AN IMPROVED METHOD FOR THE CALCULATION OF THERMAL CONDUCTIVITIES IN THE LOW TEMPERATURE REGION OF THERMAL PLASMA PROCESSES

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Dedicated to Professor Emil Pfender in honor of his 70th birthday.

Abstract

For exact modelling of plasma applications, where the components of air and hydrogen are present, transport effects due to the multiple neutral components have to be regarded carefully. In this paper we present an advanced method for calculating the energy transfer in weakly ionized hydrogen or methane/air mixtures. Results of thermal conductivity and thermal diffusion calculations for different methane/air mixtures are given. The discussions are focused on the relative importance of the main contributions to the energy flux in a reactive environment.

Introduction

Much work has been done on transport properties of high temperature plasmas ($T > 5000\,K$), where the molecules are dissociated and the atoms are partially ionized. In many plasma applications, as in water/air stabilized electric arcs, coal gasification or in the synthesis of acetylene from methane, oxygen/air or water are present. Further examples are plasma processes where quenching methods are applied. For advanced numerical modeling of the heat transfer in those plasma processes, especially the areas where temperatures are below 5000 K have to be considered carefully. In this temperature region, with gas mixtures of a neglectable degree of ionization, the large number of species and possible chemical reactions complicate the evaluation of transport data. Therefore, we present an improved method for calculating molecular transport properties of mixtures composed of the above-mentioned components up to 5000 K. The modeling is performed using exact intermolecular and interatomic data. The calculations are based on an extended Chapman-Enskog approach to solve the Boltzmann equation, following the nonequilibrium approach proposed by Brun.

Heat Conductivity Equations

Gas-kinetic models like the classical Chapman-Enskog method do not described the molecular heat conductivity as acurate as the viscosity and the diffusion, even at a high approximation levels [1]. For exact modelling the exchange of internal energy has to be described more carefully. To overcome this theoretical limitations Brun [2] has developed a heat transfer model assuming thermal nonequilibrium for the internal degrees of freedom, i.e. relaxation effects are introduced to the theorie. As described in former papers this model was extended for the general case of relaxing gas mixtures [3, 1]. Using these results and applying known solutions for the limiting case of the equilibrium proximity, the following generalized equations (1)–(5) were developed [4, 1]. The heat conductivity due to translation in a gas mixture with ν components can be obtained by solving a linear equation system, which has been developed in respect of the Chapman-Enskog solution. An analogous equation system can be used for the evaluation of the viscosity η and as described further below for the calculation of the diffusive mass flux j [5].

$$\hat{L}^{10,10} \times \boldsymbol{\lambda}^{\mathrm{tr}} = \boldsymbol{x} \tag{1}$$

The mixture value is calculated by the summation over all components. The definition of the matrix elements L_{ij} is modified compared to those of the classical theory [6, 7]. They are functions of the molar mass M_i, the molar fractions x_i and the ratios of the elastic collision integrals

$$\begin{aligned} L_{ii}^{10,10} &= \frac{x_i^2}{[\lambda_i]_1} Eu_i + \frac{4T}{25p} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} Eu_{ik} \frac{x_i x_k \left[\frac{15}{2} M_i^2 + \frac{25}{4} M_k^2 - 3 M_k^2 B_{ik}^* + 4 M_i\, M_k\, A_{ik}^*\right]}{(M_i + M_k)^2\, \mathcal{D}_{ik}} \\ L_{ij}^{10,10} &= -\frac{4T}{25p} Eu_{ij} \frac{x_i x_j\, M_i\, M_j \left(\frac{55}{4} - 3B_{ij}^* - 4A_{ij}^*\right)}{(M_i + M_j)^2\, \mathcal{D}_{ij}} \; ; \; i \neq j \; . \end{aligned} \tag{2}$$

The term $[\lambda]_1$ represents the 1st approximation of the heat conductivity according to Chapman and Enskog [6]. The Eucken correction values Eu_{ii} and Eu_{ij} introduce the relaxation influences to the translational heat conductivity

$$Eu_{ii} = 1 + \frac{10}{3\pi} \left(1 - \frac{2}{5} \frac{\varrho D_i^{\mathrm{int}}}{\eta_i}\right) \sum_{\mathrm{int}} \frac{C_{\mathrm{int},i}}{R Z_{\mathrm{int},i}} \quad ; \quad Eu_{ij} = \sqrt{Eu_{ii} \cdot Eu_{jj}} \; . \tag{3}$$

Coupling effects of the translational heat conductivity with the internal degrees of freedom are described by the summation over all the species in the mixture.

$$\sum_{\mathrm{int}} \frac{C_{\mathrm{int},i}}{R} \frac{1}{Z_{\mathrm{int},i}} = \sum_{\mathrm{int}} \frac{C_{\mathrm{int},i}}{R} \left(\sum_{k=i}^{\nu} \frac{x_k}{\mathcal{D}_{ik}} \frac{F_{ik}}{Z_{\mathrm{int},ik}} \; \Big/ \; \sum_{k=1}^{\nu} \frac{x_k}{\mathcal{D}_{ik}} \right) \; . \tag{4}$$

The sum is taken for all internal degrees of freedom, whereby $C_{\mathrm{int},i}$ denotes the molar heat capacity $C_{v,i}$ of every individual internal degree of freedom for every species i. Thermal nonequilibrium is represented by the sum containing F_{ik}. The complete formulation can be found in [1]. The internal heat conductivity can be regarded as an approximation of a quasi elastic diffusion process [8]. For non polar or weakly polar molecules, Mason and Monchick derived the approximation $D_i^{\mathrm{int}} \stackrel{!}{=} \mathcal{D}_{ii}$ [9]. For non spherical and inelastic interaction a more exact solution is given by $D_i^{\mathrm{int}} \stackrel{!}{=} \mathcal{D}_{ii}/(1 + \delta_i)$ whereby for diatomic molecules δ_i is positive but distinctly smaller than 1 [1]. The heat conductivity of an internal degree of freedom relaxing from strong thermal nonequilibrium to near equilibrium in an ν-component mixture can be approximated by a decoupled ν-dimensional equation system,

$$\hat{L}^{01,01} \times \boldsymbol{\lambda}^{\text{int}} = \boldsymbol{x} \quad ; \quad L^{01,01}_{i,j\neq i} = 0 \tag{5}$$

where the definition of $L^{01,01}_{ii}$ depends on the type of the internal degree of freedom. The total heat conductivity is obtained by summation over all degrees of freedom. The explicit formulation for the general case of the relaxing internal degree of freedom can be simplified if it is assumed that the temperature does not differ significantly from the translational temperature and that fast relaxation takes place in equilibrium proximity. Additionaly, in the framework of this investigation ($T < 5000\,\mathrm{K}$), slow relaxation processes and electron exitation effects can be neglected. Apart from the distribution of the heat capacities on the various degrees of freedom , the relaxation of the rotational degrees of freedom has to be known as well. Experimental investigations behind shock waves show that the rotational degrees of freedom of N_2 relax within two mean free paths at low temperatures [10]. The results for thermal plasma also show that, despite the vibration and electron nonequilibrium, the rotation stays in the proximity of the translational equilibrium [11]. As a result, the term $1/Z_{\text{rot},ij}$ tends towards 1, making a conditional equation for $Z_{\text{rot},ij}$ necessary, which is given in [1] and is based on molecular data.

In chemically reactive gas mixtures the total molecular energy transport is a function of the temperature and the concentration gradients. According to the work of Obermeier and Schaber [12], the mass flux (denoted by $\boldsymbol{j}^x$) due to concentration and pressure gradients and due to external forces can be determined by solving the linear equation system (6) in the direction of the diffusion force $\boldsymbol{d}_i$.

$$\hat{K} \times \boldsymbol{j}^x = \boldsymbol{d} \tag{6}$$

The elements of the matrix $\hat{K}$ are defined as a function of the binary diffusion coefficients $\mathcal{D}_{ij}$, the molar fractions x_i and the molar masses M_i in Eq. (7). The binary diffusion coefficient is written in terms of the collision integral, the temperature and the reduced mass in Eq. (8).

$$i = j: \quad K_{ij} = 0 \qquad i \neq j: \quad K_{ij} = R \cdot \frac{T}{p} \cdot \left(\frac{x_i}{\mathcal{D}_{ij}\, M_j} + \frac{1}{M_i} \sum_{\substack{k=1 \\ k\neq i}}^{\nu} \frac{x_k}{\mathcal{D}_{ik}} \right) \tag{7}$$

$$\mathcal{D}_{ij} = \frac{3}{16} \frac{T}{p} \cdot \frac{k^2}{\mu_{ij}} \cdot \frac{T}{\Omega^{(1,1)}_{ij}} \tag{8}$$

The coupling of the thermal diffusion with the Fourier heat conductivity following the 2nd approximation according to Hirschfelder et al. [6, page 537] can be neglected for the mixtures discussed here [1]. However, the magnitude of the Dufour and Soret effect must be considered. Analogous to Fourier's law, both energy flows can be described by a heat conductivity coefficient.

$$q_{\text{Dufour}} = -\lambda_{\text{Dufour}}\, \mathrm{grad}\, T \quad ; \quad q_{\text{Soret}} = -\lambda_{\text{Soret}}\, \mathrm{grad}\, T \tag{9}$$

The quantification of the Soret and the Dufour effect necessitates the evaluation of the thermal diffusion coefficient D^{T}_i. Based on the moment method by Grad [13] and the Chapman-Enskog method, Straub has developed a formulation valid for all multi-component systems [14]. With regard to the computing expenditure, this solution is the only satisfying calculation method. Compared to other solutions, the consistent transition of the solution for trivial boundary conditions is only guaranteed by this formulation [15].

Results and Discussion

The individual shares of the molecular heat conductivity of reacting gas mixtures were calculated under the assumption of chemical equilibrium. Hereby, the various magnitudes of the different shares of λ_{total} were compared: a) Fourier heat conductivity of the translational and the internal degrees of freedom, b) Heat conductivity due to concentration diffusion, c) Heat conductivity due to concentration diffusion and due to thermal diffusion effects, d) Heat conductivity due to the Soret and the Dufour effect.

Energy transport in equilibrium air. In the dissociation regime, air can be accurately described as a 5 component mixture consisting of N_2, O_2, NO, N and O. Fig. 1 shows the sum of all heat conductivities compared to those calculated by neglecting the thermal diffusion shares for the four pressures 10^3, 10^4, 10^5 and 10^6 Pa. In this case, thermal diffusion effects can be neglected, while keeping the resulting error much smaller than the uncertainty of the underlying data. Compared to the results of Straub [15] and Raffanel [16] there are distinct deviations at high temperatures despite using the same collision data (Yun's integrals [17]). Maybe different thermodynamic data lead to deviations of the compositions and therefore to different heat conductivities.

Methane/oxygen(air) mixtures. For these mixtures, experimentally derived comparative values are not available. The applied collision integral data are proved by experimental values up to ≈ 1500 K and were adapted using a generic algorithm [5]. The error due to data uncertainty is lower than 5% in the lower temperature range, and increases to over 10% for higher temperatures ($T > 2000$ K). A methane/oxygen mixture in the dissociation range can be described by a 9-component mixture consisting of CH_4, CO_2, H_2O, CO, H_2, OH, O_2, H and O. Fig. 2 shows the heat conductivity shares for a stoichiometric mixture in the temperature range from 500 to 4000 K. Thermal diffusion yields its major influence up to 2000 K. For higher temperatures the heat conductivity is mainly influenced by reaction. For a methane/air system additionally the components N_2, NO and N must be considered. Fig. 3 shows the results for a stoichiometric methane/air mixture which are qualitatively identical to the results for the methane/oxygen mixture. In the lower temperature range thermal diffusion influences can still be discerned, but

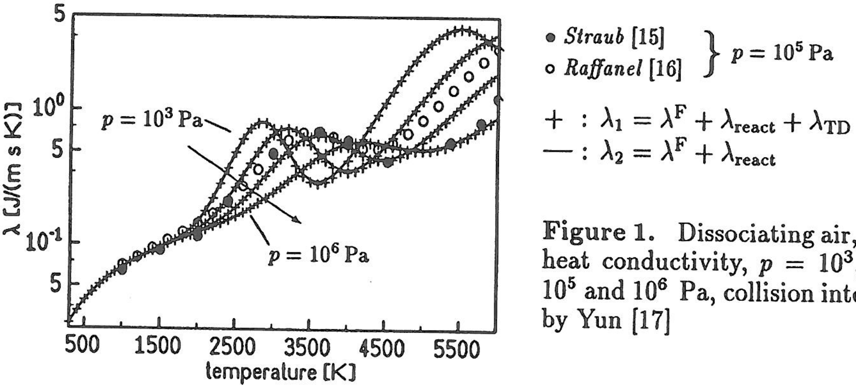
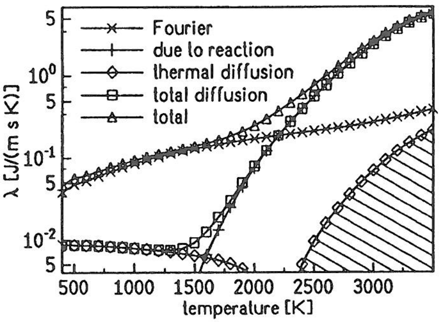


Figure 1. Dissociating air, total heat conductivity, $p = 10^3$, 10^4, 10^5 and 10^6 Pa, collision integrals by Yun [17]



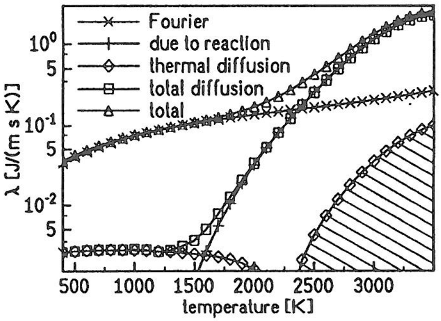


Figure 2. Methane/oxygen mixture, $\alpha = 1$, stoichiometric, chemical equilibrium, $p = 10^5$ Pa

Figure 3. Methane/air mixture, $\alpha = 1$, stoichiometric, chemical equilibrium, $p = 10^5$ Pa

they are much smaller than for a methane/oxygen mixture. As the main results of these calculations and those not jet published, it can be stated, that a) the Fourier heat conductivity makes up the main share of the total heat conductivity for low temperatures and weak composition changes, b) the heat conductivity due to concentration diffusion can greatly surpass the Fourier heat conductivity in areas with strong composition changes, c) the Soret and Dufour effect are approximately one magnitude smaller than the Fourier heat conductivity, whereby the Dufour effect always follows the heat conductivity due to reaction and is neglectably small compared to this and d) that the thermal diffusion has a significant influence on the total heat conductivity of all presented mixtures, as long as hydrogen atoms are one of their main atomic components.

Computational effectivity. The relative computation times in respect to the solution of the linear equation system (LES) (6) are displayed in Fig. 4 (see next page), comparing three different methods of calculating the mass flux. Caused by the high numerical effort for calculating determinants, the exact solution according to Hirschfelder et al. [6, page 541] is ineffective. The method of calculating the multicomponent diffusion coefficients D_{ij} proposed by Obermeier and Schaber [12] yields less accurate results with even higher numerical effort than the exact reference method. As a result, the used direct solution of equation system (6) holds the optimal results in terms of accuracy and computation time.

Conclusion

This article deals with calculation methods for the energy transport in methane/air (oxygen) mixtures which are relevant for technical plasma applications as in water/air stabilized electric arcs, coal gasification or in the synthesis of acetylene from methane. An extension of the Chapman-Enskog method exceeding the classical 1^{st} approximation for elastic collisions is applied for the evaluation of suitable calculation methods, following the method according to Brun for strongly relaxing thermal nonequilibrium. The equations presented here have optimal accuracy and at the

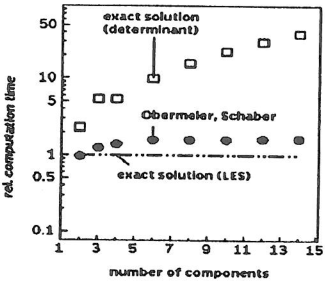


Fig. 4. Comparison of computation times for different methods

same time demand minimal numerical effort. Instead of the higher order $3\nu \times 3\nu$ heat conductivity and diffusion matrix proposed by Dixon-Lewis, the two $\nu \times \nu$ linear systems ((1), (5)) should be used without any loss of accuracy. The exact solution in the form of a linear equation system (6) for the calculation of the mass transfer rates is recommended. Thermal diffusion effects should be included in combustible mixtures using Straub's formula. Thermal diffusion processes, especially the Soret effect, are not neglectable in the methane/air mixtures investigated in this article. The importance of the various diffusive transport processes in reactive gas mixtures are subject to a dilution effect, if air is applied as oxidant or if the methane/air ratio tends towards the boundary values. As a result of this work, exact transport properties and molecular collision data for hydrogen/air(oxygen) and methane/air(oxygen) mixtures up to 5000 K are available.

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