A Transport Model for Ionized Species in Reactive Flows

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Introduction

The knowledge of transport coefficients is an essential pre-requisite for numerical simulations of reacting flows. Typical industrial applications, in which ionized species are important, are hypersonic flows around re-entry bodies, spark ignition processes in internal combustion engines, plasma etching for semiconductor manufacturing and the switching behavior of current-limiting circuit breakers.

The disadvantage of common transport models of ionized species is the high cost of the determination of the binary transport properties: The number of combinations increases with the total number of species in the mixture squared. For this reason, often models are developed, which are only valid for a fixed gas composition or for definite conditions of pressure, temperature and degree of ionization. The aim of this work is the development of a universally applicable transport model of ionized species to overcome this problem.

The new transport model is based on the classical theory of dilute gases of Chapman and Enskog. The transport coefficients in multicomponent mixtures are calculated from intermolecular potential functions (Stockmayer-(12-6-3), exponential repulsive, (n-6-4), and screened Coulomb potential) or cross sections (collisions between electrons and heavy particles). Inelastic collisions, resonant charge transfer effects and ambipolar processes are considered. Combination rules are used to determine the potential parameters from molecular input data of the pure species. This reduces the expense of the search and determination of the input properties, which now increases only linearly with the total number of species.

The example "dissociated and ionized air" is chosen to validate the new transport model, because reference values from literature are available. For a 15-species model (N_2, O_2, NO, N, O, N_2^+, O_2^+, NO^+, N^+, O^+, N^{2+}, O^{2+}, N^{3+}, O^{3+} and e^-) at pressures of $1.01325 \cdot \{10^1, 10^5 \text{ and } 10^7\}$ Pa in the temperature range from 300 to 30 000 K the equilibrium compositions are computed as steady states of a homogeneous rate equation model. Sensitivity and reaction flow analyses are performed to investigate the reaction mechanism. The calculated transport properties on the basis of these equilibrium compositions are in good agreement with the experimental and theoretical literature values.

Multicomponent Transport Formulation

The ordinary diffusion coefficients of the mixture are determined by solving a linear equation system by matrix inversion. The thermal diffusion coefficients are calculated from binary thermal diffusion ratios. Ambipolar diffusion effects are included. The viscosity and the frozen thermal conductivity of the mixture are calculated using conjugate gradient methods. The Eucken-Hirschfelder formalism [1] takes into account contributions from internal degrees of

freedom. Therefore, the thermal conductivities of the pure species are calculated by considering a modified Eucken-correction [2]. Contributions due to chemical reactions are included as (ambipolar) diffusion of specific enthalpies. All these transport coefficients are computed in the first approximation of the CE-theory, except for the transport properties of electrons. Simplified expressions for the calculation of the thermal conductivity (third approximation) and diffusion coefficients (second approximation) of electrons are used [3]. The electrical conductivity is derived from ordinary diffusion coefficients.

Simplified Model: Mixing Rules

Mixing rules are used to save computational time. The mass flux of the species i in the mixture is

$$\vec{j}_i = -\left(\rho \frac{Y_i}{X_i} D_i^{\mathrm{M}}\right) \mathrm{grad} X_i \quad , \tag{1}$$

when thermal diffusion, pressure diffusion and external forces are neglected. ρ is the total mass density, X_i and Y_i denote the mole and mass fraction of species i, respectively. The effective diffusion coefficient [2]

$$D_i^{\mathrm{M}} = \frac{1 - Y_i}{\sum\limits_{k \neq i} X_k / \left[\mathcal{D}_{ik}\right]_1} \tag{2}$$

is calculated from the binary diffusion coefficient in the first approximation of the CE-theory $[\mathcal{D}_{ik}]_1$. The ambipolar diffusion coefficients of ions are obtained by multiplying the effective diffusion coefficients by the factor of two: $\tilde{D}_i^{\mathrm{M}} \approx 2 D_i^{\mathrm{M}}$ for $i =$ ion [4]. Then the mass flux of electrons is calculated by the conservation of charge neutrality $\vec{j}_{\mathrm{e}} = \sum\limits_{i \neq \mathrm{e}}^{N_{\mathrm{g}}} Z_i \frac{M_{\mathrm{e}}}{M_i} \vec{j}_i$, whereas M_i denotes the molar mass of species i. Finally, all mass fluxes are corrected to guarantee the vanishing of the total mass flux. The viscosity η and the frozen thermal conductivity λ of the mixture are computed by a simple mixing formula [8]:

$$\nu = \left(\sum_{i=1}^{N_{\mathrm{g}}} X_i \left([\nu_i]_1 \right)^{\zeta} \right)^{1/\zeta} \quad . \tag{3}$$

The parameter ζ is set to $1/4$ in the case of $\nu = \eta$ and to $2/3$ in the case of $\nu = \lambda$. The electrical conductivity is given by [3]:

$$\sigma = \frac{e^2 X_{\mathrm{e}}}{m_{\mathrm{e}} k_{\mathrm{B}} T} \left(\rho \frac{Y_{\mathrm{e}}}{X_{\mathrm{e}}} D_{\mathrm{e}}^{\mathrm{M}} \right) \quad . \tag{4}$$

Results and Discussion

The equilibrium composition of the dissociated and ionized air is calculated as the steady-state of a rate equation model (perfectly stirred reactor) which consists of 42 elementary reactions and 15 species.

The transport coefficients of the mixture are computed on the basis of the calculated equilibrium gas compositions. The binary transport coefficients can be determined without knowing the plasma composition, and therefore they are pre-calculated as a function of temperature, except for the transport coefficients derived from collisions between charged particles. The molecular input data of the air species is taken from Ref. [9]

Binary Difussion Coefficients

In a system of 15 species 120 binary diffusion coefficients occur. Fig. 1 shows two important of them as a function of temperature at atmospheric pressure. The binary diffusion coefficients of

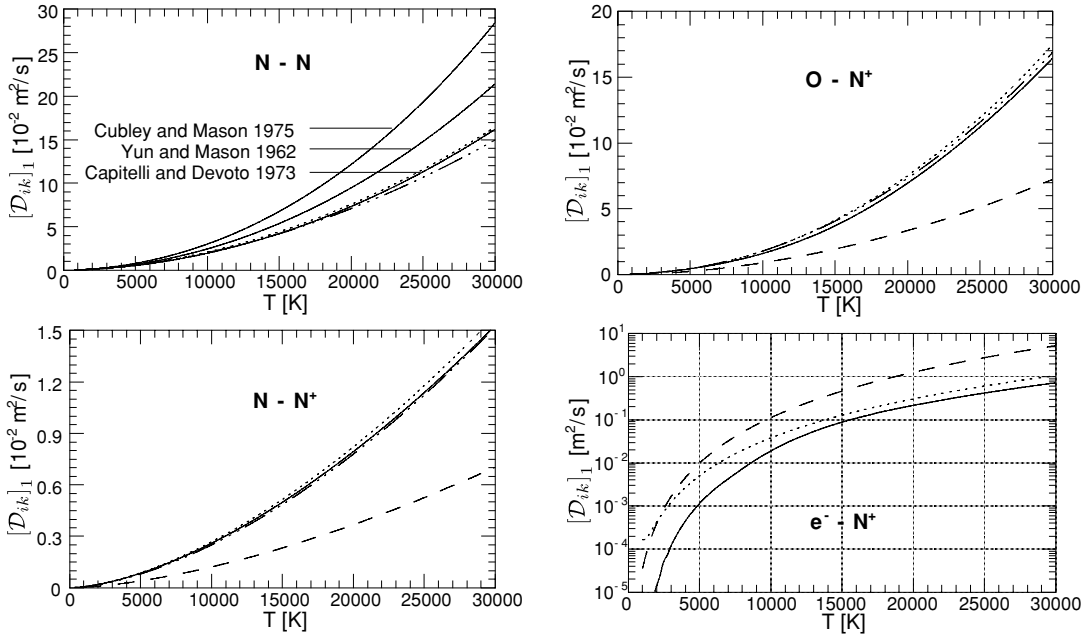

Figure 1: Binary diffusion coefficients of N-N, O-N^+, and N-N^+: Solid lines: this work, dashed lines: Yos (1963), dotted lines: Levin *et al.* (1990/91), dashed-dotted lines: Capitelli *et al.* (1998). The binary diffusion coefficients of N-N interactions are calculated for three different sets of Born-Mayer parameters. Binary diffusion coefficients of e^--N^+: Solid line: this work, dashed line: Gupta *et al.* (1990) for a fully ionized gas, dotted line: Gupta *et al.* (1990) with the electron pressure-correction.

the N-N interactions are computed for three different sets of Born-Mayer parameters. The result obtained with the set of Capitelli and Devoto [13] is in good agreement with the calculation of Levin *et al.* [12] and the recent results of Capitelli *et al.* [14], whereas the other two sets of Yun and Mason [10] and Cubley and Mason [11] lead to significant higher values. Therefore, in the present model the Born-Mayer parameters of Capitelli and Devoto are used.

The binary diffusion coefficients of the O-N^+ interactions are similar to the results from Partridge *et al.* [5]. and Capitelli *et al.* [14], but significantly higher than the computations of Yos [15]. The resonant charge transfer decreases the binary diffusion coefficients as shown in the case of the N-N^+ interaction. The result is consistent with the calculations of Stallcop *et al.* [6] and Capitelli *et al.* [14] but differs again from the calculation of Yos [15].

The binary diffusion coefficients of the e^--N^+ interactions depend on the plasma composition and vary over a wide range. Gupta *et al.* [16] have used pre-calculated collision integrals on the basis of the computations of Yos [15]. They were calculated for a fully ionized gas and then corrected by a function depending on the partial pressure of electrons. The slope of the corrected curve is similar to the one of this work, but nevertheless a difference about a factor of two is found.

Summary

To summarize, the model presented is well suited to be implemented in CFD simulations of plasma applications, where the computational time needed to compute transport quantities is an important issue in parametric studies. Higher approximations of transport properties of electrons must be included to guarantee accurate results. The simple mixing rules are more than twice as fast as the multicomponent formulation and in usual cases the accuracy is adequate, except for the computations of viscosity of ionized gases. Here, further explorations are necessary.

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