Highlights

*Ab initio* modelling of transport phenomena in multi-component mixtures of rarefied gases.

Felix Sharipov

- Reduced shear stress of a mixture is smaller than that for a single gas

- Reduced heat flux through a mixture is larger than that for a single gas

- Thermal diffusion phenomenon leads to non-uniform chemical composition

- Velocity and temperature of each species in a mixture can be different from each other
Ab initio modelling of transport phenomena in multi-component mixtures of rarefied gases.

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Abstract
The direct simulation Monte Carlo method based on ab initio potentials is applied to model transport phenomena in binary, ternary and quaternary mixtures of noble gases. To this end, the Couette and Fourier problems are solved over the whole range of the rarefaction parameter spanning the near free-molecular, transitional, and slip flow regimes. Moreover, analytical solutions are obtained in the limits of the free-molecular and continuous medium regimes of flow. As a result, the shear stress, heat flux through multi-component mixtures, distributions of velocity, temperature, and mole fractions of each species are calculated as a function of the gas rarefaction. An analysis of these data points out the properties which are strongly affected by the chemical composition. It is found that the largest deviations of characteristics of mixtures from those of a single gas are observed for the binary mixture of helium and krypton, while their deviations for the ternary and quaternary mixtures are smaller. A temperature variation in a mixture leads to non-uniform distributions of chemical composition due to the thermal diffusion phenomenon. Such redistributions are analyzed in both problems and their effect on the heat and momentum transfer is evaluated. The reported results can be used to evaluate the main factors determining transport phenomena in practical applications such as vacuum systems, microfluidics, gas separation technology, space research etc.

Keywords: Couette flow, Fourier flow, gaseous mixture, ab initio potential, diffusion, thermal diffusion

1. Introduction

Most works related to non-equilibrium phenomena in microfluidics and vacuum systems report results concerning flows of single gases. Many textbooks are also restricted by only single gas theory [1, 2]. However in practice, one deals with gaseous mixtures more often than with a single gas. This fact motivated a study of flows of binary gaseous mixtures over a wide range of the Knudsen number, see e.g. Refs. [3–17]. It was found that the behavior of binary mixtures is significantly different from that of single gas. Moreover, the intermolecular potential affects significantly mixture flows according to Refs. [3, 4]. Ternary and quaternary gaseous mixtures are also often met in practice, but such flows were not studied deeply yet. The textbooks [18–22] describe a general kinetic theory of multi-component mixtures of dilute gases. The diffusion phenomenon in multi-component mixtures was studied in Refs. [23–30] where the authors tried to relate the diffusion coefficients of a multi-component mixture to those of binary mixtures. The transport coefficients of mixtures such as viscosity, thermal conductivity, diffusion and thermal diffusion are reported in Refs. [31–38]. The moment method for quaternary mixtures based on the Boltzmann equation was proposed in the paper [39]. All above mentioned papers concern transport phenomena in the limit of continuous medium, i.e. when the molecular mean free path is quite smaller than a characteristic size of flow. The slip boundary conditions for a mix-
ture moving near a solid wall obtained in Refs.[40–42] allow to extend the continuous theory to slightly rarefied gases. However, the information about multi-component mixture flows over the whole range of the gas rarefaction is very poor. Szalmas solved couple of problems on flows of ternary mixtures of rarefied gases [43–45] applying a simplified Boltzmann equation elaborated by McCormack [46], which is valid for weakly non-equilibrium systems. To the best of knowledge of the author, there is no any information about strong non-equilibrium ternary and quaternary gaseous mixtures over the whole range of the gas rarefaction covering the free-molecular and transitional regimes of flow.

In the present work, an approach based on the direct simulation Monte Carlo (DSMC) method to a modelling of strong non-equilibrium multi-component mixtures over the whole range of the rarefaction parameter spanning the free-molecular, transitional, and viscous regimes is developed. Since the effect of interatomic potential on mixture flows is strong [3, 4], the collisions are modelled applying \textit{ab initio} potentials, which are most reliable at the moment. Two benchmark problems, namely, Couette and Fourier flows are solved. The solutions of these problems for a single gas are compared to those for binary, ternary and quaternary mixtures. The integral characteristics such as shear stress and heat flux as well as distributions of temperature, bulk velocity and mole fraction of each component are analyzed. The influence of the chemical composition on these characteristics is pointed out. The main finding of the present study is that some characteristics of ternary and quaternary mixtures deviate from those of single gas less than the corresponding characteristics of binary mixture.

2. Statement of the problem

We consider a mixture of $K$ monatomic gases confined between two parallel planar surfaces fixed at $x = \pm H/2$. In equilibrium state, the mixture has the pressure $p_0$ and the temperature $T_0$. The chemical composition of the equilibrium mixture can be characterized by the mole fraction of each species defined as

$$C_{0i} = n_{0i}/n_0, \quad n_0 = \sum_{i=1}^{K} n_{0i}. \tag{1}$$

where $n_{0i}$ is the equilibrium number density of species $i$. The equilibrium of mixture can be disturbed by two factors: a relative motion of the surfaces and by different temperatures of the surfaces. The first problem called Couette flow assumes that both surfaces are kept at the same temperature $T_0$, but the surface at $x = H/2$ is moving with a speed $U/2$ in the $y$-direction, while the plate $x = -H/2$ is moving with the same speed in the opposite direction. We are interested in the shear stress $P_{xy}$ and velocity profiles of each component. When the speed $U$ is large enough, the temperature of the mixture is not constant. As a result, the gaseous species are distributed non-uniformly because of the thermal diffusion phenomenon. These distributions are also of our interest. The second problem called Fourier flow means that the surfaces are at rest, but the one of them at $x = H/2$ is kept at a higher temperature $T_0 + \Delta T/2$, while the other at $x = -H/2$ has a lower temperature $T_0 - \Delta T/2$. Now, our aim is the heat flux $q_{xy}$ and distributions of the temperature and mole fractions of each species.

The main parameter determining the solution of both problems is the rarefaction parameter inversely proportional to the Knudsen number and defined as [2]

$$\delta = \frac{H}{\ell_0}, \quad \ell_0 = \frac{\mu_0 v_0}{p_0}, \tag{2}$$

where $\ell_0$ is the equivalent free path and $\mu_0$ is the viscosity of the mixture at the temperature $T_0$, $v_0$ is the characteristic molecular speed

$$v_0 = \sqrt{2k_B T_0/m_0}, \tag{3}$$

$k_B$ is the Boltzmann constant, $m_0$ is the mean mass of the mixture

$$m_0 = \sum_{i=1}^{K} C_{0i} m_i, \tag{4}$$

$m_i$ is the atomic mass of species $i$. The viscosity $\mu$ reported in the papers [37, 47, 48] for a wide range of the temperature are used to determine the rarefaction parameter. The limit of small rarefaction parameter ($\delta \to 0$) represents the free-molecular regime when the particles interact mostly with the surfaces, but not between them. The values $\delta \sim 1$ correspond to the transitional regime, when the interatomic collisions and gas-surface interaction play the same role in the transport phenomena. The
large values of the rarefaction parameter $\delta \to \infty$ describe the continuous limit, when the interatomic collisions prevail over the gas-surface scattering.

When the system is out of equilibrium, its main characteristics are calculated via the velocity distribution function $f_i(x, v_i)$ obeying the Boltzmann equation [18, 19]. Here, $v_i$ is the molecular velocity of species $i$. The local number density of each species and that of the mixture are given as

$$n_i(x) = \int f_i(x, v_i) \, dv_i, \quad n = \sum_{i=1}^{K} n_i. \tag{5}$$

Then, the local mole fraction can be calculated as

$$C_i = n_i / n. \tag{6}$$

The mean velocity of each species is expressed via the velocity distribution function $f_i$ as

$$u_i(x) = \frac{1}{n_i} \int v_j f_i(x, v_i) \, dv_i, \tag{7}$$

which has only the $y$-component. The hydrodynamic (or bulk) velocity of mixture is defined as

$$u = \frac{\sum_{i=1}^{K} m_i n_i u_i}{\sum_{i=1}^{K} m_i n_i}. \tag{8}$$

The temperature of each species is defined relative to the bulk velocity of the mixture

$$T_i(x) = \frac{m_i}{3 k_B n_i} \int \left[ v_{yi}^2 + (v_{yi} - u)^2 + v_{zi}^2 \right] f_i(x, v_i) \, dv_i. \tag{9}$$

Then, the mixture temperature is calculated as the mean value of all temperatures $T_i$

$$T = \sum_{i=1}^{K} C_i T_i \tag{10}$$

with $C_i$ defined by (6). The shear stress $P_{xy}$ and heat flux $q_x$ of the mixture are just the sum of the corresponding quantities of all species

$$P_{xy} = \sum_{i=1}^{K} P_{xyi}, \quad q_x = \sum_{i=1}^{K} q_{xi}. \tag{11}$$

related to the distribution function as

$$P_{xyi} = m_i \int v_{yi} v_{yi} f_i(x, v_i) \, dv_i, \tag{12}$$

$$q_{xi} = \frac{1}{2} m_i \int v_{yi}^2 v_{xi} f_i(x, v_i) \, dv_i. \tag{13}$$

Note, the quantities $P_{xyi}$ and $q_{xi}$ depend on the coordinate $x$, while both $P_{xy}$ and $q_x$ are constant over the gap between the plates because of momentum and energy conservation for the whole mixture. The results of these two problems will be given in terms of the dimensionless quantities defined via the relative plate speed $U/v_0$ and relative temperature difference $\Delta T/T_0$ as

$$\Pi = -P_{xy} v_0 / (p_0 U), \tag{14}$$

$$Q = -q_x T_0 / (p_0 v_0 \Delta T), \tag{15}$$

therefore $\Pi$ and $Q$ are always positive.

As stated above, a correct description of the interatomic collisions is important to model transport phenomena through rarefied gases. In addition, such phenomena are determined also by the gas-surface interaction. Each species has its own accommodation coefficients which depend on surface characteristics too. The effect of the accommodation coefficients on the problems in question was studied in Refs.[49, 50]. An implementation of non-diffuse scattering on a solid surface into the DSMC method was also done, see e.g. [51]. However, the purpose of the present study is to investigate the effect of the mixture chemical composition on transport phenomena hence it is reasonable to assume that all species are reflected from the surfaces according to the same model. The accommodation coefficients of most gases are close to unity [52] so that we assume that all species are reflected diffusely from both surfaces.

### 3. Free-molecular limit

The solutions of the Couette and Fourier problems in the free-molecular regime are well known for a single gas [2, 53] and for binary mixtures [3, 4]. These solutions are easily generalized for multi-component mixtures.
3.1. Couette flow

In the case of the Couette flow, the local chemical composition of the mixture is not affected by the plate motion so that the mole fractions are kept equal to their value in the equilibrium state $C_{0i}$. The shear stress is calculated as a superposition of those for each species composing the mixture. According to [2], the shear stress caused by one species under the diffuse scattering reads

$$P_{xy,i} = \frac{p_{0i}}{\sqrt{\pi}} \sqrt{\frac{m_i}{2k_bT_0}} U_i,$$

where $p_{0i} = n_0 k_b T_0$ is the partial pressure of species $i$. Substituting (16) into (12) and then into (14), we obtain

$$\Pi = \frac{1}{\sqrt{\pi}} \sum_{i=1}^{K} C_{0i} \sqrt{\frac{m_i}{m_0}}.$$  

(17)

Since $\sum_{i=1}^{K} C_{0i} \sqrt{m_i/m_0} < 1$, the dimensionless shear stress $\Pi$ for a mixture is always smaller than that for a single gas.

The velocity of each component in this regime is just zero $u_i = 0$ so that the mean velocity of the whole mixture is zero too. The temperatures of all species are the same and equal to that of the whole mixture

$$T = T_0 \left[ 1 + \frac{1}{6} \left( \frac{U}{v_0} \right)^2 \right],$$

(18)

i.e. the temperature of the mixture in the gap is constant and larger than the equilibrium temperature $T_0$ even in the collisionless regime of flow. Naturally, the temperature $T$ increases when the relative speed of the surfaces $U/v_0$ increases.

3.2. Fourier flow

The heat flux $q_{si}$ through a single species reflected diffusely from the surfaces is expressed in term of the relative temperature difference $\theta = \Delta T/2T_0$ as [2]

$$q_{si} = \frac{4p_{0i}}{\sqrt{\pi}} \frac{\theta \sqrt{1-\theta^2}}{\sqrt{1-\theta} + \sqrt{1+\theta}} \sqrt{\frac{2k_bT_0}{m_i}}.$$  

(19)

Its substitution into (11) and (15) leads to

$$Q = 2 \frac{1}{\sqrt{\pi}} \frac{\sqrt{1-\theta^2}}{\sqrt{1-\theta} + \sqrt{1+\theta}} \sum_{i=1}^{K} C_{0i} \sqrt{\frac{m_0}{m_i}}.$$  

(20)

Note, since $\sum_{i=1}^{K} C_{0i} \sqrt{m_0/m_i} > 1$, the heat flux $Q$ through a mixture is always larger than that for a single gas. The temperature of all species and of the mixture is smaller than the equilibrium temperature and equal to

$$T = T_0 \sqrt{1 - \theta^2}.$$  

(21)

The local number densities of species of the mixture for this problem are not affected so that they are equal to their value in the equilibrium state $n_{0i}$.

4. Limit of continuous media

4.1. Main equations

In the limit of continuous media ($\delta \to \infty$), the solution is based on the Navier-Stokes and Fourier equations. However, the transport coefficients, namely, viscosity, thermal conductivity, diffusion and thermal diffusion coefficients are functions of the mixture temperature and its chemical composition. Because of this feature, the solution of the problems in question become non-trivial even in an one-dimensional stationary case. In general, such problems can be solved only numerically using the database of the transport coefficients [37, 38]. Below, some simplifications are made in order to obtain an analytical solution.

First, the mass, momentum, and energy conservation laws valid for any rarefaction parameter $\delta$ are employed in the following form

$$\frac{1}{H} \int_{-H/2}^{H/2} n_i(x) \, dx = n_{0i},$$

(22)

$$\frac{dP_{xy}}{dx} = 0, \quad \frac{dq_{xy}}{dx} + P_{xy} \frac{dt}{dx} = 0.$$  

(23)

Then, the constitutive equations valid only in the continuous limit ($\delta \to \infty$) are used.

When the temperature is spatially variable, a non-uniform mole fraction is established because of the thermal diffusion phenomenon [18, 19, 29, 38]

$$\frac{dC_i}{dx} = -C_i(1 - C_i) \alpha_{si} \frac{d\ln T}{dx},$$

(24)

where $\alpha_{si}$ are the thermal diffusion factors. According to the definition of $\alpha_{si}$ introduced in Ref.[38], they obey the
relation

$$\sum_{i=1}^{K} C_i (1 - C_i) \alpha_{ij} = 0,$$

(25)

which means there are $K - 1$ independent thermal diffusion factors for mixture of $K$ species.

The first constitutive equation, namely, the Newton law relating the pressure tensor to the rate-of-shear tensor has the same form as that for a single gas [2, 19]. For the planar Couette flow, this law reads

$$P_{xy} = -\mu \frac{d\mathbf{u}}{dx}.$$

(26)

The heat flux $q_x$ through a mixture being at rest is given by the second constitutive equation, i.e., Fourier law [2, 19, 32]

$$q_x = -\kappa \frac{dT}{dx},$$

(27)

where $\kappa$ is the thermal conductivity of the mixture. The peculiarity of this coefficient for a mixture is that it depends not only on the local temperature and mole fraction, but also on the local gradients of the mole fraction [32]. Here, we will use that one corresponding to the stationary state when time-independent mole fraction distributions are established. Thus, the Couette problem requires a solution of the system of equations (22)-(27), while the Fourier problems is based on Eqs. (22), (23), (24), and (27). The numerical data of the transport coefficients of multi-component mixtures reported in Refs. [37, 38, 47, 48, 54] can be used for a numerical solution. However, some approximations of these coefficients allow to solve both problems analytically.

Usually, the dependence of viscosity and thermal conductivity on the temperature is approximated as [19, 53]

$$\mu(T) = \mu_0 \left( \frac{T}{T_0} \right)^{\omega_{\mu}}, \quad \kappa(T) = \kappa_0 \left( \frac{T}{T_0} \right)^{\omega_{\kappa}},$$

(28)

where $\mu_0$ and $\kappa_0$ correspond to the temperature $T_0$. The indexes $\omega_{\mu}$ and $\omega_{\kappa}$ are assumed to be constant and equal to each other. Indeed, for a single gas we have $\omega_{\mu} = \omega_{\kappa}$, but their values are dependent on the temperature [55]. The quantities $\omega_{\mu}$ and $\omega_{\kappa}$ for some equimolar mixtures based on the data [37] are plotted against the temperature in Figure 1. In this case, the indexes $\omega_{\mu}$ and $\omega_{\kappa}$ are also temperature dependent and, in addition, $\omega_{\mu}$ and $\omega_{\kappa}$ are different.

The transport coefficients also depend on the chemical composition that must be taken into account in numerical calculations by Eq. (24). However, the dependence of these coefficients on the mole fractions is not trivial that does not allow to obtain the analytical solution. Below, the analytical solution will be obtained assuming the quantities $\mu_0$ and $\kappa_0$ in Eq. (28) to be constant. Moreover, we assume that the indexes $\omega_{\mu}$ and $\omega_{\kappa}$ are constant and equal to each other, i.e., $\omega_{\mu} = \omega_{\kappa} = \omega$. Then, the error of these approximations will be estimated by a comparison
the analytical solution with the DSMC results.

To extend the solution based on the continuous medium equations to the slip flow regime, the boundary conditions should take into account the velocity slip and temperature jump phenomena \[2, 52, 56–58\] written down as

\[
\begin{align*}
    u = \pm \left( \frac{U}{2} - \sigma_s \ell \frac{du}{dx} \right) & \quad \text{at} \quad x = \pm \frac{H}{2}, \\
    T = T_0 \pm \left( \frac{\Delta T}{2} - \zeta_t \ell \frac{dT}{dx} \right) & \quad \text{at} \quad x = \pm \frac{H}{2},
\end{align*}
\]

respectively. Here, \(\ell\) is the local equivalent free path. The values of the velocity slip and temperature jump coefficients for single gases and binary mixtures can be found in Ref.\[52\]. In the case of ternary and quaternary mixtures considered here they are unknown. However, the coefficients can be extracted from the numerical data of the velocity \(v_u\) and temperature \(v_T\) gradients reported in Ref.\[55\] for the weakly disturbed Couette and Fourier flows, i.e.

\[
\begin{align*}
    v_u = \frac{H}{U} \frac{du}{dx} \bigg|_{x=0} = \frac{1}{1 + 2\sigma_s/\delta}, \\
    v_T = \frac{H}{\Delta T} \frac{dT}{dx} \bigg|_{x=0} = \frac{1}{1 + 2\zeta_t/\delta},
\end{align*}
\]

when \(U \ll v_0\) and \(\Delta T \ll T_0\).

The analytical solution contains the Prandtl number \(Pr\), which is expressed in terms of the viscosity and thermal conductivity as

\[
Pr = c_p \frac{\mu_0}{k_0}, \quad c_p = \frac{5k_0}{2m_0},
\]

with \(c_p\) being the specific heat at a constant pressure.

The numerical values of the Prandtl number \(Pr\), thermal diffusion factors \(\alpha_{ij}\), velocity slip \(\sigma_s\), and temperature jump \(\zeta_t\) coefficients based on the data reported in Refs.\[37, 38, 55\] are summarized in Table 1 for the mixture temperature of \(T = 300\) K.

4.2. Couette flow

A combination of Eqs.\(23\), \(26\), \(27\) and \(28\) leads to the following system of two differential equations

\[
\frac{d}{dx} T_s \frac{du}{dx} + \mu_0 T_s \left( \frac{du}{dx} \right)^2 = 0. \tag{35}
\]

An analytical solution of the system under the boundary conditions \(29\) and \(30\) can be obtained in terms of expansion with respect to the parameter \(\epsilon\) defined as

\[
\epsilon = \left( \frac{U/v_0}{1 + 2\sigma_s/\delta} \right)^2 \frac{Pr}{15}. \tag{36}
\]

The behaviour of the Prandtl number \(Pr\) for multi-component mixtures is analyzed in Ref.\[55\]. It is close to \(2/3\) for a single gas. It is even smaller for gaseous mixtures so that the parameter \(\epsilon\) is smaller than unity in a wide range of the wall speed \(U\). Thus, expanding the quantities \(u\) and \(T\) with respect to \(\epsilon\) up to the second order \((\epsilon^2)\), the solution of the system \(34\) and \(35\) reads

\[
\begin{align*}
    u(x) &= \frac{U x}{1 + 2\sigma_s/\delta} \left[ 1 - 2\omega \epsilon \left( \frac{1}{4} \frac{x^2}{H^2} + \frac{\sigma_s}{\delta} \right) \\
    &\quad + \frac{\omega \epsilon^2}{100} \left( \frac{1}{4} \frac{x^2}{H^2} \right) \right] \times \left( 3\omega + 7 - 4(7\omega + 3) \frac{x^2}{H^2} \right) + O(\epsilon^3), \tag{37}
\end{align*}
\]

\[
\begin{align*}
    T(x) &= T_0 \left[ 1 + 6\epsilon \left( \frac{1}{4} \frac{x^2}{H^2} + \frac{\zeta_t}{\delta} \right) \right] \\
    &\quad + \frac{4\omega \epsilon^2}{5} \frac{x^2}{H^2} \left( \frac{1}{4} \frac{x^2}{H^2} \right) + O(\epsilon^3). \tag{38}
\end{align*}
\]

To obtain the terms of the order of \(\epsilon^2\), the velocity slip and temperature jump were disregarded, i.e. the terms of the order \(\epsilon^3/\delta\) were neglected. The expressions similar to \(37\) and \(38\) were obtained previously \[3\] without the terms of the order \(\epsilon^2\). Here, the terms of this order were obtained to show that their contributions are small even for large values of the wall speed. For instance, they are about 0.02% if \(U = 2v_0\). Thus, the expressions \(37\) and \(38\) provide and accurate analytical solution in a wide range of the wall speed \(U\).

Substituting \(37\) into \(26\) and using \(14\), the dimensionless shear stress is obtained

\[
\Pi = \frac{1}{(\delta + 2\sigma_s)} \left[ 1 + \epsilon \omega \left( 1 + 2 \frac{3\zeta_t - \sigma_s}{\delta} \right) \right]
\]

6
In this case, the term of the order $\epsilon^2$ contributes with 0.15% when $U = 2v_0$.

Using the relations (22) and (24), the mole fraction is obtained as

$$C_i(x) = C_0 \left[ 1 + \epsilon (1 - C_0) \alpha_{ii} \left( 6\epsilon^2 - \frac{1}{2} \right) + O(\epsilon^3) \right].$$

(40)

### 4.3. Fourier problem

The solution of the Fourier problem is based on Eq. (35) assuming $u = 0$. Then, the solution can be written down in the following form

$$T = T_0 (A + Bx)^{1/(\omega+1)},$$

(41)

where the constant $A$ and $B$ are obtained from the boundary condition. First, these constants are found from the temperature continuity condition, i.e.

$$T = T_0 (1 \pm \theta) \quad \text{at} \quad x = \pm \frac{H}{2}.$$

(42)

In this case, we have

$$A_0 = \frac{1}{2} \left[ (1 + \theta)^{\omega+1} + (1 - \theta)^{\omega+1} \right],$$

(43)

$$B_0 = \frac{1}{H} \left[ (1 + \theta)^{\omega+1} - (1 - \theta)^{\omega+1} \right].$$

(44)

The solution (41) with the coefficients (43) and (44) was obtained previously in Refs.[4, 59, 60]. Here, these coefficients are corrected taking into account the temperature jump condition (30) with the local equivalent free path

$$\ell^* = \ell_0 (1 \pm \theta)^{\omega+1/2} \quad \text{at} \quad x = \pm \frac{H}{2}.$$  

(45)

The corrected coefficients $A$ and $B$ read

$$A = A_0 + \left[ (1 - \theta)^{\omega+1/2} - (1 + \theta)^{\omega+1/2} \right] \frac{H\ell_i}{2\delta} B_0,$$

(46)

$$B = B_0 \left[ 1 - \left[ (1 - \theta)^{\omega+1/2} + (1 + \theta)^{\omega+1/2} \right] \frac{\ell_i}{\delta} \right].$$

(47)

Assuming that the factor $C_0(1 - C_0) \alpha_{ii}$ in the right-hand side of (24) is constant and using the temperature profile (41), the mole fraction profiles are obtained as

$$C_i = C_0 \left[ 1 - \frac{(1 - C_0) \alpha_{ii}}{\omega + 1} \ln (A + Bx) \right].$$

(48)

The dimensionless heat flux (15) is calculated with the help of the Fourier law (27) and temperature profile (41)

$$Q = \frac{5}{4\delta Pr} \frac{BT_0}{(\omega + 1)\Delta T}.$$  

(49)

### 5. Transitional regime

In the transitional regime, the DSMC method [53] based on ab initio potentials [55, 61, 62] is applied. The main principles to implement the quantum scattering and

<table>
<thead>
<tr>
<th>gas/mixture</th>
<th>$Pr$</th>
<th>$\alpha_{ii}$</th>
<th>$\omega$</th>
<th>$\sigma_r$</th>
<th>$\zeta_\ell$</th>
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<td>1.95</td>
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Table 1: Prandtl number $Pr$, thermal diffusion factors $\alpha_{ii}$, velocity slip $\sigma_r$ and temperature jump $\zeta_\ell$ coefficients for equimolar mixtures at $T = 300$ K based on the data reported in Refs.[37, 38, 55].
The dimensionless stress tensor $\Pi$ is plotted against the rarefaction parameter $\delta$ in Figure 2. The results for the single helium are also plotted in this figure. The free-molecular solution (17) is shown in Figure 2 by the dashed lines. As expected, the quantity $\Pi$ for all mixtures considered here is smaller than that for a single gas. The smallest value of $\Pi$ corresponds to the binary mixture He-Kr, while the ternary and quaternary mixtures have the value of $\Pi$ intermediate between those for the single gas and binary mixture.

The asymptotic behaviour of $\Pi$ at large rarefaction parameter can be seen better in Figure 3 where the product $\delta \Pi$ is plotted against rarefaction parameter $\delta$. The symbols represent the DSMC results, while the solid lines show the analytical solution (39). The trend that the maximum of $\Pi$ corresponds to the single gas and its minimum corresponds to the binary mixture He-Kr is confirmed also in the limit $\delta \to \infty$. According to the data shown in Figure 3, the analytical solutions for the single gas and all mixtures are in agreement with the corresponding DSMC results within 0.2% at the largest rarefaction parameter considered here $\delta = 80$. As expected, the discrepancy between the two approaches increases when the rarefaction parameter decreases. However, the discrepancy for the single gas is qualitatively different from those for the mixtures. Indeed, the DSMC solution for pure helium leads to a smaller value of $\Pi$ than that obtained by the analytical solution, while the DSMC values of $\Pi$ for the mixtures overstate the corresponding analytical results. The discrepancies are different quantitatively too. For instance at $\delta = 10$, the relative difference between the DSMC and analytical results are 1%, 3.6%, 1%, and 0.4% for He, He-Kr, He-Ne-Kr, and He-Ne-Ar-Kr, respectively. To explain such a difference we should bear in mind that the constitutive equations (26) and (27) used to obtain the analytical solutions are valid under the local equilibrium condition, which is broken when the rarefaction parameter $\delta$ decreases. However, this condition works in a wider range of $\delta$ for a single gas and in a smaller range of $\delta$ for a mix-
ture with significantly different masses like He-Kr. When a species with an intermediate atomic mass (Ne or Ar) is added, the mixture becomes closer to the local equilibrium and the range of validity of the constitutive equation increases.

The relative difference of $\Pi$ for the mixtures from that for the single gas is plotted in Figure 4 which shows that the deviation is significant (about 5%) even in the continuous limit ($\delta \rightarrow \infty$). The main reason of such a deviation is the difference of the Prandtl number $Pr$ and the viscosity index $\omega$ (see Table 1) that appear in the second term inside of the brackets of Eq. (39). Note, the larger the wall speed $U$, the larger the deviation $\Delta \Pi$.

The additional calculation carried out for $T_0 = 50$ K and 5000 K showed that the dimensionless shear stress $\Pi$ just slightly differs from that corresponding to $T_0 = 300$ K. Its relative deviation is plotted in Figure 5 which reveals the deviation close to 1% in the transitional and continuous regimes. This deviation is due to the temperature dependence of both viscosity index $\omega$ and Prandtl number $Pr$ being parts of the second term in the brackets of (39). Naturally, the deviation vanishes in the limit $\delta \rightarrow 0$ according to the analytical solution (17) which is independent of the temperature $T_0$.

The velocities of each species and of the whole mixtures are zero in the free-molecular regime while in the limit of large $\delta$ they are given by (37). According to the analytical solution (37), the velocity is practically independent of the chemical composition. This trend is confirmed also in the transitional regime. The velocity profiles of the quaternary mixture are plotted in Figure 6 for some values of the rarefaction parameter. The profiles for $\delta = 10$ and 40 based on the DSMC method are compared with the analytical solution (37). The comparison points out an excellent agreement even in the case of the relatively small rarefaction parameter $\delta = 10$.

An analysis of the velocity profiles of each species in mixtures shows that they are the same in the continuous limit ($\delta \rightarrow \infty$) and given by (37). In the free molecular regime, the velocities of all species are zero. However, the profiles of some species can be different from others in the transitional regime ($\delta \sim 1$) even if all species are reflected by the walls in accordance with the same law, namely diffuse scattering. The typical profiles at $\delta = 0.5$ for the quaternary mixtures are plotted in Figure 7, which shows that the lighter species (He) has a smaller velocity, while the heavier species (Kr) is faster. The difference of the velocities near the wall reaches 20%.

The temperature profile in the free-molecular regime

Figure 3: Product $\delta \Pi$ vs. rarefaction parameter $\delta$: symbols - DSMC results, solid lines - analytical solution in the continuous limit (39).

Figure 4: Relative deviations of shear stress $\Delta \Pi / \Pi = (\Pi_{\text{He}} - \Pi_{\text{mix}}) / \Pi_{\text{He}}$ of mixtures from that for single helium vs. rarefaction parameter $\delta$: symbols - DSMC solution, dashed lines - analytical solution (39).
Figure 5: Relative deviations of shear stress $\Pi$ of quaternary mixtures at $T_0 = 50$ K and 5000 K from that $\Pi_{300}$ corresponding to $T_0 = 300$ K vs. rarefaction parameter $\delta$: $\Delta \Pi/\Pi = (\Pi - \Pi_{300})/\Pi_{300}$.

Figure 6: Velocity profile of quaternary mixture in the Couette problem: solid lines - DSMC solution, dashed lines - analytical solution (37).

Figure 7: Velocity profiles of each component and of quaternary mixture itself in the Couette problem at $\delta = 0.5$.

(18) is constant over the gap and independent of the chemical composition of the mixture so that it is determined only by the surface speed $U/v_0$. The profile becomes parabolic with increasing rarefaction parameter and tends to the analytical solution (38). In the continuous limit ($\delta \to \infty$), the temperature profile strongly depends on the chemical composition because of the Prandtl number in the second term of the brackets of Eq.(38). The profiles of the single gas and mixtures obtained by both DSMC and analytically are plotted in Figure 8 for $\delta = 40$, which shows a good agreement between the numerical and analytical solutions. The single gas has the highest temperature, while the binary mixture has the smallest one. The ternary and quaternary mixtures have intermediate temperatures. Such a behavior is in agreement with the analytical solution (38). Indeed, the temperature in the center of the gap ($x = 0$) is proportional to the parameter $\epsilon$ given by (36), which contains the Prandtl number $Pr$. According to Table 1, the values of $Pr$ of the ternary and quaternary mixtures are smaller than that for the single gas and larger than that of the binary mixture.

The chemical composition of mixture in the Couette problem is not uniform due to the thermal diffusion phenomenon. The mole fraction profiles of each species of the quaternary mixture at $\delta = 1$ and $\delta = 40$ obtained by the DSMC are shown by the solid lines in Figure 9.

It is observed that the mole fraction profiles at $\delta = 1$
and $\delta = 40$ are very close to each other. However, a further decrease of the rarefaction parameter leads to smaller variations of the mole fractions, which vanish in the limit $\delta \to 0$. The analytical solution (40) is also given in Figure 9 for $\delta = 40$ by the dashed lines. The DSMC and analytical solutions at $\delta = 40$ are in a good agreement between each other. Since the thermal diffusion factor of the lightest species (He) is negative, see Table 1, its mole fraction profile has the same gradient sign as that of the temperature, i.e. the concentration of helium is larger in the gap center and smaller near the walls. The second light component (Ne) has the same behaviour with a smaller variation of the mole fraction. In contrast, the heaviest species (Kr) has a concentration in the gap middle smaller than near the walls. The argon gas has a similar behaviour. It is curious that all profiles intersect the equilibrium value $C_{ni}$ in the same coordinate $x$. This behaviour is consistence with the analytical solution (40), which points out the intersection point being always at $x/H = 1/\sqrt{12} \approx 0.29$.

6.2. Fourier flow

The Fourier problem was solved for the same mixtures and rarefaction parameter as the Couette flow problem. The dimensionless heat fluxes $Q$ for the single gas and mixtures are presented in Figure 10 as function of the rarefaction parameter $\delta$. The dashed lines in this figure cor-
respond to the free-molecular solution (20). In contrast to the shear stress, the quantity $Q$ for a single gas is smallest, while it is largest for the binary mixture He-Kr.

A comparison of the numerical results with the asymptotic behaviour of $Q$, Eq.(49), at large rarefaction parameter is performed in Figure 11 where the product $\delta Q$ based on the DSMC method is plotted by symbols against the rarefaction parameter $\delta$. The minimum of $Q$ for the single gas and its maximum for the binary mixture are verified also in the continuous limit $\delta \to \infty$, which is plotted by the solid lines. It can be seen that the numerical solution tends to the analytical one with increasing rarefaction parameter $\delta$. The discrepancy between the DSMC and analytical solutions for the single gas at $\delta = 80$ is within the numerical error 0.1%, but the same discrepancy for the mixtures exceeds the numerical error and reaches 3.4% in the case of He-Kr. The explanation of such a disagreement is the assumption about the independence of the thermal conductivity of chemical composition adopted to obtain the solution (49). Actually, the thermal conductivity depends on the chemical composition [37], which is variable in the Fourier problem. In spite of the assumption, the approximate analytical solution provides a reasonable result. If more exact solution in the continuous limit is needed, the corresponding equations should be solved numerically using a database of the transport coefficients reported in Refs.[37, 38]. Naturally, the discrepancy between the DSMC and analytical solutions increases when the rarefaction parameter decreases. For instance, the difference at $\delta = 10$ varies from 10% to 21% being the smallest for pure helium and largest for the binary mixture.

The relative deviation of $Q$ for the mixtures from that for the single gas is shown in Figure 12. In this case, the deviation is strong and it increases when the rarefaction parameter increases. The Prandtl number and the viscosity index are the main reasons for these significant deviations which are kept even for a small temperature difference $\Delta T$.

The effect of the equilibrium temperature $T_0$ on the dimensionless heat flux $Q$ is shown in Figure 13. As can be seen, this effect is about 1% in the transitional regime, but it sharply increases up to 12% in the continuous regime when $T_0 = 50$ K. In the case of $T_0 = 5000$ K, the influence of the equilibrium temperature does not exceed 4.2%. Indeed, the heat flux $Q$ at $\delta \to \infty$ is determined
basically by the Prandtl number $Pr$ and viscous index $\omega$ in accordance with (49). In turn, these two quantities are sensitive to the temperature [55].

The temperature profile of a mixture varies from the constant value (21) in the free-molecular regime to the almost linear function in the continuous limit (41). The temperatures of the mixtures are weakly affected by their chemical compositions and similar to that of a single gas. Some temperature profiles of the quaternary mixture are shown in Figure 14. A comparison of the profile based on the DSMC solution at $\delta = 40$ with the analytical solution (41) performed in Figure 14 shows a perfect agreement between them. Concerning the temperature of each species of a mixture, all of them are the same when $\delta \to 0$ and also when $\delta \to \infty$. However, the profiles of the species are different from each other in the transitional regime ($\delta \sim 1$) even if of all species interact with the surface equally. An example of such difference is shown in Figure 15 where the profiles of each species of the quaternary mixture at $\delta = 0.5$ are plotted. As can be seen, the lighter species (He) has a smaller temperature and the heavier species (Kr) has a higher temperature near the hot surface. The difference of the temperatures is about 10%. The other species Ne and Ar have intermediate temperatures. Near the colder plate, all temperature are close to each other.

The strong temperature gradient leads to a non-uniform
chemical composition of mixtures because of the thermal diffusion phenomenon. This phenomenon does not exist in the free-molecular regime so that the chemical composition does not vary in this limit. In the continuous limit, the mole fraction varies according to Eq. \(48\). The mole fraction of each species in the quaternary mixture at \(\delta = 40\) obtained by the DSMC are plotted by the solid lines in Figure 16. The corresponding analytical solution \(48\) is shown by the dashed lines. The solutions are in a good agreement with each other. A small disagreement is due to the fact that the thermal diffusion factors are sensitive to the chemical composition, but they were assumed to be constant to derive \(48\). Since the thermal diffusion factors of He and Ne are negative, their concentration near the hotter plate is larger, while Ar and Kr having the negative factors \(\alpha_{ij}\) move to the colder plate.

7. Conclusions

Heat, mass and momentum transfers through multi-component mixtures of rarefied gas were studied over the whole range of the gas rarefaction covering the free-molecular, transitional, and continuous regimes of flow. The transport phenomena were modeled by solving the Couette and Fourier problems. As an example, binary mixture of helium and krypton, ternary mixture of helium, neon and krypton, and quaternary mixture of helium, neon, argon and krypton were considered. In the free-molecular limit, the problems were solved analytically. This regime does not represent any computational difficulty, but indicates the trends of solutions due to the chemical composition of mixtures. The solutions in the continuous limit are based on the Navier-Stokes and Fourier equations and require knowledge of the transport coefficients such as viscosity, thermal conductivity, diffusion and thermal diffusion. Moreover, the velocity slip and temperature jump coefficients are needed to extend the continuous solution to the slip flow regime. Since all these coefficients depend on the chemical composition and temperature, some assumptions are needed to obtain the analytical solution even in the simple one-dimensional flow. In the transitional regime, the problems were solved by direct simulation Monte Carlo method based on \textit{ab initio} potentials of interatomic interactions. The main calculations were carried out for the equilibrium temperature \(T_0 = 300\) K.

The results on the shear stress and heat flux are presented in dimensionless forms, which are weakly dependent on the species of a single gas. However, these quantities are sensitive to the chemical composition in the case of multi-component mixtures. The shear stress for a mixture is always smaller than that for a single gas, while the heat flux is always larger for mixtures. The largest deviations of these quantities from those for a single gas are observed for the binary mixture of helium and kryp-
ton. The deviations for the ternary and quaternary mixtures are smaller than those for the binary mixture. Additional calculations performed for the equilibrium temperature $T_0 = 50$ K and $5000$ K showed that the dimensionless shear stress is weakly (about 1%) affected by $T_0$, while the dimensionless heat flux varies within 12% when the temperature $T_0$ changes from 300 K to 50 K.

The temperature variation of the mixture in the Couette problem depends significantly on its chemical composition. As a result of the non-uniform temperature, the components of the mixtures are distributed also non-uniformly. Usually, the lighter components are concentrated in the middle between the plates, while the heavier components move in the opposite direction. The temperature profiles of mixtures in the Fourier problems are weakly affected by their chemical compositions. The temperature gradient in a mixture leads to a redistribution of its components, i.e. lighter species move to the hotter plate and the heavier ones move to the colder plate. A comparison of the numerical solution with the analytical one at large values of the gas rarefaction shows that the adopted assumption work well for the Couette problem, while they leads to a discrepancy of 3% for the Fourier problem.

The reported results can be used to evaluate the main factors determining transport phenomena in multi-component mixture which are met in many practical applications such as vacuum systems, microfluidics, gas separation technology, space research etc.

**Supplementary material**

The supplementary material contains numerical values of the shear stress $\Pi$ and heat flux $Q$ used to build the plots in Figures 2 - 5 and 10 - 13.

**Declaration of Competing Interest**

The author declares that he has no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data used for the research and omitted in the paper and Supplementary material will be made available on request.

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**References**


