Slip/jump boundary conditions for rarefied reacting/non-reacting multi-component gaseous flows

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ABSTRACT

General concentration-jump, velocity-slip, and temperature-jump conditions on solid surfaces in a rarefied multi-component gas flow are developed using the kinetic theory of gases. The surface is allowed to be catalytic and hence some or all of the species may take part in surface reactions. The presented model provides general boundary conditions which can be simplified according to the problem under consideration. In some limiting cases, the results of the current work are compared to the previously available and widely used boundary conditions. The details of the mathematical procedure are also provided to give a better insight about the physical importance of each term in the slip/jump boundary conditions. Also the disagreements between previously reported results are investigated to arrive at the most proper expressions for the slip/jump boundary conditions. The temperature-jump boundary condition is also modified to handle polyatomic gas flows unlike previously reported studies which were mostly concerned with monatomic gases.

1. Introduction

In recent years, there has been intensive research on microfluidic systems for compact reactor technologies. Investigations have been conducted to better understand and predict the flow, heat transfer and mass transfer properties of so-called microreactors. The microreactor technology combines several advantages such as high material compatibility, high surface area to volume ratio, and large potential for heat and mass transfer, with highly sophisticated and economic fabrication processes.

The continuum equations for mass, momentum and energy conservation are usually employed to study the motion of a fluid, in which the properties of the fluid in each point can be defined as an average of microscopic characteristics of the neighbouring points. The Knudsen number, defined as the ratio of molecular mean-free-path to the characteristic length scale of the problem, can be used to estimate the applicability of the continuum equations in dealing with problems that involve very small length scales or rarefied conditions. For finite values of the Knudsen number Kn, the continuum equations cannot be applied directly and either they should be modified or molecular models should be employed. In the case of rarefied gas flow, it is known that for $Kn < 0.001$ the continuum models are valid, and for $Kn > 10$ the free-molecular models should be employed. In the mid range, neither continuum models nor free-molecular models are satisfactory and another classification is needed: slip flow for the range $0.001 < Kn < 0.1$ and transition flow for the range $0.1 < Kn < 10$ are considered to be appropriate descriptions [1]. In the slip flow regime, the continuum equations can still be employed but proper velocity-slip and temperature and concentration-jump boundary conditions should be specified, which is the subject matter of the present work.

As the pressure is lowered, i.e., the gas is rarefied, or the characteristic length scale of the problem approaches the mean molecular free path, i.e., micro flows, the number of inter-molecular collisions decreases and eventually there comes a stage in which the number of collisions between molecules are rare compared to the number of collisions with other bodies such as the surrounding walls, in which case each molecule acts independently to bring forth the gas properties [2]. This behavior is also confirmed by experimental observations. As the pressure is lowered, it is observed that the gas loses its intimate contact with solid bodies. In viscous flow over solid bodies, the gas "slips" over the surface, and in the case of heat or mass transfer, a temperature or concentration-jump is observed between the solid surface and the adjacent gas layer. According to Kennard [2], Knudt and Warburg reported the velocity-slip in low-pressure gases for the first time.

Fluid flow cannot be described by the Navier–Stokes equations within the Knudsen layer at the wall, which is of the order of 1 molecular mean-free-path in thickness. The presence of gradients causes the velocity distribution function to deviate from the equilibrium distribution significantly. Ideally, the Boltzmann equation should be solved in the Knudsen layer and matched with the solution of the Navier–Stokes equations in the bulk flow region.

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Nomenclature

$\vec{d}$	species diffusion vector
D	species diffusion coefficient
D^{T}	thermal diffusion coefficient
e^{int}	internal energy of molecule
f	velocity distribution function
F	molecular mass flux
J	mass flux
k_{B}	Boltzmann constant
k_{w}	reaction rate constant
K	thermal conductivity
Kn	Knudsen number
m	molecular mass
n	number density
N	number density flux
p	pressure
Pr	Prandtl number
R	specific gas constant, k_{B}/m
T	temperature
U	mass averaged velocity
V	total velocity
V'	peculiar (thermal) velocity
x, y, z	cartesian coordinates
$\vec{X}$	body force vector

Greek symbols

γ	recombination coefficient
$\bar{\gamma}$	specific heat ratio, c_p/c_v
ζ	number of internal degrees of freedom
θ	accommodation coefficient
λ	molecular mean-free-path
μ	viscosity
ξ	number of terms in the Sonine polynomial
ρ	density
σ	total degrees of freedom
τ	Newtonian stress
Φ	normalized perturbation

Subscript and superscripts

+/−	outward/inward directions normal to the wall
M	Maxwellian
NS	number of species
s	edge of the Knudsen layer
w	wall

However, without solving the Boltzmann equation, it is possible to find an approximate Navier–Stokes solution by using suitable slip conditions [1–7]. The first velocity-slip model to address this issue was proposed by Maxwell, who derived a velocity-slip equation based on a Taylor series expansion retaining terms up to first-order. Some other arbitrary extensions to this model have been proposed by others involving higher order or non-linear *Kn* terms.

The effects of velocity-slip and temperature-jump on flow and heat transfer characteristics have been extensively studied. However, there exists very limited work on non-equilibrium transport in reacting flows. In the case of multi-species transport, another important effect analogous to temperature-jump should be taken into account, i.e., the concentration-jump. The investigation of the concentration-jump was initially performed by Kramers et al. [12] based on the work of Maxwell on velocity-slip and temperature-jump. Concentration-jump not only affects the rate of reaction and local species concentration, but also velocity-slip and temperature-jump in both reacting and non-reacting systems.

Many rate-limiting adsorption/desorption reactions are very sensitive to local temperatures and hence the proper modeling and computation of temperature along with the local species concentration is vital for an accurate prediction of the behavior of such systems. The effect of temperature-jump on the performance of reactive systems was investigated and verified experimentally by Shankar et al. [9] using low-pressure catalytic combustion systems. The concentration-jump phenomenon has been detected in simulations of reacting gas mixtures by Bird [10] and Papadopoulos and Rosner [11]. Neglecting the concentration-jump can cause problems in predicting the performance of reactive systems both directly (inaccurate local concentration) and indirectly (inaccurate temperature field).

Generally, the slip (jump) condition is assumed to occur in a very thin layer adjacent to the solid boundary, normally of the order of the mean-free-path of molecules. Two main approaches are usually followed to arrive at proper slip/jump boundary conditions. The first approach is the so-called half-flux method in which the flux of conserved quantities such as mass, momentum and energy are assumed to be constant across the Knudsen layer. The second method, initially proposed by Grad [3], employs essentially the same assumptions, but it is a more rigorous mathematical description of the problem, which alleviates some of the difficulties encountered in the half-flux method associated with reference velocities and calculation of fluxes.

One of the most detailed investigations on the concentration-jump as well as velocity-slip and temperature-jump was performed by Scott [13,14] and Gupta et al. [15]. They followed the half-flux method to determine the velocity-slip and temperature and concentration-jump boundary conditions for a multi-component reacting flow. However, as pointed out by Goniak et al. [16], the choice of reference velocity in the definition of fluxes at the edge of the Knudsen layer was inconsistent with the fluxes at the wall. This issue will be discussed in detail later. Also, in the derivation of the velocity-slip and temperature-jump boundary conditions, Gupta et al. [15] have neglected possible chemical reactions at the surface. Based on the similarity between heat and mass transfer, Rosner et al. [17] developed an expression for concentration-jump in the transport of multi-species flows without accounting for reaction terms.

The most accurate, but the least acknowledged, study on slip boundary conditions for a multi-component monatomic gas flow on catalytic surfaces is given by Kiryutin and Tirskii [18]. They employed the half-flux method in order to arrive at the boundary conditions by choosing a proper reference velocity for the velocity distribution function and fluxes across the edge of Knudsen layer and at the wall. The only major restriction in their model is that it is for monatomic gases, and therefore, their model fails to reproduce the commonly used temperature-jump boundary condition for polyatomic gases.

Recently Xu and Ju [19] derived an expression for the concentration-jump based on the kinetic theory, following the half-flux method. They investigated the effect of concentration-jump on the rate of catalytic reactions in the numerical modeling of microscale chemical reactors. Their model is based on a simplified velocity distribution function in which terms such as viscous stresses, mass fluxes and thermal diffusion are neglected. Also, in modeling the velocity distribution of molecules reflected from the wall, the effect of possible wall reactions was not considered. However, more recently, Xu and Ju [20] derived a more general expression

for concentration-jump compared to their previous work, but it carries some simplifying assumptions and is inconsistent with well-established expressions in special or limiting cases. They have assumed that all of the molecules leaving the wall have a Maxwellian velocity distribution with no specular reflection.

In the present work, general slip/jump boundary conditions are derived for velocity, temperature and concentration in a multi-component gas flow on a catalytic surface following Grad's method [3]. In order for the model to be applicable to practical problems (i.e., polyatomic gas flows) correction terms are added to the temperature-jump boundary condition as well. It should be noted that a key objective of the current work is to present a clearer picture of the underlying principles and assumptions in the complex derivation of slip/jump boundary conditions so that they can be well understood and properly simplified in practical engineering problems.

2. Slip model

In order to avoid the complexity of solving the Boltzmann equation in rarefied gas flows, in the slip flow regime one can assign *imaginary* velocity, temperature and concentration values (slip/jump values) at the boundary so that the standard continuum equations can still be employed safely outside the Knudsen layer [1–7]. The macroscopic properties of the gas can be obtained if the velocity distribution of the molecules f is known.

Consider a wall with gas molecules impinging on it where catalytic reactions could also take place. In order to derive the slip boundary conditions, the velocity distribution function for wall-reflected molecules f^+ should be specified provided that the incident distribution f^- is given. The most commonly used reflection model is the so-called specular-diffusive model which, assuming the boundary is perpendicular to the y direction, can be written as [3]

$$
\begin{aligned}
f_i^+(V_{ix}, V_{iy}, V_{iz}) &= (1-\theta_i)f_i^-(V_{ix}, -V_{iy}, V_{iz}) \\
&+ (\theta_i - \gamma_i)\frac{n_{i,w}}{(2\pi k_B T_w/m_i)^{3/2}} \exp\left(-\frac{V_i^2}{2k_B T_w/m_i}\right); \\
& V_{iy} > 0
\end{aligned}
\tag{1}
$$

where T_w is the wall temperature, θ_i is the accommodation coefficient and γ_i is the recombination coefficient, which represents the probability of appearance ($\gamma_i < 0$) or disappearance ($\gamma_i > 0$) of species i at the surface due to chemical reactions. This expression states that a certain fraction ($1 - \theta_i$) of the incident molecules are specularly reflected by the wall (without reaching the equilibrium state), while the remaining molecules are captured by the wall and are either consumed (or produced) or re-emitted with an equilibrium distribution at the prevailing wall temperature. It is important to note that $n_{i,w}$ is defined as the wall number density *prior* to chemical reactions on the catalytic surface. Thus, double-accounting of the reaction effects through both γ_i and $n_{i,w}$ in Eq. (1) is avoided. This definition of number density is also appropriate for determining the rate of production (or consumption) of species at the wall, since it represents the reactant concentration required for a typical catalytic reaction rate expression as shown later.

In order to be consistent with the approximation level associated with the Navier–Stokes equations, the velocity distribution function near the wall can be described by the first-order accurate Chapman–Enskog distribution function [1]. To this approximation, the velocity distribution function for each species "i" in a non-uniform multi-component mixture can be written as

$$
f_i(V_{ix}, V_{iy}, V_{iz}) = f_i^M(1 + \Phi_i)
\tag{2.a}
$$

$$
f_i^M(V_{ix}, V_{iy}, V_{iz}) = \frac{n_i}{(2\pi k_B T/m_i)^{3/2}} \exp\left(-\frac{V_i'^2}{2k_B T/m_i}\right)
\tag{2.b}
$$

where f_i^M is the Maxwellian distribution function, n_i and m_i are the number density and molecular mass of species "i", T is the temperature, k_B is the Boltzmann constant and $\vec{V}'_i = \vec{V}_i - \vec{U}$ is the peculiar (or thermal) velocity of the gas molecules with $\vec{V}_i$ and $\vec{U}$ being the molecular velocity and mass averaged gas velocity, respectively. The normalized perturbation to the equilibrium distribution Φ_i corresponds to the Navier–Stokes approximation in the solution of the Boltzmann equation. Using the Chapman–Enskog method to first-order approximation, Φ_i is given by [1]

$$
\begin{aligned}
\Phi_i = &-\left[a_{i0} + a_{i1}\left(\frac{5}{2} - \frac{m_i V_i'^2}{2k_B T}\right)\right]\left(\vec{V}'_i \cdot \frac{\partial \ln T}{\partial \vec{r}}\right) \\
&- \frac{m_i}{2k_B T}\left[\left(\vec{V}'_i \vec{V}'_i - \frac{1}{3}V_i'^2 I\right) : \frac{\partial \vec{U}}{\partial \vec{r}}\right]b_{i0} + n\sqrt{\frac{m_i}{2k_B T}}\sum_{j=1}^{NS} c_{i0}^j \vec{V}'_i \cdot \vec{d}_j
\end{aligned}
\tag{3}
$$

where a_{i0}, a_{i1}, b_{i0} and c_{i0}^j are coefficients of expansions in the Sonine polynomials which will be described later, $\vec{r}$ is the position vector, I is the unit tensor, and $\vec{d}_j$ is the diffusion vector related to the diffusion velocity of species "j" given by [7]

$$
\vec{d}_j = \vec{\nabla}\left(\frac{n_j}{n}\right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho}\right)\vec{\nabla}\ln p - \frac{n_j m_j}{p}\left(\vec{X}_j - \frac{1}{\rho}\sum_{k=1}^{NS} n_k m_k \vec{X}_k\right)
\tag{4}
$$

where $\vec{X}_j$ is the body force acting on species j.

2.1. Concentration-jump

In order to derive the concentration-jump boundary condition, the net mass flux of each species normal to the boundary is determined as

$$
\begin{aligned}
F_i = \int_{-\infty}^{+\infty}\int_0^{+\infty}\int_{-\infty}^{+\infty} m_i V_{iy}[&f_i^+(V_{ix}, V_{iy}, V_{iz}) \\
&- f_i^-(V_{ix}, -V_{iy}, V_{iz})]dV_{ix}\,dV_{iy}\,dV_{iz}
\end{aligned}
\tag{5}
$$

On the other hand, the net mass flux of each species normal to the wall can be written in terms of macroscopic properties as [7]

$$
F_i = \frac{m_i n_{i,s}}{2}\left(\frac{2k_B T_s}{m_i}\right)^{1/2}\left(-a_{i0}\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS} c_{i0}^j d_{jy}\right)_s
\tag{6}
$$

where d_{jy} is the y component of the diffusion velocity of species j (see Eq. (4)). Equating these two equations and calculating the integrals involved results in the following concentration-jump boundary condition:

$$
\begin{aligned}
\frac{n_{i,w}}{n_{i,s}}\left(\frac{T_w}{T_s}\right)^{1/2} = &\frac{\theta_i}{\theta_i - \gamma_i}\left[1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right]_s \\
&+ \frac{(2-\theta_i)\sqrt{\pi}}{2(\theta_i - \gamma_i)}\left(-a_{i0}\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS} c_{i0}^j d_{jy}\right)_s
\end{aligned}
\tag{7}
$$

It should be noted that the above equation is not an explicit expression for $n_{i,s}$ because the coefficients a_{i0} and c_{i0}^j are functions of $n_{i,s}$. Explicit expressions for $n_{i,s}$ can be obtained by specifying the surface reaction rate, which will be discussed for special cases in Section 3.

2.2. Velocity-slip

In order to arrive at the velocity-slip boundary condition, one can multiply Eq. (1) by $m_i V'_{ix} V'_{iy} = m_i(V_{ix} - U_x)V_{iy}$ and integrate to obtain

$$
S_{i,xy}^+ + (1-\theta_i)S_{i,xy}^- + (\theta_i - \gamma_i)U_x n_{i,w} m_i\sqrt{\frac{k_B T_w}{2\pi m_i}} = 0
\tag{8}
$$

where

$$
S_{i,xy}^\pm = \pm\int_{-\infty}^{+\infty} dV_{ix}\int_{-\infty}^{+\infty} dV_{iz}\int_0^{+\infty} m_i V'_{ix} V'_{iy} f_i^\pm(V_{ix}, \pm V_{iy}, V_{iz})dV_{iy}
\tag{9}
$$

Integration of the above equation using Eqs. (2) and (3) yields

$$S_{i,xy}^{\pm} = \pm \frac{n_{i,s}k_B}{4\sqrt{\pi}}(a_{i1} - 2a_{i0})\left(\frac{\partial T}{\partial x}\right)_s - \frac{n_{i,s}k_B T_s}{4}b_{i0}\left(\frac{\partial U_x}{\partial y} + \frac{U_y}{\partial x}\right)_s$$

$$\pm \left(\frac{n n_{i,s}k_B T_s}{2\sqrt{\pi}}\sum_{j=1}^{NS} c_{i0}^j d_{jx}\right)_s \qquad (10)$$

Substituting this in Eq. (8) and summing over all species, the following velocity-slip expression is obtained:

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{\frac{k_B T_s}{2}}\left[\theta_i\left(\left(a_{i0} - \frac{a_{i1}}{2}\right)\frac{\partial \ln T}{\partial x} - n\sum_{j=1}^{NS}c_{i0}^j d_{jx}\right)_s + (2-\theta_i)\sqrt{\pi}\frac{b_{i0}}{2}\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)_s\right]}{\sum_{i=1}^{NS}(\theta_i - \gamma_i)n_{i,w}\sqrt{\frac{T_w}{T_s}}\sqrt{m_i}} \qquad (11)$$

Considering Eq. (7), the velocity-slip boundary condition can also be written as

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{\frac{k_B T_s}{2}}\left[\theta_i\left(\left(a_{i0} - \frac{a_{i1}}{2}\right)\frac{\partial \ln T}{\partial x} - n\sum_{j=1}^{NS}c_{i0}^j d_{jx}\right)_s + (2-\theta_i)\sqrt{\pi}\frac{b_{i0}}{2}\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)_s\right]}{\sum_{i=1}^{NS} n_{i,s}\sqrt{m_i}\left[\theta_i\left(1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right)_s + \frac{(2-\theta_i)\sqrt{\pi}}{2}\left(n\sum_{j=1}^{NS}c_{i0}^j d_{jy} - a_{i0}\frac{\partial \ln T}{\partial y}\right)_s\right]} \qquad (12)$$

Note that in order to arrive at the above relation for velocity-slip in the x direction, Eq. (1) was multiplied by $m_i V'_{ix}V'_{iy} = m_i(V_{ix} - U_x)V_{iy}$. In the same manner, one can multiply Eq. (1) by $m_i V'_{iz}V'_{iy} = m_i(V_{iz} - U_z)V_{iy}$ and follow the same steps to arrive at a velocity-slip boundary condition in the z direction as

$$U_z = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{\frac{k_B T_s}{2}}\left[\theta_i\left(\left(a_{i0} - \frac{a_{i1}}{2}\right)\frac{\partial \ln T}{\partial z} - n\sum_{j=1}^{NS}c_{i0}^j d_{jz}\right)_s + (2-\theta_i)\sqrt{\pi}\frac{b_{i0}}{2}\left(\frac{\partial U_z}{\partial y} + \frac{\partial U_y}{\partial z}\right)_s\right]}{\sum_{i=1}^{NS}(\theta_i - \gamma_i)n_{i,w}\sqrt{\frac{T_w}{T_s}}\sqrt{m_i}} \qquad (13)$$

2.3. Temperature-jump

In order to proceed with the temperature-jump boundary condition, Eq. (1) is multiplied by $m_i V'_{iy}V'^2_i = m_i V_{iy}(V_i^2 - 2\vec{V}_i \cdot \vec{U} + U^2)$ and integrated to obtain

$$h_{i,y}^+ + (1 - \theta_i)h_{i,y}^- = (\theta_i - \gamma_i)h_{i,y}^M \qquad (14)$$

where

$$h_{i,y}^{\pm} = \pm \int_{-\infty}^{+\infty} dV_{ix} \int_{-\infty}^{+\infty} dV_{iz} \int_0^{+\infty} m_i V'_{iy}V'^2_i f_i^{\pm}(V_{ix}, \pm V_{iy}, V_{iz})dV_{iy} \qquad (15)$$

and

$$h_{i,y}^M = \int_{-\infty}^{+\infty} dV_{ix} \int_{-\infty}^{+\infty} dV_{iz} \int_0^{+\infty} m_i V'_{iy}V'^2_i f_i^M(V_{ix}, V_{iy}, V_{iz})dV_{iy} \qquad (16)$$

Performing the integrations in the above equations yields

$$h_{i,y}^{\pm} = \pm \frac{n_{i,s}m_i}{\sqrt{\pi}}\left(\frac{2k_B T_s}{m_i}\right)^{3/2} + 5n_{i,s}m_i\left(\frac{k_B T_s}{2m_i}\right)^{3/2}(a_{i1} - a_{i0})\frac{\partial \ln T}{\partial y}$$

$$\pm \frac{n_{i,s}m_i}{4\sqrt{\pi}}\left(\frac{2k_B T_s}{m_i}\right)b_{i0}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)_s$$

$$+ \left(5n n_{i,s}m_i\left(\frac{k_B T_s}{2m_i}\right)^{3/2}\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)_s \qquad (17)$$

and

$$h_{i,y}^M = n_{i,w}m_i U^2\sqrt{\frac{k_B T_w}{2\pi m_i}} + \frac{n_{i,w}m_i}{\sqrt{\pi}}\left(\frac{2k_B T_w}{m_i}\right)^{3/2} \qquad (18)$$

These expressions account only for the translational energy of molecules and do not include the internal (rotational and vibrational) energy of the incident and reflected molecules, which becomes important in the case of polyatomic gases. In order to include the internal energy of molecules, one can simply multiply the number flux N_i of incident (or reflected) species by the average internal energy carried by each molecule. Thus, the above expressions are modified using:

$$H_{i,y}^{\pm} = h_{i,y}^{\pm} + N_i^{\pm}e_{i,s}^{int} \qquad (19)$$

and

$$H_{i,y}^M = h_{i,y}^M + N_i^M e_{i,w}^{int} \qquad (20)$$

in which $e_i^{int} = k_B T\zeta$ is the internal energy of the molecule characterized by the number of internal degrees of freedom ζ. The internal number of degrees of freedom is related to the total degrees of freedom σ through

$$\sigma = \zeta + 3 \qquad (21)$$

This way, the three degrees of freedom associated with the translational motion of molecules is excluded in the calculation of internal energy. The number density flux of the incident and reflected molecules can be determined as

$$N_i^+ = \int_{-\infty}^{+\infty} dV_{ix} \int_{-\infty}^{+\infty} dV_{iz} \int_0^{+\infty} V_{iy}f_i(V_{ix}, V_{iy}, V_{iz})dV_{iy} \qquad (22.a)$$

$$N_i^- = \int_{-\infty}^{+\infty} dV_{ix} \int_{-\infty}^{+\infty} dV_{iz} \int_{-\infty}^{0} V_{iy}f_i(V_{ix}, V_{iy}, V_{iz})dV_{iy} \qquad (22.b)$$

$$N_i^M = \int_{-\infty}^{+\infty} dV_{ix} \int_{-\infty}^{+\infty} dV_{iz} \int_0^{+\infty} V_{iy}f_i^M(V_{ix}, V_{iy}, V_{iz})dV_{iy} \qquad (22.c)$$

Next, Eq. (22) are substituted into Eqs. (19) and (20) and incorporated in Eq. (14) with h_i replaced by H_i. Finally, summing over all

species and rearranging, the following temperature-jump equation is obtained

$$\left(\frac{T_s}{T_w}\right)^{3/2} = \frac{\sum_{i=1}^{NS}(\theta_i - \gamma_i)\frac{n_{i,w}}{\sqrt{m_i}}\left(1 + \frac{U^2 m_i}{4k_B T_w} + \frac{\zeta}{4}\right)}{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}[(2-\theta_i)Z_1 + \theta_i Z_2]} \tag{23.a}$$

where

$$Z_1 = \frac{5\sqrt{\pi}}{8}\left((a_{i1} - a_{i0})\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)_s \tag{23.b}$$

$$Z_2 = \left(1 + \frac{\zeta}{4}\right) + \frac{b_{i0}}{12}\left(3 + \frac{\zeta}{2}\right)\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)_s$$
$$+ \frac{\zeta\sqrt{\pi}}{8}\left(a_{i0}\frac{\partial \ln T}{\partial y} - n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)_s \tag{23.c}$$

Considering Eq. (7), the temperature-jump boundary condition can also be written as

$$\frac{T_s}{T_w} = \frac{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta_i\left(1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right)_s + \frac{(2-\theta_i)\sqrt{\pi}}{2}\left(n\sum_{j=1}^{NS}c_{i0}^j d_{jy} - a_{i0}\frac{\partial \ln T}{\partial y}\right)_s\right]\left(1 + \frac{U^2 m_i}{4k_B T_w} + \frac{\zeta}{4}\right)}{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}[(2-\theta_i)Z_1 + \theta_i Z_2]} \tag{24}$$

3. Simplified boundary conditions

The previously obtained slip/jump conditions are for the general case and the coefficients in the Sonine polynomials need to be expressed in terms of the usual transport properties in order to be applicable to practical engineering problems. The Sonine expansion coefficients a_{i0}, a_{i1}, b_{i0} and c_{i0}^j are obtained using variational techniques and are expressed in terms of collision integrals. However, they can also be directly related to transport properties as follows [7]:

$$D_i^T(\xi) = \frac{n_i m_i}{2}\sqrt{\frac{2k_B T}{m_i}}a_{i0}(\xi) \tag{25}$$

$$K(\xi) = -\frac{5}{4}k_B\sum_{i=1}^{NS}n_i\sqrt{\frac{2k_B T}{m_i}}a_{i1}(\xi) \tag{26}$$

$$\mu(\xi) = \frac{1}{2}k_B T\sum_{i=1}^{NS}n_i b_{i0}(\xi) \tag{27}$$

$$D_{ij}(\xi) = \frac{\rho n_i}{2nm_j}\sqrt{\frac{2k_B T}{m_i}}c_{i0}^j(\xi) \tag{28}$$

where $D_i^T(\xi)$, $K(\xi)$, $\mu(\xi)$, and $D_{ij}(\xi)$ are the thermal diffusion coefficient, thermal conductivity, viscosity, and the species diffusion coefficient, respectively. The parameter ξ in these expressions refers to the number of terms used in the Sonine polynomial expansion [7]. Usually $\xi = 1$ gives acceptable results in approximating the transport properties, except for the thermal diffusion D_i^T which vanishes for $\xi = 1$, and therefore, at least two terms should be considered in the Sonine expansion. It is apparent that a_{i1} and b_{i0} cannot be obtained explicitly from the above equations, and rather cumbersome equations given in reference [7] have to be solved to determine them exactly. However, the following approximations may be employed to obtain explicit expressions for these coefficients [8]:

$$\mu \approx \sum_{i=1}^{NS}\frac{n_i}{n}\mu_i \tag{29}$$

$$K \approx \sum_{i=1}^{NS}\frac{n_i}{n}K_i \tag{30}$$

Thus, Eqs. (26) and (27) yield

$$a_{i1} \approx -\frac{4}{5}\frac{K_i}{nk_B}\sqrt{\frac{m_i}{2k_B T}} \tag{31}$$

$$b_{i0} \approx \frac{2}{nk_B T}\mu_i \tag{32}$$

Having determined the Sonine expansion coefficients a_{i0}, a_{i1}, b_{i0} and c_{i0}^j in terms of the usual transport properties, they can be employed to establish the slip/jump conditions at a solid boundary. The concentration-jump condition (Eq. (7)) can be rewritten as

$$\frac{n_{i,w}}{n_{i,s}}\left(\frac{T_w}{T_s}\right)^{1/2} = \frac{\theta_i}{\theta_i - \gamma_i}\left[1 + \frac{\mu_i}{3nk_B T_s}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right]_s$$
$$+ \frac{(2-\theta_i)}{2(\theta_i - \gamma_i)}\sqrt{\frac{\pi m_i}{2k_B T_s}}\left[\frac{2n^2}{n_i\rho}\sum_{j=1}^{NS}m_j D_{ij}d_{jy} - \frac{2D_i^T}{n_i m_i}\frac{\partial \ln T}{\partial y}\right]_s \tag{33}$$

Before proceeding with the velocity-slip and temperature-jump equations, it would be useful to make a connection between the recombination coefficient γ_i and the reaction rate constant $k_{w,i}$ so that the applicability of the concentration-jump in reacting/non-reacting flows is clarified. Utilizing Eqs. (25) and (28), the net flux of species i at the surface (see Eq. (6)) can be expressed as

$$F_i = -D_i^T\frac{\partial \ln T}{\partial y} + \sum_{j=1}^{NS}\frac{n^2 m_i m_j}{\rho}D_{ij}d_{jy} \tag{34}$$

If the wall is non-catalytic and no reaction occurs at the wall, the net flux at the outer edge of the Knudsen layer should be zero. Therefore, the concentration-jump expression at the wall is no longer needed (since the wall number density is only useful in determining the reaction rate) and Eq. (34) can be used directly as the proper boundary condition as follows:

$$-D_i^T\frac{\partial \ln T}{\partial y} + \sum_{j=1}^{NS}\frac{n^2 m_i m_j}{\rho}D_{ij}d_{jy} = 0 \tag{35}$$

On the other hand, if reaction takes place at the wall, then the net flux of species i at the edge of the Knudsen layer should match the production rate of the same species at wall. As an example, consider a first-order recombination reaction on a catalytic surface. For this case, the net flux at the edge of the Knudsen layer is given by:

$$-D_i^T\frac{\partial \ln T}{\partial y} + \sum_{j=1}^{NS}\frac{n^2 m_i m_j}{\rho}D_{ij}d_{jy} = -k_{w,i}n_{i,w}m_i \tag{36}$$

where the right-hand side represents the rate at which species i is consumed at the wall and the minus sign indicates that the net flux is in the direction opposite to the surface normal. For a first-order recombination, the reaction rate constant $k_{w,i}$ can be expressed in terms of the recombination coefficient γ_i as [13]

$$k_{w,i} = \gamma_i\sqrt{\frac{k_B T_w}{2\pi m_i}} \tag{37}$$

Therefore, Eq. (36) can be expressed as

$$-D_i^T \frac{\partial \ln T}{\partial y} + \sum_{j=1}^{NS} \frac{n^2 m_i m_j}{\rho} D_{ij} d_{jy} = -\gamma_i n_{i,w} m_i \sqrt{\frac{k_B T_w}{2\pi m_i}} \tag{38}$$

Note that the consumption (or production) rate of species depends on the wall number density prior to reaction on the surface. Substituting $n_{i,\,w}$ from Eq. (33) into Eq. (38), the following explicit expression for $n_{i,\,s}$ is obtained:

$$n_{i,s} = \frac{\left(\frac{2\theta_i - \theta_i \gamma_i}{2\theta_i \gamma_i}\right)\left(\frac{2\pi}{k_B T_s m_i}\right)^{\frac{1}{2}}\left[D_i^T \frac{\partial \ln T}{\partial y} - \sum_{j=1}^{NS} \frac{n^2 m_i m_j}{\rho} D_{ij} d_{jy}\right]_s}{1 + \frac{\mu_i}{3nk_B T_s}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)_s} \tag{39}$$

This expression can be used as the boundary condition at the outer edge of the Knudsen layer when there is a first-order recombination reaction at the wall. For more complicated reactions, the same procedure can be followed except that the proper production rates of species at the wall should be specified for the flux matching condition at the edge of the Knudsen layer (Eq. (36)).

Using the same procedure as concentration-jump, the velocity-slip in the x direction (Eq. (11)) can be rewritten in terms of the usual transport properties as

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s} \sqrt{m_i}\left[\theta_i\left(\left(\frac{D_i^T}{n_i m_i} + \frac{K_i}{5k_B n}\right)\frac{\partial \ln T}{\partial x} - \frac{n^2}{\rho n_i}\sum_{j=1}^{NS} m_j D_{ij} d_{jx}\right) + (2-\theta_i)\frac{\mu_i}{nm_i}\sqrt{\frac{\pi m_i}{2k_B T}}\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)\right]_s}{\sum_{i=1}^{NS} n_{i,s} \sqrt{m_i}\left[\theta_i\left(1 + \frac{\mu_i}{3nk_B T_s}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + \frac{(2-\theta_i)}{2}\sqrt{\frac{\pi m_i}{2k_B T_s}}\left(\frac{2n^2}{n_i \rho}\sum_{j=1}^{NS} m_j D_{ij} d_{jy} - \frac{2D_i^T}{n_i m_i}\frac{\partial \ln T}{\partial y}\right)\right]_s} \tag{40}$$

Note that the velocity-slip in the z direction can be obtained similarly.

In order to simplify the temperature-jump expression (Eq. (24)), one can first relate the number of internal degrees of freedom ζ to the specific heat ratio $\bar{\gamma}$ as [21]

$$\bar{\gamma} = \frac{\sigma + 2}{\sigma} = \frac{\zeta + 5}{\zeta + 3} \tag{41}$$

Thus the temperature-jump can be rewritten as

$$\frac{T_s}{T_w} = \frac{\sum_{i=1}^{NS} \frac{n_{i,s}}{\sqrt{m_i}}\left[\left(\frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \frac{U^2 m_i}{4k_B T_w}\right)\right]\left[\theta_i\left(1 + \frac{\mu_i}{3nk_B T_s}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + \frac{(2-\theta_i)}{2}Y_1\right]_s}{\sum_{i=1}^{NS} \frac{n_{i,s}}{\sqrt{m_i}}\left[(2-\theta_i)Y_2 + \theta_i Y_3\right]_s} \tag{42.a}$$

where

$$Y_1 = \sqrt{\frac{\pi m_i}{2k_B T_s}}\left(\frac{2n^2}{n_i \rho}\sum_{j=1}^{NS} m_j D_{ij} d_{jy} - \frac{2D_i^T}{n_i m_i}\frac{\partial \ln T}{\partial y}\right)_s \tag{42.b}$$

$$Y_2 = \frac{5}{8}\sqrt{\frac{\pi m_i}{2k_B T_s}}\left[-\left(\frac{4K_i}{5k_B n} + \frac{2D_i^T}{n_i m_i}\right)\frac{\partial \ln T}{\partial y} + \frac{2n^2}{\rho n_i}\sum_{j=1}^{NS} m_j D_{ij} d_{jy}\right]_s \tag{42.c}$$

$$Y_3 = \frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \left[\frac{\mu_i}{12nk_B T_s}\frac{3\bar{\gamma}-1}{(\bar{\gamma}-1)}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right.$$
$$\left. + \frac{5-3\bar{\gamma}}{8(\bar{\gamma}-1)}Y_1\right]_s \tag{42.d}$$

Before further simplification, it is useful to rewrite these equations in terms of Newtonian viscous stresses and species mass fluxes given by

$$\tau_i^{yy} = \frac{2\mu_i}{3}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right) \tag{43.a}$$

$$\tau_i^{xy} = -\mu_i\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right) \tag{43.b}$$

$$J_{iy} = \frac{n^2 m_i}{\rho}\sum_{j=1}^{NS} m_j D_{ij} d_{jy} - D_i^T \frac{\partial \ln T}{\partial y} \tag{43.c}$$

$$J_{ix} = \frac{n^2 m_i}{\rho}\sum_{j=1}^{NS} m_j D_{ij} d_{jx} - D_i^T \frac{\partial \ln T}{\partial x} \tag{43.d}$$

Thereby, (33), (40) and (42.a) can be written as

$$\frac{n_{i,w}}{n_{i,s}}\left(\frac{T_w}{T_s}\right)^{1/2} = \frac{\theta_i}{\theta_i - \gamma_i}\left(1 + \frac{\tau_i^{yy}}{2p}\right)_s + \frac{(2-\theta_i)}{(\theta_i - \gamma_i)}\left(\frac{J_{iy}}{n_i m_i}\sqrt{\frac{\pi m_i}{2k_B T_s}}\right)_s \tag{44}$$

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{m_i}\left[\theta_i\left(\frac{K_i}{5k_B n}\frac{\partial \ln T}{\partial x} - \frac{J_{ix}}{n_i m_i}\right) - (2-\theta_i)\frac{\tau_i^{xy}}{nm_i}\sqrt{\frac{\pi m_i}{2k_B T_s}}\right]_s}{\sum_{i=1}^{NS} n_{i,s}\sqrt{m_i}\left[\theta_i\left(1 + \frac{\tau_i^{yy}}{2p}\right) + (2-\theta_i)\frac{J_{iy}}{n_i m_i}\sqrt{\frac{\pi m_i}{2k_B T_s}}\right]_s} \tag{45}$$

$$\frac{T_s}{T_w} = \frac{\sum_{i=1}^{NS} \frac{n_{i,s}}{\sqrt{m_i}}\left(\frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \frac{U^2 m_i}{4k_B T_w}\right)\left[\theta_i\left(1 + \frac{\tau_i^{yy}}{2p}\right) + \frac{J_{iy}(2-\theta_i)}{n_i m_i}\sqrt{\frac{\pi m_i}{2k_B T_s}}\right]_s}{\sum_{i=1}^{NS} \frac{n_{i,s}}{\sqrt{m_i}}\left[\frac{5(2-\theta_i)}{4}\sqrt{\frac{\pi m_i}{2k_B T_s}}\left(\frac{J_{iy}}{n_i m_i} - \frac{2K_i}{5k_B n}\frac{\partial \ln T}{\partial y}\right) + \theta_i\left(\frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \frac{\tau_i^{yy}}{8p}\frac{(3\bar{\gamma}-1)}{(\bar{\gamma}-1)} + \frac{(5-3\bar{\gamma})}{4(\bar{\gamma}-1)}\frac{J_{iy}}{n_i m_i}\sqrt{\frac{\pi m_i}{2k_B T_s}}\right)\right]_s} \tag{46}$$

4. Simplifications for a single-component gas

As a practical case of the slip/jump equations obtained in the previous sections, a single-component gas is considered here. In this case, the recombination coefficient is set equal to zero (no reaction at the wall) and, ignoring self-diffusion, the terms involving molecular diffusion are zero. Hence, for a single-component gas, the slip/jump boundary conditions become

$$\frac{\rho_w}{\rho_s}\left(\frac{T_w}{T_s}\right)^{1/2} = \left(1 + \frac{\tau^{yy}}{2p}\right)_s - \left(\frac{2-\theta}{\theta}\right)\sqrt{\frac{\pi}{2RT_s}}\frac{D^T}{\rho_s}\frac{\partial \ln T}{\partial y} \tag{47}$$

$$U_x = \frac{\left[\left(\frac{D^T}{\rho} + \frac{K}{5k_B n}\right)\frac{\partial \ln T}{\partial x} - \left(\frac{2-\theta}{\theta}\right)\frac{\tau^{xy}}{\rho}\sqrt{\frac{\pi}{2RT_s}}\right]_s}{\left(1 + \frac{\tau^{yy}}{2p}\right)_s - \left(\frac{2-\theta}{\theta}\right)\sqrt{\frac{\pi}{2RT_s}}\frac{D^T}{\rho_s}\frac{\partial \ln T}{\partial y}} \tag{48}$$

$$\frac{T_s}{T_w} = \frac{\left(\frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \frac{U^2}{4RT_w}\right)\left[\left(1 + \frac{\tau^{yy}}{2p}\right) - \frac{(2-\theta)}{\theta}\frac{D^T}{\rho}\sqrt{\frac{\pi}{2RT_s}}\frac{\partial \ln T}{\partial y}\right]_s}{\frac{\bar{\gamma}+1}{4(\bar{\gamma}-1)} + \left[\frac{3\bar{\gamma}-1}{4(\bar{\gamma}-1)}\frac{\tau^{yy}}{2p} + \frac{D^T}{\rho}\sqrt{\frac{\pi}{2RT}}\left(\frac{5-3\bar{\gamma}}{4(\bar{\gamma}-1)} - \frac{5(2-\theta)}{4\theta}\right)\frac{\partial \ln T}{\partial y} - \sqrt{\frac{\pi}{2RT_s}}\frac{2-\theta}{2\theta}\frac{K}{k_B n}\frac{\partial \ln T}{\partial y}\right]_s} \tag{49}$$

where $\rho_s = mn_s$ and $\rho_w = mn_w$ are the densities of the gas at the edge of the Knudsen layer and at the wall, respectively. In deriving these equations, no simplifying assumptions were made, and therefore, they can be used for any general single-species gas flow over solid surfaces. However, the form of velocity-slip and temperature-jump boundary conditions is still different from those usually encountered in the literature. In order to further simplify these equations, some assumptions must be made. First, consider the velocity-slip equation. Neglecting thermal diffusion, Eq. (48) can be written as:

$$U_x\left(1 + \frac{\tau^{yy}}{2p}\right)_s = \left[\frac{K}{5p}\frac{\partial T}{\partial x} + \left(\frac{2-\theta}{\theta}\right)\frac{\mu}{\rho}\sqrt{\frac{\pi}{2RT_s}}\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)\right]_s \tag{50}$$

where τ^{xy} has been substituted from Eq. (43.b). Next, thermal conductivity K and viscosity μ can be expressed, to a first-order approximation, in terms of the mean-free-path λ as [1]

$$\mu = \frac{5}{16}\rho\lambda\sqrt{2\pi RT} \tag{51.a}$$

$$K = \frac{15}{4}R\mu \tag{51.b}$$

Substituting these equations into Eq. (50) results in

$$U_x\left(1 + \frac{\tau^{yy}}{2p}\right)_s = \left[\frac{3\mu}{4\rho T_s}\frac{\partial T}{\partial x} + \frac{5\pi}{16}\left(\frac{2-\theta}{\theta}\right)\lambda\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)\right]_s \tag{52}$$

The numerical factor of $5\pi/16$ is almost equal to unity. The normal viscous stress τ^{yy} is usually much smaller (if not zero) than the total pressure, which makes the term $\tau^{yy}/2p$ negligible compared to 1. Moreover, in many flows $\partial U_y/\partial x \ll \partial U_x/\partial y$. All of these can be easily used to further simplify Eq. (52).

In the same manner, the temperature-jump boundary condition for single-species gas flows can be further simplified if thermal diffusion is neglected. Setting $D^T = 0$ and rearranging Eq. (49) yields

$$T_s - T_w = \left[\frac{5\pi}{16}\left(\frac{2-\theta}{\theta}\right)\left(\frac{2\bar{\gamma}}{\bar{\gamma}+1}\right)\frac{\lambda}{Pr}\frac{\partial T}{\partial y} - \frac{\tau^{yy}}{2p}\left(\frac{3\bar{\gamma}-1}{\bar{\gamma}+1}T_s - T_w\right)\right.$$
$$\left. + \left(\frac{\bar{\gamma}-1}{\bar{\gamma}+1}\right)\left(1 + \frac{\tau^{yy}}{2p}\right)\frac{U^2}{R}\right]_s \tag{53}$$

As indicated above, $5\pi/16 \cong 1$, and $\tau^{yy}/2p \ll 1$ if not zero. Thus, the temperature-jump equation takes the following simplified form:

$$T_s - T_w = \left(\frac{2-\theta}{\theta}\right)\left(\frac{2\bar{\gamma}}{\bar{\gamma}+1}\right)\frac{\lambda}{Pr}\frac{\partial T}{\partial y} + \left(\frac{\bar{\gamma}-1}{\bar{\gamma}+1}\right)\frac{U^2}{R} \tag{54}$$

Note that the last term on the right-hand side of Eq. (54) is widely stated as $U^2/4R$ in the literature without acknowledging the associated monatomic gas assumption. Clearly, the term $(\bar{\gamma}-1)/(\bar{\gamma}+1)$ is equal to 1/4 only for a monatomic gas for which $\bar{\gamma} = 5/3$.

5. Comparison with existing models

In order to compare the results of the present study with existing expressions, the underlying assumptions in each investigation should be scrutinized. First of all, it should be emphasized that the boundary conditions obtained in the current work are for the general case of multi-component polyatomic gas flows. In this section, the results of the current work will be compared with the results found in references [13,15,18].

The expression for concentration-jump in reference [13] matches exactly the one obtained in the present work. The velocity-slip and temperature-jump expressions of reference [13], in the current notation, can be written as

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{\frac{k_B T_s}{2}}\left[\theta\left((a_{i0}-a_{i1})\frac{\partial \ln T}{\partial x} - n\sum_{j=1}^{NS}c_{i0}^j d_{jx}\right) + (2-\theta)\sqrt{\pi}\frac{b_{i0}}{2}\left(\frac{\partial U_x}{\partial y} + \frac{\partial U_y}{\partial x}\right)\right]_s}{\sum_{i=1}^{NS}\theta n_{i,s}\sqrt{m_i}} \tag{55}$$

$$\frac{T_s}{T_w} = \frac{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta\left(1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + (2-\theta)\frac{\sqrt{\pi}}{2}\left(-a_{i0}\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)\right]_s}{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta\left(1 + \frac{b_{i0}}{4}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + \frac{5\sqrt{\pi}}{8}(2-\theta)\left((a_{i1}-a_{i0})\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)\right]_s} \tag{56}$$

The accommodation coefficient is assumed to be the same for all species in references [13 and 15] in the derivation of velocity-slip and temperature-jump boundary conditions. Therefore, for comparison purposes, we will also assume that $\theta_i = \theta$. The improper choice of reference velocity in the calculation of fluxes is responsible for the incorrect velocity-slip expression given above. In the context of kinetic theory, three different velocities are usually involved: the total molecular velocity V, the mass averaged velocity U, and the peculiar (thermal) velocity $V' = V - U$. When dealing with conserved quantities (mass, momentum and energy) there might be confusion about which velocity to use, especially in the half-flux method. Although the velocity distribution functions, i.e., the Chapman–Enskog and Maxwellian distributions, are written in terms of the peculiar velocity [1,2], the fluxes of conserved quantities should be expressed in terms of the total velocity. However, in [13 and 15], the peculiar velocity was used in the description of conserved quantities. Furthermore, it should be noted that in the specular-diffusive reflection model, the velocity distribution of the molecules diffusively released from the wall should be a normal distribution centered around zero, as given in the last term of Eq. (1). However, [13 and 15] incorrectly used a Maxwellian

distribution centered around the mass averaged velocity for the diffusively released molecules. Finally, a comparison of Eq. (55) with (12), shows that there is a difference in the coefficient of a_{i1}, which is likely due to an error in reference [13], since the results of the current work yield a correct expression in the case of a single-component gas.

concentration-jump expression in this reference is not in agreement with the present work.

The expression for concentration-jump and velocity-slip in reference [18] matches exactly with the ones obtained in the current work. The temperature-jump boundary condition of reference [18], in the present notation, can be written as

$$\left(\frac{T_s}{T_w}\right)^{3/2} = \frac{\sum_{i=1}^{NS}(\theta_i - \gamma_i)\frac{n_{i,w}}{\sqrt{m_i}}\left(1 + \frac{U^2 m_i}{4k_B T_w}\right)}{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta_i\left(1 + \frac{b_{i0}}{4}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + (2 - \theta_i)\frac{5\sqrt{\pi}}{8}\left((a_{i1} - a_{i0})\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)\right]_s} \tag{60}$$

The first difference that is evident when comparing the temperature-jump expressions is the effect of polyatomic gas flows, characterized by ζ. Since in reference [13] the change in internal energy of gas molecules upon receding from the wall is not included, the resulting temperature-jump expression is for the special case of $\zeta = 0$. Setting $\zeta = 0$ in Eq. (24), the denominator of the expressions is observed to be the same. The term $U^2 m_i/4k_B T_w$, which is related to friction at the surface due to velocity-slip, is missing in the expression provided in reference [13]. This difference in the nominator of the two expressions also originates from the improper choice of reference velocity in calculation of fluxes at the edge of the Knudsen layer, as discussed earlier.

The concentration-jump, velocity-slip and temperature-jump expressions of reference [15], in the present notation, can be written as

The only difference here with the current work is the effect of internal energy of polyatomic gases. In fact Eq. (60) is the special case of the temperature-jump boundary condition, Eq. (23), in which the gas molecules are assumed to be monatomic, i.e., $\zeta = 0$.

6. Conclusions

Based on the kinetic theory of gases, general concentration-jump, velocity-slip and temperature-jump boundary conditions were developed for reacting/non-reacting multi-component polyatomic gaseous flows over catalytic surfaces. The method used here follows the approach taken by Grad [3] as an alternative to the half-flux method usually employed in the derivation of the slip/jump boundary conditions. A key objective of the present work was to show in a clear and systematic manner the derivation of

$$\frac{n_{i,w}}{n_{i,s}}\left(\frac{T_w}{T_s}\right)^{1/2} = 1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)_s + \frac{\sqrt{\pi}}{2}\left(a_{i0}\frac{\partial \ln T}{\partial y} - n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)_s \tag{57}$$

$$U_x = \frac{\sum_{i=1}^{NS} n_{i,s}\sqrt{\frac{k_B T_s}{2}}\left[\theta\left(\left(a_{i0} - \frac{a_{i1}}{2}\right)\frac{\partial \ln T}{\partial x} - n\sum_{j=1}^{NS}c_{i0}^j d_{jx}\right) + (2 - \theta)\sqrt{\pi}\frac{b_{i0}}{2}\left(\frac{\partial U_y}{\partial y} + \frac{\partial U_x}{\partial x}\right)\right]_s}{\sum_{i=1}^{NS}\theta n_{i,s}\sqrt{m_i}} \tag{58}$$

$$\frac{T_s}{T_w} = \frac{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta\left(1 + \frac{b_{i0}}{6}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + \frac{\sqrt{\pi}}{2}\left(a_{i0}\frac{\partial \ln T}{\partial y} - n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)\right]_s}{\sum_{i=1}^{NS}\frac{n_{i,s}}{\sqrt{m_i}}\left[\theta\left(1 + \frac{b_{i0}}{4}\left(\frac{\partial U_x}{\partial x} + \frac{\partial U_z}{\partial z} - 2\frac{\partial U_y}{\partial y}\right)\right) + \frac{5\sqrt{\pi}}{8}(2 - \theta)\left((a_{i1} - a_{i0})\frac{\partial \ln T}{\partial y} + n\sum_{j=1}^{NS}c_{i0}^j d_{jy}\right)\right]_s} \tag{59}$$

The concentration-jump expression in reference [15] is incomplete since the surface reaction parameter γ_i is not present in the general expression, unlike all other references and the current work. Also, although not mentioned explicitly, it seems that θ is assumed to be equal to unity in the final presentation of the concentration-jump expression. Taking the above remarks into account, Eq. (57) resembles the concentration-jump boundary condition of the current work, Eq. (7), assuming $\gamma_i = 0$ and $\theta = 1$, except for a minus sign in the last term. Considering the results of other references [13,18], it seems that this difference arises from a calculus or typographical error in the result of reference [15].

Similar to reference [13], in reference [15] the improper choice of reference velocity results in the omission of some important terms in the denominator of Eq. (58) as compared to Eq. (12). Also, the effect of polyatomic gas flows, characterized by ζ, is not included in the derivation of the temperature-jump expression of reference [15]. Furthermore, friction at the surface due to velocity-slip, $U^2 m_i/4k_B T_w$, is missing in their expression. These differences are due to the reasons discussed earlier about the results of reference [13]. Another important difference is the second term in the numerator of Eq. (59) involving thermal diffusion a_{i0} and species diffusion d_{jy}. This difference arises from the fact that the

these complex boundary conditions and to identify the origins of different terms in each expression. This is expected to permit easier assessment of various terms, and thereby allow correct simplifications to be made in specific cases.

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