State-to-state modeling of oxygen relaxation taking into account electron kinetics

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Abstract. Coupled vibrational, chemical and electronic kinetics in oxygen is studied using the detailed state-to-state model. Simulation of zero-dimensional oxygen relaxation in the presence of free electrons in the temperature range 300 – 1000 K is carried out; the master equations for the vibrational state populations and densities of excited species are solved together with the Boltzmann equation for the electron density distribution. Different models for heavy-particle interactions are assessed. It is shown that the forced harmonic oscillator model is suitable in the entire temperature range. The effect of the initial conditions and the presence of free electrons is discussed; it is shown that including electrons modifies the main relaxation mechanisms. Recommendations are given for extending the kinetic scheme to high-temperature regimes.

1. Introduction
One of challenging problems in modern aerothermodynamics is simulation of high-speed vehicle flights in planetary atmospheres. The range of applications of these studies comprises aviation and rocket science, as well as space exploration programs. In recent years, increasing of computing power caused growing need in accurate models of non-equilibrium gas flows. One of the most important processes occurring in non-equilibrium gases is the exchange of molecular vibrational energy and its transfer to other types of energy. There are several approaches for describing these processes, but the most accurate is the state-to-state (STS) approach [1, 2]. Its particular feature is treating of each vibrational state as a separate species. The advantages of this approach are especially evident under conditions of strong non-equilibrium, when vibrational-translational (VT) and vibrational-vibrational (VV) energy exchanges proceed at the macroscopic time scale, whereas dissociation and recombination reactions are strongly coupled to the vibrational energy transitions.

At the same time, computational complexity still does not allow taking into account a large number of processes and interactions in reacting flows of real geometry. This imposes restrictions on the conditions under which the STS approach is applicable. For example, when gas is ionized at high temperatures, a significant number of free electrons appears, which, in turn, essentially influences the evolution of fluid-dynamic variables. Previously, attempts have been made to take into account state-resolved interactions with electrons in high-temperature flows, but mainly using approximate models based on the Maxwell energy distribution of electrons [3, 4].

On the other hand, in modeling gas discharges, low computational complexity of zero-dimensional problem simulations makes it possible to take into account with much greater accuracy the electronic kinetics, which plays one of the main roles in these problems. For
example, in [5], modeling of reacting oxygen was performed in the STS approach taking into account 80 types of interactions leading to several hundreds of state-resolved reactions. Special attention deserves the description of the electron energy distribution by solving the Boltzmann equation for free electrons. This approach is computationally demanding and difficult to implement. To solve this equation in low-temperature discharge simulations, the LoKI-B [6] software package can be used. The package was developed by the research group of the University of Lisbon and allows to calculate the distribution of free electrons over energy for given conditions.

The objective of the present study is to assess whether the low-temperature state-resolved models and LoKI-B software can be extended for simulations of gas flows with significantly higher temperatures. We apply both the approach proposed in [5] and the one recently developed for high-temperature kinetics of neutral gases [2] to study the STS oxygen relaxation and evaluate the influence of vibrational excitation, dissociation, and recombination of heavy particles and kinetics of free electrons on the mixture composition and vibrational distribution functions (VDF). The comparison of schemes without and with allowance for free electrons is carried out.

2. Kinetic scheme
We consider zero-dimensional oxygen relaxation under isothermal conditions. 11 species are included in the mixture: \( \text{O}_2(X^3\Sigma_g^-, i = 0 - 41), \text{O}_2(a^1\Delta_g), \text{O}_2(b^1\Sigma_g^+), \text{O}_2^+, \text{O}^{(3P)}, \text{O}^{(1D)}, \text{O}^+, \text{O}^-, \text{O}_3, \text{O}_3^* \) (vibrationally excited ozone) and \( e^- \); 42 vibrational levels of the \( \text{O}_2 \) ground electronic state are taken into account. The kinetic scheme was taken from Annuov et al 2018 [5] with minor additions and model variations. In this model, a large number of interactions are taken into account. In particular, we include to the kinetic scheme VT-exchanges (\( i, j \) stand for vibrational levels)

\[
\text{O}_2(X,i) + M \leftrightarrow \text{O}_2(X,j) + M, \quad M = \text{O}_2, \text{O}, \tag{1}
\]

VV-exchanges

\[
\text{O}_2(X,i) + \text{O}_2(X,j) \leftrightarrow \text{O}_2(X,i') + \text{O}_2(X,j'), \tag{2}
\]

eV-exchanges

\[
e^- + \text{O}_2(X,i) \leftrightarrow e^- + \text{O}_2(X,j), \tag{3}
\]

electronic excitation (\( Z \) stands for the electronic state)

\[
\text{O}_2(Z) + M \leftrightarrow \text{O}_2(Z') + M, \quad M = \text{O}_2, \text{O}, \text{O}_3, e^-, \tag{4}
\]

\[
\text{O}_2(Z_1) + \text{O}_2(Z_2) \leftrightarrow \text{O}_2(Z'_1) + \text{O}_2(Z'_2), \tag{5}
\]

\[
\text{O}(Z) + M \leftrightarrow \text{O}(Z') + M, \quad M = \text{O}_2, \text{O}, \text{O}_3, e^-, \tag{6}
\]

dissociation and recombination

\[
\text{O}_2(Z_1,i) + M \leftrightarrow \text{O}(Z_2) + \text{O}(Z_3) + M, \quad M = \text{O}_2, \text{O}, \text{O}_3, e^-, \tag{7}
\]

\[
\text{O}_2(Z_1) + M \leftrightarrow \text{O}_2(Z_2) + \text{O}(Z_3) + M, \quad M = \text{O}_2, \text{O}, \text{O}_3, e^-, \tag{8}
\]

ionization

\[
e^- + M \rightarrow e^- + e^- + M^+, \quad M = \text{O}_2, \text{O}, \tag{9}
\]

\[
e^- + \text{O}_2(Z_1) \rightarrow \text{O}(Z_2) + \text{O}^-, \tag{10}
\]

and different kinds of exchange reactions

\[
AB + CD \leftrightarrow AD + CB, \tag{11}
\]

\[
A + B + CD \leftrightarrow AC + BD \tag{12}
\]
which correspond to a large number of processes involving \( \text{O}_2 \), \( \text{O}_3 \), \( \text{O} \) and ions. More details can be found in [5] (Table 2).

For the rate coefficients of VT-, VV-exchanges and dissociation, two model sets were used: 1) the models proposed by Annuov et al [5] and Esposito et al [7] based on quasi-classical trajectory calculations, and 2) the theoretical forced harmonic oscillator model (FHO) [8] for vibrational transitions, and the Marrone–Treanor model [9, 10] for dissociation. The first set of rate coefficients yields good accuracy under low-temperature discharge conditions, whereas the second was assessed in high-temperature shock heated flows [2] and provides the best agreement with experimental data of [11]. For electron-impact processes, the rate coefficients from [5] are used. For free electrons, the Boltzmann equation was solved, and the reaction rate coefficients were calculated by averaging corresponding cross-sections with the electron energy distribution function (EEDF).

Initial conditions are varied to observe different effects. The initial vibrational distribution is taken both equilibrium and non-equilibrium. To consider the effects of interactions with free electrons, simulations are carried out in the presence of a reduced electric field with a constant intensity. To assess the role of electrons, corresponding test cases neglecting electrons are also considered.

3. Results

Simulations were carried out in the MATLAB software environment. For the solution of the Boltzmann equation for free electrons we used LoKI-B [6], an open-source simulation tool. The calculations were performed at a pressure \( p = 1 \), 10 Torr, gas temperature \( T_g = 300, \ 400, \ 650, \ 1000 \) K, initial Boltzmann distribution with vibrational temperatures \( T_{v0} = 0.5T_g, \ T_g, \ 1.2T_g \), and reduced electric field intensity \( E/N = 50, \ 70 \) Td. The choice of initial conditions is based on data [5] and data obtained from the Lisbon University group working on the LoKI software. Calculations were also carried out without the field to analyze the impact of free electrons. In total, simulations were performed for more than 40 test cases.
3.1. Effect of rate coefficients
The effect of the model for heavy-particles interactions is shown in Figures 1–3. First, we compare the VDFs at $t \approx 100$ s corresponding to equilibrium values of species number densities. In Figure 1 (left), the VDF obtained with the Marrone–Treanor dissociation model and two sets of vibrational energy transition models (FHO vs Annuov and Esposito) are compared. In Figure 1 (right), the ladder-climbing and Marrone–Treanor models of dissociation are assessed using the Annuov and Esposito models for vibrational transitions. In the latter test case, initial distribution is not the Boltzmann one, but all $O_2$ molecules are assumed on the ground vibrational state. The VDF for the ladder-climbing model is kindly provided by Tiago Cunha Dias. One can see that for both model sets, the VDFs are significantly non-Boltzmann; this is due to the account of electronically excited states, as well as efficient dissociation and ionization processes. The effect of rate coefficients of VV and VT transitions is significant for low and
Figure 4. Rate coefficients of VT transitions in collision O$_2$-O$_2$ as functions of $T$. Models of Annušov [5] and FHO [8]; transitions 7 → 6 and 30 → 29.

intermediate states, whereas the VDFs at high states are almost the same. This is explained by the large difference in the VT rate coefficients for O$_2$-O collision obtained by the FHO model and the Esposito model. On the contrary, the effect of dissociation model is important for high states; using the preferential Marrone–Treanor model leads to the considerable depletion of high levels.

The influence of vibrational relaxation model on the number densities of O$_2$ molecules in the ground and excited electronic states is shown in Figure 2, and on the number densities of high-energy states of O$_2^+$ and O($^1$D) in Figure 3. For ozone and electronically excited atoms, there is some difference in the density profiles, but the overall effect is small. For oxygen molecules, the discrepancy increases with time. It is worth mentioning that the final values of species number densities differ for two sets of rate coefficients, which is not completely self-consistent. The explanation is that in the kinetic scheme used in [5], some of kinetic processes have no corresponding backward reactions. This may lead to different, model-dependent, equilibrium mixture compositions. For the sake of consistency, we recommend upgrading the model of [5] by including missing backward processes, at least for heavy-particle collisions.

Except this small discrepancy, the two sets of models for heavy-particle interactions provide similar results, and therefore, both models can be implemented under low-temperature conditions. However, the model of [5] cannot be used under high-temperature conditions due to the limited range of validity of interpolation formulas for the rate coefficients; $T = 1000$ K is indicated in [5] as the upper limit. On the other hand, the FHO model provides good accuracy in a wide temperature range. Comparison of the VT rate coefficients calculated using two models is presented in Figure 4. In the low-temperature range, the rate coefficients are rather close, but at $T > 1500$ K, those of [5] show sharp increase, and thus cannot be used. Moreover, the ladder-climbing dissociation model is not applicable in high-temperature flows, where heavy-particle collisions are important, since it underpredicts the thermal dissociation rate. Taking into account the above analysis, we recommend using the FHO model of vibrational transitions and the Marrone–Treanor model of dissociation in the entire range of conditions.
3.2. Influence of initial conditions and electrons

Let us now discuss the effect of initial conditions on the relaxation process. All calculations considered below were carried out using the Marrone–Treanor model for dissociation. Varying the initial temperature and pressure in the range 1-10 Torr does not yield qualitative differences; the time distributions of species number densities remain similar. For an isothermal process, the effect of initial non-equilibrium on the mixture composition turned out to be rather weak. The main influence was found when considering the populations of vibrational states. Figure 5 (left) shows the evolution of the population of the first vibrational state for $T_g = 1000$ K and three different initial values $T_{v0}$. It can be seen that the main difference is observed before the peak of the population. The populations converge immediately after the peak, and further relaxation occurs in the same way.

In addition to vibrational populations, initial non-equilibrium affects highly excited particles, such as ions and $O_3^*$. Figure 5 (right) demonstrates evolution of $O_3^*$ number densities for various initial non-equilibrium. The main differences are observed in the zone of the number density maximum. It is also interesting to note that the largest values for the $O_3^*$ density are observed at a lower initial internal oxygen energy ($T_{v0} = 0.5T_g$).

For several test cases, simulation was carried out neglecting free electrons. It was found that in the absence of electrons, relaxation proceeds much slower. The formation of particles with high internal energy practically ceases. Figure 6 (left) presents the VDF of $O_2(X, i)$ for two initial values of $T_{v0}$ at different times; electrons are not included to the kinetic scheme. One can see that the final distribution, although being the same for two test cases, differs from the Boltzmann distribution and rather tends to a kind of quasi-steady state. This, once again, can be explained by neglecting some of backward processes in the model [5], in particular, by the fact that highly excited $O_2(X, i)$ molecules go to the electronically excited states. Figure 6 (right) shows a comparison of the final vibrational distributions with and without electrons for initial $T_{v0} = 0.5T_g$. It can be seen that the presence of electrons strongly affects the distribution, populating high-energy states. At the same time, the number of oxygen molecules at the lower levels is reduced. This occurs as a consequence of internal energy pumping, as well as the formation of other mixture components. It can also be noted that the final quasi-steady state in the presence of a field occurs a little earlier than without it.
Figure 6. VDF at various times $t$. $p = 1$ Torr, $T = 1000$ K, $E/N = 70$ Td; vibrational kinetics models of [5] and [7]; Marrone–Treanor model of dissociation. (left): no electrons, two values of initial vibrational temperature $T_v^0 = 0.5T_g$ and $T_v^0 = 1.2T_g$; (right): final VDF in the presence of free electrons and without them. $T_v^0 = 0.5T_g$.

Figure 7. Number densities of O$_3$ (left) and O($^3P$) (right) as functions of time in the presence of free electrons and without them. $p = 1$ Torr, $T = 1000$ K, $T_v^0 = 0.5T_g$, $E/N = 70$ Td; vibrational kinetics models [5] and [7]; Marrone–Treanor model of dissociation.

Figure 7 shows the time evolution of ozone and oxygen atom number density for the kinetic schemes accounting for electrons and neglecting them. One can see that under the present conditions, the main role in O$_2$ dissociation and formation of excited species belongs to electrons; in the absence of electrons these processes are practically frozen at $T < 1000$ K. The electrons are also efficient in excitation of high vibrational states. Neglecting electrons completely modifies dominating relaxation mechanisms. However, under high-temperature conditions, we expect that contributions of heavy-particle interactions to the overall relaxation processes becomes much more important. This will be assessed in our further studies.

4. Conclusion
Coupled vibrational-chemical-electronic kinetics in oxygen was studied using the detailed state-to-state approach and the Boltzmann equation for the electron density distribution. The effect
of different initial conditions, kinetic scheme and models for the rate coefficients of heavy-particle interactions was assessed.

Simulations were performed for different initial values of $p$, $T$, $T_{e0}$ and $E/N$ in the presence and absence of free electrons and varying the models for heavy-particles interactions, such as VV, VT vibrational energy transitions and dissociation. Comparison of the results obtained at $T < 1000$ K using the FHO model and that of Annuov and Esposito shows relatively small difference, consisting mainly in the evolution of VDF; in the considered range of conditions, the discrepancy decreases with the gas temperature. In addition, for low temperatures, small differences are observed in the quasi-equilibrium number densities of the mixture species. This, as well as the depletion of the VDF tail below the equilibrium values, may be a consequence of the absence of some reverse processes in the kinetic scheme [5]. Therefore, we recommend to improve the model by including backward processes to the kinetic scheme, at least for heavy-particle collisions. Also it is shown that while the FHO model is suitable for both low and high temperatures, the model [5] cannot be applied for VT- and VV-processes at high temperatures. For high-temperature regimes, there is a need to replace the models of vibrational relaxation in $O_2-O_2$ collisions and heavy-particles dissociation. We suggest the FHO model and the Marrone–Treanor model.

Varying the initial conditions yields some small differences in the relaxation rate, VDF and densities of highly excited particles, but in general does not lead to large deviations. This is partly due to the isothermal formulation of the problem. On the contrary, the absence or presence of electrons completely modifies relaxation mechanisms. When electrons are not included to the kinetic scheme, formation of high-energy electronically excited species and population of high vibrational levels of $O_2$ ground electronic state are not observed. The contribution of heavy-particle interactions is expected to be greater under high-temperature conditions.

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