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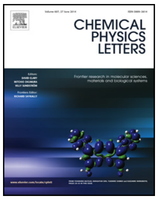

Effect of molecular diameters on state-to-state transport properties: The shear viscosity coefficient

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ABSTRACT

Shear viscosity coefficient is calculated for both equilibrium and strongly non-equilibrium state-to-state vibrational distributions taking into account increasing diameters of vibrationally excited molecules. Under conditions of local thermal equilibrium, the effect of vibrational excitation on the shear viscosity coefficient is found to be negligible for temperatures below 5000 K. For $T > 10\,000$ K, the contribution of excited states becomes important. Under non-equilibrium conditions characteristic for shock heated and supersonic expanding flows vibrational level populations deviate strongly from the Boltzmann distribution. Nevertheless, estimated coupled effect of molecular size and non-Boltzmann distributions on the shear viscosity coefficient is negligible.

1. Introduction

State-to-state modelling of non-equilibrium flows is based on the assumption that the rates of vibrational relaxation and chemical reactions are comparable with the rate of fluid dynamic parameters variation whereas translational and rotational relaxations terminate much faster. The main advantage of this approach is that it does not postulate the existence of some quasi-stationary molecular distributions over vibrational states. The idea originated in 1950s [1] for a long time was not applied to real gas flows due to considerable computational efforts required for its implementation. In 1990s, the first studies for non-equilibrium kinetics in shock waves [2–4], nozzles [5,6], flows along the stagnation line [7] have been conducted revealing an important effect of state-to-state kinetics on the dynamics of inviscid flows. Development of the kinetic theory for calculation of state-to-state transport coefficients [8,9] and chemical reaction rates [10,11] allowed applying the state-to-state approach for studying heat transfer in viscous flows. Calculations performed in Refs. [12–17] showed important peculiarities of mass and heat transfer in the absence of quasi-stationary vibrational distributions, in particular, the role of diffusion of vibrational states.

The state-to-state transport model developed in Refs. [8,9] has however a serious limitation since, to derive the final expressions for collision integrals, it is assumed that the elastic collision cross sections do not depend on the vibrational state of colliding molecules. This assumption was not systematically validated up to now. To the authors' knowledge, there is only one paper [18] containing rough estimates for the effect of excited molecule size on the state-to-state heat conductivity coefficient; for the particular case considered in that reference the effect was found to be negligible, and in all further studies it was neglected. One should mention the study performed by Nyeland and Billing [19] to calculate collision integrals accounting for excited rotational and vibrational states at low temperatures; the results are however applicable only to one-temperature thermal equilibrium gas flows. On the other hand, growing interest to the state-to-state simulations of hypersonic flows [20] requires development of accurate models for the high-temperature transport properties.

It is known that the size of molecules varies considerably for different excited states thus affecting the collision cross sections. Hirschfelder in 1957 [21] noted that electronically excited atoms become huge and therefore applying commonly used expressions for collision integrals is questionable. The effect of atomic diameters on transport properties of equilibrium plasmas is discussed in Ref. [22]; in Ref. [23] the heat conductivity of electronically excited atoms and molecules under non-equilibrium conditions was studied. It was found that at high temperature the size of atoms influences significantly the collision integrals. One can expect a similar effect in high-temperature vibrationally excited gases.

The diameters of rotationally and vibrationally excited molecules are studied in Refs. [24,25]. In these papers it was shown

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that for high vibrational states, the size of the oscillators is significantly larger compared to that of the ground state. Some new data on the vibrationally resolved collision cross sections for N_2+N system are provided in the recent papers [26,27].

The objective of the present study is to evaluate the effect of the diameter of rotationally and vibrationally excited diatomic molecules on the collision integrals required for the calculation of state-to-state shear viscosity coefficient. We consider five diatomic species, N_2, O_2, NO, H_2, Cl_2. First we calculate the size of these molecules for different excited states according to the model proposed in Refs. [24,28]. Then we evaluate the contribution of rotational states to the size of the oscillator. Next, we consider the influence of the molecular diameter on the collision integrals and shear viscosity coefficient assuming thermal equilibrium Boltzmann distribution over vibrational states. Finally, we study the shear viscosity coefficient for strongly non-equilibrium state-to-state vibrational distributions obtained under various flow conditions. Comparing the results, we establish the limits of applicability of the state-to-state transport model proposed in Refs. [8,9].

2. State-to-state transport model

The state-to-state model for transport properties was derived in Ref. [8] and then simplified in Ref. [9] to make it suitable for implementation to computational fluid dynamics. The model is based on the assumption that translational and rotational degrees of freedom equilibrate fast whereas vibrational relaxation and chemical reactions occur at the macroscopic (fluid dynamic) time scale. In such a strong non-equilibrium situation, the macroscopic variables providing the closed flow description are number densities of molecules of chemical species c at the vibrational state i, n_{ci}, gas velocity $\mathbf{v}$ and temperature T. The set of fluid dynamic equations includes the continuity, momentum and energy equations coupled to the equations of detailed vibrational–chemical kinetics for n_{ci}. Using the modification of the Chapman–Enskog method, the stress tensor, the total energy flux as well as diffusion velocities for each vibrational level can be expressed in terms of gradients of macroscopic variables and transport coefficients. The peculiarity of the state-to-state model is that the heat transfer is specified not only by heat conduction (which is associated with the transfer of rotational and translational energy), mass and thermal diffusion, but also by diffusion of vibrational states. The number of independent diffusion coefficients is determined by the total number of vibrational states in the mixture.

Although the state-to-state approach has many distinctive features, the general Chapman–Enskog procedure still can be applied for the calculation of transport coefficients. The state-resolved algorithm for evaluating the transport properties is described in details in Refs. [8,9,11]. In the general Chapman–Enskog procedure to determine the non-equilibrium distribution function for molecular gases from the Boltzmann equation, the scalar coefficients which appear in the first-order approximation of the distribution function are expanded in terms of Sonine–Waldmann-Trübenbacher polynomials. Using this algorithm, all transport coefficients can be expressed in terms of bracket integrals depending on chemical species and vibrational states of the collision partners. The bracket integrals are determined by the cross sections of rapid processes, i.e. elastic collisions and those resulting in the rotational energy exchange [8].

In this work we are interested in the influence of the size of vibrationally and rotationally excited molecules on the collision integrals and viscosity coefficient of a single gas. In the case of binary collisions between two molecules of the same species with mass m whose vibrational levels are denoted by i, k and rotational states by j, l, the shear viscosity coefficient η is expressed in terms of the scalar coefficients b_i of the first Sonine–Waldmann-Trübenbacher polynomial representation by [14]

$$\eta = \frac{kT}{2}\sum_i x_i b_i, \tag{1}$$

where k denotes the Boltzmann constant and $x_i = n_i/n$ is the molar fraction of molecules at the ith vibrational state (n_i is its number density, $n = \sum_i n_i$). Keeping only the first non-vanishing terms in the expansions we can determine the system of algebraic equations for the calculation of the scalar coefficients b_i

$$\sum_k H_{ik} b_k = \frac{2}{kT} x_i, \quad i, k = 0, \ldots, i_{\max}, \tag{2}$$

where $i_{\max}$ is the maximum number of considered vibrational levels. Here, the bracket integrals H_{ik} are given by

$$H_{ik} = \frac{1}{2}\frac{x_i x_k}{\eta_{ik}}\left(1 - \frac{5}{3A_{ik}}\right), \quad \forall i \neq k, \tag{3}$$

$$H_{ii} = \frac{1}{2}\sum_{k \neq i}\frac{x_i x_k}{\eta_{ik}}\left(1 + \frac{5}{3A_{ik}}\right) + \frac{x_i^2}{\eta_{ii}}, \tag{4}$$

where the following quantities were introduced

$$\eta_{ik} = \frac{5}{8}\frac{kT}{\Omega_{ik}^{(2,2)}}, \quad A_{ik} = \frac{1}{2}\frac{\Omega_{ik}^{(2,2)}}{\Omega_{ik}^{(1,1)}}, \tag{5}$$

$$\Omega_{ik}^{(1,1)} = \sqrt{\frac{kT}{\pi m}}\sum_{jj'll'}\frac{(2j+1)(2l+1)}{[Z^{\mathrm{rot}}(T)]^2}\int e^{-\gamma^2-\epsilon_j-\epsilon_l}\left(\gamma^2 - \gamma\gamma'\cos\chi\right) \times\sigma_{ijkl}^{j'l'}\, d^2\Omega\, \gamma^3\, d\gamma, \tag{6}$$

$$\Omega_{ik}^{(2,2)} = \sqrt{\frac{kT}{\pi m}}\sum_{jj'll'}\frac{(2j+1)(2l+1)}{[Z^{\mathrm{rot}}(T)]^2} \times\int e^{-\gamma^2-\epsilon_j-\epsilon_l}\left(\gamma^4 - \gamma^2\gamma'^2\cos\chi - \frac{(\Delta\epsilon^{\mathrm{rot}})^2}{6}\right)\sigma_{ijkl}^{j'l'}\, d^2\Omega\, \gamma^3\, d\gamma. \tag{7}$$

Above $Z^{\mathrm{rot}}(T) = \sum_j (2j+1)\exp(-\epsilon_j)$ is the rotational partition function, $\gamma = \sqrt{g^2/4kT}$ is a dimensionless relative velocity and $\epsilon_j = \varepsilon_j/kT$ a dimensionless molecular energy in the rotational level j. Furthermore, the binary collision is characterized by the inelastic differential cross-section $\sigma_{ijkl}^{j'l'}$, the element of solid angle $d^2\Omega$, the scattering angle χ, and the primes refer to post-collision values of relative velocities and rotational levels. The dimensionless energy conservation law is expressed by $\gamma'^2 - \gamma^2 = \Delta\epsilon^{\mathrm{rot}} = \epsilon_j - \epsilon_{j'} + \epsilon_l - \epsilon_{l'}$.

Other transport coefficients are given in terms of bracket integrals which are defined similarly in terms of the same variables.

The main problem in evaluating the bracket integrals is the lack of knowledge on the elastic and inelastic collision cross sections. A commonly used practice is to assume that the cross section $\sigma_{ijkl}^{j'l'}$ is equal to that for the elastic collision and does not depend on the quantum states of colliding particles. This assumption allows simplifications in the calculation of the linear systems for the transport coefficients [9]. However the limits of applicability for this assumption have not been established up to now. In the next sections we discuss the dependence of the collision integrals and shear viscosity coefficient on the molecular diameters.

3. Molecular diameters

As was previously pointed out we are interested in investigating the influence of the quantum states on the bracket integrals. In