Progress in Flight Physics **9** (2017) 327-334
DOI: 10.1051/eucass/201709327

HEAT FLUX AND DIFFUSION VELOCITIES BEHIND SHOCK WAVE: STATE-TO-STATE APPROACH

O. Kunova, E. Kustova, M. Mekhonoshina,
and E. Nagnibeda

Department of Mathematics and Mechanics
St. Petersburg State University
28 Universitetskiy Pr., St. Petersburg 198504, Russia

The influence of vibrational populations and dissociation–recombination reactions on the heat and mass transfer in the relaxation zone behind shock waves is studied. The contribution of various processes and influence of different initial conditions on diffusion velocities and total energy flux in the flows of shock heated air components is estimated.

1 INTRODUCTION

In the present paper, nonequilibrium vibration–dissociation kinetics of N_2/N and O_2/O mixtures and its influence on diffusion and heat transfer in relaxation zone behind shock waves are studied. For the description of nonequilibrium reacting gas flows, the most accurate model [1] based on detailed state-to-state molecular distributions over internal energy levels is used. This approach receives much attention for investigation of different gas flows; in shock heated gases, the state-to-state kinetics has been studied in a number of papers [2–6]. Unfortunately, the practical implementation of the state-to-state approach for viscous reacting mixtures occurs extremely computationally consuming since a large number of equations for vibrational distributions should be solved; moreover, at each time and space step of numerical simulation, the state-dependent transport coefficients have to be computed solving the high-rank transport linear systems containing equations for each chemical component and vibration level. A simplified algorithm for the transport coefficients calculation which reduces noticeably the number of equations has been proposed in [7]. Nevertheless, direct implementation of state-to-state transport algorithms is still complicated. In the present paper, a simplified approach applying a postprocessing procedure is used: first, the gasdynamic parameters and their derivatives are calculated for an inviscid flow and then, the transport terms are evaluated on the basis of this solution. In this way, the impact of nonequilibrium kinetics on the heat transfer has been studied in shock heated mixtures. The contribution of various processes and the influence of different initial conditions on diffusion velocities and total energy flux in the flows of air components have been estimated.

2 KINETICS BEHIND THE SHOCK WAVE

In the present paper, inviscid flows of N_2/N and O_2/O mixtures in the relaxation zone have been considered behind a plane shock wave. The kinetic scheme for the binary mixtures includes vibrational energy exchanges at the collisions of molecules (VV), exchanges of translational and vibrational energies (VT), and dissociation and recombination reactions. A nonequilibrium flow under the considered conditions is described by the equations for the vibrational level populations n_i of molecular species and number densities of atoms n_a coupled to the conservation equations for the momentum and total energy [1]:

$$\frac{d(v\,n_i)}{dx} = R_i^{\mathrm{VT}} + R_i^{\mathrm{VV}} + R_i^{\text{diss-rec}}\,, \quad i = 0, 1, \ldots l; \tag{1}$$

$$\frac{d(v\,n_a)}{dx} = -2\sum_i R_i^{\text{diss-rec}}\,; \tag{2}$$

$$\rho_0 v_0^2 + p_0 = \rho\, v^2 + p\,; \tag{3}$$

$$h_0 + \frac{v_0^2}{2} = h + \frac{v^2}{2}\,. \tag{4}$$

Here, x is the distance from the shock front; $p = nk_BT$ is the pressure; n is the mixture number density; T is the gas temperature; k_B is the Boltzmann constant; v is the macroscopic velocity; and the subscript "0" denotes the parameters in the free stream. In Eq. (4),

$$h = h_m\frac{\rho_m}{\rho} + h_a\frac{\rho_a}{\rho}$$

where ρ is the mixture density and ρ_m, ρ_a, h_m, and h_a are the mass densities and specific enthalpy of molecular and atomic components:

$$h_a = \frac{5}{2}\,\bar{R}_aT + \frac{\varepsilon_a}{m_a}\,; \qquad h_m = \frac{7}{2}\,\bar{R}_mT + \frac{1}{\rho_m}\sum_i \varepsilon_i n_i\,,$$

with $\bar{R}_m$ and $\bar{R}_a$ being the specific gas constants of molecules N_2 and O_2 and atoms N and O, m_a being the atom mass, ε_i being the vibrational energy of a molecule at the ith vibrational level, and ε_a being the formation energy of atoms. In calculations, the vibrational energy is simulated by the anharmonic oscillator model with total numbers of vibrational levels $l = 46$ for N_2 and $l = 35$ for O_2.

The right-hand sides of Eqs. (1) and (2) contain the state-dependent rate coefficients of considered VV and VT energy transitions and dissociation–recombination reactions. The rate coefficients for vibrational energy transitions in the source terms R_i^{VT} and R_i^{VV} are calculated using the generalized Schwartz, Slawsky, and Herzfeld formulas [8, 9], rate coefficients of dissociation are described by the Treanor–Marrone model [10] modified for state-to-state approach [1]. Rate coefficients of forward and backward kinetic processes are connected by the detailed balance principle.

3 DIFFUSION AND HEAT FLUX

Expressions for diffusion velocities and heat flux can be written on the basis of state-to-state approach as follows [1]:

$$\mathbf{V}_i = \mathbf{V}_i^{\mathrm{TD}} + \mathbf{V}_i^{\mathrm{MD}} + \mathbf{V}_i^{\mathrm{DVE}}\,; \quad \mathbf{V}_a = \mathbf{V}_a^{\mathrm{TD}} + \mathbf{V}_a^{\mathrm{MD}}\,;$$

$$\mathbf{q} = \mathbf{q}^{\mathrm{HC}} + \mathbf{q}^{\mathrm{MD}} + \mathbf{q}^{\mathrm{TD}} + \mathbf{q}^{\mathrm{DVE}}\,.$$

Here, $\mathbf{V}_i^{\mathrm{MD}}$, $\mathbf{V}_a^{\mathrm{MD}}$, $\mathbf{V}_i^{\mathrm{TD}}$, $\mathbf{V}_a^{\mathrm{TD}}$, and $\mathbf{V}_i^{\mathrm{DVE}}$ are the contributions of the mass diffusion, thermal diffusion, and diffusion of vibrational energy:

$$\mathbf{V}_i^{\mathrm{MD}} = -D_{mm}\mathbf{d}_m - D_{ma}\mathbf{d}_a\,; \quad \mathbf{V}_i^{\mathrm{TD}} = -D_{Tm}\nabla \ln T\,;$$

$$\mathbf{V}_i^{\mathrm{DVE}} = -n\left(\frac{n_m}{D_{mm}} + \frac{n_a}{D_{ma}}\right)^{-1} \nabla \ln \frac{n_i}{n_m}\,;$$

$$\mathbf{V}_a^{\mathrm{MD}} = -D_{ma}\mathbf{d}_m - D_{aa}\mathbf{d}_a\,; \quad \mathbf{V}_a^{\mathrm{TD}} = -D_{Ta}\nabla \ln T\,;$$

$\mathbf{q}^{\mathrm{HC}}$, $\mathbf{q}^{\mathrm{MD}}$, $\mathbf{q}^{\mathrm{TD}}$, and $\mathbf{q}^{\mathrm{DVE}}$ are the energy fluxes associated with the heat conductivity of translational and rotational degrees of freedom (Fourier flux), mass diffusion, thermal diffusion, and the transfer of vibrational energy carried by excited molecules:

$$\mathbf{q}^{\mathrm{HC}} = -\lambda'\nabla T\,; \quad \mathbf{q}^{\mathrm{MD}} = \rho_m h_m \mathbf{V}_m^{\mathrm{MD}} + \rho_a h_a \mathbf{V}_a^{\mathrm{MD}}\,;$$

$$\mathbf{q}^{\mathrm{TD}} = -p(D_{Tm}\mathbf{d}_m + D_{Ta}\mathbf{d}_a) + \rho_m h_m \mathbf{V}_m^{\mathrm{TD}} + \rho_a h_a \mathbf{V}_a^{\mathrm{TD}}\,;$$

$$\mathbf{q}^{\mathrm{DVE}} = \sum_i \left(\frac{5}{2}k_B T + \langle \varepsilon^i \rangle_{\mathrm{rot}} + \varepsilon_i\right) n_i \mathbf{V}_i^{\mathrm{DVE}}\,.$$

Here, D_{mm}, D_{ma}, D_{aa}, D_{Tm}, and D_{Ta} are the multicomponent diffusion and thermal diffusion coefficients for each molecule and atom; $\mathbf{d}_m$ and $\mathbf{d}_a$ are the diffusive driving forces depending on gradients of the level populations and atom densities; and λ' is the thermal conductivity coefficient.

4 RESULTS

First, let us present the flow parameters obtained as a solution of Eqs. (1)–(4) in the relaxation zone behind the shock wave under the following conditions in the free stream: $T_0 = 271$ K; $p_0 = 100$ Pa; $M_0 = 15$ and 18; $n_m = p_0/(k_B T_0)$; and $n_a = 0$. Initial distributions in the free stream are assumed to be the Boltzmann ones with the temperature T_0. The gas parameters just behind the shock are found with the use of the Rankine–Hugoniot relations under the assumption of frozen vibrational distributions and mixture composition within the shock front.

Figure 1*a* shows the variation of the gas temperature in N_2/N and O_2/O mixtures with respect to the distance from the shock front. One can notice that the relaxation process in O_2/O mixture proceeds much faster and more actively than in the mixture of nitrogen molecules and atoms. In particular, one can see slower decrease in the gas temperature for N_2/N mixture than for O_2/O in the beginning of the relaxation zone. Then, the value of temperature in N_2/N mixture occurs about twice higher than in O_2/O mixture for both Mach numbers.

Figure 1*b* depicts number densities of N and O atoms as functions of x and shows intensive dissociation of O_2 molecules for both cases. The difference between $n_{\rm N}$ and $n_{\rm O}$ is explained, firstly, by the high rates of the vibrational energy transfer of O_2 molecules, in consequence of which the excitation of the oxygen molecules occurs in a narrow zone behind the shock front compared to the nitrogen molecules. Secondly, dissociation of oxygen is considerably more active than dissociation of nitrogen. These facts are illustrated also in Fig. 2 which show the level populations of nitrogen and oxygen molecules in the relaxation zone for different M_0. One can see that level populations (for $i > 0$) rise in the beginning

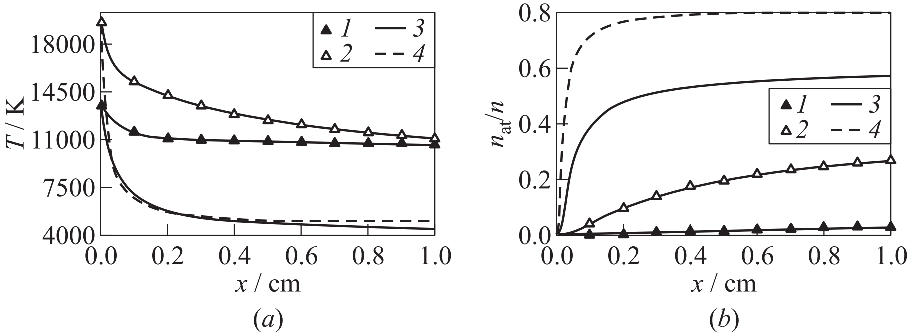
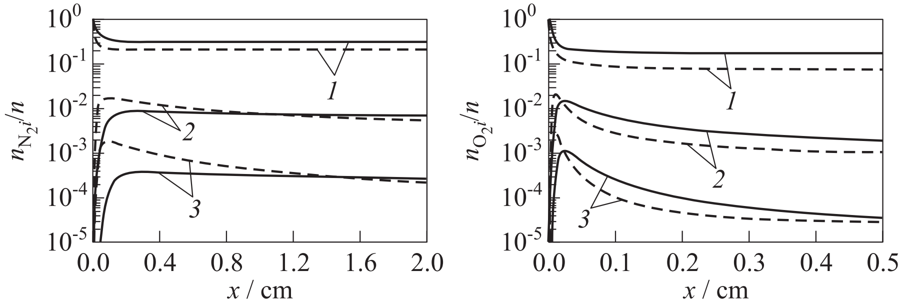
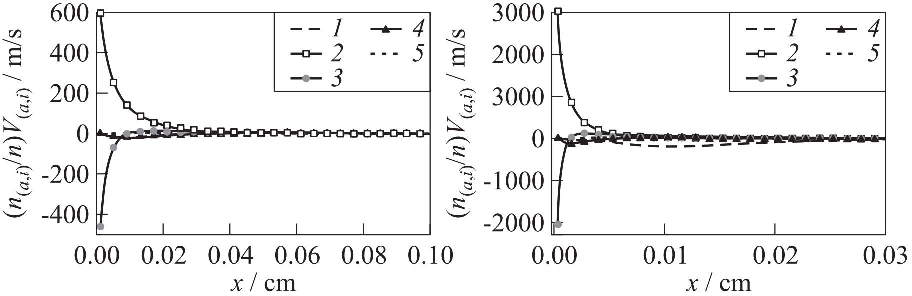


Figure 1 Temperature T (*a*) and atomic molar fractions $n_{\rm N}/n$ and $n_{\rm O}/n$ (*b*) as functions of x: *1* — N_2/N, $M_0 = 15$; *2* — N_2/N, $M_0 = 18$; *3* — O_2/O, $M_0 = 15$; and *4* — O_2/O, $M_0 = 18$



(*a*) (*b*)

Figure 2 Vibrational level populations $n_{N_2 i}/n$ (a) and $n_{O_2 i}/n$ (b) as functions of x: *1* — $i = 0$; *2* — 10; *3* — $i = 20$; solid curves — $M_0 = 15$; and dashed curves — $M_0 = 18$



(*a*) (*b*)

Figure 3 Diffusion fluxes behind the shock as a function of x for $M_0 = 18$; (a) N_2/N; (b) O_2/O; *1* — atoms; *2* — $i = 0$; *3* — 1; *4* — 5; and *5* — $i = 30$

of relaxation zone as a consequence of TV excitation and then slightly decrease due to VT deactivation and dissociation.

Self-consistent calculation of the transport terms is extremely time-consuming, it requires the solution of transport linear systems at each step of computations. Since we are interested in preliminary estimates of qualitative behavior of the fluxes, let us use a simplified approach. For the investigation of transport processes, let us substitute the macroparameters and their gradients obtained as solutions of the inviscid flow equations into the expressions of diffusion velocities and total heat flux.

As one can see (Fig. 3), diffusion fluxes of high vibrational states are weak; the most important contribution is given by $i = 0$ and 1. It is seen that the mass diffusion flux for nitrogen atoms is negligible since dissociation of N_2 molecules

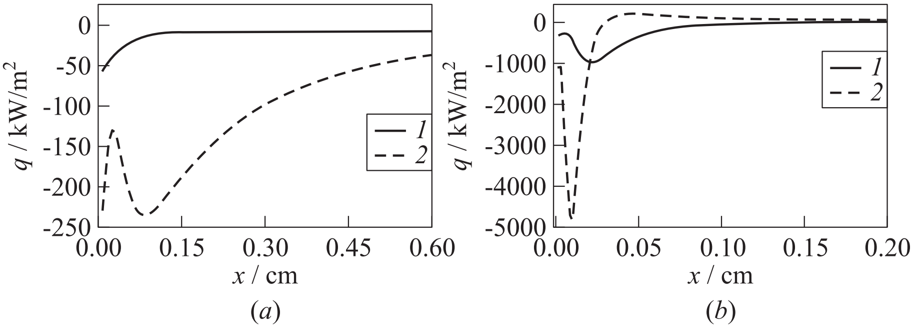


Figure 4 Total heat flux behind the shock as a function of x for $M_0 = 15$ (*1*) and 18 (*2*): (*a*) N_2/N; and (*b*) O_2/O

is rather slow; for oxygen atoms, the mass diffusion reaches its maximum, when diffusion fluxes for all molecular vibrational states n_iV_i/n become zero. For both mixtures, n_aV_a/n is small near the shock front due to the existence of finite incubation time for the dissociation reaction. Since vibrational excitation proceeds faster in oxygen, the values of n_iV_i/n are greater in O_2/O mixture.

Figure 4 presents the variation of the total heat flux in the relaxation zone for different Mach numbers. Let us discuss first the nitrogen mixture. One can see that for $M_0 = 15$, the total heat flux varies strongly near the shock front, then (for $x > 0.2$ cm), it is almost constant. One can notice nonmonotonic behavior of the total heat flux with x for $M_0 = 18$ which is explained by the strong competition of different dissipative processes near the shock front. For oxygen mixture, one can see qualitatively similar results. But competition of different processes and, as a consequence, nonmonotonic heat flux behavior occurs already for $M_0 = 15$. The absolute value of total heat flux is significantly larger for oxygen, because all the processes proceed faster and the gradients of gasdynamic variables are larger than for nitrogen.

To understand the reason for different behavior of the total heat flux for various initial conditions, let us consider the contributions of multiple dissipative processes to the total energy flux (Fig. 5). The Fourier flux due to heat conductivity q^{HC} and the flux caused by the diffusion of vibrational energy q^{DVE} give the contribution of the same order near the shock front and their absolute values are rather high near the shock front. The signs of these terms are opposite which causes a strong compensation effect leading to much lower values of the total flux q. The contribution of the vibrational energy diffusion to the heat flux in shock heated flows occurs dominating and it leads to the negative sign of q. The influence of mass diffusion becomes noticeable only at $x > 0.05$ cm for nitrogen and at $x > 0.02$ cm for oxygen mixture due to the dissociation incubation time. At such distance from the shock front, the influence of q^{HC} and q^{DVE}

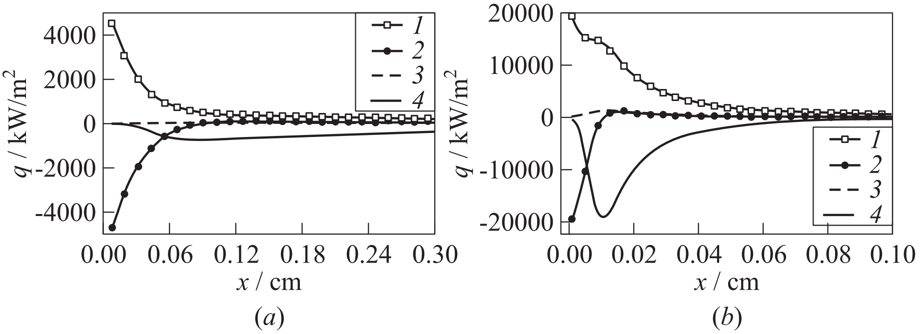


Figure 5 The total heat flux behind the shock as a function of x for $M_0 = 18$; (*a*) N_2/N; (*b*) O_2/O; *1* — q^{HC}; *2* — q^{DVE}; *3* — q^{TD}; and *4* — q^{MD}

becomes smaller than of q^{MD}. Thus, the total heat flux behavior in the state-to-state approach is nonmonotonic with x for N_2/N mixture at $M_0 = 18$ and O_2/O mixture at $M_0 = 15$ and 18. For lower Mach numbers, dissociation of molecules is not enough efficient to provide a considerable effect of mass diffusion; thus, the heat flux decreases monotonically with the distance. The thermal diffusion flux is practically zero behind the shock wave.

5 CONCLUDING REMARKS

Diffusion and heat flux in the relaxation zone behind the shock wave in state-to-state approximation have been considered for nitrogen and oxygen mixtures for Mach numbers 15 and 18. It is seen that for higher Mach numbers, kinetic and dissipative processes proceed more efficiently. The contribution of heat conductivity, thermal diffusion, mass diffusion, and diffusion of vibrationally excited molecules to the total energy flux is analyzed. Comparison of oxygen and nitrogen shows that for O_2/O, fast vibrational relaxation and dissociation lead to the sharp variation of gasdynamic parameters near the shock front and, as a consequence, to greater values of the total heat flux.

ACKNOWLEDGMENTS

This study is supported by Saint Petersburg State University, projects Nos. 6.50.2522.2013 and 6.37.163.2014, and by the Russian Foundation for Basic Research, grants Nos. 15-01-02373 and 15-08-03371.

REFERENCES

1. Nagnibeda, E., and E. Kustova. 2009. *Non-equilibrium reacting gas flows: Kinetic theory of transport and relaxation processes*. Heat and mass transfer ser. Berlin–Heidelberg: Springer-Verlag. 266 p.
2. Adamovich, I., S. Macheret, J. Rich, and C. Treanor. 1995. Vibrational relaxation and dissociation behind shock waves. *AIAA J.* 33(6):1064–1075.
3. Lordet, F., J. Meolans, A. Chauvin, and R. Brun. 1995. Nonequilibrium vibration–dissociation phenomena behind a propagating shock wave: Vibrational population calculation. *Shock Waves* 4:299–312.
4. Kustova, E., and E. Nagnibeda. 1997. The effect of level nonequilibrium kinetics on transport properties of dissociating gas flow behind a shock wave. *21st Symposium (International) on Shock Waves Proceedings*. Ed. A. Houwing. Brisbane: The University of Queensland. Paper 4231.
5. Kustova, E., and E. Nagnibeda. 2000. Nonequilibrium vibrational kinetics in carbon dioxide flow behind a shock wave. *22nd Symposium (International) on Shock Waves Proceedings*. Eds. G. Ball, R. Hillier, and G. Roberts. Southhampton: University of Southhampton. 1:777–782.
6. Park, C. 2006. Thermochemical relaxation in shock tunnels. *J. Thermophys. Heat Tr.* 20:689–698.
7. Kustova, E. V. 2001. On the simplified state-to-state transport coefficients. *Chem. Phys.* 270(1):177–195.
8. Schwartz, R., Z. Slawsky, and K. Herzfeld. 1952. Calculation of vibrational relaxation times in gases. *J. Chem. Phys.* 20:1591–1599.
9. Gordiets, B., A. Osipov, and L. Shelepin. 1988. *Kinetic processes in gases and molecular lasers*. Amsterdam: Gordon and Breach Science Publs. 688 p. (Transl. from Russian: 1980. *Kineticheskie protsessy v gazakh i molekulyarnye lazery*. Moscow: Nauka. 512 p.)
10. Marrone, P. V., and C. E. Treanor. 1963. Chemical relaxation with preferential dissociation from excited vibrational levels. *Phys. Fluids* 6(9):1215–1221.