Chemical Physics 445 (2014) 82–94

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Chemical reaction rates and non-equilibrium pressure of reacting gas mixtures in the state-to-state approach

Elena V. Kustova [a,*], Gilberto M. Kremer [b]

[a] Department of Mathematics and Mechanics, Saint Petersburg State University, 198504 Universitetskiy pr. 28, Saint Petersburg, Russia
[b] Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19044, 81531-980 Curitiba, Brazil

ARTICLE INFO

Article history:
Received 25 August 2014
In final form 24 October 2014
Available online 1 November 2014

Keywords:
Rate of vibrational transitions and chemical reactions
Non-equilibrium pressure
Transport coefficients

ABSTRACT

Viscous gas flows with vibrational relaxation and chemical reactions in the state-to-state approach are analyzed. A modified Chapman–Enskog method is used for the determination of chemical reaction and vibrational transition rates and non-equilibrium pressure. Constitutive equations depend on the thermodynamic forces: velocity divergence and chemical reaction/transition affinity. As an application, N_2 flow with vibrational relaxation across a shock wave is investigated. Two distinct processes occur behind the shock: for small values of the distance the affinity is large and vibrational relaxation is in its initial stage; for large distances the affinity is small and the chemical reaction is in its final stage. The affinity contributes more to the transition rate than the velocity divergence and the effect of these two contributions are more important for small distances from the shock front. For the non-equilibrium pressure, the term associated with the bulk viscosity increases by a small amount the hydrostatic pressure.

1. Introduction

The molecules of gas mixtures at high temperatures in supersonic and hypersonic flows are often characterized by equilibration of translational and rotational degrees of freedom in a time that is shorter than those of vibrational relaxation and chemical reactions. In this case one may split the collisional operator of the Boltzmann equation into one operator that describes the rapid processes (elastic and rotational energy exchanges) and another connected with the slow processes (vibrational energy exchanges and chemical reactions). While the local equilibrium description is determined by Maxwell–Boltzmann distribution functions over the velocities and rotational energy levels, it is necessary to represent the non-equilibrium vibrational and chemical kinetics in terms of master equations which take into account the cross sections for the chemical reactions and the vibrational transition probabilities (the so-called state-to-state approach).

The idea of using the state-to-state model for investigation of vibrational kinetics belongs to Montroll and Shuler [1]. It took almost forty years to start applying this detailed description to real gas flows because of its high computational costs and lack of data on the state-specific rate coefficients of internal energy transitions. First, inviscid flows behind shock waves [2–4] and in nozzles [5,6] were studied. Recently, due to increased computer power, advanced numerical methods and new data sets for the cross sections of inelastic collisions allowed investigating the case of coupled state-to-state rovibrational relaxation [7,8] in inviscid flows. In the meanwhile the need for the state-to-state simulations of viscous flows was revealed to be important to analyze heat and mass transfer. First attempts to study viscous shock and boundary layers were done in Refs. [9,10]. However in these studies a rigorous formulation of transport phenomena was missing. In [11,12], the kinetic theory algorithms for the state-specific transport properties were developed, and then applied to the assessment of heat fluxes in various flows of air species [13–16] and carbon dioxide [17,18]. The weakness of these studies is that the rates of non-equilibrium processes are calculated neglecting deviations of the distribution function from the Maxwell–Boltzmann.

Interest in the effect of non-Maxwell distributions on chemical reaction rates arises starting from the works by Prigogine [19] and successors [20–25]. First results were obtained neglecting internal degrees of freedom. Later, chemical reaction rates in gases with internal modes under conditions of weak thermal and strong chemical non-equilibrium were studied theoretically in Refs. [26,23,27,15,28,29] but no applications to compressible gas flows were considered up to the present time except for a few examples given in [28]. Non-equilibrium reaction rates in multi-temperature viscous flows with vibrational–translational relaxation were discussed in [30,15,31–33] but never used in viscous flow

* Corresponding author.
E-mail addresses: e.kustova@spbu.ru (E.V. Kustova), kremer@fisica.ufpr.br (G.M. Kremer).

http://dx.doi.org/10.1016/j.chemphys.2014.10.019
0301-0104/

simulations. We do not discuss here different CVDV (Coupled-Vibration–Dissociation-Vibration) models like the widely used Treanor–Marrone model [34] since they are not derived in a self-consistent way from kinetic theory principles and can be applied only to inviscid flows. Some basic ideas of the correct description for the state-to-state reaction and internal energy transition rates in viscous flows are proposed in [35,15,36]; however the theory is not completed and no application to real gas flows have been given so far. It is worth noting that the analysis of the state-to-state model is formally similar to that of equilibrium reactive mixtures, where the species are taken as pseudo-species and by assuming that each vibrational state is considered to be a distinct molecule.

The objective of this work is to develop a self-consistent kinetic model for the chemical reaction and vibrational energy transition rates in the state-to-state approach; to derive the constitutive equations for the rates of non-equilibrium processes and to calculate the corresponding transport coefficients. The chemical reaction rates and normal mean stress are functions of two scalar forces, the generalized affinity and the divergence of the hydrodynamic velocity, and the kinetic coefficients associated with these forces are obtained from integral equations that follow by applying the modified Chapman–Enskog formalism to the system of Boltzmann equations written in the Wang Chang–Uhlenbeck form [15,29,36]. Zero- and first-order approximations of the Chapman–Enskog method are considered; the detailed algorithm for the calculation of the first-order corrections to the rates of non-equilibrium processes and pressure tensor is proposed. As an application, a nitrogen flow is analyzed where only a few lowest vibrational states of N_2 are taken into account. The mutual effect of different energy transitions is evaluated for this simplified case.

2. Boltzmann equation for reacting gas mixtures

We are interested in analyzing a reacting gas mixture with bimolecular reactions and reactions of dissociation–recombination. A bimolecular reaction is represented by

$$A_c(\mathbf{u}_c, i, j) + A_d(\mathbf{u}_d, k, l) \rightleftharpoons A_{c'}(\mathbf{u}'_{c'}, i', j') + A_{d'}(\mathbf{u}'_{d'}, k', l'), \tag{1}$$

where $\mathbf{u}_c$ and $\mathbf{u}_d$ denote the linear velocities of the molecules of the constituents c and d with i, k designating their vibrational levels, while j, l their corresponding rotational states. After the reaction the values of the velocities, vibrational and rotational levels are labeled by a prime.

The dissociation reaction for a diatomic molecule can be written as

$$A_c(\mathbf{u}_c, i, j) + A_d(\mathbf{u}_d, k, l) \rightleftharpoons A_{c'}(\mathbf{u}_{c'}) + A_{f'}(\mathbf{u}_{f'}) + A_d(\mathbf{u}'_d, k', l'), \tag{2}$$

with c', f' indicating the atomic species which are formed as reaction products, while $\mathbf{u}_{c'}, \mathbf{u}_{f'}, \mathbf{u}'_d$ are the particle velocities after the collision.

In the phase space spanned by the coordinates $\mathbf{r}$ and velocities $\mathbf{u}_c$ we introduce the distribution function $f_{cij} = f_{cij}(\mathbf{r}, \mathbf{u}_c, t)$ of constituent c in the vibrational and rotational levels i, j. The evolution of f_{cij} is ruled by the Boltzmann equation – which without external forces and torques – reads

$$\frac{\partial f_{cij}}{\partial t} + \mathbf{u}_c \cdot \nabla f_{cij} = J^E_{cij} + J^I_{cij} + J^R_{cij}, \quad J^R_{cij} = J^{RE}_{cij} + J^{RD}_{cij}. \tag{3}$$

For gases without chemical reactions this form of the Boltzmann equation was proposed by Wang Chang–Uhlenbeck [37]. The elastic J^E_{cij}, inelastic J^I_{cij}, and reactive J^R_{cij} (J^{RE}_{cij} for exchange and J^{RD}_{cij} for dissociation reactions) collision terms in (3) are given by

$$J^E_{cij} = \sum_d \sum_k \sum_l \int \left(f'_{cij} f'_{dkl} - f_{cij} f_{dkl} \right) \sigma^{ijkl}_{ijkl} g\, d^2\Omega\, d\mathbf{u}_d, \tag{4}$$

$$J^I_{cij} = \sum_d \sum_{i',k',k} \sum_{j',l',l} \int \left(f'_{ci'j'} f'_{dk'l'} \frac{s^{ci}_j s^{dk}_l}{s^{c'i'}_{j'} s^{d'k'}_{l'}} - f_{cij} f_{dkl} \right) \times \sigma^{i'j'k'l'}_{ijkl} g\, d^2\Omega\, d\mathbf{u}_d, \tag{5}$$

$$J^{RE}_{cij} = \sum_{c',d',d} \sum_{i',k',k} \sum_{j',l',l} \int \left[f_{c'i'j'} f_{d'k'l'} \frac{s^{ci}_j s^{dk}_l}{s^{c'i'}_{j'} s^{d'k'}_{l'}} \left(\frac{m_c m_d}{m_{c'} m_{d'}} \right)^3 - f_{cij} f_{dkl} \right] \\ \times \sigma^{c'd'i'j'k'l'}_{cd\,ijkl} g\, d^2\Omega\, d\mathbf{u}_d, \tag{6}$$

$$J^{RD}_{cij} = \sum_d \sum_{k',k} \sum_{l',l} \int \left[f_{dk'l'} f_{c'} f_{f'} h^3 s^{ci}_j \left(\frac{m_c}{m_{c'} m_{f'}} \right)^3 - f_{cij} f_{dkl} \right] \\ \times g \sigma^{c'f'dk'l'}_{cd\,ijkl}\, d\mathbf{u}_{c'}\, d\mathbf{u}_{f'}\, d\mathbf{u}'_d\, d\mathbf{u}_d. \tag{7}$$

Here $\sigma^{ijkl}_{ijkl}, \sigma^{i'j'k'l'}_{ijkl}$ and $\sigma^{c'd'i'j'k'l'}_{cd\,ijkl}, \sigma^{c'f'dk'l'}_{cd\,ijkl}$ represent the elastic, inelastic, and reactive differential cross-sections for exchange and dissociation reactions, respectively, and $d^2\Omega$ the element of solid angle that characterizes the binary collisions in the direction of outgoing relative velocity. Furthermore m_c, m_d are the masses of the constituents, s^{ci}_j, s^{dk}_l the statistical weight of the molecular state degeneracy with internal energy ε^c_{ij} and h the Planck constant.

We shall assume that (i) the rotational cross sections are averaged over degenerated states, so that they do not depend on the magnetic quantum numbers – which are related with the angular momentum projection on a fixed axis – and (ii) the rotational statistical weight corresponds to the equiprobable distribution on the directions of internal momentum which is given by $s^{ci}_j = 2j + 1$. This last assumption is not valid for asymmetrical molecules, where three unequal moments of inertia about the principal axes could be found. These two assumptions are commonly used if the gas mixture is not in the presence of magnetic or electrical fields. In order to simplify the calculations we introduce also the following additional assumptions: (iii) the cross sections of vibrational and rotational transitions are independent and (iv) the molecular rotations are simulated by the rigid rotor. The assumption (iii) must be taken with some care, since rovibrational relaxations could be important in the analysis of some viscous flows. Here we assume that the reacting mixture is in a temperature range where the rotational degrees of freedom are completely excited, so that the influence of the vibrational modes do not have an important contribution to the rotational ones.

The last assumptions imply that the rotational ε^c_j and vibrational ε^c_i energies are independent from each other and that the inelastic collision operator may be split into two terms $J^I_{cij} = J^{\text{rot}}_{cij} + J^{\text{vibr}}_{cij}$, where the rotational and vibrational collision operators are given by

$$J^{\text{rot}}_{cij} = \sum_d \sum_{j',l',l,k} \int \left(f'_{cij'} f'_{dkl'} \frac{(2j+1)(2l+1)}{(2j'+1)(2l'+1)} - f_{cij} f_{dkl} \right) \times \sigma^{j'l'}_{jl} g\, d^2\Omega\, d\mathbf{u}_d, \tag{8}$$

$$J^{\text{vibr}}_{cij} = \sum_d \sum_{i',k',k,l} \int \left(f_{ci'j} f_{dk'l} - f_{cij} f_{dkl} \right) \sigma^{i'k'}_{ik} g\, d^2\Omega\, d\mathbf{u}_d. \tag{9}$$

Above we have introduced the differential cross-sections $\sigma^{j'l'}_{jl} \equiv \sigma^{ij'kl'}_{ijkl}$ and $\sigma^{i'k'}_{ik} \equiv \sigma^{i'jk'l}_{ijkl}$.

3. Characteristic times and dimensionless Boltzmann equation

In this work we shall consider the state-to-state model of coupled vibrational relaxation and chemical reactions based on the following characteristic time relations:

$$\tau_E < \tau_{\text{rot}} \ll \tau_{\text{vibr}} < \tau_R \sim \theta. \tag{10}$$

Above θ is the gas-dynamic time scale and