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Abstract. A system of coupled Boltzmann equations (BE) is here proposed for a binary gaseous mixture undergoing elastic and reactive collisions. Reactive cross sections without activation energy, i.e. without barriers, are adopted to model the chemical process, whereas differential cross sections of rigid spheres are assumed for elastic scattering. The possibility of a pair of molecules to collide through an elastic mechanism or a reactive process is described by means of probability coefficients which are introduced in the collision terms. The rate of reaction and temperature exchange rate are explicitly computed using the non-equilibrium solution of the BE obtained through the Chapman-Enskog method in a chemical regime such that the reactive process is in its initial stage. Spatially homogeneous solutions are examined for the number density of reactants and mixture temperature.

Keywords: Boltzmann equation, Chemical reactions
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INTRODUCTION

In the literature of the Boltzmann equation extended to chemically reacting gases, most research papers introduce reactive cross sections with activation energy whereas only few works consider reactive models for processes without activation energy [1]. On the other hand, chemical reactions without barriers have become an interesting topic in many engineering applications of reactive flows, in particular in combustion phenomena, but also in other fields such as astrophysics, organic chemistry, chemical physics and biophysics [2, 3]. The modeling of reactions without barriers can help to interpret the related experimental data and provide some useful information about the kinetics of the reaction. Following this idea, a kinetic model of the Boltzmann equation is here proposed for a binary mixture undergoing elastic and reactive scattering. An appropriate model of reactive cross section without barriers can be found in the literature (see [4, 5]) and it will correspond to the choice of the proposed non-barrier kinetic theory. At the microscopic scale, the key idea is to modify the collision terms of the Boltzmann equation, introducing probability coefficients that describe the possibility of a pair of molecules to collide through an elastic mechanism or a reactive process. This improvement accounts for the fact that a great number of reactive interactions corresponds to a small number of elastic collisions, and vice-versa. In this sense, the considered model represents a new approach, since almost all existent papers introduce reactive cross sections with activation energy and control the presence of both elastic and reactive collisions assuming rather large activation energies and a steric factor which reduce the number of reactive collisions.

In a chemical regime of slow reaction, the chemical non-equilibrium effects induced on the solution of the Boltzmann equation are also characterized using the Chapman-Enskog method and a second order Sonine polynomial expansion of the distributions. The chemical process is considered in its early stage so that reactive collisions among molecules of reaction products can be disregarded since the products of the reaction are in a small amount with respect to the reactants. Moreover, it was considered that the heat of reaction is a small quantity which can be neglected. At last, as an application of the thermodynamic model proposed here, spatially homogeneous field equations for reactant number density and mixture temperature are solved and the time evolution of the reactive system is examined.

BOLTZMANN EQUATION AND MACROSCOPIC DESCRIPTION

Consider a binary mixture of constituents $\alpha = A, B$ with binding energies ε_A and ε_B and equal molecular masses, $m_A = m_B = m$, undergoing a reversible reaction of type $A + A \rightleftharpoons B + B$. Gas molecules may participate in binary elastic collisions preserving momentum and kinetic energy,

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

as well as in binary reactive interactions preserving momentum and total energy,

$$m\mathbf{c}_A + m\mathbf{c}_{A_1} = m\mathbf{c}_B + m\mathbf{c}_{B_1}, \qquad \varepsilon_A + \frac{1}{2}mc_A^2 + \varepsilon_A + \frac{1}{2}mc_{A_1}^2 = \varepsilon_B + \frac{1}{2}mc_B^2 + \varepsilon_B + \frac{1}{2}mc_{B_1}^2. \tag{2}$$

Above, $(\mathbf{c}_\alpha, \mathbf{c}_\beta)$ and $(\mathbf{c}'_\alpha, \mathbf{c}'_\beta)$ denote pre and post collisional velocities, whereas $(\mathbf{c}_A, \mathbf{c}_{A_1})$ and $(\mathbf{c}_B, \mathbf{c}_{B_1})$ refer to the the velocities of reactants and products of the forward reaction, respectively. Sub-index 1 is used to distinguish two molecules of the same species. The relative velocities of the reactants and products is given by $\mathbf{g}_A = \mathbf{c}_{A_1} - \mathbf{c}_A$ and $\mathbf{g}_B = \mathbf{c}_{B_1} - \mathbf{c}_B$, and the reaction heat is defined as $Q_R = 2(\varepsilon_A - \varepsilon_B)$. A pertinent choice of reactive cross sections to describe chemical reactions without a barrier should not consider an activation energy. Accordingly, assuming an attractive potential energy of the form $V(r) = -K/r^n$, the following reactive cross sections model is adopted (see Refs. [4, 5]),

$$\sigma_\alpha^* = \frac{d_r^2}{4}\left(\frac{mg_\alpha^2}{4kT_0}\right)^{n-1/2}, \tag{3}$$

where T_0 is a characteristic temperature, d_r a reactive collision diameter and the exponent n may range from $-3/2$ to $1/2$, with the particular values $1/2$, 0 and $1/6$ standing for hard-spheres reactions, ion-molecule reactions and reactions of neutral species, respectively. For what concerns the differential cross sections of elastic encounters, the simple model of rigid spheres is adopted, namely $\sigma_{\alpha\beta} = d^2/4$, where d is the molecular diameter.

The Boltzmann equation proposed here for the considered mixture contains, as usual, distinct contributions for elastic collisions and reactive interactions, but now suitable probability coefficients $0 \le \chi_A, \chi_B \le 1$ are introduced in order to account for the possibility of a pair of molecules interact through an elastic collision or a reactive process. In absence of external body forces, the BE for f_α is written then in the form

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

$$+ \int \left[\chi_\beta f_\beta f_{\beta_1} \sigma_\beta^\star \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha f_{\alpha_1} \sigma_\alpha^\star \right] g_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1}, \tag{4}$$

The first term on the r.h.s. of (4) refers to elastic collisions and the second one to chemical interactions where one has to take $\alpha \ne \beta = A, B$. Elastic contributions referred to AA and BB encounters are affected by a reduced factor, namely $1 - \chi_\alpha$, $\alpha = A, B$, which is compensated by the corresponding factor χ_α relative to reactive encounters among AA and BB molecules, respectively.

The macroscopic picture of the mixture can be described by the number densities n_α and internal energy densities $\rho_\alpha e_\alpha$ of both constituents, together with the mixture velocity v_i, given by

$$n_\alpha = \int f_\alpha d\mathbf{c}_\alpha = \frac{\rho_\alpha}{m}, \qquad v_i = \frac{1}{\rho} \sum_{\alpha=A}^{B} \int mc_i^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad \rho_\alpha e_\alpha = \int \frac{m}{2}\xi_\alpha^2 f_\alpha d\mathbf{c}_\alpha, \tag{5}$$

with $\xi_i^\alpha = c_i^\alpha - v_i$ the peculiar velocity of constituent α, and $n = \sum_{\alpha=A}^{B} n_\alpha$, $\rho = \sum_{\alpha=A}^{B} \rho_\alpha$. Each constituent is assumed to have the same temperature T which is the mixture's temperature, so that its internal energy density becomes $\rho_\alpha e_\alpha = 3n_\alpha kT/2$. By rather standard arguments, the balance equations for the fields defined in expressions (5) are obtained from Eq. (4), in the form

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial x_i}(n_\alpha u_i^\alpha + n_\alpha v_i) = \tau_\alpha \tag{6}$$

$$\frac{\partial \rho v_i}{\partial t} + \frac{\partial}{\partial x_j}(p_{ij} + \rho v_i v_j) = 0, \tag{7}$$

$$\frac{3}{2}\frac{\partial n_\alpha kT}{\partial t} + \frac{\partial}{\partial x_i}\left(q_i^\alpha + \frac{3}{2}n_\alpha kT v_i\right) - \frac{\rho_\alpha}{\rho}u_i^\alpha\frac{\partial p_{ij}}{\partial x_j} + p_{ij}^\alpha\frac{\partial v_j}{\partial x_i} = \zeta_\alpha. \tag{8}$$

Above, τ_α is the rate of reaction and ζ_α the production term of internal energy density of constituent α, given by

$$\tau_\alpha = \int \left[\chi_\beta f_\beta f_{\beta_1} \sigma_\beta^\star \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha f_{\alpha_1} \sigma_\alpha^\star \right] g_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1} d\mathbf{c}_\alpha, \quad \text{with} \quad \tau_B = -\tau_A, \tag{9}$$

$$\zeta_\alpha = \sum_{\beta=A}^{B} (1 - \chi_\beta \delta_{\alpha\beta}) \int \frac{1}{2} m(\xi_\alpha'^2 - \xi_\alpha^2) f_\alpha f_\beta g_{\beta\alpha} \sigma_{\beta\alpha} d\Omega_{\beta\alpha} d\mathbf{c}_\beta d\mathbf{c}_\alpha$$

$$+ \int \frac{m}{4} (\xi_\alpha^2 + \xi_{\alpha_1}^2) \left[\chi_\beta f_\beta f_{\beta_1} \sigma_\beta^\star \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha f_{\alpha_1} \sigma_\alpha^\star \right] g_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1} d\mathbf{c}_\alpha. \tag{10}$$

Moreover, u_i^α, q_i^α and p_{ij}^α are the diffusion velocity, heat flux and pressure tensor of each constituent, defined by

$$u_i^\alpha = \frac{1}{n_\alpha} \int \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad q_i^\alpha = \int \frac{1}{2} m \xi_\alpha^2 \xi_i^\alpha f_\alpha d\mathbf{c}_\alpha, \qquad p_{ij}^\alpha = \int m \xi_i^\alpha \xi_j^\alpha f_\alpha d\mathbf{c}_\alpha,$$

with

$$\sum_{\alpha=A}^{B} \rho_\alpha u_i^\alpha = 0, \qquad q_i = \sum_{\alpha=A}^{B} q_i^\alpha, \qquad p_{ij} = \sum_{\alpha=A}^{B} p_{ij}^\alpha.$$

THE NON-EQUILIBRIUM DISTRIBUTION FUNCTION

The deviations induced by the chemical reaction on the distribution functions can be explicitly computed using the Chapman-Enskog method [9] with Sonine polynomial representation of the distributions. Assuming a chemical regime of slow processes, for which the reaction is close to its initial stage, reactive collisions are less frequent than elastic encounters and the chemical relaxation time is larger than the elastic one. This means that reactive collision terms of the Boltzmann Eqs. (4) and material time derivatives, $\mathscr{D} = (\partial/\partial t) + v_i \partial/\partial x_i$, are of the same order, whereas the gradients of the fields are of successive order. This means that the Boltzmann equation (4) can be written as

$$\mathscr{D} f_\alpha + \lambda \xi_i^\alpha \frac{\partial f_\alpha}{\partial x_i} - \int \left[\chi_\beta f_\beta f_{\beta_1} \sigma_\beta^\star \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha f_{\alpha_1} \sigma_\alpha^\star \right] g_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1} \tag{11}$$

$$= \frac{1}{\lambda} \sum_{\beta=A}^{B} (1 - \chi_\beta \delta_{\alpha\beta}) \int \left[f_\alpha' f_\beta' - f_\alpha f_\beta \right] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_\beta,$$

where λ is a formal parameter of the order of the Knudsen number [9]. Proceeding with the insertion of the expansions

$$f_\alpha = f_\alpha^M + \lambda f_\alpha^{(0)} + \lambda^2 f_\alpha^{(1)} + \dots \quad \text{and} \quad \mathscr{D} = \mathscr{D}^{(0)} + \lambda \mathscr{D}^{(1)} + \lambda^2 \mathscr{D}^{(2)} + \dots, \tag{12}$$

into the Boltzmann Eqs. (11) and equating equal powers of λ, one obtains the integral equations for f_α^M and $f_\alpha^{(0)}$ in the form,

$$\sum_{\beta=A}^{B} (1 - \chi_\beta \delta_{\alpha\beta}) \int \left[f_\alpha^{M'} f_\beta^{M'} - f_\alpha^M f_\beta^M \right] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_\beta = 0, \tag{13}$$

$$\mathscr{D}^{(0)} f_\alpha^M - \int \left[\chi_\beta f_\beta^M f_{\beta_1}^M \sigma_\beta^\star \frac{g_\beta^2}{g_\alpha^2} - \chi_\alpha f_\alpha^M f_{\alpha_1}^M \sigma_\alpha^\star \right] g_\alpha d\Omega_\beta d\mathbf{c}_{\alpha_1} \tag{14}$$

$$= \sum_{\beta=A}^{B} (1 - \chi_\beta \delta_{\alpha\beta}) \int \left[f_\alpha^{(0)\prime} f_\beta^{M\prime} + f_\alpha^{M\prime} f_\beta^{(0)\prime} - f_\alpha^{(0)} f_\beta^M - f_\alpha^M f_\beta^{(0)} \right] g_{\beta\alpha} \sigma_{\alpha\beta} d\Omega_{\alpha\beta} d\mathbf{c}_\beta.$$

The solution of the integral equation (13) is the Maxwellian distribution function, given by

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

with partial number densities n_α completely uncorrelated, since no chemical equilibrium condition is involved.

Concerning Eq. (14), since the field gradients are absent, one admits that its solution is a small deviation from the Maxwellian distribution, expressed in terms of Sonine polynomials as

$$f_\alpha^{(0)} = f_\alpha^M \left[a_1^\alpha \left(\frac{3}{2} - \frac{m\xi_\alpha^2}{2kT} \right) + a_2^\alpha \left(\frac{15}{8} - \frac{5m\xi_\alpha^2}{4kT} + \frac{m^2\xi_\alpha^4}{8k^2T^2} \right) \right],$$ (16)

where a_1^α and a_2^α are scalar coefficients to be determined. First, the insertion of distributions (16) into definition $(5)_2$ of the internal energy density and integration of the resulting equation lead to $a_1^A = a_1^B = 0$. Afterwards, the balance Eqs. (6-8) for an Eulerian mixture where $u_i^\alpha = 0$, $p_{ij} = p\delta_{ij}$ and $q_i = 0$ are used to eliminate the material derivatives in Eq. (14). The successive multiplication of the resulting equation by m and $(3/2 - m\xi_\alpha^2/2kT)$ and further integration over $\mathbf{c}_\alpha$ lead to identities, whereas the multiplication by $(15/8 - 5m\xi_\alpha^2/4kT + m^2\xi_\alpha^4/8k^2T^2)$ and integration give the following system of coupled equations for a_2^A and a_2^B

$$-v_\alpha \frac{\chi_A n_A^2}{2} \left(\frac{T}{T_0} \right)^{n-\frac{1}{2}} \Gamma\left(n + \frac{3}{2} \right) n(n-1) \left(\frac{d\mathbf{r}}{d} \right)^2 = -4(1 - \chi_\alpha)n_\alpha^2 a_2^\alpha + \frac{n_\alpha n_\beta}{4}(15a_2^\beta - 31a_2^\alpha), \quad \alpha \neq \beta = A, B,$$ (17)

where $v_A = -v_B = -1$ are stoichiometric coefficients. For the purpose of the present study, it was considered that in the early stage of the reaction the probability of a reactive collision between B molecules is negligible so that $\chi_B \approx 0$. Furthermore, the heat of reaction is a small quantity so that it can be neglected. These assumptions have been taken into account to deduce Eqs. (17). More details about the approximating procedure here employed are reported in a paper in preparation, concerning the kinetic theory of chemical reactions without barriers (see Ref. [10]).

From the system of equations (17) one obtains

$$a_2^A = \frac{2\chi_A x_A}{15x_A^2\chi_A + 16x_A\chi_A - 31} \left(\frac{T}{T_0} \right)^{n-\frac{1}{2}} \Gamma\left(n + \frac{3}{2} \right) n(n-1) \left(\frac{d\mathbf{r}}{d} \right)^2,$$ (18)

$$a_2^B = \frac{x_A(x_A\chi_A - 1)}{1 - x_A} a_2^A,$$ (19)

where $x_A = n_A/n$ and $x_B = 1 - x_A$ represent the molar fraction of the constituents.

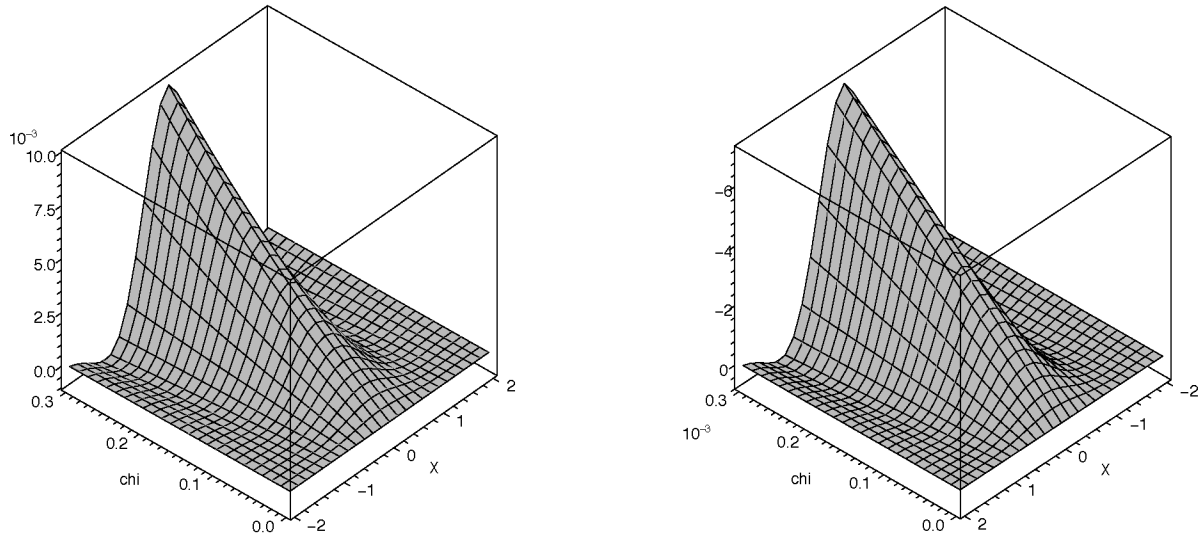**FIGURE 1.** Deviations of the non-equilibrium distribution function with respect to the Maxwellian distribution, versus X and chi $\equiv \chi_A$, for $x_A = 0.9$. Left frame: F_A; right frame: F_B.

All the representative effects induced on the non-equilibrium distribution function are illustrated in Fig. 1, where the deviations with respect to the Maxwellian distribution function, namely

$$F_\alpha \equiv \frac{1}{n}\left(\frac{2\pi kT}{m}\right)^{3/2} f_\alpha^{(0)} = x_\alpha e^{-X^2} a_2^\alpha \left(\frac{15}{8} - \frac{5}{2}X^2 + \frac{1}{2}X^4\right), \qquad \alpha = A, B \tag{20}$$

are plotted versus chi=χ_A and $X = \sqrt{m\xi_A^2/2kT}$, when $\mathsf{d_r} = \mathsf{d}$ and $x_A = 0.9$ for the case of hard-spheres reactions without barrriers, i.e., for $\mathsf{n} = 1/2$. The left frame refers to the Maxwellian deviation for the reactants whereas the right frame to the corresponding deviations for the products. One can infer from the figures that the modulus of deviation from a Maxwellian distribution function becomes larger when the probability of reactive encounters among the reactants increases. Furthermore, the deviation is positive for the reactants and negative for the products, which means that the non equilibrium distribution is larger than the Maxwellian one for the reactants and smaller for the products.

Note that for $\chi_A = 0$ the distribution is Maxwellian and all collisions are elastic, i.e., no reactive encounter occurs.

A SPATIALLY UNIFORM PROBLEM

From the knowledge of the non-equilibrium distribution function previously obtained, it is now possible to evaluate the reaction rate and internal energy exchange rate of the reactants. In fact, it is enough to insert expressions (16) into definitions (9) and (10) and performing the corresponding integrations. One obtains

$$\tau_A = -\sqrt{\frac{\pi kT}{m}}\left(\frac{T}{T_0}\right)^{\mathsf{n}-\frac{1}{2}}\Gamma\left(\mathsf{n}+\frac{3}{2}\right)\chi_A n_A^2 \mathsf{d_r^2}\left[4 + \mathsf{n}(\mathsf{n}-1)a_2^A\right], \tag{21}$$

$$\zeta_A = -kT\sqrt{\frac{\pi kT}{m}}\left\{n_A n_B \mathsf{d}^2(a_2^A - a_2^B) + \frac{1}{2}\left(\frac{T}{T_0}\right)^{\mathsf{n}-\frac{1}{2}}\Gamma\left(\mathsf{n}+\frac{3}{2}\right)\chi_A n_A^2 \mathsf{d_r^2}\left[12 + 4\mathsf{n} + \mathsf{n}(5 + 4\mathsf{n} + \mathsf{n}^2)a_2^A\right]\right\}, \tag{22}$$

with a_2^A and a_2^B given by expressions (18) and (19), respectively.

In the particular case of chemical reactions of ion-molecule type ($\mathsf{n} = 0$), the effects related to the coefficients a_2^α disappear from the production terms (21) and (22), and also from the non-equilibrium deviations $f_\alpha^{(0)}$.

From the balance equations (6) and (8), with the production terms (21) and (22) referred to the present case, one obtains the spatially uniform evolution equations for particle number density and internal energy density of the reactants,

$$\frac{dx_A}{d\mathsf{t}} = -\frac{\sqrt{\pi}}{2}\chi_A x_A^2 \qquad \text{and} \qquad \frac{3}{2}k\frac{d(x_A T)}{d\mathsf{t}} = -\frac{3}{2}kT\frac{\sqrt{\pi}}{2}\chi_A x_A^2 \tag{23}$$

with

$$\mathsf{t} = \frac{t}{t_c}, \qquad t_c = \frac{1}{4n_0 \mathsf{d}^2}\sqrt{\frac{m}{\pi kT_0}},$$

where t_c is the mean free time of elastic collisions, and n_0, T_0 denote the number density and temperature of the mixture in a reference initial state. Moreover the collision diameters have been considered equal to each other, i.e. $\mathsf{d_r} = \mathsf{d}$.

The solution of the differential equations (23) is given by

$$x_A = \frac{x_A^0}{\frac{\sqrt{\pi}}{2}x_A^0 \chi_A \mathsf{t} + 1}, \qquad T = T_0. \tag{24}$$

From the above equations, one concludes that the temperature of the mixture remains constant while the reactant concentration decreases with time and that the decay is more pronounced when the probability χ_A of reactive encounters increases. This last result can be observed in Figure 2 where the ratio x_A/x_A^0 is represented as function of t and chi=χ_A for $x_A^0 = 0.9$.
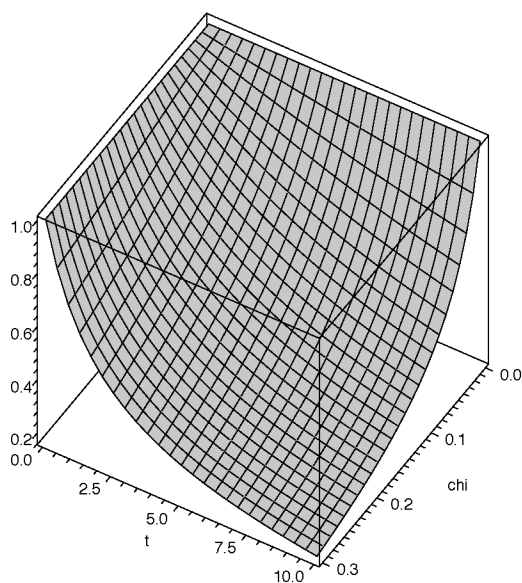
FIGURE 2. Ratio x_A/x_A^0 as function of t and chi=χ_A for $x_A^0 = 0.9$.

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