Chemical kinetics in a five-component air behind shock waves

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Abstract. The influence of non-equilibrium kinetic processes on macroscopic parameters in air flows is a challenging and an important problem. Particularly, simulation of flows with high-temperature effects is important near the surface of spacecraft or meteorites when they enter the Earth’s atmosphere. Non-equilibrium flows of a reacting five-component air mixture consisting of $N_2$, $O_2$, NO, $N$, $O$ behind a shock wave at different altitudes in the Earth’s atmosphere and different speeds of the inlet flow are investigated. The lengths of the relaxation zones are considered to evaluate the applicability of one-temperature thermodynamics model for calculating the macroscopic fluid quantities behind the shock wave. The results of the flow simulation are obtained with in-house code developed for super- and hypersonic applications. The results from the code are compared with the results of numerical calculations computed with the equilibrium thermodynamics model.

1. Introduction
One of the important problems in modern physical and chemical gas dynamics is the study of non-equilibrium kinetics in air flows behind shock waves. The influence of non-equilibrium kinetic processes on macroscopic parameters in air flows is a challenging and an important problem. Particularly, simulation of flows with high-temperature effects is important near the surface of spacecraft or meteorites when they enter the Earth’s atmosphere.

A significant difference between the relaxation times of different degrees of freedom is observed in air flow behind the shock wave. The time of establishing equilibrium in the translational and rotational degrees of freedom is significantly less than the time of vibrational and chemical relaxation. Theoretical models describing the flow of high-temperature air under various non-equilibrium conditions have been developed in \cite{1} taking into account the relations between the characteristic times of the kinetic processes.

The most detailed and rigorous description of relaxation processes is based on solving the equations for the population of vibrational levels of molecules and densities of atoms with the equations of gas dynamics \cite{2}. However, the difficulties that arise in the numerical study of the level-by-level kinetics in the flows of multicomponent mixtures are associated with the...
need to solve a large number of equations for the population of the vibrational levels of all molecular components of the mixture together with the equations for macro-quantities. Therefore, this study uses a single-temperature model of non-equilibrium kinetics, which requires less computational resources and retains satisfactory accuracy [3].

Non-equilibrium flows of a reacting five-component air mixture consisting of $N_2$, $O_2$, $NO$, $N$, $O$ behind a shock wave at different altitudes in the Earth’s atmosphere and different speeds of the inlet flow are investigated. The lengths of the relaxation zones are considered to evaluate the applicability of one-temperature thermodynamics models for calculating the macro-quantities behind the shock wave. The results of the flow simulation are obtained with in-house code developed for super- and hypersonic applications. The results from the code are compared with the results of numerical calculations computed with the equilibrium thermodynamics model [4].

2. One-temperature approach

Air is considered as a five-component mixture of $N_2$, $O_2$, $NO$, $N$, $O$. The following chemical processes take place in the mixture:

- dissociation and recombination
  \[
  N_2 + M \rightleftharpoons N + N + M; \\
  O_2 + M \rightleftharpoons O + O + M; \\
  NO + M \rightleftharpoons N + O + M;
  \]

- chemical exchange reactions
  \[
  N_2 + O \rightleftharpoons NO + N; \\
  O_2 + N \rightleftharpoons NO + O.
  \]

Here, $M = N_2$, $O_2$, $NO$, $N$, $O$.

There are various approaches to the description of non-equilibrium flows: one-temperature, multi-temperature, level-by-level [1]. The most detailed description of non-equilibrium kinetics is given by the level-by-level approach, but the computational speed of this approach is low, due to the need to solve a large number of equations. The study uses a simple one-temperature approximation, which requires less computation time and is often used to solve applied problems. In this case, the processes of ionization and electronic excitation are not taken into account, since the temperature ranges at which the influence of these processes on the flow parameters is weaker than the influence of vibrational excitation and chemical reactions.

The vibrational energy of molecules $\varepsilon^c_i$ of $c$ type on $i$ level is calculated based on the Morse model of anharmonic oscillator

\[
\varepsilon^c_i = \varepsilon^c_0 + \hbar c (\omega^c e^{-\omega^c e^c - \omega^c e^c_0} e^{\varepsilon^c i}) \rightleftharpoons \varepsilon^c = \hbar c \left( \frac{1}{2} \omega^c e^{-\omega^c e^c_0} \right) .
\]

Here, $\hbar$ is Planck’s constant, $c$ is speed of light, $\omega^c e^c$ and $\omega^c e^c_0$ are spectroscopic constants characterizing the frequency and anharmonicity of molecular vibrations ($c = N_2$, $O_2$, $NO$).

For the populations of the vibrational levels of air components, under the assumption that the distribution of molecules over vibrational levels is quasi-stationary and corresponds to the Boltzmann distribution, the relation is

\[
n^c_i(T) = \frac{n^c}{Z^\text{vib}(T)} \exp \left( \frac{\varepsilon^c_i}{kT} \right) , \quad Z^\text{vib}(T) = \sum_i \exp \left( \frac{\varepsilon^c_i}{kT} \right) .
\]
3. Governing equations

The equations describing non-equilibrium air flows in the one-temperature approximation are considered. Within the framework of this approach, the determining macro-parameters of the flow are the numerical densities of molecules and atoms \( n_{N_2}, n_{O_2}, n_{NO}, n_N, n_O \), gas temperature \( T \) and macroscopic velocity \( v \). A closed system of equations for macro-parameters contains equations for one-temperature non-equilibrium chemical kinetics, equations for conservation of momentum and total energy. In the case of a stationary one-dimensional flow of an inviscid and non-conducting mixture, these equations have the form [1]

\[
\begin{align*}
&v \frac{dn_{N_2}}{dx} + n_{N_2} \frac{dv}{dx} = R_{N_2}^{2+2} + R_{N_2}^{2+3}; \\
&v \frac{dn_{O_2}}{dx} + n_{O_2} \frac{dv}{dx} = R_{O_2}^{2+2} + R_{O_2}^{2+3}; \\
&v \frac{dn_{NO}}{dx} + n_{NO} \frac{dv}{dx} = R_{NO}^{2+2} + R_{NO}^{2+3}; \\
&v \frac{dn_N}{dx} + n_N \frac{dv}{dx} = R_N^{2+2} + R_N^{2+3}; \\
&v \frac{dn_O}{dx} + n_O \frac{dv}{dx} = R_O^{2+2} + R_O^{2+3}; \\
&\rho v \frac{dv}{dx} + \frac{dp}{dx} = 0; \\
&v \frac{dE}{dx} + (p + E) \frac{dv}{dx} = 0.
\end{align*}
\]

Here, \( \rho = \sum_M n_M m_M \) is density of mixture, \( p = nkT \) is pressure, \( n = \sum_M n_M \) is numerical density of mixture, \( E \) is total energy per unit volume. The total energy per unit volume is found from the relation

\[
E = E^{tr} + E^{rot} + E^{vibr} + E^f,
\]

where \( E^{tr}, E^{rot}, E^{vibr} \) are translational, rotational, vibrational energies per unit volume, and \( E^f \) is energy of formation of mixture species per unit volume. The component of the total energy are found as

\[
\begin{align*}
E^{tr} &= \frac{3}{2} nkT; \\
E^{rot} &= \sum_{c=N_2,O_2,NO} n_c kT; \\
E^{vibr} &= \sum_{c=N_2,O_2,NO} \left( \sum_i (\varepsilon_{c}^{i} + \varepsilon_{\varepsilon}^{i}) \right) n_c(T); \\
E^f &= \sum_{d=N,O,NO} n_d \varepsilon_{d}^f.
\end{align*}
\]

Here, \( \varepsilon_{N}^f, \varepsilon_{O}^f, \varepsilon_{NO}^f \) are energies of formation of \( NO \) molecule, \( N \) and \( O \) atoms. They are determined as

\[
\varepsilon_{N}^f = \frac{1}{2} D_{N_2}, \quad \varepsilon_{O}^f = \frac{1}{2} D_{O_2}, \quad \varepsilon_{NO}^f = \frac{1}{2} (D_{N_2} + D_{O_2}) - D_{NO}.
\]
These equations form a closed system of non-linear ordinary differential equations (ODE) describing the one-dimensional flow of the air mixture taking into account the reactions of exchange, dissociation and recombination. The implicit Gear method with backward differentiation formulas is applied.

The one-temperature approach assumes that only the chemical composition of the mixture is retained at the front. When modelling relaxation behind the shock front, the parameters in the incident flow are set as the initial conditions: pressure $p_0$ (or the numerical density of the mixture $n_0$), temperature of the mixture $T_0$, Mach number $M_0$ (or gas velocity $v_0$), the initial composition of the mixture. After that, it is necessary to calculate the parameters of the gas immediately behind the shock front, and these parameters are used as the initial ones when solving the system.

4. Relaxation terms

To close the system of equations, it is necessary to express the relaxation terms $R^{2+2}_c$ and $R^{2+3}_c$ in terms of macro-parameters.

The terms $R^{2+2}_c$ describe changes in the number density of molecules due to exchange reactions $(4)-(5)$ and take the form [1]

$$
R^{2+2}_N = n_{NO}^n n_{NO}^N k^{N->O}_{NO} n_{N2}^2 k^{O->N}_{N2->NO} - n_{N2} n_{O}^n k^{N->O}_{N2->NO};
$$

$$
R^{2+2}_O = n_{NO}^n n_{NO}^O k^{O->N}_{NO} n_{O2}^2 k^{N->O}_{O2->NO} - n_{O2} n_{N}^n k^{O->N}_{O2->NO};
$$

$$
R^{2+2}_R = -R^{2+2}_N - R^{2+2}_O;
$$

$$
R^{2+2}_N = -2R^{2+2}_N + R^{2+2}_O;
$$

$$
R^{2+2}_O = R^{2+2}_N - R^{2+3}_O.
$$

Here, $k^{O->N}_{NO}(T)$ and $k^{N->O}_{NO}(T)$ are rate coefficients of direct exchange reactions depending on temperature; $k^{N->O}_{NO->N2}(T)$ and $k^{O->N}_{NO->O2}(T)$ are back reaction rate coefficients.

The terms $R^{2+3}_c$ describe dissociation and recombination processes $(1)-(3)$ and take the form

$$
R^{2+3}_{N2} = \sum_{M=N2,O2,NO,N,O} n_M (n^{M}_{N\text{rec},N2} - n^{M}_{N2\text{diss}});\n$$

$$
R^{2+3}_{O2} = \sum_{M=N2,O2,NO,N,O} n_M (n^{M}_{O\text{rec},O2} - n^{M}_{O2\text{diss}});\n$$

$$
R^{2+3}_{NO} = \sum_{M=N2,O2,NO,N,O} n_M (n^{M}_{NNO\text{rec},NO} - n^{M}_{NNO\text{diss}});\n$$

$$
R^{2+3}_N = -2R^{2+3}_N - R^{2+3}_NO;\n$$

$$
R^{2+3}_O = -2R^{2+3}_O - R^{2+3}_NO.
$$

Here, $k^{M}_{N2\text{diss}}(T)$, $k^{M}_{O2\text{diss}}(T)$, $k^{M}_{NNO\text{diss}}(T)$ are dissociation rate coefficients of $N_2$, $O_2$, $NO$ molecules upon collision with a particle $M$; $k^{M}_{N\text{rec},N2}(T)$, $k^{M}_{O\text{rec},O2}(T)$, $k^{M}_{\text{rec},NO}(T)$ are coefficients of the rate of recombination of atoms with the formation of molecules $N_2$, $O_2$, $NO$.

To calculate the one-temperature coefficients of the rate of direct reactions of exchange and dissociation, the Arrhenius law is used, which is valid in a thermally equilibrium gas

$$
k^{M}_{c,eq}(T) = A_M T^n \exp \left( -\frac{E_a}{kT} \right),
$$
where $E_\sigma(D_c)$ is activation energy in the case of exchange reactions and the dissociation energy in the case of decay reactions; $A_M$ and $n$ are constants that are determined based on experimental data or numerical calculations. The calculations use the dissociation rate coefficients recommended in [5].

The coefficients of the rate of recombination and reverse exchange reactions are calculated using the relations following from the principle of detailed balance [1]

$$k_{\text{rec},N_2}(T) = k_{\text{N}_2,\text{diss}}^{M}(T) \left( \frac{m_{N_2}}{m_N} \frac{h^2}{2\pi kT} \right)^{3/2} Z_{N_2}^{\text{rot}}(T) Z_{N_2}^{\text{vibr}}(T) \exp \left( \frac{D_{N_2}}{kT} \right);$$

$$k_{\text{rec},O_2}(T) = k_{\text{O}_2,\text{diss}}^{M}(T) \left( \frac{m_{O_2}}{m_O} \frac{h^2}{2\pi kT} \right)^{3/2} Z_{O_2}^{\text{rot}}(T) Z_{O_2}^{\text{vibr}}(T) \exp \left( \frac{D_{O_2}}{kT} \right);$$

$$k_{\text{rec},NO}(T) = k_{\text{NO},\text{diss}}^{M}(T) \left( \frac{m_{NO}}{m_Nm_O} \frac{h^2}{2\pi kT} \right)^{3/2} Z_{NO}^{\text{rot}}(T) Z_{NO}^{\text{vibr}}(T) \exp \left( \frac{D_{NO}}{kT} \right);$$

$$k_{\text{NO} \rightarrow N_2}(T) = k_{\text{N}_2 \rightarrow NO}^{N}(T) \left( \frac{m_{N_2}m_O}{m_{NO}m_N} \right) \frac{Z_{N_2}^{\text{rot}}(T) Z_{N_2}^{\text{vibr}}(T)}{Z_{NO}^{\text{rot}}(T) Z_{NO}^{\text{vibr}}(T)} \exp \left( \frac{D_{N_2} - D_{NO}}{kT} \right);$$

$$k_{\text{NO} \rightarrow O_2}(T) = k_{\text{O}_2 \rightarrow NO}^{N}(T) \left( \frac{m_{O_2}m_N}{m_{NO}m_O} \right) \frac{Z_{O_2}^{\text{rot}}(T) Z_{O_2}^{\text{vibr}}(T)}{Z_{NO}^{\text{rot}}(T) Z_{NO}^{\text{vibr}}(T)} \exp \left( \frac{D_{O_2} - D_{NO}}{kT} \right).$$

Here, $Z_{rot}^{\text{rot}}(T)$ is statistical sum of rotational degrees of freedom, $Z_{vibr}^{\text{vibr}}(T)$ is statistical sum of vibrational degrees of freedom, $\sigma_{N_2} = \sigma_{O_2} = 2$, $\sigma_{NO} = 1$ are factors of symmetry, $\theta^c_c$ is characteristic rotational temperature. The statistical sum of rotational degrees of freedom is found from $Z_{c}^{\text{rot}}(T) = T/\sigma_c \theta^c_c$.

5. Results and discussion

The chemical reactions behind a normal shock wave at different altitudes and flight speeds are considered. To determine the parameters of the inlet flow at different flight altitudes, data corresponding to the standard atmosphere are used. The flight Mach number varies from $M = 10$ to $16$. The upper limit is associated with the fact that, at Mach numbers above 16, the temperature and pressure immediately behind the shock layer have values at which the ionization processes have a significant effect on the flow parameters [6].

The lengths of the zones behind the shock front, in which the parameters change by more than 1% of the final result, depending on the Mach number at different flight altitudes, are compared. In Figures 1–4, the vertical axis shows the length of the relaxation zone in which the specified parameter differs from the final result by 1%. The zone in which all flow parameters differ from the final result by 1% is referred to as the relaxation zone.

With an increase in the Mach number, the zone of chemical reactions decreases. On the one hand, the velocity behind the shock wave increases with an increase in the Mach number, which leads to an increase in the length of relaxation zone. On the other hand, the pressure also increases, which leads to a decrease in the relaxation zone. As the pressure increases much faster than the speed, the chemical reaction zone decreases. The establishment of macro-parameters occurs at a shorter distance than the establishment of certain concentrations of the mixture components. The establishment of the NO concentration is the slowest. The length of the relaxation zone is $x = 0.383$ mm at an altitude of $h = 0$ km from the ground level, $x = 8.5$ mm at an altitude of $h = 10$ km, $x = 55$ mm at an altitude of $h = 24$ km, $x = 3211$ mm at an altitude of $h = 60$ km.
The lengths of the zones of variation of the flow parameters behind the shock wave depending on the flight altitude at Mach numbers $M = 10$, $13$ and $16$ are presented in Figure 5. The solid lines show the lengths of the zones of chemical reactions, where the relative error of the macro-parameters (temperature, pressure, number density) relative to their final values exceeds 1%. Dash-dotted lines show the lengths of the zones of chemical reactions, where the relative error of the numerical components of the mixture relative to their final values exceeds 1%. The length of the zone of change in macro-parameters is much less than the length of the zone of change in the numerical densities of the components.

With the Mach number $M=10$, the conditional relaxation zone is more than 1 mm already.
Figure 3. The lengths of relaxation zone at altitude of $h = 24$ km

Figure 4. The lengths of relaxation zone at altitude of $h = 60$ km

...at an altitude of 4 km above sea level (in this case, the length of the zone of changes in macro-parameters at the same altitude is $x = 0.32$ mm). At an altitude of 10 km, the length of the zone is more than 1 cm (for macro-parameters $x = 2.5$ mm), at an altitude of 32 km it is more than 10 cm (for macro-parameters $x = 1.57$ cm), at an altitude of 60 km it is about 3 m (for macro-parameters $x = 2.6$ m). The lengths of the zones at the Mach number $M=10$ are much longer than at other Mach numbers.

With the Mach number $M=13$, the length of the zone of variation of flow parameters is more than 1 mm at an altitude of 25 km above sea level (while the length of the zone of variation of macro-parameters at the same height is $x = 0.2$ mm). At an altitude of 42 km, the length of...
the zone is more than 1 cm (for macro parameters $x = 0.57$ cm), at an altitude of 53 km it is more than 10 cm (for macro-parameters $x = 4.7$ cm), at an altitude of 60 km it is about 47 cm (for macro parameters $x = 23$ cm).

With the Mach number $M=16$, the length of the zone of variation of flow parameters is more than 1 mm at an altitude of 35 km above sea level (in this case, the length of the zone of variation of macro-parameters at the same height is $x = 0.5$ mm). At an altitude of 46 km, the length of the zone is more than 1 cm (for macro-parameters $x = 0.58$ cm), at an altitude of 57 km it is more than 10 cm (for macro-parameters $x = 5$ cm), at an altitude of 60 km it is about 21 cm (for macro-parameters $x = 10$ cm).

6. Conclusion
Non-equilibrium flows of a reacting five-component air mixture consisting of $N_2$, $O_2$, $NO$, $N$, $O$ behind a shock wave at different altitudes in the Earth’s atmosphere and different speeds of the incoming flow are investigated. The lengths of the relaxation zones are considered to evaluate the applicability of equilibrium thermodynamics models for calculating the macro-quantities behind the shock wave. The results of the flow simulation are obtained with in-house code developed for super- and hypersonic applications. The results from the code are compared with the results of numerical calculations computed with the equilibrium thermodynamics model.

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