Reduced description of local equilibrium monatomic oxygen flows with multiple ionization

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Abstract. A new scheme to describe ionized monatomic gases with multiple kinds of ions is suggested. The conservation equations of the momentum, energy, numbers of nuclei and electrons (both bound and free) are derived. Local equilibrium flows of dissociated ionized oxygen are considered. Temperature dependence of oxygen atoms, ions and free electrons concentrations is calculated for the case when the initial density of oxygen atoms is equal to the Loschmidt’s number. The dependence of pressure on temperature is also emphasized.

1. Introduction
Studies of ionized gases local equilibrium flows are necessary for the solution of many technological and scientific problems. In connection with development of space technologies the studies of dissociated air mixtures and their separate ionized components have a particular importance. Therefore, in this paper the flows of the monatomic ionized oxygen are considered under the various values of temperatures. The oxygen mixtures are assumed enough rarefied to be treated as ideal gases even after multiple ionization steps.

If we do not know the gas ionization degree in advance, then at a relatively high temperature $T$, the gas mixture may contain neutral atoms $A_0$, ions $A(c)$ with charges $c$ ranging from $c = +1$ to $c = +N$ ($N$ is a number of chemical element $A$ in the periodic table) and free electrons $e^-$. The number of oxygen in the periodic table is equal to 8. Therefore, hypothetically, in the ionized flow of oxygen one can discover the neutral atoms O, ions $O(c)$ with a charge $c = +1, \ldots, +8$, and free electrons $e^-$. The description of unmagnetized plasma flows with multiple ion species is usually realised on the basis of the transport equations for the momentum, energy, densities of all species of ions and free electrons (see, for example, [1, 2, 3]). These equations are similar to the transport equations for the neutral gas mixtures with internal degrees of freedom and chemical reactions [4, 5, 6]. Our paper is devoted to derivation of the conservation equations systems for the flows of ionized mixture under consideration. It is shown that these reduced systems allow one to investigate the set of the local equilibrium flow characteristics of ionized monatomic oxygen, on the basis of the special form of the equilibrium distribution functions [7].

2. The systems of conservation equations for the ionized oxygen flows
2.1. Conservation equations
In any ionized gas mixture the momentum, total energy, the numbers of the nuclei and electrons are conserved in any collision. For derivation of the corresponding conservation equations one
can use the methods of fluid dynamics and the methods of kinetic theory. When studying ionized monatomic oxygen flows, along with the equations for the momentum and energy one can write the conservation equations for the oxygen nuclei \( \text{O} \) and the electrons \( \text{e} \) (both bound and free).

As a result, we obtain the system of following equations:

\[
\frac{dv}{dt} = F - \frac{1}{\rho} \nabla \cdot \mathbf{P}, \tag{1}
\]

\[
\frac{de}{dt} + e \nabla \cdot \mathbf{v} + \mathbf{P} : \nabla \mathbf{v} + \nabla \cdot \mathbf{q} = 0, \tag{2}
\]

\[
\frac{d\tilde{n}_s}{dt} + \tilde{n}_s \nabla \cdot \mathbf{v} + \nabla \cdot \mathbf{q}_s = 0, \tag{3}
\]

\[
\frac{d\tilde{n}_{-e}}{dt} + \tilde{n}_{-e} \nabla \cdot \mathbf{v} + \nabla \cdot \mathbf{q}_{-e} = 0. \tag{4}
\]

Here \( \mathbf{v}(r, t) \) is the macroscopic velocity of the gas flow; \( \mathbf{F} \) is the specific external force; \( \mathbf{P} \) is the stress tensor; \( \rho(r, t) \) is the mass density; \( e(r, t), \tilde{n}_s(r, t), \tilde{n}_{-e}(r, t) \) are total energy, total numbers of nuclei \( \text{O}^* \) and electrons \( \text{e}^- \) (both bound and free) in the unit volume, respectively; \( \mathbf{q}(r, t), \mathbf{q}_s(r, t) \) and \( \mathbf{q}_{-e}(r, t) \) are fluxes of the total energy, and diffusive fluxes of nuclei \( \text{O}^* \) and all electrons \( \text{e}^- \).

Using kinetic methods, one can introduce the distribution functions \( f_{ci}(r, \mathbf{u}, t) \) for oxygen particles with charge \( c \) (\( c = 0, 1, \ldots, 8 \)), internal electronic energy \( \varepsilon_{ci} \) and velocity \( \mathbf{u} \), as well as \( f_{-e}(r, \mathbf{u}, t) \) for the free electrons \( \text{e}^- \) with velocity \( \mathbf{u} \). Under these conditions velocity \( \mathbf{v}(r, t) \) is determined by the equation:

\[
\sum_{c,i} \int f_{ci}(r, \mathbf{u}, t)m_{ci}\mathbf{u}d\mathbf{u} + \int f_{e^-}(r, \mathbf{u}, t)m_{e^-}\mathbf{u}d\mathbf{u} = \rho(r, t)v(r, t).
\]

After the transition to peculiar velocities \( \mathbf{c}(r, t) = \mathbf{u} - \mathbf{v}(r, t) \), one can write the relations:

\[
\sum_{c,i} \int f_{ci}m_{ci}\mathbf{cdc} + \int f_{e^-}m_{e^-}\mathbf{cdc} = 0, \tag{5}
\]

\[
e(r, t) = \sum_{c,i} \int f_{ci} \left( \frac{m_{ci}c^2}{2} + \varepsilon_{ci} \right) d\mathbf{c} + \int f_{e^-} \frac{m_{e^-}c^2}{2} d\mathbf{c}, \tag{6}
\]

\[
\tilde{n}_s(r, t) = \sum_{c,i} \int f_{ci}d\mathbf{c}, \tag{7}
\]

\[
\tilde{n}_{-e}(r, t) = \sum_{c,i} (8 - c) \int f_{ci}d\mathbf{c} + \int f_{e^-}d\mathbf{c}, \tag{8}
\]

\[
\mathbf{P}(r, t) = \sum_{c,i} \int f_{ci}m_{ci}\mathbf{ccd} + \int f_{e^-}m_{e^-}\mathbf{ccd} = 0, \tag{9}
\]
\[ q(r, t) = \sum_{c,i} \int f_{ci} \left( \frac{m_{ci}c^2}{2} + \varepsilon_{ci} \right) \, dc + \int f_e \frac{m_{e^-}c^2}{2} \, dc, \quad (10) \]

\[ q_s(r, t) = \sum_{c,i} \int f_{ci} \, dc, \quad (11) \]

\[ q_e^-(r, t) = \sum_{c,i} (8 - c) \int f_{ci} \, dc + \int f_e \, dc. \quad (12) \]

Here \( m_c \) and \( m_{e^-} \) are the masses of ions \( O^c \) and electrons \( e^- \). If \( m_s \) is a mass of nucleus \( O^s \), then \( m_c = m_s + (8 - c) m_{e^-} \).

2.2. Continuity equation

It should be noted that the continuity equation

\[ \frac{dp}{dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (13) \]

is a consequence of Eq. (3) and Eq. (4).

Indeed, the mass density \( \rho(r, t) \) can be represented as:

\[ \rho = m_s n_s + m_{e^-} n_{e^-} = \sum_{c=0}^{8} m_c n_c + m_{e^-} n_{e^-}, \quad (14) \]

where \( n_c(r, t) \) and \( n_{e^-}(r, t) \) are the number densities of the oxygen particles with charge \( c \) and free electrons.

If we sum Eq. (3) and Eq. (4) after multiplying them by the oxygen nucleus mass \( m_s \) and the electron mass \( m_{e^-} \), we obtain the equality:

\[ \frac{dp}{dt} + \rho \nabla \cdot \mathbf{v} + m_s \nabla \cdot \mathbf{q}_s + m_{e^-} \nabla \cdot \mathbf{q}_{e^-} = 0, \quad (15) \]

where in accordance with formulae (11), (12) and (5) one can write the relation:

\[ m_s \nabla \cdot \mathbf{q}_s + m_{e^-} \nabla \cdot \mathbf{q}_{e^-} = \nabla \cdot \left( \sum_{c,i} \int f_{ci} m_c \, dc + \int f_e m_{e^-} \, dc \right) = 0. \]

As a result, Eq. (15) takes the form Eq. (13).

3. Description of the local equilibrium flows of ionized oxygen

The equilibrium flows of plasma have been widely discussed in the literature (see, for example, [8, 9, 10, 11, 12]). In Ref. [7] it was proposed to use for the study of equilibrium states of ionized gas systems the distribution functions which correspond to the entropy maximum under the constraint of conservation of the numbers of atoms nuclei and the electrons (both bound and free) in the systems.

In the local equilibrium flows of ionized monatomic oxygen such functions can be represented in the form [13]:

\[ f_{ci}^{0}(r, c, t) = s_{ci} \frac{m_c^3}{h^3} \exp \left( -\frac{m_c c^2/2 + \varepsilon_{ci}}{kT} + \gamma_1 + \gamma_2 (8 - c) \right), \quad (16) \]
\[ f_{e^-}(r, c, t) = \frac{m_{e^-}^3}{h^3} \exp \left( -\frac{m_{e^-}c^2}{2kT} + \gamma_2 \right). \] (17)

Here \( h \) and \( k \) are the Planck constant and the Boltzmann constant. \( T(r, t) \) is the temperature; multipliers \( \gamma_1(r, t) \) and \( \gamma_2(r, t) \) are pre-collision invariants which are connected with the nuclei and the electrons conservation.

After substitution of the distribution functions (16)–(17) to formulae (9)–(12) we obtain the relation:

\[
P = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix},
\] (18)

where \( p = nkT \) is a pressure, and the flux terms are equal to zero:

\[
q = 0, \quad q_e = 0, \quad q_{e^-} = 0.
\] (19)

Thus, the system (1)–(4) can be written in the form [13]:

\[
\frac{dv}{dt} = F - \frac{1}{\rho} \nabla p,
\] (20)

\[
\frac{de}{dt} = -(e + p) \nabla \cdot v,
\] (21)

\[
\frac{dn_s}{dt} = -\tilde{n}_s \nabla \cdot v,
\] (22)

\[
\frac{dn_{e^-}}{dt} = -\tilde{n}_{e^-} \nabla \cdot v.
\] (23)

The solution of system (20)–(23) allows us not only to determine the functions \( v(r, t), T(r, t), \tilde{n}_s(r, t), \tilde{n}_{e^-}(r, t) \), but also to find equilibrium concentrations of the oxygen atoms \( n_0(r, t) \), ions \( n_c(r, t) \ (c = 1, 8) \) and free electrons \( n_{e^-}(r, t) \), corresponding to functions (16)–(17) and represented in the form:

\[
n_c = Z_c(T)x^8 - c, \quad c = 0, 8,
\] (24)

\[
n_{e^-} = Z_{e^-}(T)y.
\] (25)

Here the notation \( Z_c(T) \) and \( Z_{e^-}(T) \) is used for partition functions of the particles \( O(c) \) with charge \( c = 0, 1, \ldots, 8 \), and for free electrons \( e^- \). Also \( x = e^\gamma_1 \) and \( y = e^\gamma_2 \).

Indeed, relations (7) and (8) can be represented in the form:

\[
\sum_{c=0}^{\infty} n_c = \tilde{n}_s,
\] (26)

\[
\sum_{c=0}^{8} n_c(8 - c) + n_{e^-} = \tilde{n}_{e^-}.
\] (27)

After substituting Eq. (24) and Eq. (25) into expressions (26) and (27), we obtain a system of two equations from two unknowns \( x \) and \( y \). In [7] it was shown that this system has a unique solution.
4. Results and discussion
For illustration, we present the equilibrium concentrations of the oxygen atoms, ions and free electrons, normalized by the oxygen particles density \( \tilde{n}_e = N_L \) (\( N_L \) is Loschmidt’s number) and also the pressure of ionized mixture in the wide temperature range (see Fig. 1 and Fig. 2). In calculation of the partition functions the data of [14] are used.

![Equilibrium composition of monatomic ionized oxygen.](image1)

**Figure 1.** Equilibrium composition of monatomic ionized oxygen.

![Dependence of pressure on the mixture temperature.](image2)

**Figure 2.** Dependence of pressure on the mixture temperature.

Figure 1 clearly shows the presence of only oxygen atoms \( \left( \frac{n_0}{N_L} = 1 \right) \) in an equilibrium mixture in the temperature range \( T \leq 10000 \) K and a further monotonic decrease in the density of atoms. One can also see the sequential relative ion concentrations \( \frac{n_c}{N_L} \) \( (c = 1, 6) \). Each of these concentrations increases to a certain maximum and then decreases monotonically. The
increase in the last two relative ion concentrations $\frac{n_{c}}{N_{L}}$ ($c = 7, 8$) are not shown here, since a higher temperature is required to detach the last two electrons from the atomic shell. Moreover, Figure 1 clearly shows a monotonic increase in the relative concentration of free electrons $\frac{n_{e}}{N_{L}}$.

Figure 2 shows the monotonic growth of the pressure, which is due to the change in the number of particles, as well as the growth of free electrons density. That is why a non-linear growth is reflected here.

5. Conclusion
The flows of monatomic oxygen with multiple ionization are investigated. The conservation equations system for ionized oxygen flows is derived. Equilibrium distribution functions of ionized particles and free electrons are used. Under these conditions a reduced system of equations describing the local equilibrium flows of ionized oxygen is obtained. This system significantly simplifies the determination of equilibrium flow parameters and calculation of the gas mixture equilibrium composition.

Equilibrium concentrations of oxygen atoms, ions and free electrons are presented for illustration. A non-linear dependence of pressure on temperature is also emphasized.

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