



# Enskog's kinetic theory of dense gases for chemically reacting binary mixtures, II: Light scattering and sound propagation

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## ABSTRACT

Enskog's kinetic theory for a symmetric moderately dense reaction  $A + A \rightleftharpoons B + B$  is used to determine Fick's and Fourier's law. The transport coefficients of diffusion, thermal-diffusion rate and thermal conductivity are represented graphically for endothermic and exothermic reactions and are analyzed as a function of the activation energy and of the density of the mixture. The Onsager reciprocity relations are numerically investigated and verified. The problems related to sound propagation and light scattering are investigated for such a mixture and it is shown that the influence of chemical reactions on phase velocity, attenuation coefficient and light scattering spectra is more pronounced for rarefied gases although there is a considerable change in these quantities as the mixture becomes denser.

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## 1. Introduction

The determination of the effects of chemical reactions on the transport properties of gas mixtures within the framework of the Boltzmann equation was investigated by several researchers, starting from the pioneering works of Prigogine and collaborators [1,2] in the beginning of the fifties. The subsequent research were devoted mainly to the determination of the reaction rate coefficient (see, e.g. the papers [3–11]) and the effects of chemical reactions on transport coefficients (see e.g. the Refs. [12–16]) for ideal gas mixtures. For an extensive list of other works on kinetic theory of chemically reacting gases one is referred to Ref. [17]. Furthermore, the influence of chemical reactions on mixtures of dense gases were also investigated in the works [18–23].

This paper is a continuation of a former work [22] – henceforth denoted by I. – on the linear transport coefficients of Enskog's theory for a symmetric moderately dense gas reaction  $A + A \rightleftharpoons B + B$  by considering the last stage of a chemical reaction where the thermodynamic affinity can be considered a small quantity, i.e., within the framework of the theory of linear irreversible thermodynamics [24]. In this kind of reaction – known as a fast reaction – the frequencies of the elastic and reactive collisions are of the same order.

While in the first paper we gave a detailed analysis of the transport coefficients of the forward reaction rate, “bulk” reaction rate, shear, bulk and “chemical” viscosities, here we will focus on the diffusion coefficient, the thermal-diffusion

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rate and the thermal conductivity coefficient. The difference between these two types of approaches is directly connected with the choice of thermodynamic forces to describe the gas system. In a chemically reacting gas mixture it is possible to identify at least 4 types of thermodynamic forces: the temperature gradient  $\partial T/\partial x_i$ , the concentration gradient  $\partial x_A/\partial x_i$ , the velocity gradient  $\partial v_i/\partial x_j$  and the affinity  $\mathcal{A}$ . In a previous work, the momentum transport and the reaction rate density were analyzed and for that purpose we have considered the last two types of force. In the present work we are concerned with Fick's and Fourier's law, which means that is necessary to investigate the relations involving the concentration and temperature gradients.

The main objective of this work is to show how these transport coefficients change when a chemical reaction proceeds and the mixture becomes denser.

As in the previous work I, we shall use the so-called Standard Enskog Theory (SET). In fact, while the Revised Enskog Theory (RET) (see Refs. [25–28]) is consistent with the irreversible thermodynamics and satisfies all requirements of the Onsager relations, one of the problems which involves the SET – apart from violating Onsager's reciprocity relations – is the nonphysical prediction of negative diffusion coefficients [28]. However, we will show that here the diffusion coefficient is positive and it is also possible to verify the Onsager's reciprocity relations, i.e., the model developed here does not violate any physical principle. Besides, the central point between SET and RET lies in the way of evaluating the radial function  $\chi$ , since in general the molecules of the mixtures have different diameters and mass. The problem of three possible choices to evaluate does not appear here since we are dealing with a binary mixture whose components have molecules with the same mass and same diameter ( $m_A = m_B = m$  and  $d_A = d_B = d$ ) and all three choices coincide, as in the original one-component Enskog theory. Moreover, the RET theory is very complex and the structure of the equations is heavier, while the SET theory is less sophisticated but it supplies the correct behavior of the transport coefficients when the mixture evolves from an ideal to a dense phase. Therefore after we have confirmed the veracity of reciprocity relations of our results, we were convinced that the model developed here does not violate any physical principle.

The molecules of the gases are supposed to behave as monatomic particles with formation energies but the degrees of freedom such as rotational and vibrational modes are not taken into account. The collision integrals are determined analytically by considering a rigid sphere model for the elastic cross section and a line-of-centers energy model for the reactive cross section.

We begin in Section 2 by introducing the balance equations for the partial particle number densities, momentum density and temperature of the mixture, where the constitutive quantities – namely, diffusion flux, reaction rate, pressure tensor and heat flux of the mixture – are given in terms of the distribution functions of each constituent.

By using the Chapman–Enskog method, the non-equilibrium distribution functions are determined in Section 3 from a coupled system of integral equations for each constituent and expressed in terms of the thermodynamic forces, namely, temperature gradient and concentration gradient of one of the constituents. From a knowledge of the non-equilibrium distribution functions the remaining constitutive equations corresponding to the diffusion flux and mixture's heat flux – which are related to Fick's and Fourier's laws, respectively – are established. The behavior of the transport coefficients of diffusion, thermal-diffusion rate and thermal conductivity are represented graphically for two cases corresponding to endothermic and exothermic reactions. The results for the transport coefficients are analyzed as a function of the activation energy and also of the density of the mixture. Also in Section 3 the Onsager reciprocity relations are numerically investigated, since the algebraic expressions for the coefficients are too heavy to handle. The Onsager reciprocity relations are verified showing that the assumption of using the SET theory does not violate any reciprocity relationship.

In Section 4, the problems concerning sound propagation and light scattering in chemically reacting mixtures of moderately dense gases are analyzed following the methodology of the previous works [29–31]. It is shown that the effects of chemical reaction on the phase velocity, attenuation coefficient and light scattering spectra is more pronounced for rarefied gases but there is a strong dependence of these quantities as the mixture becomes denser. Finally, in the Section 5 some concluding remarks are presented.

Cartesian notation for tensors is used and the Einstein summation convention over repeated indices will be adopted throughout the paper.

## 2. Basic definitions and balance equations

In the preceding article a general formalism was introduced for deriving the distribution function with the purpose of investigating some constitutive equations, namely, the reaction rate density and the pressure tensor of the mixture. In order to analyze Fick's and Fourier's law we will reintroduce in this work some variables from part I, among them the six scalar fields that describe the chemically reacting gas mixture  $A + A \rightleftharpoons B + B$ : the partial particle number densities  $n_A$  and  $n_B$ , the velocity  $v_i$  of the mixture and its temperature  $T$  which are defined in terms of the one particle distribution functions by

$$n_\alpha = \int f_\alpha \mathbf{d}\mathbf{c}_\alpha, \quad v_i = \frac{1}{n} \sum_{\alpha=A}^B \int c_i^\alpha f_\alpha \mathbf{d}\mathbf{c}_\alpha, \quad \frac{3}{2}nkT = \sum_{\alpha=A}^B \int \frac{m}{2} \xi_\alpha^2 f_\alpha \mathbf{d}\mathbf{c}_\alpha. \quad (1)$$

In the above relations  $n = n_A + n_B$  is the particle number density of the mixture,  $k$  is the Boltzmann constant,  $\xi_i^\alpha = c_i^\alpha - v_i$  is the velocity of the molecule of constituent  $\alpha$  in the mixture's rest frame and  $f_\alpha \equiv f(\mathbf{x}, \mathbf{c}_\alpha, t)$  with  $\alpha = A, B$  is the one-particle distribution function.

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