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From the transport coefficients of a relaxation kinetic model to harmonic wave solutions

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Summary. — For a gas system of four constituents which experiences the bimolecular chemical reaction $A_1 + A_2 \rightleftharpoons A_3 + A_4$, and in a regime close to the chemical equilibrium, the BGK-type model proposed by the authors in a previous paper is here considered with the aim of studying plane harmonic wave solutions to the system of the reactive field equations. The Chapman-Enskog method has been used to determine a first-order approximate solution to the BGK equations, which includes the transport features of shear viscosity, diffusion and thermal conductivity. Such approach leads to the constitutive equations and permits to close the reactive field equations at the Navier-Stokes, Fourier and Fick level. The propagation of plane harmonic waves in a reactive mixture where the transport effects are relevant can then be studied by a normal mode analysis. Numerical results are provided for two different mixtures of the hydrogen-chlorine system where the elementary reaction $H_2 + Cl \rightleftharpoons HCl + H$ takes place. The behavior of diffusion, shear viscosity and thermal conductivity coefficients, as well as the one of phase velocity and attenuation coefficient, is described focusing the influence of the chemical reaction on the transport properties and harmonic wave solutions.

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1. – Introduction and preliminaries

The relaxation kinetic model proposed by the authors in [1] extends the BGK-type model, derived by Garzó, Santos and Brey for an inert gas mixture in [2], to a quaternary reacting gas mixture undergoing a reversible reaction of type $A_1 + A_2 \rightleftharpoons A_3 + A_4$. The model equations are

$$\frac{\partial f_\alpha}{\partial t} + c_i^\alpha \frac{\partial f_\alpha}{\partial x_i} = -\sum_{\beta=1}^{4} \zeta_{\alpha\beta}^E \left(f_\alpha - f_{\alpha\beta}^E\right) - \zeta_{\alpha\gamma}^R \left(f_\alpha - f_{\alpha\gamma}^R\right), \quad \alpha = 1, \ldots, 4, \tag{1}$$

where the repeated index i denotes a summation over $i = 1, 2, 3$ for the space components, and $(\alpha, \gamma) = (1, 2), (2, 1), (3, 4), (4, 3)$. The gas constituents have molecular mass m_α, molecular velocity $\boldsymbol{c}_\alpha$, and chemical binding energy ε_α. In the model equations (1), f_α denotes the one-particle distribution function, $\zeta^E_{\alpha\beta}$, $\zeta^R_{\alpha\gamma}$ are elastic and reactive collision frequencies which are expressed in terms of cross-sections of rigid spheres [3] for elastic collisions, and in terms of line-of-centers energy model [4] for encounters with chemical reactions. Moreover $f^E_{\alpha\beta}$, $f^R_{\alpha\gamma}$ are the elastic and reactive reference distribution functions which have been determined in paper [1] so that the consistency with respect to balance equations and mixture conservation laws is assured. More in detail, the reference distributions have been determined by imposing that the production terms of mass, momentum and total energy are the same for the BGK-type model and for the exact reactive Boltzmann equation (BE), that is

$$\text{(2)} \qquad \begin{cases} -\int \psi_\alpha \zeta^E_{\alpha\beta}(f_\alpha - f^E_{\alpha\beta})\mathrm{d}\mathbf{c}_\alpha = \int \psi_\alpha \mathcal{Q}^E_{\alpha\beta}\mathrm{d}\mathbf{c}_\alpha, \\ -\int \psi_\alpha \zeta^R_{\alpha\gamma}(f_\alpha - f^R_{\alpha\gamma})\mathrm{d}\mathbf{c}_\alpha = \int \psi_\alpha \mathcal{Q}^R_{\alpha}\mathrm{d}\mathbf{c}_\alpha, \end{cases} \qquad \text{for} \quad \psi_\alpha = \begin{cases} m_\alpha, \\ m_\alpha c^\alpha_i, \\ \frac{1}{2} m_\alpha c^2_\alpha + \varepsilon_\alpha. \end{cases}$$

Here $\mathcal{Q}^E_{\alpha\beta}$ and $\mathcal{Q}^R_{\alpha\beta}$ are the elastic and reactive collision terms of the exact reactive BE, whose explicit expressions are well known (see, for instance, ref. [5]). The explicit computation of the integrals is performed by assuming that all constituents have the same temperature T and by taking an input function $\widehat{f_\alpha}$ defined by

$$\text{(3)} \qquad \widehat{f_\alpha} \approx n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m_\alpha \xi^2_\alpha}{2kT}\right]\left[1 + \frac{m_\alpha \xi^\alpha_i}{kT} u^\alpha_i\right],$$

where $\xi^\alpha_i = c^\alpha_i - v_i$ and $u^\alpha_i = v^\alpha_i - v_i$ are the peculiar velocity and the diffusion velocity of each constituent, respectively. Detailed computations of the production terms (2) lead to the following expressions for the elastic and reactive reference distributions:

$$\text{(4)} \quad f^E_{\alpha\beta} = n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} \mathrm{e}^{-\frac{m_\alpha \xi^2_\alpha}{2kT}} \left\{1 + \frac{m_\alpha \xi^\alpha_i}{kT} \frac{m_\alpha u^\alpha_i + m_\beta u^\beta_i}{m_\alpha + m_\beta}\right\}, \quad \alpha, \beta = 1, \ldots, 4,$$

$$\text{(5)} \quad f^R_{\alpha\gamma} = n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} \mathrm{e}^{-\frac{m_\alpha \xi^2_\alpha}{2kT}} \left\{1 + \nu_\alpha \left[1 - M_\gamma\left(\epsilon^\star_\sigma + \frac{1}{2}\right)\left(1 - \frac{m_\alpha \xi^2_\alpha}{3kT}\right)\right]\frac{\mathcal{A}}{kT}\right.$$
$$\left. + \frac{m_\alpha \xi^\alpha_i}{kT}\left[u^\alpha_i + \sigma \sum_{\beta=1}^{4} \nu_\beta M_\beta u^\beta_i - \frac{2}{3}(\epsilon^\star_\sigma + 2) M_\gamma (u^\alpha_i - u^\gamma_i)\right]\right\},$$

where $M_\alpha = m_\alpha/(m_\alpha + m_\gamma)$ is a mass ratio, $\epsilon^\star_\sigma = \epsilon_\sigma/kT$ is the activation energy of the forward ($\sigma = 1$) and of the backward ($\sigma = -1$) reaction in units of kT, $\mathcal{A} = kT \ln\left(\frac{n_1 n_2 n_3^{\mathrm{eq}} n_4^{\mathrm{eq}}}{n_3 n_4 n_1^{\mathrm{eq}} n_2^{\mathrm{eq}}}\right)$ is the affinity of the forward reaction and ν_α are the stoichiometric coefficients such that $\nu_1 = \nu_2 = -\nu_3 = -\nu_4 = -1$.

The kinetic equations (1) with reference distributions (4) and (5) define the relaxation model and constitute the basis of the present analysis. Observe that in eqs. (1) the elastic and reactive collision terms are approximated separately, so that both the inert mechanism and the chemical interaction preserve their own role. The model is then appropriate to investigate the deviation of the mixture from the equilibrium induced by the chemical reaction, in a hydrodynamic regime for which the diffusion velocities are assumed to be small ($|u_i^\alpha| \ll 1$).

The work is organized as follows. The transport properties of diffusion, shear viscosity and thermal conductivity are detailed in sect. **2**. The plane harmonic wave propagation in the reacting mixture is studied in sect. **3**, starting from the system of the field equations closed at the Navier-Stokes, Fourier and Fick level. At last, numerical results for transport coefficients and harmonic wave solutions are provided in sect. **4** for the chemical reaction $H_2 + Cl \rightleftharpoons HCl + H$.

2. – Transport properties

In a flow regime where the chemical reaction is in its final stage and the affinity is a small parameter, $|\mathcal{A}| < 1$, the elastic and reactive frequencies are of the same order of magnitude and the mixture is near chemical equilibrium.

The model equations (1), adopting a first-order Chapman-Enskog expansion for the distribution function of type $f_\alpha = f_\alpha^{(0)} + f_\alpha^{(1)}$, transform to

$$\frac{\partial f_\alpha^{(0)}}{\partial t} + c_i^\alpha \frac{\partial f_\alpha^{(0)}}{\partial x_i} = -\sum_{\beta=1}^{4} \zeta_{\alpha\beta}^E (f_\alpha^{(0)} + f_\alpha^{(1)} - f_{\alpha\beta}^E) - \zeta_{\alpha\gamma}^R (f_\alpha^{(0)} + f_\alpha^{(1)} - f_{\alpha\gamma}^R). \tag{6}$$

Proceeding with the usual steps of the Chapman-Enskog method, one obtains

$$f_\alpha^{(0)} = n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m_\alpha \xi_\alpha^2}{2kT}\right], \tag{7}$$

$$\begin{aligned} f_\alpha^{(1)} = \frac{-f_\alpha^{(0)}}{\sum_{\beta=1}^4 \zeta_{\alpha\beta}^E + \zeta_{\alpha\gamma}^R} \Bigg\{ & \frac{m_\alpha}{kT} \xi_i^\alpha \xi_j^\alpha \left(\frac{\partial v_i}{\partial x_j} - \frac{1}{3}\frac{\partial v_r}{\partial x_r}\delta_{ij}\right) + \frac{n^{\mathrm{eq}}}{n_\alpha^{\mathrm{eq}}} \xi_i^\alpha d_i^\alpha \\ & + \xi_i^\alpha \left(\frac{m_\alpha \xi_\alpha^2}{2kT} - \frac{5}{2}\right) \frac{1}{T}\frac{\partial T}{\partial x_i} - \sum_{\beta=1}^4 \zeta_{\alpha\beta}^E \frac{m_\alpha \xi_i^\alpha}{kT} \frac{m_\alpha u_i^\alpha + m_\beta u_i^\beta}{m_\alpha + m_\beta} \\ & + \zeta_{\alpha\gamma}^R \left[\frac{n_\alpha^{\mathrm{eq}}}{n^{\mathrm{eq}}} E^\star + \nu_\alpha M_\gamma \left(\epsilon_\sigma^\star + \frac{1}{2}\right)\right] \left(1 - \frac{m_\alpha \xi_\alpha^2}{3kT}\right) \frac{\mathcal{A}}{kT} \\ & - \zeta_{\alpha\gamma}^R \frac{m_\alpha \xi_i^\alpha}{kT} \left[u_i^\alpha + \sigma \sum_{\beta=1}^4 \nu_\beta M_\beta u_i^\beta - \frac{2}{3}(\epsilon_\sigma^\star + 2) M_\gamma (u_i^\alpha - u_i^\gamma)\right] \Bigg\}, \end{aligned} \tag{8}$$

where d_i^α denotes the generalized diffusion force defined by $d_i^\alpha = \frac{1}{p}\left[\frac{\partial p_\alpha}{\partial x_i} - \frac{\varrho_\alpha}{\varrho}\frac{\partial p}{\partial x_i}\right]$ with the condition $\sum_{\alpha=1}^4 d_i^\alpha = 0$. The expansion of f_α, together with expressions (7) and (8) for $f_\alpha^{(0)}$ and $f_\alpha^{(1)}$, is then introduced in the kinetic definitions of the constituent diffusion velocities u_i^α, mixture pressure tensor p_{ij} and heat flux q_i,

$$u_i^\alpha = \frac{1}{\varrho_\alpha} \int m_\alpha c_i^\alpha f_\alpha \mathrm{d}\boldsymbol{c}_\alpha, \qquad p_{ij} = \sum_{\alpha=1}^4 \int m_\alpha \xi_i^\alpha \xi_j^\alpha f_\alpha \mathrm{d}\boldsymbol{c}_\alpha, \tag{9}$$

$$q_i = \sum_{\alpha=1}^4 \left(\frac{1}{2}\int m_\alpha \xi_\alpha^2 \xi_i^\alpha f_\alpha \mathrm{d}\boldsymbol{c}_\alpha + n_\alpha \varepsilon_\alpha u_i^\alpha\right). \tag{10}$$

Therefore the actual computation of the involved integrals permits to obtain

$$d_i^\alpha = -\sum_{\beta=1}^{4} \frac{x_\alpha^{\rm eq} x_\beta^{\rm eq}}{D_{\alpha\beta}} \left(u_i^\alpha - u_i^\beta \right), \tag{11}$$

$$q_i = -\lambda \frac{\partial T}{\partial x_i} + \sum_{\alpha=1}^{4} \left(\frac{5}{2} kT + \varepsilon_\alpha \right) n_\alpha^{\rm eq} u_i^\alpha, \tag{12}$$

$$p_{ij} = p\delta_{ij} - \mu \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} - \frac{2}{3} \frac{\partial v_r}{\partial x_r} \delta_{ij} \right). \tag{13}$$

Equations (11) and (12) represent the generalized laws of Fick and Fourier, respectively, while eq. (13) expresses the constitutive law of a Newtonian fluid which, in kinetic theory, is also called Navier-Stokes law. Furthermore, $x_\alpha^{\rm eq} = n_\alpha^{\rm eq}/n^{\rm eq}$ denotes the equilibrium concentration of the constituent α. The above laws give the link between the transport fluxes u_i^α, p_{ij}, q_i and the diffusion forces, mixture velocity gradient, temperature gradient, respectively, through the transport coefficients of diffusion $D_{\alpha\beta}$ ($D_{\alpha\beta} = D_{\beta\alpha}$), shear viscosity μ and thermal conductivity λ. Such transport coefficients are given by the expressions

$$\frac{1}{D_{12}} = \frac{m_{12}}{kTx_2^{\rm eq}} \left[\zeta_{12}^E + \frac{2}{3} \zeta_{12}^R \left(\epsilon_1^\star + \frac{1}{2} \right) \right], \qquad \frac{1}{D_{13}} = \frac{m_{13}}{kTx_3^{\rm eq}} \left[\zeta_{13}^E + \zeta_{12}^R \frac{m_1 + m_3}{m_1 + m_2} \right], \tag{14}$$

$$\frac{1}{D_{14}} = \frac{m_{14}}{kTx_4^{\rm eq}} \left[\zeta_{14}^E + \zeta_{12}^R \frac{m_1 + m_4}{m_1 + m_2} \right], \qquad \frac{1}{D_{23}} = \frac{m_{23}}{kTx_3^{\rm eq}} \left[\zeta_{23}^E + \zeta_{21}^R \frac{m_2 + m_3}{m_1 + m_2} \right],$$

$$\frac{1}{D_{24}} = \frac{m_{24}}{kTx_4^{\rm eq}} \left[\zeta_{24}^E + \zeta_{21}^R \frac{m_2 + m_4}{m_1 + m_2} \right], \qquad \frac{1}{D_{34}} = \frac{m_{34}}{kTx_4^{\rm eq}} \left[\zeta_{34}^E + \frac{2}{3} \zeta_{34}^R \left(\epsilon_{-1}^\star + \frac{1}{2} \right) \right],$$

$$\mu = \frac{n_1^{\rm eq} kT}{\sum_{\beta=1}^4 \zeta_{1\beta}^E + \zeta_{12}^R} + \frac{n_2^{\rm eq} kT}{\sum_{\beta=1}^4 \zeta_{2\beta}^E + \zeta_{21}^R} + \frac{n_3^{\rm eq} kT}{\sum_{\beta=1}^4 \zeta_{3\beta}^E + \zeta_{34}^R} + \frac{n_4^{\rm eq} kT}{\sum_{\beta=1}^4 \zeta_{4\beta}^E + \zeta_{43}^R}, \tag{15}$$

$$\lambda = \frac{5}{2} \left[\frac{n_1^{\rm eq} k^2 T/m_1}{\sum_{\beta=1}^4 \zeta_{1\beta}^E + \zeta_{12}^R} + \frac{n_2^{\rm eq} k^2 T/m_2}{\sum_{\beta=1}^4 \zeta_{2\beta}^E + \zeta_{21}^R} + \frac{n_3^{\rm eq} k^2 T/m_3}{\sum_{\beta=1}^4 \zeta_{3\beta}^E + \zeta_{34}^R} + \frac{n_4^{\rm eq} k^2 T/m_4}{\sum_{\beta=1}^4 \zeta_{4\beta}^E + \zeta_{43}^R} \right]. \tag{16}$$

Equations (14)-(16) clearly show the dependence of transport coefficients on the chemical process through the presence of the reactive collision frequencies $\zeta_{\alpha\gamma}^R$ and activation energies $\epsilon_1^\star$ and $\epsilon_{-1}^\star$ related to the forward and backward reaction.

3. – Plane harmonic waves

The model equations (1) with reference distributions (4) and (5) lead to the following balance equations for the number density of each constituent and to the conservation laws for momentum and total energy of the mixture, namely

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial x_i}(n_\alpha u_i^\alpha + n_\alpha v_i) = \tau_\alpha, \qquad \tau_\alpha = \int \left(\sum_{\beta=1}^{4} \mathcal{Q}_{\alpha\beta}^E + \mathcal{Q}_\alpha^R \right) \mathrm{d}\mathbf{c}_\alpha, \tag{17}$$

$$\frac{\partial \varrho v_i}{\partial t} + \frac{\partial}{\partial x_j}(p_{ij} + \varrho v_i v_j) = 0, \tag{18}$$

$$\frac{\partial}{\partial t}\left[\frac{3}{2}nkT + \sum_{\alpha=1}^{4} n_\alpha \varepsilon_\alpha + \frac{1}{2}\varrho v^2\right] + \frac{\partial}{\partial x_i}\left[q_i + p_{ij}v_j + \left(\frac{3}{2}nkT + \sum_{\alpha=1}^{4} n_\alpha \varepsilon_\alpha + \frac{1}{2}\varrho v^2\right) v_i\right] = 0. \tag{19}$$

The form of the system (17)-(19) is the same as in the case of the exact reactive BE, due to the requirement (2) of equal production terms for both the BGK-type model and reactive BE. The closure of the above system at the Navier-Stokes, Fourier and Fick level is assured by the constitutive equations (11), (12), which guarantee that u_i^α, p_{ij} and q_i are expressed in terms of the basic fields n_α, v_i and T.

The closed system of the reactive field equations (17)-(19) and constitutive equations (11), (12) will now be solved by searching sound wave solutions through a normal mode analysis. At this end, a linearization around an equilibrium state of the mixture, characterized by constant individual number densities n_α^{eq}, mixture temperature T_0 and vanishing mean velocity, is introduced in the closed system. The basic fields are expanded in the form

$$n_\alpha = n_\alpha^{\mathrm{eq}} + \widetilde{n}_\alpha, \qquad v_i = \widetilde{v}_i, \qquad T = T_0 + \widetilde{T}, \tag{20}$$

where $\widetilde{n}_\alpha$, $\widetilde{v}_i$ and $\widetilde{T}$ represent small perturbations of the corresponding equilibrium state fields. By introducing the expansions (20) into the field equations (17)-(19) and referring them to one space dimension ($v_1 = v$), one obtains the linearized one-dimensional equations in the form

$$\frac{\partial \widetilde{n}_\alpha}{\partial t} + n_\alpha^{\mathrm{eq}} \frac{\partial \widetilde{u}_\alpha}{\partial x} + n_\alpha^{\mathrm{eq}} \frac{\partial \widetilde{v}}{\partial x} = \nu_\alpha n_\alpha^{\mathrm{eq}} n_\gamma^{\mathrm{eq}} k_\sigma^{(0)} \frac{\mathcal{A}}{kT_0}, \qquad \alpha = 1, \dots, 4, \tag{21}$$

$$\varrho_0 \frac{\partial \widetilde{v}}{\partial t} + \frac{\partial \widetilde{p}_{11}}{\partial x} = 0, \tag{22}$$

$$\frac{3}{2}kn_0 \frac{\partial \widetilde{T}}{\partial t} + p_0 \frac{\partial \widetilde{v}}{\partial x} + \frac{\partial \widetilde{q}}{\partial x} - \sum_{\alpha=1}^{4} n_\alpha^{\mathrm{eq}} \left(\frac{3}{2}kT_0 + \varepsilon_\alpha\right) \frac{\partial \widetilde{u}_\alpha}{\partial x} = -\sum_{\alpha=1}^{4} \varepsilon_\alpha \nu_\alpha n_\alpha^{\mathrm{eq}} n_\gamma^{\mathrm{eq}} k_\sigma^{(0)} \frac{\mathcal{A}}{kT_0}, \tag{23}$$

where $k_\sigma^{(0)}$ is the first approximation to the forward ($\sigma = 1$) and backward ($\sigma = -1$) rate constants [1], and $\widetilde{u}_\alpha$, $\widetilde{p}_{11}$, $\widetilde{q}$ are the first-order perturbations of u_α, p_{11}, q, respectively. The explicit form of such perturbations states their dependence on the transport coefficients $D_{\alpha\beta}$, μ, λ, besides the field perturbations $\widetilde{n}_\alpha$, $\widetilde{v}$, $\widetilde{T}$, since the closure of the reactive field equations has been performed at the Navier-Sokes, Fourier and Fick level. Longitudinal harmonic waves propagating along the x-axis are characterized by assuming that the perturbations $\widetilde{n}_\alpha$, $\widetilde{v}$, $\widetilde{T}$ are given by small complex amplitudes $\overline{n}_\alpha$, $\overline{v}$, $\overline{T}$ multiplied by exponential factors depending on the complex wave number κ and real angular frequency ω of the wave, that is

$$\widetilde{n}_\alpha = \overline{n}_\alpha \exp[\imath(\kappa x - \omega t)], \qquad \widetilde{v} = \overline{v} \exp[\imath(\kappa x - \omega t)], \qquad \widetilde{T} = \overline{T} \exp[\imath(\kappa x - \omega t)]. \tag{24}$$

The phase velocity v_{ph} and the attenuation coefficient α of the wave are defined by $v_{\mathrm{ph}} = \omega / \operatorname{Re}\kappa$, $\alpha = \operatorname{Im}\kappa$, and the affinity $\mathcal{A}$ can be written in terms of the perturbation amplitudes of the particle number densities in the form $\mathcal{A} = -kT_0 \sum_{\alpha=1}^{4} \nu_\alpha \bar{n}_\alpha / n_\alpha^{\mathrm{eq}}$.

After inserting the constitutive equations (11), (12) together with the perturbations (24) and the expression for the affinity, the linearized field equations (21)-(23) transform into the following linear algebraic system for the amplitudes:

$$A\overline{z} = 0, \qquad \overline{z}^{\mathrm{T}} = [\overline{n}_1\, \overline{n}_2\, \overline{n}_3\, \overline{n}_4\, \overline{v}\, \overline{T}]^{\mathrm{T}}, \tag{25}$$

where $A = [A_{ij}]$ is a six-order square matrix whose elements depend on the equilibrium state of the reactive mixture, transport coefficients and wave parameters. The explicit expressions of the matrix elements are here omitted for brevity.

The algebraic system (25) has a non-trivial solution if the determinant of the matrix A vanishes. This condition leads to the dispersion relation for the normal modes (24), namely, $\sum_{j=0}^{6} a_j (\kappa/\omega)^{2j} = 0$, where the coefficients a_j depend on the equilibrium number densities n_α^{eq}, equilibrium mixture temperature T_0, molecular masses m_α, transport coefficients μ, λ, $D_{\alpha\beta}$, rate constant $k_1^{(0)}$, as well as angular frequency ω and wave number κ.

4. – Results

Two mixtures of the H_2-Cl system undergoing the bimolecular chemical reaction $H_2 + Cl \rightleftharpoons HCl + H$ with different equilibrium constituent concentrations and at the same equilibrium temperature $T_0 = 1500\,\mathrm{K}$ are considered in two cases, namely:

Case (a) $x_1^{\mathrm{eq}} = 0.1$, $x_2^{\mathrm{eq}} = 0.618$, $x_3^{\mathrm{eq}} = 0.082$, $x_4^{\mathrm{eq}} = 0.2$;

Case (b) $x_1^{\mathrm{eq}} = 0.2$, $x_2^{\mathrm{eq}} = 0.424$, $x_3^{\mathrm{eq}} = 0.076$, $x_4^{\mathrm{eq}} = 0.3$.

In both cases the concentrations x_1^{eq} and x_4^{eq} of the constituents H_2 and H were chosen, while the concentrations x_2^{eq} and x_3^{eq} of Cl and HCl were obtained from the constraint $x_1^{\mathrm{eq}} + x_2^{\mathrm{eq}} + x_3^{\mathrm{eq}} + x_4^{\mathrm{eq}} = 1$ and from the mass action law,

$$\frac{E}{kT_0} = \frac{3}{2} \ln\left(\frac{m_3 m_4}{m_1 m_2}\right) + \ln \frac{x_1^{\mathrm{eq}} x_2^{\mathrm{eq}}}{x_3^{\mathrm{eq}} x_4^{\mathrm{eq}}},$$

where $E = 3.98\,\mathrm{kJ/mol}$ represents the reaction heat of the reaction $H_2 + Cl \rightleftharpoons HCl + H$.

The theoretical analysis of sects. **2** and **3** is applied to the reacting mixtures of the above cases (a) and (b), with the aim of studying the transport properties and characterizing the harmonic wave solutions in the hydrogen-chlorine system. More in detail, the influence of the chemical reaction on transport coefficients and wave solutions can be appreciated through the comparison of the reacting mixtures of cases (a) and (b) with the non-reacting mixtures for which the same choice of constituent concentrations is considered.

TABLE I. – *Case (a). Influence of chemical reaction on the transport coefficients.*

	$\mu(10^{-5}$ Pa s)	λ(W/mK)	$D_{12}(10^{-4}$ m^2/s)	$D_{13}(10^{-4}$ m^2/s)
Reacting	3.388	0.139	2.375	1.251
Non-reacting	3.431	0.141	2.553	1.529
	$D_{14}(10^{-4}$ m^2/s)	$D_{23}(10^{-4}$ m^2/s)	$D_{24}(10^{-4}$ m^2/s)	$D_{34}(10^{-4}$ m^2/s)
Reacting	5.081	0.548	6.880	3.035
Non-reacting	5.124	0.709	7.108	3.565

TABLE II. – *Case (b). Influence of chemical reaction on the transport coefficients.*

	$\mu(10^{-5}$ Pa s)	λ(W/mK)	$D_{12}(10^{-4}$ m^2/s)	$D_{13}(10^{-4}$ m^2/s)
Reacting	1.965	0.182	2.375	1.313
Non-reacting	2.000	0.185	2.553	1.529
	$D_{14}(10^{-4}$ m^2/s)	$D_{23}(10^{-4}$ m^2/s)	$D_{24}(10^{-4}$ m^2/s)	$D_{34}(10^{-4}$ m^2/s)
Reacting	5.104	0.434	6.807	3.041
Non-reacting	5.124	0.709	7.108	3.565

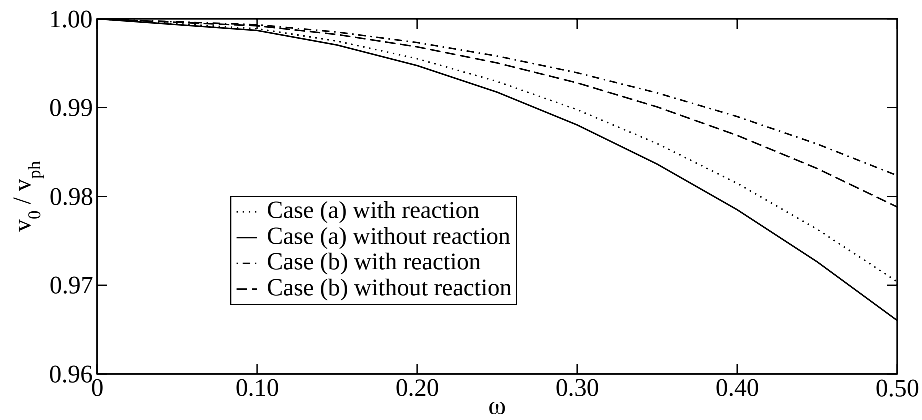

Fig. 1. – Influence of the chemical reaction on phase velocity *vs.* angular frequency.

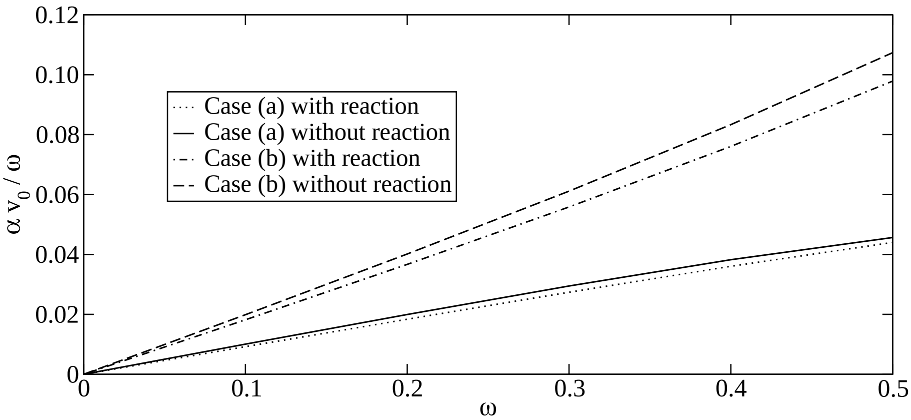

Fig. 2. – Influence of the chemical reaction on attenuation coefficient *vs.* angular frequency.

The transport coefficients μ, λ and $D_{\alpha\beta}$ of the reacting mixture are shown in comparison with the non-reacting mixture in table I with reference to case (a), and in table II with reference to case (b). The results in tables I and II show that: i) the chemical reaction contributes to decrease the transport coefficients with respect to the non-reacting mixtures and ii) the chemical influence is more appreciable in the diffusion coefficients. Such conclusion is in agreement with the results obtained in paper [6] for the transport coefficients of an analogous mixture of the hydrogen-chlorine system, starting from the exact reactive BE.

Moreover, figs. 1 and 2 describe the behavior of the phase velocity and attenuation coefficient as functions of the angular frequency of the wave, for a low-frequency regime ($\omega \leq 0.5$). The two cases (a) and (b) are considered in both figures and again, the comparison of the reacting mixtures with the corresponding inert systems allows to appreciate the influence of the chemical reaction on the harmonic solutions.

The figures illustrate that: i) the phase velocities and the attenuation coefficients for reacting mixtures are smaller than the corresponding ones for non-reactive mixtures, because the transport coefficients show also the same behavior; ii) the chemical influence on the phase velocities and attenuation coefficients becomes negligible in the limit of low frequencies and iii) by increasing the concentrations of the lighter constituents (H_2, H), the phase velocity decreases and the attenuation coefficient increases.

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