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# Slip Boundary Conditions for Gas Mixture Flows with State-to-State Vibrational-Chemical Kinetics

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**Abstract.** The extension of recently developed theoretical approach allowing to obtain slip boundary conditions for non-equilibrium multi-component gas flows by means of rigorous kinetic theory techniques is proposed. Gaseous mixture in the present work is described on the basis of the detailed state-to-state (STS) model, but all the assumptions made can be easily implemented for the one- and multi-temperature approximations. New form of the approach was developed with the objective of taking into consideration not only scattering but other non-equilibrium surface processes and examining their influence on the form of conditions. The proposed scheme allows to obtain conditions only in terms of transport coefficients and probabilities of surface processes along with macroparameters and to be further extended in order to account for more complex time-dependent kinetics of particles-solid wall interaction. Commonly applied Maxwell and Cercignani–Lampis (CL) scattering kernels are considered and it is shown that discrepancies in resulting expressions appear only in the temperature jump. The comparison of boundary conditions with other theoretical and phenomenological models is performed.

## INTRODUCTION

In the case of highly non-equilibrium gas flows considered on the basis of continuum approximation one of the most detailed approach is the state-specific. Simulations performed on its basis can describe with high accuracy vibrational-chemical kinetics and mass and heat transfer. The STS approach can be applied in such practical problems as hypersonic aerodynamics, aerospace applications, low-temperature plasma science, but the implementation is still limited for the cases of quasi-one-dimensional and one-dimensional problems [1, 2, 3, 4, 5]; and simple two-dimensional inviscid gas flows [6, 7]. There are still challenging problems arising while performing STS simulations. One is related with its computational cost, which makes the approach hardly applicable to viscous reacting 2-D and 3-D flows [8]; this problem becomes less critical with increasing performance of modern computers. Another issue is the absence of formal kinetic-theory methods for deriving vibrational state-specific wall boundary conditions, and, consequently, the expressions for velocity slip, temperature jump and variation of vibrational level populations and species concentrations on the surface. The latter is essential since the description of a flow near the solid wall in the frame of the STS approach requires consideration of non-equilibrium surface effects. In our recent work [9] we overcame the last issue and developed the approach based on the kinetic boundary condition. Here the extension of the approach allowing to include more accurate description of surface processes is proposed.

The slip boundary conditions is a convenient model, which allows one to use continuum approximation for non-equilibrium rarefied flows near solid wall with non-zero, but small values of Knudsen number (Kn). The gas flows in this case are considered on the basis of transient and near-continuum regimes ( $0.001 < \text{Kn} < 0.25$ ). Conditions are established as the boundary conditions at the external edge of the Knudsen layer near the solid wall, that is why one can avoid applying numerical kinetic modeling or molecular dynamics techniques in the layer. The conditions include velocity slip and temperature jump, which effects will enhance with the increase of gas rarefaction. Another important issue of slip conditions is connected with consideration of non-equilibrium surface processes and their influence on gas dynamics near solid wall. This can be done by establishing additional wall boundary conditions for species concentrations, or the so called concentration jump expressions. When STS approximation is chosen such processes should include vibrational excitation/deactivation of molecules impinging the wall, heterogeneous reactions and adsorption/desorption. In our recent work, the mentioned processes, except for adsorption/desorption, were considered on the basis of coefficients, which absolute values give the extension of recombination probabilities, and included in the scheme through the normalization condition [9]. Besides that we showed for the particular case of specular-diffusive scattering that conditions, when reduced to the one-temperature approximation, are equivalent to the ones, obtained by the common Grad and Patterson-Shidlovsky methods [10, 11, 12]. Despite these facts, the approach has an issue connected with obtained boundary conditions for species concentrations. The main drawback

is in the dependence of the mass flux of the given species normal component on the wall solely on the density of that given species, which is not correct since such a dependence cannot account for different species contribution to the given flux. As the approach is equivalent to the other known theoretical ones, the same issue arises for them either [13, 14].

In the present study, an extended approach is developed, which allows to overcome the mentioned issue and obtain conditions for species concentration in the form similar to some phenomenological models [15, 16].

## APPROACH BASED ON THE KINETIC BOUNDARY CONDITION

Slip boundary conditions can be obtained by the approach similar to derivation of transport equations from the Boltzmann equation. The difference is that the Boltzmann equation is replaced by the kinetic boundary condition and integration is performed over the half-space  $u_{cn} > 0$ , where  $u_{cn}$  is the particle  $c$  molecular velocity normal to the surface component. The advantage of such a procedure is in relatively easy derivation of boundary conditions for different types of scattering kernels, and the expression of conditions only in terms of macroscopic parameters and coefficients related to the recombination/dissociation and vibrational state change processes, in contrast to the Grad's and half-flux techniques [9, 17].

The state-specific kinetic boundary condition has the following form [9]:

$$f_{cij}^+ \mathbf{u}_{cn} |_{u_{cn} > 0} = - \sum_l \int_{u'_{cn} < 0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t) u'_{cn} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}'_c. \quad (1)$$

Here,  $f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t)$ ,  $f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t)$  are distribution functions of incident and reflected particles of chemical species  $c$ , vibrational level  $i$  and rotational level  $j$ ;  $\mathbf{u}_c$  and  $\mathbf{u}'_c$  are the velocities of reflected and incident particles;  $T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c)$  is the scattering kernel, for which non-negativeness and reciprocity relations must be established [18]. The common normalization condition for the kernel is valid only if surface processes other than scattering are neglected:

$$\sum_j \int_{u_{cn} > 0} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}_c = 1. \quad (2)$$

The loss and gain in the number of particles due to chemical reaction and vibrational deactivation/excitation can be included in the above relation. This can be done by modifying the right-hand side by the sum of above mentioned coefficients  $\sum \gamma_{ci}^p$ . Here  $p$  denotes a particular surface process: recombination/dissociation, vibrational excitation/deactivation or adsorption/desorption. It is supposed that  $\gamma_{ci}^p > 0$  if particles of species  $ci$  change their vibrational or chemical state due to the surface process  $p$ ;  $\gamma_{ci}^p < 0$  if particles of species  $ci$  are formed as a result of the  $p$  process [9]. These coefficients is an extension of the common recombination coefficients initially adapted in slip conditions by Scott [19]. The normalization condition (2) with such assumption is rewritten as

$$\sum_j \int_{u_{cn} > 0} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}_c = 1 - \sum \gamma_{ci}^p. \quad (3)$$

The scheme based on (1), (3), when reduced to the one-temperature approximation, allows one to write the distribution function of reflected particles equivalent to the ones written e.g. in [13, 14, 20]. Here we start with proposing an alternative way of accounting for the loss and gain in the number of particles, which is based on the next scheme:

$$f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t) u_{cn} |_{u_{cn} > 0} = - \sum_l \int_{u'_{cn} < 0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t) u'_{cn} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}'_c + \sum_{dk, dk \neq ci} \gamma_{dk}^i \tilde{f}_{cij}^+(\mathbf{r}, \mathbf{u}_c, t) u_{cn} |_{u_{cn} > 0}, \quad (4)$$

with modified normalization condition for the scattering kernel  $T_l^{cij}$ :

$$\sum_j \int_{u_{cn} > 0} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}_c = 1 - \sum_{dk, dk \neq ci} \gamma_{ci}^{dk}. \quad (5)$$

Here,  $\gamma_{dk}^i$  is the independent of the rotational state of a molecule probability that particle of chemical species  $d$  with vibration level  $k$  changes its state to  $ci$ . Relation (4) implies that the number flux of reflected by solid wall particles

consists of: 1) the number flux of scattered particles, transformed by the kernel  $T_l^{cij}$ ; 2) the flux of particles obtained as a result of heterogeneous reactions and vibrational deactivation/excitation due to the wall impinging. It is assumed that the latter particles are then desorbed into the gas phase with the distribution function  $\tilde{f}_{cij}^+(\mathbf{r}, \mathbf{u}_c, t)$ .

Obvious disadvantages of the proposed scheme (4), (5) are that it cannot take into account: 1) the distribution of incident particles before their change of state and 2) how the change of state of particles of  $cij$  species affects the number flux of reflected particles of other species that are involved in the surface chemical processes with  $cij$  particles. Besides that the concentration jump expressions are written in the form similar to that mentioned in the introduction, i.e. the mass flux of a given species normal component on the wall  $\mathbf{J}_{ci} \cdot \mathbf{n}|_w$  depends only on the density  $\rho_{ci}$  of a given species:  $\mathbf{J}_{ci} \cdot \mathbf{n}|_w = -\tilde{k}_{ci}^w \rho_{ci}$ . Here, the rate constants  $\tilde{k}_{ci}^w$  differ from the ones, written for the initial scheme (1), (3). Thus, the problem of incorrect description of non-equilibrium surface processes remains.

The first issue can be resolved by the following modification of (4):

$$\begin{aligned} f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t)u_{cn}|_{u_{cn}>0} = & - \sum_l \int_{u'_{cn}<0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t)u'_{cn}T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c)d\mathbf{u}'_c \\ & - \sum_{dkl, dk \neq ci} \gamma_{dk}^{ci} \int_{u'_{cn}<0} f_{dil}^-(\mathbf{r}, \mathbf{u}'_d, t)u'_{cn}\tilde{T}_l^{cij}(\mathbf{u}_c, \mathbf{u}'_d)d\mathbf{u}'_d, \end{aligned} \quad (6)$$

where kernels  $\tilde{T}_l^{cij}$  and  $T_l^{cij}$  satisfy normalization conditions (3) and (5) accordingly. The above scheme with such assumptions is equivalent to the initially considered (1), (3). But one can see that the second term in the right-hand side of equation (6) does not actually show the increase in the number of particles of the given species, since it considers the number flux of particles of the same species. This statement explains the reason why concentration jump has the mentioned above limitation. Finally, in order to overcome mentioned above issues for the schemes (4), (5) and (6), the kinetic boundary condition should be rewritten correspondingly:

$$\begin{aligned} f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t)u_{cn}|_{u_{cn}>0} = & - \sum_l \int_{u'_{cn}<0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t)u'_{cn}T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c)d\mathbf{u}'_c \\ & - \sum_{dkl, dk \neq ci} \gamma_{dk}^{ci} \int_{u'_{dn}<0} f_{dnl}^-(\mathbf{r}, \mathbf{u}'_d, t)u'_{dn}\tilde{T}_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}'_d)d\mathbf{u}'_d. \end{aligned} \quad (7)$$

The conditions for kernels remains the same. In the scheme (7) the number flux of reflected particles of  $cij$  consists of the number flux of scattered particles, transformed by the kernel  $T_l^{cij}$ , and the fluxes of particles of different species that are transformed into particles of given species due to the wall chemical reactions or vibrational state change. The probability of such a transformation is  $\gamma_{dk}^{ci}$ , and subsequent reflection into the gas phase is described by the kernel  $\tilde{T}_{dkl}^{cij}$ .

The adsorption and desorption processes should also be considered, so the scheme could better capture the surface chemistry effect on gas dynamics. The first can be included on the basis of sticking coefficient  $S_{ci}$ , described as the fraction of incident atoms impinging on a surface that are really adsorbed [21]. In order to account for this process, the sticking coefficients should be included in the normalization condition for the kernel that describes scattering as follows

$$\sum_j \int_{u_{cn}>0} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c)d\mathbf{u}_c = 1 - \sum_{dk, dk \neq ci} \gamma_{ci}^{dk} - S_{ci}. \quad (8)$$

The desorption can be included on the basis of similarly introduced desorption coefficient  $D_{ci}$ , defined as the ratio of desorbed particles and incident particles. There are at least two obvious ways of adding the flux of desorbed particles into the scheme (7). One of the options suggests that we will not take into account distribution of particles before their adsorption and assume their reflection then with the local Maxwell-Boltzmann distribution  $\tilde{f}_{cij}^{+,M}(\mathbf{r}, \mathbf{u}_c, t)$  at the given time moment:

$$\begin{aligned} f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t)u_{cn}|_{u_{cn}>0} = & - \sum_l \int_{u'_{cn}<0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t)u'_{cn}T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c)d\mathbf{u}'_c + D_{ci}\tilde{f}_{cij}^{+,M}(\mathbf{r}, \mathbf{u}_c, t)u_{cn}|_{u_{cn}>0} \\ & - \sum_{dkl, dk \neq ci} \gamma_{dk}^{ci} \int_{u'_{dn}<0} f_{dnl}^-(\mathbf{r}, \mathbf{u}'_d, t)u'_{dn}\tilde{T}_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}'_d)d\mathbf{u}'_d. \end{aligned} \quad (9)$$

The other accounts for their distribution, but implies the immediate desorption:

$$\begin{aligned}
f_{cij}^+(\mathbf{r}, \mathbf{u}_c, t) u_{cn} |_{u_{cn} > 0} = & - \sum_l \int_{u'_{cn} < 0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_c, t) u'_{cn} T_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}'_c - D_{ci} \sum_l \int_{u'_{cn} < 0} f_{cil}^-(\mathbf{r}, \mathbf{u}'_d, t) u'_{cn} \tilde{T}_l^{cij}(\mathbf{u}_c, \mathbf{u}'_c) d\mathbf{u}'_c \\
& - \sum_{dkl, dk \neq ci} \gamma_{dk}^{ci} \int_{u'_{dn} < 0} f_{dki}^-(\mathbf{r}, \mathbf{u}'_d, t) u'_{dn} \tilde{T}_{dki}^{cij}(\mathbf{u}_c, \mathbf{u}'_d) d\mathbf{u}'_d.
\end{aligned} \tag{10}$$

Here we will consider the first option (9), which affects the balance law on the surface. Besides that it is also worth mentioning that the distribution of desorbed particles from the surface  $\tilde{f}_{cij}^{+,M}(\mathbf{r}, \mathbf{u}_c, t)$  depends on the wall temperature, but not on the one, considered on the external edge of the Knudsen layer.

It should be emphasized that the scheme considered here is noticeably different from the one, applied in our previous work [9]. As is shown later, it allows one to overcome the mentioned issues in the concentration jump description and obtain conditions that account for the introduced complex surface mechanisms.

## SLIP CONDITIONS FOR MAXWELL AND CERCIGNANI–LAMPIS KERNELS

In this section boundary conditions for the STS set of fluid-dynamic variables [8] will be obtained for two most widely used model, which are those proposed by Maxwell [22] and Cercignani–Lampis [23]. The first one suggests that some particles are reflected specularly by solid wall, while the other part — diffusely, and the fraction of these particles is given by the accommodation coefficient. The Cercignani–Lampis model includes two accommodation coefficients for better representation of physical properties of the solid surface, that is why express more efficient transport phenomena of gas flows near the surface.

The procedure to obtain the slip conditions for the new scheme (9) will be held for the first-order state-specific distribution function, which can be written in terms of the expansion coefficients as follows [8]:

$$\begin{aligned}
f_{cij}^{(1)} = f_{cij}^{(0)} + \frac{f_{cij}^{(0)}}{n} \left[ \frac{m_c}{2kT} \mathbf{c}_c \cdot \nabla \ln T \left( a_{ci,00} S_{3/2}^{(0)} P_j^{(0)} + a_{ci,10} S_{3/2}^{(1)} P_j^{(0)} + a_{ci,01} S_{3/2}^{(0)} P_j^{(1)} \right) - \frac{m_c}{2kT} \sum_{dk} d_{ci,0}^{dk} \mathbf{c}_c \cdot \mathbf{d}_{dk} S_{3/2}^{(0)} \right. \\
- \frac{m_c}{2kT} b_{ci,0} \left( \mathbf{c}_c \mathbf{c}_c : \nabla \mathbf{v} - \frac{1}{3} c_c^2 \nabla \cdot \mathbf{v} \right) S_{5/2}^{(0)} - \left( f_{ci,10} S_{1/2}^{(1)} P_j^{(0)} + f_{ci,01} S_{1/2}^{(0)} P_j^{(1)} \right) \nabla \cdot \mathbf{v} - g_{ci,10} S_{1/2}^{(1)} P_j^{(0)} \\
\left. - g_{ci,01} S_{1/2}^{(0)} P_j^{(1)} \right],
\end{aligned} \tag{11}$$

where the form of the expansion, provided by the set of Sonine and Waldmann–Trübenbacher polynomials  $S_n^{(v)}, P_j^{(p)}$  with coefficients  $a_{ci,rp}, b_{ci,r}, d_{ci,r}^{dk}, f_{ci,rp}, g_{ci,rp}$ , is chosen accordingly to the right-hand sides of corresponding integral equations. The zero-order local thermal equilibrium Maxwell-Boltzmann distribution  $f_{cij}^{(0)}$  has the form:

$$f_{cij}^{(0)} = \frac{n_{ci}}{Z_{rot,ci}} \left( \frac{m_c}{2\pi kT} \right)^{3/2} s_j^{ci} \exp \left( -\frac{m_c \mathbf{c}_c^2}{2kT} - \frac{\boldsymbol{\varepsilon}_j^{ci}}{kT} \right). \tag{12}$$

In the above relations  $m_c$  is the mass of particle  $c$ ;  $k$  is the Boltzmann constant;  $n$  is the total number density per unit volume;  $T$  is the gas temperature;  $\mathbf{c}_c$  is the particle peculiar or thermal velocity;  $\mathbf{v}$  is the macroscopic mixture velocity;  $\mathbf{d}_{ci}$  is the diffusive driving force for species  $ci$ ;  $n_{ci}$  is the number density of chemical species  $c$  in the vibrational state  $i$ ;  $s_j^{ci}$  is the statistical weight;  $Z_{rot,ci}$  is the rotational partition function depending on the vibrational state  $i$ ;  $\boldsymbol{\varepsilon}_j^{ci}$  is the particle's rotational energy. The transport coefficient expressions in terms of the expansion coefficients are introduced

by the following relations [8]:

$$D_{cidk} = \frac{1}{2n} a_{ci,0}^{dk}; \quad (13)$$

$$D_{T,ci} = -\frac{1}{2n} a_{ci,00}; \quad (14)$$

$$\lambda' = \sum_{ci} \frac{n_{ci}}{n} \left( \frac{5}{4} k a_{ci,10} + \frac{m_c}{2} c_{rot,ci} a_{ci,01} \right) = \sum_{ci} \frac{n_{ci}}{n} (\lambda'_{ci,tr} + \lambda_{ci,rot}) = \sum_{ci} \frac{n_{ci}}{n} \lambda'_{ci}; \quad (15)$$

$$\eta = \sum_{ci} \frac{n_{ci}}{n} \frac{kT}{2} b_{ci,0} = \sum_{ci} \frac{n_{ci}}{n} \eta_{ci}; \quad (16)$$

$$\zeta = -\sum_{ci} \frac{n_{ci}}{n} kT f_{ci,10} = \sum_{ci} \frac{n_{ci}}{n} \zeta_{ci}; \quad (17)$$

$$p_{rel} = -\sum_{ci} \frac{n_{ci}}{n} kT g_{ci,10} = \sum_{ci} \frac{n_{ci}}{n} p_{rel,ci}. \quad (18)$$

Here,  $D_{cidk}$  and  $D_{T,ci}$  are multi-component state-specific diffusion and thermal diffusion coefficients,  $\lambda'$  is the partial thermal conductivity coefficient of translational and rotational degrees of freedom,  $\eta$  and  $\zeta$  are shear and bulk viscosity coefficients,  $p_{rel}$  is the relaxation (dynamic) pressure and  $c_{rot,ci}$  is the rotational specific heat depending on the vibrational state. For the convenience, the effective transport coefficients  $\lambda'_{ci}$ ,  $\eta_{ci}$ ,  $\zeta_{ci}$ ,  $p_{rel,ci}$  are introduced, which are not the true mixture transport coefficients but are needed to give the physical interpretation of obtained slip conditions. The transport terms expressions, which in the STS approximation include diffusion velocity  $\mathbf{V}_{ci}$ , viscous stress tensor  $\mathbf{P}$  and total heat flux  $\mathbf{q}$  are written in terms of the transport coefficients in the form

$$\mathbf{P} = (p - \zeta \nabla \cdot \mathbf{v} - p_{rel}) \mathbf{I} - 2\eta \mathbf{S}, \quad (19)$$

$$\mathbf{V}_{ci} = -\sum_{dk} D_{cidk} \mathbf{d}_{dk} - D_{T,ci} \nabla \ln T, \quad (20)$$

$$\mathbf{q} = -\lambda' \nabla T - p \sum_{ci} D_{T,ci} \mathbf{d}_{ci} + \sum_{ci} n_{ci} \mathbf{V}_{ci} \left( \frac{5}{2} kT + \langle \varepsilon_j^{ci} \rangle_{rot} + \varepsilon_i^e + \varepsilon_c \right), \quad (21)$$

where  $p$  is pressure,  $\mathbf{S}$  is the traceless symmetric part of the strain rate tensor,  $\varepsilon_i^e$  is the vibrational energy of the  $i$ th state,  $\varepsilon_c$  is the energy of formation,  $\langle \dots \rangle_{rot}$  denotes averaging over rotational energy with local equilibrium Boltzmann distribution.

As it was in the initial approach we will assume that the velocity component along normal is zero near the surface. Such an assumption provides us the following balance law at the wall:

$$\sum_{ci} n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} = \sum_{ci} \frac{S_{ci}}{2} \left[ n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} - \sqrt{\frac{kT}{2\pi n \sqrt{m_c}}} \left( 2n - b_{ci,0} S_{nn} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10} \right) \right] + \sqrt{\frac{kT}{2\pi}} \sum_{ci} D_{ci} \frac{n_{ci}}{\sqrt{m_c}}. \quad (22)$$

Here and hereafter the notation that all the terms are taken on the wall  $-|_w$  (which is actually the external edge of the Knudsen layer) is omitted. When adsorption and desorption are neglected, we have the simplified relation, which can be interpreted as the conservation of number flux near the wall for the introduced scheme (9):

$$\sum_{ci} n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} = 0. \quad (23)$$

Also it is worth mentioning that, as in the previous approach, the concentration jump expressions do not depend on the chosen models of scattering kernels, that is why they can be obtained on the basis of only the considered approximation of distribution function (11). Implementation of the mentioned above procedure for the concentration

jump case [9] yields the following expression for the new scheme:

$$\begin{aligned}
n_{ci} \left( 2 - \sum_{dk} \gamma_{ci}^{dk} - S_{ci} \right) \left( \frac{1}{2n} a_{ci,00} \frac{\partial \ln T}{\partial n} - \frac{1}{2n} \sum_{dk} a_{ci,0}^{dk} \mathbf{d}_{dk} \cdot \mathbf{n} \right) &= - \left( \sum_{dk} \gamma_{ci}^{dk} + S_{ci} \right) \frac{n_{ci}}{n} \sqrt{\frac{kT}{2\pi m_c}} \left( 2n - b_{ci,0} S_{nm} \right. \\
&+ \left. f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10} \right) + D_{ci} n_{ci} \sqrt{\frac{2kT}{\pi m_c}} - \sum_{dk} \gamma_{dk}^{ci} n_{dk} \left( \frac{1}{2n} a_{dk,00} \frac{\partial \ln T}{\partial n} - \frac{1}{2n} \sum_{fl} a_{dk,0}^{fl} \mathbf{d}_{fl} \cdot \mathbf{n} \right) + \sqrt{\frac{kT}{2\pi}} \sum_{dk} \frac{\gamma_{dk}^{ci} n_{dk}}{n \sqrt{m_d}} \\
&\times \left( 2n - b_{dk,0} S_{nm} + f_{dk,10} \nabla \cdot \mathbf{v} + g_{dk,10} \right). \tag{24}
\end{aligned}$$

Alternatively, it can be written in a more compact form in terms of diffusion velocity:

$$\begin{aligned}
n_{ci} \left( 2 - \sum_{dk} \gamma_{ci}^{dk} - S_{ci} \right) \mathbf{V}_{ci} \cdot \mathbf{n} &= - \left( \sum_{dk} \gamma_{ci}^{dk} + S_{ci} \right) \frac{n_{ci}}{n} \sqrt{\frac{kT}{2\pi m_c}} \left( 2n - b_{ci,0} S_{nm} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10} \right) \\
&+ D_{ci} n_{ci} \sqrt{\frac{2kT}{\pi m_c}} - \sum_{dk} \gamma_{dk}^{ci} n_{dk} \mathbf{V}_{dk} \cdot \mathbf{n} + \sqrt{\frac{kT}{2\pi}} \sum_{dk} \frac{\gamma_{dk}^{ci} n_{dk}}{n \sqrt{m_d}} \left( 2n - b_{dk,0} S_{nm} + f_{dk,10} \nabla \cdot \mathbf{v} + g_{dk,10} \right). \tag{25}
\end{aligned}$$

The difference from the expression, presented in [9], is in the last three additional terms appearing in the RHS of the above relation and the accounted fraction of particles loss after scattering  $\sum_{dk} \gamma_{ci}^{dk} + S_{ci}$ . The last sum has replaced the sum of coefficients  $\sum \gamma_{ci}^p$ , which allowed to account for both loss and gain in the particles number (3). The obtained concentration jump implies that the number flux of particles of given species near the surface  $n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n}$  consists of: 1) the number flux of desorbed particles with the mean non-slip velocity  $\sqrt{\frac{2kT}{\pi m_c}}$ ; 2) the opposite number flux of particles of given species that change their state due to surface processes; 3) fluxes of particles that are a part of  $ci$  species formation.

## Maxwell model

In the case of the state-to-state approximation, the specular-diffusive kernel can be written as follows:

$$T_{l,M}^{cij}(\mathbf{u}_c, \mathbf{u}'_c) = (1 - \sigma_{ci}) \delta_{lj} \delta(\mathbf{u}'_c - \mathbf{u}_c + 2u_{cn} \mathbf{n}) + \sigma_{ci} \frac{2}{\pi} \left( \frac{m_c}{2kT^w} \right)^2 \frac{s_j^{ci}}{Z_{rot,ci}(T^w)} \exp \left( -\frac{m_c u_c^2}{2kT^w} - \frac{\epsilon_j^{ci}}{kT^w} \right) u_{cn}, \tag{26}$$

where  $T^w$  is the wall temperature and  $\sigma_{ci}$  is the accommodation coefficient which represents the fraction of particles of  $ci$  species that are diffusely reflected. The coefficient is usually chosen to describe the tangential momentum or total energy accommodation on the surface, which generally are not the same. It should be noted that the expression above, despite being appropriate generalization, still has a disadvantage in being unable to describe various mechanisms of rotational state change of a molecule due to the wall impinging. One of the possible ways to overcome this is to introduce the probabilities of vibrational state change due to specular and diffusive scattering, depending on the wall temperature and solid wall characteristics.

The additional kernel  $T_{dkl}^{cij}$  in the new scheme (9) is chosen, in order to simplify the calculations, to be diffusive for both considered cases of  $T_l^{cij}$  kernels. Such an assumption means that the particles, for which vibrational or chemical state change occurs during their interaction with solid wall, are reflected into the gas with the local-equilibrium Maxwell–Boltzmann distribution:

$$T_{dkl}^{cij}(\mathbf{u}_c, \mathbf{u}'_d) = \frac{2}{\pi} \left( \frac{m_c}{2kT^w} \right)^2 \frac{s_j^{ci}}{Z_{rot,ci}(T^w)} \exp \left( -\frac{m_c u_c^2}{2kT^w} - \frac{\epsilon_j^{ci}}{kT^w} \right) u_{cn}. \tag{27}$$

The procedure to obtain the slip conditions performed for the Maxwell scattering kernel  $T_{l,M}^{cij}$  yields velocity slip

and temperature jump in the form:

$$v_l = \frac{\sqrt{\frac{\pi kT}{2}} \sum_{ci} (2 - \sigma_{ci}) \frac{n_{ci}}{2n} b_{ci,0} S_{ln} - \sum_{ci} \sigma_{ci} n_{ci} \sqrt{m_c} \left( \mathbf{V}_{ci} \cdot \boldsymbol{\tau}_l - \frac{a_{ci,10}}{4n} \frac{\partial \ln T}{\partial \boldsymbol{\tau}_l} \right)}{\sqrt{\frac{\pi}{2kT}} \sum_{ci} (2 - \sigma_{ci}) m_c n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} + \sum_{ci} \sigma_{ci} \frac{n_{ci} \sqrt{m_c}}{2n} (2n - b_{ci,0} S_{nm} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10}) - \sum_{ci} n_{ci} \sqrt{m_c} D_{ci}}; \quad (28)$$

$$\frac{T}{T^w} = \frac{\sum_{ci} (2 - \sigma_{ci}) n_{ci} \left( 1 + \frac{m_c v^2}{4kT^w} \right) \mathbf{V}_{ci} \cdot \mathbf{n} + \sqrt{\frac{kT}{2\pi}} Z_1}{\sum_{ci} \frac{5(2 - \sigma_{ci}) n_{ci}}{4} \mathbf{V}_{ci} \cdot \mathbf{n} - \frac{Z_3}{2k} \frac{\partial \ln T}{\partial n} + \sqrt{\frac{kT}{2\pi}} \left( \sum_{ci} \frac{3\sigma_{ci} n_{ci}}{n \sqrt{m_c}} \left( \frac{2n}{3} - \frac{b_{ci,0}}{2} S_{nm} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10} \right) + Z_2 \right)}, \quad (29a)$$

$$Z_1 = \sum_{ci} \sigma_{ci} \frac{n_{ci}}{n \sqrt{m_c}} \left( 1 + \frac{m_c v^2}{4kT^w} \right) \cdot (2n - b_{ci,0} S_{nm} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10}), \quad (29b)$$

$$Z_2 = \sum_{ci} \sigma_{ci} \frac{n_{ci}}{n} \sqrt{m_c} \frac{c_{rot,ci}}{k} (f_{ci,01} \nabla \cdot \mathbf{v} + g_{ci,01}), \quad (29c)$$

$$Z_3 = \sum_{ci} (2 - \sigma_{ci}) \frac{n_{ci}}{2n} \left( \frac{5}{2} k a_{ci,10} + m_c c_{rot,ci} a_{ci,01} \right). \quad (29d)$$

Here,  $v_l$  is the velocity component in the tangential direction  $\boldsymbol{\tau}_l$ . The difference in equations for the new kinetic approach and for the initially proposed appears in the velocity slip expression, while the temperature jump remains to be exactly the same. The last statement will not be valid if the distribution of the particles desorped into the gas phase occurs with the temperature different from  $T^w$ . The difference in the velocity slip is expressed by the term in denominator, connected with desorption coefficients, consequently, if the desorption process is neglected, then the velocity slip coincides with that derived in the frame of the initial scheme [9].

## Cercignani–Lampis model

Generalization of the CL kernel for the case of reacting gas flows with rapid and slow processes can be introduced by the following relation:

$$T_{i,CL}^{cij}(\mathbf{u}_c, \mathbf{u}'_c) = \frac{2}{\pi} \left( \frac{m_c}{2kT^w} \right)^2 \frac{s_j^{ci}}{Z_{rot,ci}(T^w)} \frac{1}{\alpha_{n,ci} \alpha_{\tau,ci}} u_{cn} I_0 \left( \frac{2m_c \sqrt{1 - \alpha_{n,ci}} u_{cn} u'_{cn}}{2kT^w \alpha_{n,ci}} \right) \times \exp \left( -\frac{m_c (u_{cn}^2 + (1 - \alpha_{n,ci}) u_{cn}'^2)}{2kT^w \alpha_{n,ci}} \right) \exp \left( -\frac{m_c (\mathbf{u}_{c\tau} - \sqrt{1 - \alpha_{\tau,ci}} \mathbf{u}'_{c\tau})^2}{2kT^w \alpha_{\tau,ci}} \right) \exp \left( -\frac{\boldsymbol{\varepsilon}_j^{ci}}{kT^w} \right), \quad (30)$$

where  $\mathbf{u}_{c\tau}$  is the tangential velocity and  $I_0$  is the zeroth order modified Bessel function:

$$I_0(x) = \frac{1}{\pi} \int_0^\pi e^{x \cos \theta} d\theta. \quad (31)$$

The coefficients  $\alpha_{n,ci}$ ,  $\alpha_{\tau,ci}$  for  $ci$  species should be treated as the normal and tangential energy accommodation coefficients. The kernel also can be written in terms of normal and tangential momentum coefficients, but here for the convenience we prefer the first option. The above kernel, as the previous Maxwell one, is not capable to describe the rotational state change of a molecule while it is scattered from the surface. Similarly, this issue may be resolved by introducing the probability of the vibrational state change. The kernel  $\tilde{T}_{dkl}^{cij}$  here is also chosen to be diffusive.

From the obtained set of slip conditions for the present model only the temperature jump is provided, since the expression for the velocity slip is the same, as for the Maxwell model and, as it is stated above, the concentration jump is independent of scattering kernels. The temperature jump is obtained in the form

$$\frac{T}{T^w} = \frac{(\alpha_\tau + \alpha_n) \sum_{ci} \frac{n_{ci}}{2n} \mathbf{V}_{ci} \cdot \mathbf{n} + \sqrt{\frac{2kT}{\pi}} \sum_{ci} \frac{n_{ci}}{2n \sqrt{m_c}} \left( \alpha_\tau \frac{m_c v^2}{2kT^w} + \alpha_\tau + \alpha_n \right) (2n - b_{ci,0} S_{nm} + f_{ci,10} \nabla \cdot \mathbf{v} + g_{ci,10})}{(10 - (2\alpha_\tau + 3\alpha_n)) \sum_{ci} \frac{n_{ci}}{4n} \mathbf{V}_{ci} \cdot \mathbf{n} - Z_1 + \sqrt{\frac{2kT}{\pi}} (Z_2 + Z_3) + \sqrt{1 - \alpha_\tau} \sum_{ci} \frac{n_{ci}}{2n} b_{ci,0} (S_{1n} v_1 + S_{2n} v_2)}, \quad (32a)$$



$$Z_1 = (10 - (2\alpha_\tau + 3\alpha_n)) \sum_{ci} \frac{n_{ci}}{4n} a_{ci,10} \frac{\partial \ln T}{\partial n} + \sum_{ci} \frac{n_{ci}}{2n} m_c \frac{c_{rot,ci}}{k} a_{ci,01} \frac{\partial \ln T}{\partial n}; \quad (32b)$$

$$Z_2 = \sum_{ci} \frac{n_{ci}}{n} \sqrt{m_c} \frac{c_{rot,ci}}{k} (f_{ci,01} \nabla \cdot \mathbf{v} + g_{ci,01}); \quad (32c)$$

$$Z_3 = \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} ((\alpha_n + \alpha_\tau)(2n + 3f_{ci,10} \nabla \cdot \mathbf{v} + 3g_{ci,10}) - 3\alpha_n b_{ci,0} S_{nn}). \quad (32d)$$

Contrary to the Maxwell model, the temperature jump for the CL scattering kernel depends on two accommodation coefficients, and due to that has more complex expression. The coefficients are assumed here to be independent of the particle's vibrational level and chemical species. If the latter is not valid, then the resulting expression will have more complicated form and include terms, connected with tangential stress components.

## SIMPLIFICATIONS OF OBTAINED CONDITIONS

The concentration jump relation can be written in a more physically meaningful form if we use the effective transport coefficients and normal stress for given species  $P_{nn,ci} = p - 2\eta_{ci} S_{nn} - \zeta_{ci} \nabla \cdot \mathbf{v} - p_{rel,ci}$ :

$$\left(2 - \sum_{dk, dk \neq ci} \gamma_{ci}^{dk} - S_{ci}\right) n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} = - \frac{(\sum_{dk, dk \neq ci} \gamma_{ci}^{dk} + S_{ci}) n_{ci}}{n \sqrt{2\pi m_c k T}} (p + P_{nn,ci}) + \sqrt{\frac{2kT}{\pi m_c}} n_{ci} D_{ci} \quad (33)$$

$$- \sum_{dk, dk \neq ci} \gamma_{dk}^{ci} n_{dk} \mathbf{V}_{dk} \cdot \mathbf{n} + \frac{1}{\sqrt{2\pi k T}} \sum_{dk, dk \neq ci} \gamma_{dk}^{ci} \frac{n_{dk}}{n \sqrt{m_d}} (p + P_{nn,dk}), \quad c = 1, \dots, L, \quad i = 0, \dots, L_c,$$

where  $L_c$  is the number of vibrational states of  $c$  particle,  $L$  is the number of components in the mixture. For the Maxwell model, the set of conditions including velocity slip and temperature jump is written similarly:

$$v_l = \frac{(2 - \sigma) \sqrt{\frac{\pi}{2kT}} \sum_{ci} \frac{n_{ci}}{n} 2\eta_{ci} S_{ln} + \sigma \sum_{ci} n_{ci} \sqrt{m_c} \left( \frac{\lambda'_{lr,ci}}{5kn} \frac{\partial \ln T}{\partial \tau_l} - \mathbf{V}_{ci} \cdot \boldsymbol{\tau}_l \right)}{\sigma \sum_{ci} \frac{n_{ci}}{2nkT} \sqrt{m_c} (p + P_{nn,ci}) - \sum_{ci} n_{ci} \sqrt{m_c} D_{ci}}, \quad l = 1, 2; \quad (34)$$

$$\frac{T}{T^w} = \frac{(2 - \sigma) \sum_{ci} n_{ci} \mathbf{V}_{ci} \cdot \mathbf{n} + \sigma \sqrt{\frac{2}{\pi k T}} \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} \left(1 + \frac{m_c v^2}{4kT^w}\right) \cdot (p + P_{ci,nn})}{(2 - \sigma) \sum_{ci} \frac{5n_{ci}}{4} \mathbf{V}_{ci} \cdot \mathbf{n} - \frac{(2 - \sigma)\lambda'}{2k} \frac{\partial \ln T}{\partial n} + \sigma \sqrt{\frac{2}{\pi k T}} \sum_{ci} \frac{3n_{ci}}{2n} \left( \frac{-\frac{p}{3} + \eta_{ci} S_{nn} + P_{ci,nn}}{\sqrt{m_c}} + \frac{\sqrt{m_c} \delta_{ci}}{3} \right)}. \quad (35)$$

Here,  $\delta_{ci} = c_{rot,ci} T (f_{ci,01} \nabla \cdot \mathbf{v} + g_{ci,01})$ , and, as for the CL model, the accommodation coefficient is independent of particle's species. The temperature jump for the Cercignani–Lampis model is written accordingly:

$$\frac{T}{T^w} = \frac{(\alpha_\tau + \alpha_n) \sum_{ci} \frac{n_{ci}}{2n} \mathbf{V}_{ci} \cdot \mathbf{n} + \sqrt{\frac{2}{\pi k T}} \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} \left( \alpha_\tau \frac{m_c v^2}{2kT^w} + \alpha_\tau + \alpha_n \right) (p + P_{nn,ci})}{(10 - 2\alpha_\tau - 3\alpha_n) \sum_{ci} \frac{n_{ci}}{4n} \mathbf{V}_{ci} \cdot \mathbf{n} - \frac{(10 - 2\alpha_\tau - 3\alpha_n)\lambda'_r + 5\lambda'_{rot}}{5k} \frac{\partial \ln T}{\partial n} + \sqrt{\frac{2}{\pi k T}} (Z_2 + Z_3) + \frac{\sqrt{1 - \alpha_\tau} \eta}{kT} (S_{1n} v_1 + S_{2n} v_2)}, \quad (36a)$$

$$Z_2 = \sum_{ci} \frac{n_{ci} \sqrt{m_c}}{n} \delta_{ci}; \quad (36b)$$

$$Z_3 = \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} ((\alpha_n + \alpha_\tau)(2p - 3\zeta_{ci} \nabla \cdot \mathbf{v} - 3p_{rel,ci}) - 6\alpha_n \eta_{ci} S_{nn}). \quad (36c)$$

If desorption and adsorption processes are neglected, the temperature jump expressions can be written in a simplified form:

$$\frac{T}{T^w} = \frac{\sigma \sqrt{\frac{2}{\pi k T}} \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} \left(1 + \frac{m_c v^2}{4kT^w}\right) \cdot (p + P_{ci,nn})}{-\frac{(2 - \sigma)\lambda'}{2k} \frac{\partial \ln T}{\partial n} + \sigma \sqrt{\frac{2}{\pi k T}} \sum_{ci} \frac{3n_{ci}}{2n} \left( \frac{-\frac{p}{3} + \eta_{ci} S_{nn} + P_{ci,nn}}{\sqrt{m_c}} + \frac{\sqrt{m_c} \delta_{ci}}{3} \right)}. \quad (37)$$

$$\frac{T}{T^w} = \frac{\sqrt{\frac{2}{\pi kT}} \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} \left( \alpha_\tau \frac{m_c v^2}{2kT^w} + \alpha_\tau + \alpha_n \right) (p + P_{nn,ci})}{-\frac{(10-2\alpha_\tau-3\alpha_n)\lambda'_{tr}+5\lambda'_{rot}}{5k} \frac{\partial \ln T}{\partial n} + \sqrt{\frac{2}{\pi kT}} \left( \sum_{ci} \frac{n_{ci}\sqrt{m_c}}{n} \delta_{ci} + Z_3 \right) + \frac{\sqrt{1-\alpha_\tau}\eta}{kT} (S_{1n}v_1 + S_{2n}v_2)}, \quad (38a)$$

$$Z_3 = \sum_{ci} \frac{n_{ci}}{2n\sqrt{m_c}} \left( (\alpha_n + \alpha_\tau)(2p - 3\zeta_{ci}\nabla \cdot \mathbf{v} - 3p_{rel,ci}) - 6\alpha_n\eta_{ci}S_{nn} \right). \quad (38b)$$

In the above equations, the reduced form (23) of the conservation law has been used.

Here we also are interested in a particular case of only atom recombination on surface considered. For this case only the concentration jump expressions (33) will change explicitly due to the independence of above equations from the mass flux near the surface. The simplification under such an assumption yields

$$n_a \mathbf{V}_a \cdot \mathbf{n} = -\frac{\sum_{M,k} \gamma_a^{rec,M(k)}}{2 - \sum_{M,k} \gamma_a^{rec,M(k)}} \frac{n_a}{n\sqrt{2\pi m_a kT}} (p + P_{nn,a}), \quad a = 1, \dots, L_a; \quad (39)$$

$$n_{M(i)} \mathbf{V}_{M(i)} \cdot \mathbf{n} = -\sum_a \frac{\gamma_a^{rec,M(k)}}{2} n_a \mathbf{V}_a \cdot \mathbf{n} + \frac{1}{\sqrt{2\pi kT}} \sum_a \frac{\gamma_a^{rec,M(k)}}{2} \frac{n_a}{n\sqrt{m_a}} (p + P_{nn,a}), \quad M = 1, \dots, L_M, \quad i = 0, \dots, N_M, \quad (40)$$

where indices  $a$  and  $M(i)$  correspond to atom and molecule in the vibrational state  $i$ , respectively,  $\gamma_a^{rec,M(i)}$  is the recombination probability,  $L_a$  and  $L_M$  are the numbers of atoms and molecular components in the mixture,  $N_M$  is the number of considered vibrational states for a molecule  $M$ . Eq. (40) can be simplified, so each condition for species concentration will present a relation for the mass flux  $\mathbf{J}_{ci} \cdot \mathbf{n} = \rho_{ci} \mathbf{V}_{ci} \cdot \mathbf{n}$ :

$$n_{M(i)} \mathbf{V}_{M(i)} \cdot \mathbf{n} = \frac{1}{\sqrt{2\pi kT}} \sum_a \frac{\gamma_a^{rec,M(k)}}{2} \frac{n_a}{n\sqrt{m_a}} (p + P_{nn,a}) \left[ 1 + \frac{\sum_{M,k} \gamma_a^{rec,M(k)}}{2 - \sum_{M,k} \gamma_a^{rec,M(k)}} \right], \quad M = 1, \dots, L_M, \quad i = 0, \dots, N_M, \quad (41)$$

Besides the above simplifications, in order to obtain expressions in the required form, we will add the additional non-slip velocity and the Fick's law assumptions for Eqs. (39), (41):

$$D_a \frac{\partial y_a}{\partial n} = \frac{\sum_{M,k} \gamma_a^{rec,M(k)}}{2 - \sum_{M,k} \gamma_a^{rec,M(k)}} \sqrt{\frac{2kT}{\pi m_a}} y_a, \quad a = 1, \dots, L_a; \quad (42)$$

$$D_{M(i)} \frac{\partial y_{M(i)}}{\partial n} = -\sqrt{\frac{2kT}{\pi}} \sum_a \frac{\gamma_a^{rec,M(k)}}{2} \frac{m_M y_a}{\sqrt{m_a^3}} \left[ 1 + \frac{\sum_{M,k} \gamma_a^{rec,M(k)}}{2 - \sum_{M,k} \gamma_a^{rec,M(k)}} \right], \quad M = 1, \dots, L_M, \quad i = 0, \dots, N_M, \quad (43)$$

where  $y_a = \rho_a/\rho$ ,  $y_{M(i)} = \rho_{M(i)}/\rho$ . In the above relations, the terms connected with the relaxation pressure, have been omitted as well.

For the particular case of the mentioned assumptions, the slip conditions for species concentrations written above reduce to a form similar to that obtained in Refs. [15, 16]. The differences are in the considered reaction rates, which in our case are derived theoretically and, when velocity slip is considered, depend on the viscous stress of given species.

## CONCLUSIONS

In the present work, the approach allowing to obtain slip boundary conditions for the state-specific set of macroparameters, is developed in the viscous flow approximation. The advantages of the developed scheme are in extended description of various non-equilibrium surface processes and in further development in order to account for time-dependent kinetics on the wall. Slip conditions were obtained for two particular cases of commonly used scattering kernels, and, in the case of the CL kernel, the conditions for a multi-component mixture were obtained for the first

time. The differences between two sets of obtained conditions are only in temperature jump expressions. For the CL model the expression accounts for effects of two accommodation coefficients.

The procedure can be easily adapted for one- and multi-temperature approximations, and for the first one, the conditions can be already written based on the provided formulas. Still, the approach has certain limitations, which are: 1) neglecting the time that particles interact with the surface; due to that only first-order reactions are included in the concentration jump expressions; 2) fully catalytic surface case is described incorrectly since the model does not allow infinite increase of the rate coefficients. Later we plan to overcome these limitations.

The obtained slip conditions already depend only on macroparameters, accommodation coefficients and probabilities of surface processes without required further simplification, as in half-flux and Grad's methods. Due to this fact the approach should not cause any additional computational costs if all coefficients of surface processes are known. The resulting expressions for species concentrations, with several simplifications, are written in the form similar to some known phenomenological models. This fact provides us certain confidence that we are aiming at the right direction, since such models have been successfully applied to practical applications.

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