1 - \kappa_r^\star)\frac{\mathcal{A}}{kT}\right], \quad \tau_A^{\mathrm{d}} = n_A^2 \kappa^{(0)}\left[1 + \kappa_d^\star \frac{\mathcal{A}}{kT}\right], \quad \tau_A = -n_A^2 \kappa^{(0)}\left[1 - \kappa_r^\star + \kappa_d^\star\right]\frac{\mathcal{A}}{kT}. \tag{29}$$

Above, $\kappa^{(0)}$ is the first approximation to the rate constant, $\kappa_d^\star$ and $\kappa_r^\star$ are dimensionless second approximations to the direct and reverse rate constants, respectively, which are given by

$$\kappa^{(0)} = 4\chi \mathsf{d}^2 \sqrt{\frac{\pi kT}{m}}, \qquad \kappa_r^\star = -\left(\frac{1}{2} - \frac{Q}{kT}\right)\frac{n_A}{n_B}\mathsf{e}_1^A, \qquad \kappa_d^\star = \frac{1}{2}\mathsf{e}_1^A. \tag{30}$$

The expressions for the transport coefficients of diffusion D_{12}, thermal-diffusion ratio k_T shear viscosity μ and thermal conductivity λ – given above by (21), (23)$_2$ and (27)$_2$ – are the same as those of paper [13], but here the scalar coefficients, which appear in the expression (18) for the deviation $\Phi_\alpha^{(1)}$, depend on the probability factor χ and are evaluated for a differential cross section which does not depend on the activation energy. Moreover, the first approximation to the rate constant $\kappa^{(0)}$ – given by (30)$_1$ – has the same form as the pre-exponential factor of the Arrhenius equation, apart from the factor χ. In fact, $\kappa^{(0)}$ is the actual rate of reaction in the first order approximation, since in the case of non-barrier model there is no activation energy.

3.2 Results and discussions

The behavior of the transport coefficients can now be illustrated as a function of two parameters such as the mole fraction of the A-constituent, $x_A = n_A^{\mathrm{eq}}/(n_A^{\mathrm{eq}} + n_B^{\mathrm{eq}})$, and the probability χ of a reactive collision, since the reaction heat is connected to the equilibrium molar fractions through the mass action law (5), that is

$$\frac{Q}{kT} = 2\ln\left(\frac{x_A}{1 - x_A}\right). \tag{31}$$

According to the chemical regime considered in the present work, both types of encounters (elastic and reactive) are equally probable and the elastic and reactive Knudsen numbers $\mathrm{Kn_E}$ and $\mathrm{Kn_R}$ are of the same order. So we choose values for the parameter χ in the range $0.45 \leq \chi \leq 0.55$, the case $\chi = 0.5$ representing the same probability of occurrence of elastic and reactive collisions. Concerning the molar fraction x_A, we will restrict x_A to the range $0.4 \leq x_A \leq 0.6$, which represents mixtures where the proportion of the two constituents are not too disparate and the reaction heat can be considered a small quantity, according to
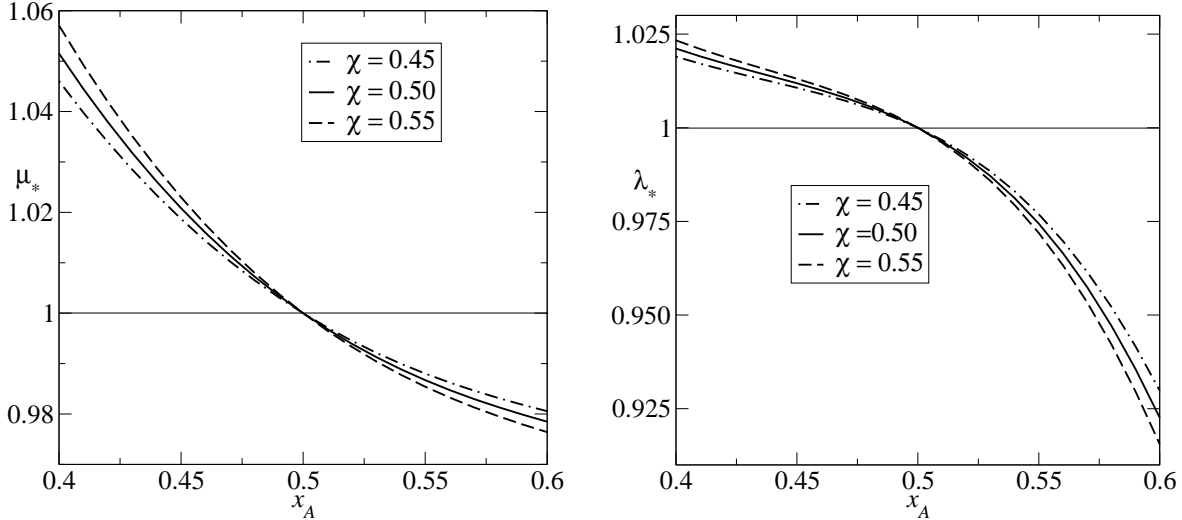
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Figure 1: Behavior of the transport coefficients as function of mole fraction x_A for three different values of the probability coefficient: (a) dimensionless shear viscosity coefficient (left) and (b) dimensionless thermal conductivity coefficient (right).

its relation with x_A given by (31). This choice is justified by the fact that we are considering a situation in which the particles are distributed in a rather uniform way, without a particular species in much greater concentration than the other.

In order to show the behavior of the transport coefficients μ, λ, D_{12}, k_T and of the rate constant κ_d^* defined in the previous Subsection 3.1, let us first introduce the dimensionless coefficients μ_*, λ_* and D_*, given by

$$\mu_* = \frac{\mu}{\mu_I}, \qquad \lambda_* = \frac{\lambda}{\lambda_I}, \qquad D_* = \frac{D_{12}}{D_{11}}. \tag{32}$$

Note that the thermal-diffusion ratio k_T and the rate constant κ_d^* are already dimensionless quantities. The μ_I and λ_I represent the shear viscosity and thermal conductivity coefficients of a single inert gas, respectively, while D_{11} is the self-diffusion coefficient of a binary mixture of hard spheres. Their expressions are given by [25]

$$\mu_I = \frac{5}{16d^2}\sqrt{\frac{mkT}{\pi}}, \qquad \lambda_I = \frac{75k}{64d^2}\sqrt{\frac{kT}{\pi m}}, \qquad D_{11} = \frac{177}{464nd^2}\sqrt{\frac{kT}{\pi m}}. \tag{33}$$

Figures 1a, 1b, 2a, 2b and 3 describe the behavior of the dimensionless coefficients μ_* and λ_* of shear viscosity and thermal conductivity, thermal-diffusion ratio k_T, dimensionless diffusion coefficient $D_\star$ and direct reaction rate κ_d^*, as functions of the molar fraction x_A, for three values of the probability coefficient χ. From all figures except that for the diffusion coefficient, we can observe that there is an inflection point common to all curves for different values of χ, when the molar fractions of both constituents are equal, i.e., $x_A = x_B = 0.5$. This point corresponds to a mixture with vanishing reaction heat (see (31)) and separates the region $x_A < 0.5$ on its left hand side, with negative reaction heat, from the region $x_A > 0.5$ on the right hand side, with positive reaction heat. Moreover, for the considered non-barrier model, the constituents are distinguished by the formation energies only, which are related to the reaction heat by $Q = 2(\epsilon_B - \epsilon_A)$. Therefore, the inflection point corresponds to a mixture for which the particles A and B become indistinguishable and the reaction process does not affect the chemical composition of the gas system. On the other hand, the region $x_A < 0.5$ corresponds to a mixture with predominant B-constituent and exothermic chemical reaction whereas the region $x_A > 0.5$ to a mixture with predominant A-constituent and endothermic chemical reaction. Other main observations that we can make here for the shear viscosity and thermal conductivity ratios – according to Figures 1a and 1b – are the following: (a) it is noticeable that the effects on both coefficients are larger when the probability of reactive collision becomes greater than 0.5, since more reactions occur; (b) for $x_A = x_B = 0.5$ the reaction heat vanishes
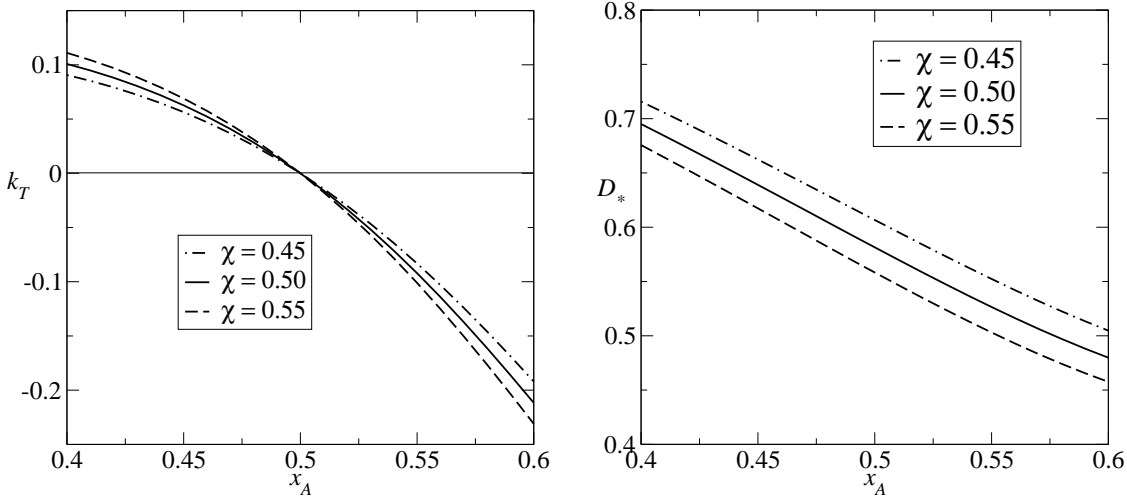
Figure 2: Behavior of the transport coefficients as function of mole fraction x_A for three different values of the probability coefficient: (a) thermal-diffusion ratio (left) and dimensionless diffusion coefficient (right).

and there is no any reactive effect on the shear viscosity μ_* and thermal conductivity λ_* ratios; **(c)** when $x_A < 0.5$, the system becomes more viscous and more heat conducting due to the chemical reaction; this feature can be explained as follows: since the reaction heat is negative, the energy is released (exothermic process), so that the temperature of the mixture increases and causes a rise in both coefficients of shear viscosity and thermal conductivity of the mixture; **(d)** when $x_A > 0.5$, just the opposite occurs and the coefficients of shear viscosity and thermal conductivity decrease as a consequence of the temperature decreasing in an endothermic process. It is important to call attention to the fact that for chemical reactions with activation energies, both coefficients of shear viscosity and thermal conductivity decrease for endothermic as well as for exothermic reactions (see e.g. [31], [32], [33], [34]).

The thermal-diffusion ratio k_T is represented in Figure 2a. With respect to this coefficient it is possible to conclude that the reaction heat is directly responsible for the observed alternation in its signal. Indeed, the change from an exothermic reaction ($x_A < 0.5$) to an endothermic one ($x_A > 0.5$) implies that the thermal-diffusion ratio alternates its signal, from a positive value to a negative one. The coefficient vanishes only when the mixture presents the same amount of reactants and products of the reaction. What is interesting here is that the resultant effect is due exclusively to the chemical reaction, since in a system composed by particles with the same mass and diameter, which do not react, a crossed effect like the thermal-diffusion does not appear.

The dimensionless coefficient D_* is shown in Figure 2b. The phenomenon of diffusion of particles in gases is common in mixtures composed of different molecules, as well as in a single gas of isotopes molecules, an effect known as self-diffusion. On account of this fact, the diffusion does not vanish when $x_A = x_B$, contrary to the thermal-diffusion ratio. The behavior shown in Figure 2b indicates that the diffusion coefficient D_* becomes smaller by increasing the concentration of the A-constituent. In terms of the reaction heat, this means that the diffusion coefficient decreases when the chemical reaction switches from an exothermic to an endothermic reaction.

With respect to the dimensionless reaction rate, its first approximation $\kappa^{(0)}$ depends only on the probability coefficient χ. This result is different from the one when an activation energy is involved and the Arrhenius equation is valid. Moreover, the second approximation is a function of both the molar fraction x_A and the probability coefficient χ, through the coefficient e_1^A. The behavior of the second approximation for the direct reaction rate κ_d^* is plotted in Figure 3 as function of the molar fraction x_A for different values of the probability factor χ. Here we also note that this coefficient vanishes when there is an equal amount of A and B-particles. Again, the largest effect is observed when the probability coefficient χ becomes larger than $\chi = 0.5$. This behavior is totally expected, since under this condition the reactions become more frequent.
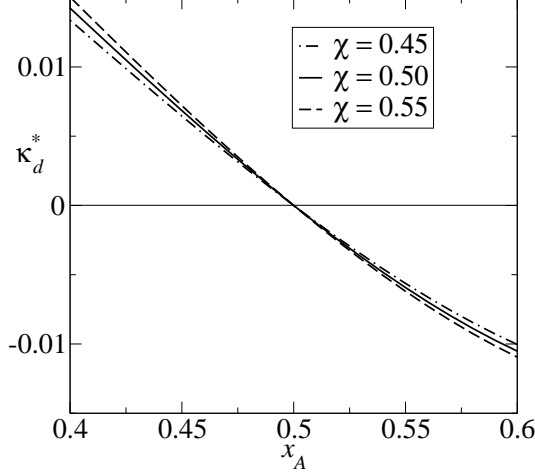
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Figure 3: Behavior of the direct reaction rate κ_d^* as function of mole fraction x_A for three different values of the probability coefficient χ.

4 Eigenmodes in a Chemically Reacting Gas Mixture

In this section we investigate the dynamical behavior of a small local disturbance from the spatially homogeneous solution caused by a spontaneous internal fluctuation. By assuming that the disturbance is sufficiently weak that only linear deviations from the homogeneous solution need to be taken into account, we define dimensionless perturbations of the hydrodynamic fields as

$$\overline{n}_\alpha(\boldsymbol{x},t) = \frac{n_\alpha(\boldsymbol{x},t)}{n_0 x_\alpha} - 1, \qquad \overline{v}_i(\boldsymbol{x},t) = \frac{v_i(\boldsymbol{x},t)}{c} \qquad \text{and} \qquad \overline{T}(\boldsymbol{x},t) = \frac{T(\boldsymbol{x},t)}{T_0} - 1, \tag{34}$$

which represent small perturbations about an equilibrium state of constant number densities n_A^{eq}, n_B^{eq}, temperature T_0 and vanishing value of the velocity. Above, $x_\alpha = n_\alpha^{\text{eq}}/n_0$ is the molar fraction of constituent α with $n_0 = n_A^{\text{eq}} + n_B^{\text{eq}}$ and c is the adiabatic sound speed of the mixture, given by

$$c = \sqrt{\frac{5}{3}\frac{kT_0}{m}}. \tag{35}$$

Insertion of the constitutive relations (20), (22), (24), (29)$_3$ together with the perturbations (34) into the balance equations (8), (9) and (10) leads to a system of linear partial differential equations for $\overline{n}_A$, $\overline{n}_B$, $\overline{v}_i$ and $\overline{T}$. Since the time evolution and decay of local disturbances are described by the so-called eigenmodes, we look for solutions of the form

$$\begin{pmatrix} \overline{n}_A(\boldsymbol{x},t) \\ \overline{n}_B(\boldsymbol{x},t) \\ \overline{v}_i(\boldsymbol{x},t) \\ \overline{T}(\boldsymbol{x},t) \end{pmatrix} = \begin{pmatrix} \overline{n}_A(\boldsymbol{\kappa},t) \\ \overline{n}_B(\boldsymbol{\kappa},t) \\ \overline{v}_i(\boldsymbol{\kappa},t) \\ \overline{T}(\boldsymbol{\kappa},t) \end{pmatrix} \exp\left[i\left(\boldsymbol{\kappa}\cdot\boldsymbol{x} - \omega t\right)\right], \tag{36}$$

where the time is given in units of an effective relaxation time $\tau_r = (4/5)(\mu_0/n_0 kT_0)$ and the position is given in units of an effective length $c\tau$. Above, $\boldsymbol{\kappa}$ and ω are the dimensionless wave-vector and the angular frequency of the disturbances, respectively. If the wave-vector is taken parallel to the x-axis, we

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obtain the following longitudinal system of algebraic equations for the amplitudes of the perturbations:

$$\begin{pmatrix} A_{11} & A_{12} & A_{13} & A_{14} \\ A_{21} & A_{22} & A_{23} & A_{24} \\ A_{31} & A_{32} & A_{33} & A_{34} \\ A_{41} & A_{42} & A_{43} & A_{44} \end{pmatrix} \begin{pmatrix} \overline{n}_A(\boldsymbol{\kappa},t) \\ \overline{n}_B(\boldsymbol{\kappa},t) \\ \overline{v}_x(\boldsymbol{\kappa},t) \\ \overline{T}(\boldsymbol{\kappa},t) \end{pmatrix} = 0, \tag{37}$$

where the elements of the above matrix are given by

$$A_{11} = \omega x_A + i\left[2\chi x_A^2 + \frac{531}{580}D_* x_A x_B \kappa^2\right], \qquad A_{12} = A_{21} = -i\left[2\chi x_A^2 + \frac{531}{580}D_* x_A x_B \kappa^2\right], \tag{38}$$

$$A_{13} = -x_A\kappa, \qquad A_{14} = -A_{24} = i\frac{531}{580}D_* k_T \kappa^2, \qquad A_{22} = \omega x_B + i\left[2\chi x_A^2 + \frac{531}{580}D_* x_A x_B \kappa^2\right], \tag{39}$$

$$A_{23} = -x_B\kappa, \qquad A_{31} = -\frac{3}{5}x_A\kappa, \qquad A_{32} = -\frac{3}{5}x_B\kappa, \qquad A_{33} = \omega + i\mu_*\kappa^2, \tag{40}$$

$$A_{34} = -\frac{3}{5}\kappa, \qquad A_{43} = -\frac{2}{3}\kappa, \qquad A_{41} = -A_{42} = i\frac{2}{3}\left[\chi x_A^2 \frac{Q}{kT_0} + \frac{531}{580}D_* x_A x_B \kappa^2\right], \tag{41}$$

$$A_{44} = \omega + i\left[\frac{15}{8}\lambda_* + \frac{177}{290}D_*\frac{k_T^2}{x_A x_B}\right]\kappa^2. \tag{42}$$

The longitudinal system of algebraic equations (37) has a non-trivial solution if the determinant of the matrix of the coefficients vanishes. This condition leads to a dispersion relation which can be used to determine the angular frequency ω as a function of the wavenumber κ or vice versa. The eigenmodes follow when we take the wavenumber real and solve the dispersion relation for the angular frequency leading to a relation of the form $\omega = \omega(\kappa)$. In this case, the real part of the angular frequency describes the frequency of oscillation of a small internal perturbation, while the imaginary part describes the decay of its amplitude in time. If we solve the dispersion relation for $\kappa = \kappa(\omega)$, we get the so-called forced modes, which describe the propagation of sound waves in a chemically reacting gas mixture [35].

The solution of the dispersion relation for the longitudinal system (37) gives four eigenmodes which can be divided into hydrodynamic modes, where $\omega(\kappa)$ tends to zero when κ goes to zero, and kinetic modes, where $\omega(\kappa)$ tends to a constant value when κ goes to zero. In the small wavenumber limit, the longitudinal eigenmodes can be determined by expanding the angular frequency as

$$\omega(\kappa) = a_0 + a_1\kappa + a_2\kappa^2 + \dots, \tag{43}$$

where the expansion coefficients a_n depend on the transport coefficients and on the reaction heat. Hence, after some algebraic work, we get

$$\omega_{1,2} = \pm\kappa - i\left\{\frac{\mu_*}{2} + \frac{3}{8}\lambda_* + \frac{177}{1450}D_*\left[\frac{k_T^2}{x_A x_B} - \frac{k_T}{2}\left(\frac{Q}{kT_0}\right)\right]\right\}\kappa^2 + \dots, \tag{44}$$

$$\omega_3 = -i\left\{\frac{9}{8}\lambda_* + \frac{531}{1450}D_*\left[\frac{k_T^2}{x_A x_B} - \frac{k_T}{2}\left(\frac{Q}{kT_0}\right)\right]\right\}\kappa^2 + \dots, \tag{45}$$

$$\omega_4 = -i\,2\frac{x_A}{x_B}\chi - i\frac{531}{580}D_*\left[1 + \frac{k_T}{3}\left(\frac{Q}{kT_0}\right)\right]\kappa^2 + \dots. \tag{46}$$

Expressions (44)–(46) show that in the small wavenumber limit there exist three hydrodynamic modes and one kinetic mode. Two of the hydrodynamic modes are sound modes that describe sound propagation in opposite directions parallel to x-axis, while the other hydrodynamic mode is purely diffusive. Furthermore, for values of the wavenumber close to zero, the kinetic mode does not propagate since its real part vanish.
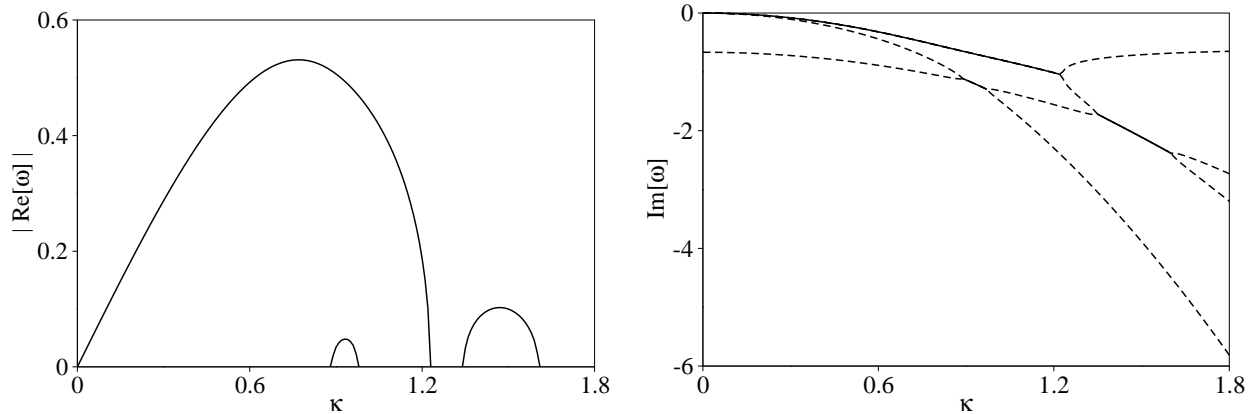
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Figure 4: Wavenumber dependence of the longitudinal eigenmodes for and exothermic reaction with $x_A = 0.4$.

Figures 4, 5 and 6 show the wavenumber dependence of the longitudinal eigenmodes for values of the molar fraction of the reactants equal to 0.4, 0.6 and 0.5, respectively. The left frames of these figures represent the wavenumber dependence of the real part of the frequency, while the right frames show the wavenumber dependence of the imaginary part of the frequency, where the solid and dashed lines correspond to the propagating and non-propagating modes, respectively. The dimensionless transport coefficients for the molar fractions 0.4, 0.5 and 0.6 and probability coefficient $\chi = 0.5$ are given in Table 1.

x_A	D_*	μ_*	λ_*	k_T
0.4	0.6951	1.0515	1.0211	0.1008
0.5	0.5815	1	1	0
0.6	0.4798	0.9785	0.9226	-0.2117

Table 1: Dimensionless transport coefficients μ_*, λ_*, D_* and k_T for molar fractions $x_A = 0.4, 0.5$ and 0.6 and probability coefficient $\chi = 0.5$.

Figure 4 shows that a kinetic sound mode that propagates slower than the hydrodynamic sound mode appears in the wavenumber interval $0.88 < \kappa < 0.98$ for the exothermic case ($Q < 0$). The occurrence of this kinetic sound mode is caused by the coupling between the purely diffusive eigenmode and the kinetic eigenmode. Besides, we infer from Figure 4 that a dispersion curve with several sound propagation gaps (i.e., when the sound oscillation frequency vanishes) follows from the usual hydrodynamic equations when $\kappa > 1.22$. At this point, it is important to mention that the usual eigenmodes can be used to describe the time evolution and the decay of small local disturbances from equilibrium caused by spontaneous internal fluctuations as long as the condition $\ell/\lambda < 1/2$ is satisfied, where λ is the wavelength of the fluctuations and ℓ is the mean free path. In terms of the dimensionless wavenumber this condition can be written as $\kappa < 1.80$ indicating that the kinetic sound model shown in Figure 4 appears in the wavenumber region where the usual hydrodynamic description is still valid. When the reaction is endothermic ($Q > 0$) we verify from Figure 5 the existence of a kinetic sound mode that also propagates slower than the hydrodynamic sound mode, which begins to propagate at larger wavenumber values than that of the exothermic case. Figure 5 also shows a dispersion curve with a sound propagation gap that appears at $\kappa = 1.32$ when the reaction is endothermic. Finally, from Figure 6, we see that no kinetic sound mode appears when the reaction heat Q vanishes. This result leads us to affirm that the appearance of a kinetic sound mode when the reaction is exothermic or endothermic is caused by the coupling between the concentration and temperature fluctuations. Furthermore, for the vanishing reaction heat case, we note that the hydrodynamic sound mode stops to propagate for wavenumber values larger than 1.30.

At this point it is noteworthy to mention that the existence of just four modes is dictated by the choice

of the four basic fields (or moments) $\overline{n}_a$, $\overline{n}_b$, $\overline{v}_x$ and $\overline{T}$. If higher moments of the distribution function are chosen as basic fields, beyond the emergence of additional kinetic modes, we expect that such extended hydrodynamics eigenmodes can be used to describe the time evolution and the decay of the spontaneous disturbances from equilibrium in a wavenumber region where the usual hydrodynamic description is no longer valid.
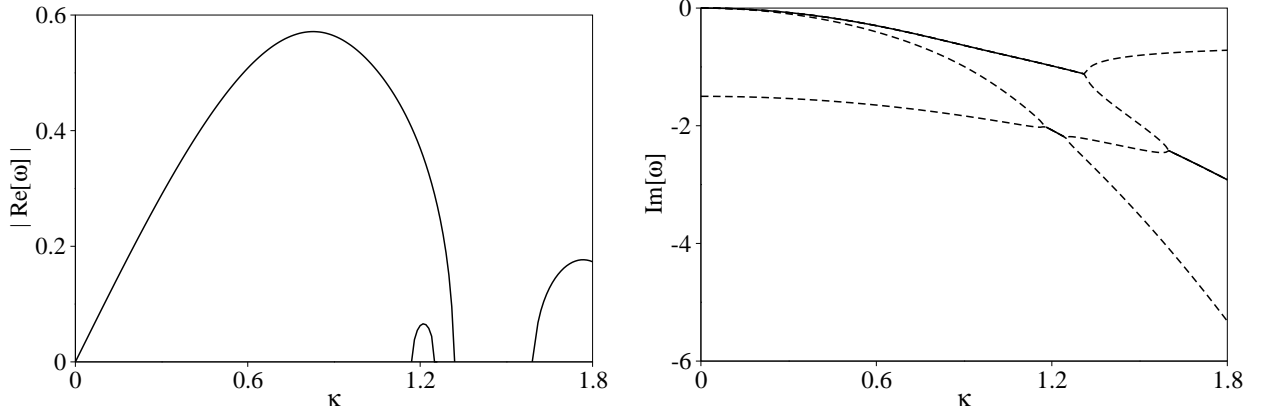

Figure 5: Wavenumber dependence of the longitudinal eigenmodes for an endothermic reaction with $x_A = 0.6$.
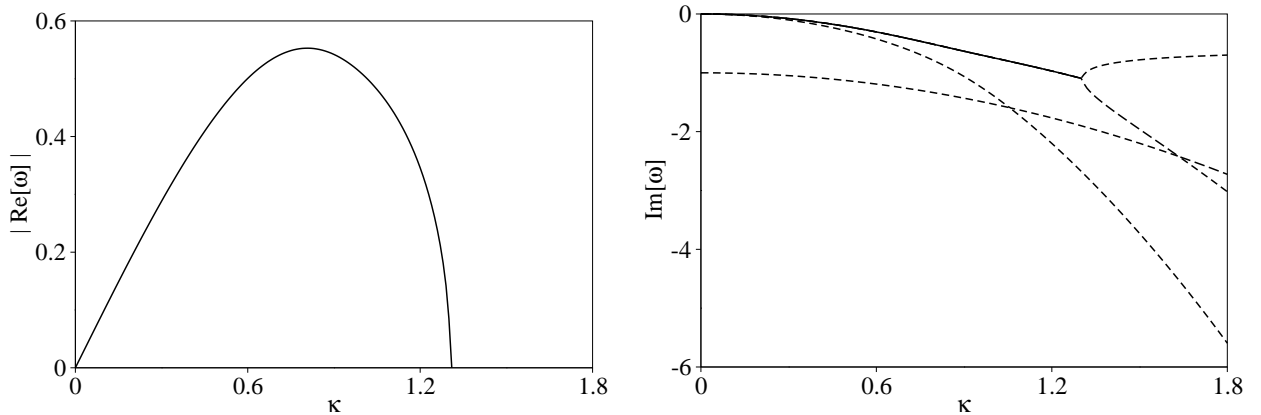

Figure 6: Wavenumber dependence of the longitudinal eigenmodes for vanishing reaction heat, i.e., when $x_A = 0.5$.

5   Conclusions

In the present paper, a new model of the Boltzmann equation has been used to describe a binary mixture undergoing the symmetric chemical reaction A+A$\rightleftharpoons$B+B that proceeds without the need of exceeding the activation energy barrier. The transport properties of the reactive mixture have been examined in a flow regime for which the reactive processes are close to the final state of chemical equilibrium. The effects of the reactive process on the transport coefficients have been investigated in detail, analyzing the contributions of the reactive collisions on the coefficients of diffusion, shear viscosity, thermal conductivity and thermal-diffusion ratio, as well as on the direct and reverse reaction rates. Both the exothermic and endothermic chemical reactions have been considered and the influence of the reaction heat on the transport properties has been investigated in depth.

The results reported in this paper have been obtained with the Chapman-Enskog method together with the first-order Sonine polynomial expansion for the considered fast chemical regime. They provide a satisfactory description of the nonequilibrium effects in the considered reactive system, when the probability χ of a reactive collision and the molar fraction x_A of the reactants are considered in the ranges $0.45 \leq \chi \leq 0.55$ and $0.4 \leq x_A \leq 0.6$, respectively.

The range of validity of the Chapman-Enskog method, as well as the convergence of the first-order Sonine expansion were not investigated in our paper. The work involved to achieve a convergence analysis is really huge and typically implies rather cumbersome calculations. This will be done in a forthcoming work.

Numerical analysis has been carried out for different sets of mixture parameters and the results provide some interesting information about the kinetics of the reactions without barriers, as underlined in Subsection 3.2. Opposed to the case of chemical reactions with activation energies, both coefficients of shear viscosity and thermal conductivity increase for exothermic reactions. Finally, the application performed in Section 4 shows that there exist four longitudinal eigenmodes: two hydrodynamic sound modes, one purely diffusive hydrodynamic mode and one kinetic mode. When the reaction heat vanishes $x_A = x_B = 0.5$, the kinetic mode does not show up indicating that the kinetic mode is due to a coupling between the concentration and temperature fluctuations.

Acknowledgments

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