CONCENTRATION SLIP AND ITS IMPACT ON HETEROGENEOUS COMBUSTION IN A MICRO SCALE CHEMICAL REACTOR

Bo Xu and Yiguang Ju

Department of Mechanical and Aerospace Engineering
Princeton University, Princeton, NJ 08544, USA

Corresponding author: Bo Xu
Address: Department of Mechanical and Aerospace Engineering
Princeton University
E-Quad, Olden Street
Princeton
NJ, 08544
E-mail: bxu@princeton.edu
Tel: (609) 258 1411
Fax: (609) 258 6109

Short Title: Concentration Slip of Microscale Combustion
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ABSTRACT

The rarefied gas effect on concentration slip and on heterogeneous combustion in microscale chemical reactors was investigated. First, a concentration slip model to describe the rarefied gas effect on the species transport in microscale chemical reactors was derived from the approximate solution of the Boltzmann equation. Second, the model was verified using the direct Monte-Carlo method for the pure diffusion problems at different Knudsen numbers. The comparison showed that the present analytical model for the concentration slip boundary condition reasonably predicted the rarefied gas effect in the slip regime. Finally, the impact of the concentration slip on the coupling between the surface catalytic reactions and the homogeneous gas phase reactions in a microscale chemical reactor was examined using the one-step overall surface reaction model with a wide range of Knudsen and Damköhler numbers. It was shown that the rarefied gas effect significantly reduced the reaction rate of the surface catalytic oxidization for large Knudsen numbers. Furthermore, it was shown that the impact of slip effects on catalytic reactions strongly depends on the competition between the reaction rate and diffusion transport. It was found that the concentration slip causes a nonlinear reaction rate distribution at large Damköhler numbers. The results also showed that an accurate prediction of the rarefied gas effect on catalytic reactions in microscale reactors has to consider both the temperature slip and the concentration slip.
### NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$a$</td>
<td>Thermal accommodation coefficient</td>
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<tr>
<td>$A$</td>
<td>Constant in Eq. 19</td>
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<tr>
<td>$B_c$</td>
<td>Density-weighted collision rate</td>
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<td>$c_p$</td>
<td>Specific heat at constant pressure</td>
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<tr>
<td>$D$</td>
<td>Diffusion coefficient</td>
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<td>$D_a$</td>
<td>Damköhler number</td>
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<tr>
<td>$E_g, E_s$</td>
<td>Activation energy of gas and surface reactions</td>
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<tr>
<td>$f^-, f^+$</td>
<td>Molecular velocity distribution function</td>
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<td>$H$</td>
<td>Channel height</td>
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<td>$h_k$</td>
<td>Enthalpy of the $k$th species</td>
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<td>$m$</td>
<td>Molecular mass</td>
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<tr>
<td>$NS$</td>
<td>Total species number</td>
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<td>Molar concentration or number density</td>
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<td>$R, R^0$</td>
<td>Gas or universal gas constant</td>
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<td>$T$</td>
<td>Temperature</td>
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<td>$U, V$</td>
<td>Flow velocity in $x$ and $y$ directions</td>
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<td>$v_{x,y,z}$</td>
<td>Molecular thermal velocity</td>
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<td>$Y$</td>
<td>Mass fraction of species</td>
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<td>Molecular transport flux</td>
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<td>Ratio of the specific heats</td>
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<td>Molecular mean free path</td>
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<td>Thermal conductivity</td>
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<td>$\mu, \mu'$</td>
<td>Fluid dynamic viscosity</td>
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<td>$b$</td>
<td>Momentum accommodation coefficient</td>
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<td>$\rho$</td>
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<td>$\omega$</td>
<td>Reaction rate</td>
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INTRODUCTION

The recent development in microfabrication technology has led to great interests in microscale combustion for power generation, chemical sensing, and fuel conversion. The research in microscale combustion has been motivated by the fact that hydrocarbon fuel has an energy density per unit mass \((50 \text{ MJ/Kg})\) or volume that is 100 times more than the most efficient lithium-ion batteries \((0.5\text{MJ/Kg})\). Furthermore, hydrocarbon fuel based microcombustors also have the advantages of lighter weight, longer life time, immediate recharge, and less environmental impact than batteries. Moreover, microscale combustion also has higher thermal efficiency than macroscale combustors due to the increased surface to volume ratio and heat recirculation. Despite the merits of microscale combustion, combustion in meso and micro scales yields challenges in understanding the impacts of heat loss, radical quenching, and non-equilibrium transport on homogeneous and heterogeneous combustion.

It is well known that with the decrease of the combustor scale, the increase of larger surface to volume ratios dramatically increases the wall heat loss and leads to flame extinction. On the other hand, the reduction of thermal inertia at small scale significantly reduces the response time of the wall and leads to strong wall flame coupling. This flame-wall interaction can dramatically change the nature of flame propagation in small scale devices. In particular, at small scale, the heat recirculation through the wall heat conduction yields new flame regimes and instabilities.

Previous studies have shown that the wall heat loss results in the so called quenching distance below which a flame cannot propagate [1]. However, Weinberg and co-workers [2-4] studied the heat recirculation effects by reversing the burned gas to preheat the unburned mixture and their results showed that the flammability limit can be extended and that there are two limits caused by heat loss and flow rate, respectively. Theoretical analyses from Ronney [5] and Ju et al.
[6, 7] repredicted this observed phenomenon and demonstrated the existence of different flame regimes in mesoscale channels caused by this wall-flame thermal interaction [7]. Numerical simulations from Norton et al. [8] and Timothy et al. [9] showed that it was possible to build microburners below the quenching distance with a proper choice of wall materials and reduced heat loss. Experimentally, a number of innovative ways have been devised to reduce thermal losses and build up micro combustors near or below the quenching distances, including the single pass [10], the Y-shaped diffusion burner [11] and the three-dimensional “Swiss Roll” [12, 13] counter flow heat-exchanger/combustor. A microburner with a scale of less than 1 mm has also been developed by Masel, Shannon and their co-workers [14] to allow self-sustained homogeneous combustion, which is achieved by using certain insulated alumina to reduce radical adsorption and heat loss.

Industry and military applications require that the micro power generators be portable as well as efficient. However, with the channel width further decreased, it becomes very difficult to sustain a stable propagating flame due to the quenching effect of the wall and the requirement of high operating and ignition temperatures of hydrocarbon fuels. On the other hand, catalytic combustion can take advantage of the high surface to volume ratio and high transport rate in microscale and generate enough radicals to sustain the reaction. This provides an opportunity for faster catalytic reactions than could be achieved with macroscale combustors. Many numerical simulations and experimental work have been conducted to study the ignition, stability and conversion efficiency of catalytic microburners [13, 15, 16]. Some catalyzed microburners have been built to achieve sustained catalytic microcombustion over a wide range of compositions and at substantially lower temperatures and pressures than macro combustors where traditional homogeneous combustion may not survive. All of these studies were focused on combustion in the continuum regime. The burner scales were so large (>100 µm) that the rarefied gas effect was
ignored.

However, when the length scale of the flow approaches the mean free path of the combustion mixture, there are no longer sufficient collisions between gas molecules to achieve thermodynamic equilibrium. For example, the mean free path of the partially burned methane-air mixture at 1000 K and one atmosphere is around 0.1 $\mu$m. The resulting Knudsen number for microcombustion is between 0.001 and 1. Norton et al. [17] have developed catalyzed microburners that allow self-sustained combustion in channels with a gap of 250 $\mu$m and peak pressure of 5000 Pa within a temperature range of 800-1000 K, which yielded a Knudsen number of 0.02. As such, in microscale combustion, the resulting non-continuum and non-equilibrium transport processes cannot be well predicted without reasonably considering the rarefied gas effect.

Slip models accounting for velocity and temperature in micro fluidics have been developed and employed in the numerically efficient continuum methods to correct the non-equilibrium processes near solid boundaries [18]. The basic idea is to relax the traditional no-slip boundary to allow for the presence of slip on the surface while the equations applicable to the continuum regime are retained. It is well known that the temperature and velocity slips on the wall can greatly affect the energy exchange between the gas and the wall [19]. In a microscale combustor, these slips will also affect the catalytic surface reaction due to the strongly temperature dependent Arrhenius law and transport properties. A recent study of catalytic conversion in micro-channels has shown that slip flow significantly affects the conversion efficiency [20]. Shankar and Glumac [21] studied the temperature slip effect in a low pressure catalytic combustion system and they observed a slip of 34K in the hydrogen/oxygen reaction system. Similar to the velocity and temperature, there is a possibility that the species concentration near the boundary may also be very different from that at the boundary [22], which significantly influences the surface reaction.
Raimondeau et al. [23] and Aghalayam et al. [24] numerically studied the role of radical wall quenching in flame stability and wall heat flux and their results showed that quenching of any of the important radicals had a significant influence on the stability of the system due to the chemical and thermal coupling between the gas and the wall. It has been shown that while the species concentration could be very uniform in a micro channel when the wall was inert, certain radicals could also have a large gradient of concentration near the reactive surface. This could have been the case especially if the reaction speed was larger than the transport speed [24], which renders a possible large radical discontinuity between the gas and the wall. The rarefied gas surface reaction is also an important issue in chemical vapor deposition because many depositions are conducted at very low pressure environments. In spite of its great practical importance and the increasing interests in studying the velocity and temperature slips in microfluidics, the radical or species concentration slip and its impact on catalytic reactions in micro and nano scales have not been well investigated.

This study was motivated by the above discussion and was aimed to develop a slip condition of species concentration for the purpose of numerical modeling of micro and nanoscale chemical reactors. First, a concentration slip model was developed from the approximate solution of the Boltzmann equation. Second, a pure diffusion problem was solved using the newly developed slip model and the results were compared with those obtained by direct simulation of the Monte-Carlo (DSMC) method [25]. Third, the impact of slip boundary conditions on the catalytic reaction was investigated using the catalytic reaction in a low pressure, two-dimensional micro channel. Finally, discussions and conclusions were made.

A SLIP MODEL FOR SPECIES CONCENTRATION

Slip model
For a rarified gaseous flow, the collision frequency between molecules and the wall are comparable with that between molecules. As a result, flow cannot be considered as a local thermodynamic equilibrium (LTE) any more. The degree that a gas deviates from the LTE can be measured by the Knudsen number ($Kn$), which is defined as $Kn=\lambda/H$, where $\lambda$ is the molecular mean free path of the gas mixture and $H$ is the characteristic length of the physical problem. A flow with a higher Knudsen number is said to be more rarefied because of the relatively less intermolecule collisions.

For medium Knudsen numbers, that is, when a gaseous flow is within the so called Slip Boundary Regime ($10^{-3} < Kn < 10^{-1}$), the effects of the thermodynamic non-equilibrium are limited only to a region of a few mean free paths near the wall surface. This thin region is called the Knudsen layer. Within the Knudsen layer, the gradients of velocity, temperature, and species concentration are so steep that these values at the edge of the Knudsen layer are significantly different from those at the boundary (wall surface). Therefore, for simulations using the continuum equations, slip models are needed to correct the non-equilibrium effects at the boundary. Different models [18-21] have been developed for velocity and temperature slips and been widely used in micro fluidics and hypersonic boundary layer problems. However, the concentration slip model has not been well established. In the following, the slip boundary condition for species concentrations from the gas kinetic theory was derived.

Figure 1 shows the schematic of the Knudsen layer. In Fig.1, variables with the subscripts "w" and "s" represent the properties on the surface of the wall and at the outer edge of the Knudsen layer, respectively. According to the slip models, if $n$ denotes the number density of the tagged molecules per unit volume, in numerical simulations based on the continuum model for the internal flow, the species number density for the tagged molecules at the boundary should be $n_s$ instead of $n_w$. Since the number density of the tagged molecules at the wall concentration is
much greater than that at the outer edge of the Knudsen layer, the number of tagged molecules
crossing the Knudsen layer via molecule collisions from the wall to the outer edge of the
Knudsen layer will exceed the number crossing the Knudsen layer in the opposite direction.

For the two-dimensional, weakly non-equilibrium gaseous flows with a zero velocity
gradient, the thermal velocity distribution functions outside the Knudsen layer and at the
boundary can be given respectively as

\[
f^- = \frac{n_s}{(2\pi kT_s / m)^{\frac{3}{2}}} \exp \left[ -\frac{(v_x - U_s)^2 + (v_y - V_s)^2 + v_z^2}{2kT_s / m} \right]
\]

\[1 + \frac{\kappa}{\rho(kT_s / m)^2} \times \left[ \frac{(v_x - U_s)^2 + (v_y - V_s)^2 + v_z^2}{5kT_s / m} \right] \times \left[ (v_x - U_s) \frac{\partial T}{\partial x} + (v_y - V_s) \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right] \}

\[
f^+ = \frac{n_w}{(2\pi kT_w / m)^{\frac{3}{2}}} \exp \left[ -\frac{(v_x - U_w)^2 + (v_y - V_w)^2 + v_z^2}{2kT_w / m} \right]
\]

\[1 + \frac{\kappa}{\rho(kT_w / m)^2} \times \left[ \frac{(v_x - U_w)^2 + (v_y - V_w)^2 + v_z^2}{5kT_w / m} \right] \times \left[ (v_x - U_w) \frac{\partial T}{\partial x} + (v_y - V_w) \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} \right] \}

The net molecule number crossing the Knudsen layer from the left to the right in the positive y-
direction per unit area and per unit time is represented by

\[
\psi = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f^+ v_y dv_y \, dv_z + \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f^- v_y dv_y \, dv_z
\]

This flux should be equal to the flux of the Stefan flow at the outer edge of the Knudsen layer,

\[
\psi = n_s V_s - D \left( \frac{\partial n}{\partial y} \right)_s
\]

where \( D = \lambda \rho / 3 \) is the diffusion coefficient.

From Eqs.3 and 4, we can obtain the following slip boundary condition for species
concentration
If the macro velocity is negligible compared with the thermal velocity, which is always true in microchannel flows, Eq. 5 reduces to

$$n_s = n_w \left( \sqrt{\frac{T_w}{T_s}} + 2n_w \frac{V_w}{\nu} + \frac{4}{3} \frac{\lambda}{\nu} \left( \frac{\partial n}{\partial y} \right)_s \right)$$

This form is similar to the slip boundary conditions of temperature and velocity. The first term on the right hand side of Eq.6 represents the molecular flux produced through molecular thermal collision and the second term denotes the correction of the molecular flux due to the concentration gradient. Therefore, the concentration slip depends both on the temperature slip and the concentration gradient on the outer edge of the Knudsen layer.

**Validation of the slip model**

In order to validate the slip boundary condition of species concentration in Eq. 6, a pure diffusion process was modeled using the DSMC method. The problem was first simplified by neglecting the convective transport and only retaining the diffusion process. As such, in the pure diffusion model, we consider the binary molecular diffusion of tagged molecules into the other molecules of the same species (so-called self-diffusion) [27], and assume uniform pressure and temperature distributions. If all the molecules of a system were exactly alike, there would be no experimental method by which one group of diffusing molecules could be distinguished from the other. However, in numerical simulations, it is possible to “tag” certain molecules so that they can be distinguished from the others and to treat the diffusion problem as if the two groups of molecules were different.
Figure 2 shows the schematic of the pure diffusion problem. The concentrations of the tagged (untagged) molecules are, respectively, maintained at 0 ($n_w = n_0$) on the boundary $A$ and $n_w$ (0) on the boundary $B$. Employing one-dimensional geometry and the isothermal approximation with the slip boundary condition, a linear distribution of the tagged molecule concentration can be obtained as

$$\frac{n}{n_w} = \left(\frac{y}{H} + \frac{4}{3} Kn\right) \left[1 + \frac{8}{3} Kn\right]$$

The DSMC method treats the tagged and untagged molecules as different kinds of molecules except that all of the properties are the same, which means that physically they are the same species.

The comparisons between the analytic solutions using the slip models and the DSMC results are shown in Figs. 3 and 4 for different Knudsen numbers ($Kn=0.01$ and $Kn=0.1$). Parameters used in the DSMC simulation are listed in Table 1. It is shown that both methods predict the existence of the concentration slip (jump) at the boundaries and that the magnitude of the concentration slip (jump) grows quickly with the increase of the Knudsen number. Figure 3 shows that the two methods agree fairly well when the Knudsen number is small. It is also seen in Fig.4 that even when the Knudsen number increases up to 0.1, the present slip model is also acceptable. However, a further increase of the Knudsen number will lead to a significant deviation between the two results, which may be because of the breakdown of the continuum assumption. Fortunately, most of the problems interested in microscale reactors fall into the range of $Kn < 0.1$.

**NUMERICAL SIMULATIONS OF CATALYTIC REACTION IN A MICRO CHANNEL**
Physical model

Here a simplified geometry was used to demonstrate how the concentration slip affects the catalytic reaction in microscale reactors. The schematic of a micro channel reactor is shown in Fig. 5. The width of the channel varies from 0.25 mm to 1 mm and the length from 1 to 5 mm. The top and bottom walls are catalytic. Since most chemical reactors involve hydrocarbon fuels, we use methane as an example fuel. The stoichiometric methane and air premixture flows into the channel at a uniform velocity. The Reynolds number is very small so that the flow is assumed to be laminar. The wall temperature of the reactor is fixed at a constant value $T_w$ because the total chemical heat release from the gas mixture is negligible compared with the thermal capacity of the wall. Fuel and air react with each other both in the gas phase and at the catalytic surface. To model the rarefied gas effect, the channel pressure is reduced to 100 Pa to increase the Knudsen number. The resulting Knudsen numbers are between 0.001 and 0.1.

Governing equations and boundary conditions

The steady-state Navier-Stokes equations, the energy equation, and the species conservation equations for the reactive internal flow are given as

$$\frac{\partial \rho U_i}{\partial x_i} = 0 \tag{8}$$

$$\rho u_j \frac{\partial U_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j} \left( \mu \frac{\partial U_i}{\partial x_j} \right) + \frac{\partial}{\partial x_j} \left( \mu' \nabla \cdot \hat{U} \right) + \frac{\partial}{\partial x_j} \left( \mu \frac{\partial U_j}{\partial x_i} \right) \tag{9}$$

$$\frac{\partial}{\partial x_i} \left( \rho c_p U_i T \right) = \frac{\partial}{\partial x_i} \left( \kappa \frac{\partial T}{\partial x_i} \right) - \sum_{k=1}^{N_s} \dot{\omega}_k h_k \tag{10}$$

$$\frac{\partial}{\partial x_i} \left( \rho U_i Y_k \right) = \frac{\partial}{\partial x_i} \left( \rho D \frac{\partial Y_k}{\partial x_i} \right) - \dot{\omega}_k \tag{11}$$
The ideal gas state equation is also included to close the problem. Since our investigation is focused on the slip effects, we only consider the one-step overall reaction mechanism in both gas phase and surface reactions and assume constant thermal properties.

In the modeling of the slip phenomena on the wall, the following three kinds of slip boundaries are considered:

(i) The velocity slip, which has been proved valid in correcting the rarefied effect, can be written as:

\[
U_s = \left(\frac{2-b}{b}\right)\lambda \left(\frac{\partial U}{\partial y}\right)_s
\]

(ii) The temperature jump can also be derived from gas dynamics theory and written as:

\[
T_s - T_w = \left(\frac{2-a}{a}\right)\left(\frac{\gamma}{\gamma+1}\right)\left(\frac{4\kappa}{\rho_s\nu_c}\right)\left(\frac{\partial T}{\partial y}\right)_s + \left(\frac{\gamma}{\gamma+1}\right)\frac{U_s^2}{c_{ps}} \left(\frac{\mu_s}{\rho_s c_p}\right)\left(\frac{\partial U}{\partial x}\right)_s
\]

(iii) The species boundary conditions on the solid surfaces depend on the reactivity as well as the transport process between the wall and the gas, which is controlled by the Knudsen number and was written in Eq.6.

By substituting \(n_k = \rho Y_k/W_k\) into Eq.6, we can get the slip boundary condition in terms of species mass fractions.

\[
\left(\rho Y_k\right)_w = \sqrt{T_s/T_w} \left[\left(\rho Y_k\right)_s - \frac{4}{3} \lambda \left(\frac{\partial (\rho Y_k)}{\partial y}\right)_s\right]
\]

The gas number density at the catalytic surface is needed in order to calculate \(Y_{k,w}\). At first sight, it seems reasonable to obtain \(\rho_w\) from the gas equation of state since the wall temperature and pressure is known. However, the gas equation of state does not apply within the Knudsen layer due to the nonequilibrium effect. Since the mass fractions of all the species add up to unity, we add up Eq.14 for all species to yield a slip boundary condition for the gas density, which is written as following
\[ \rho_w = \sqrt{\frac{T_s}{T_w}} \left[ \rho_s - \frac{4}{3} \lambda \left( \frac{\partial \rho}{\partial y} \right)_s \right] \]  

(15)

**Reaction Model**

We here emphasize the effect of slip boundary conditions on the mass transfer between the gas and the wall. As such, it is also convenient to simplify the chemistry by considering the one-step model. The time scale of the catalytic reaction can be modeled by introducing the Damköhler number. The one-step overall reaction is written as

\[ \text{CH}_4 + 2(\text{O}_2 + 4.36\text{N}_2) = \text{CO}_2 + 2\text{H}_2\text{O} + 8.72\text{N}_2 \]  

(16)

The reaction rate for the gas phase can also be written as:

\[ \dot{\omega}_g = k_g n_f n_o e^{\frac{E_g}{RT_s}} \]  

(17)

where the reaction coefficient \( k_g \) is equal to \( 1.3 \times 10^{11} \) m\(^3\)/(mol*sec), the activation energy \( E_g \) is 48.4 kcal/mole, and \( n_f \) and \( n_o \) are the mole concentrations of fuel and oxygen.

For the surface reaction, the Hougen-Watson model for methane oxidization over a palladium alumina catalyst has been developed [28, 29] and the reaction rate can be expressed as

\[ \dot{\omega}_s = \frac{k P_{\text{CH}_4}^2}{(1 + \sqrt{K_{O_2} P_{O_2} + K_{CO_2} P_{CO_2} + K_{H_2O} P_{H_2O}})^3} e^{\frac{E_s}{RT_s}} \]  

(18)

where the \( K_s \) are either interpreted as adsorption equilibrium constants for the active sites or as empirical constants with a unit in atm\(^{-1}\). Different methods such as Linear and Nonlinear Least Squares Method have been developed to determine the \( K_s \) based on the reaction rates from the experimental data at certain temperatures and pressures and the detailed reaction mechanism. It was found that the \( K_s \) are in an order of unity for many hydrocarbon catalytic reactions [28-31].
In this work, we assume the pressure is very low (0.001~0.01 \text{ atm}) so that the rarefied gas effect is significant even at mesoscales. Since the goal of this work is to study the slip effects instead of the reaction mechanism, we can simplify the problem by assuming that the product of $K$ and $P$ is much smaller than unity within the pressure range being considered. Furthermore, the reaction constant $k$ is varied and chosen in such a way that the resulting Damköhler numbers cover the whole range of time scales of the practical catalytic reactions. The denominator of Eq.18 can be evaluated with the inlet conditions and written as $A$. As such, Eq.18 reduces to

$$
\dot{\omega}_f = Ak p^2 P_{CH_4} e^{\frac{E_s}{RT}}
$$

By further normalizing the species concentration using the inlet fuel concentration, the fuel reaction rate is rewritten as the following

$$
\omega_f = A \frac{W_F (v^*_f - v^*_f)}{Y_{f,in}} \prod \left( \frac{P W}{R^0 T W_k} \sigma_{k,f} Y_{f,in} \right)^{v_k} \tilde{Y}_k^{v_i} e^{-\frac{E_s}{RT}} = -BC A \prod \tilde{Y}_k^{v_i} e^{-\frac{E_s}{RT}}
$$

where subscript $f$ represents the fuel and $in$ represents the inlet boundary; $\sigma_{k,f}$ is the stoichiometric mass ratio of species $k$ to the fuel; $W$ is the molecular weight; $v^*_k$ and $v^*'_k$ are the molar concentration coefficients of the reactants and products. By nondimensionalizing the reaction rate with $\kappa/(c_p H)$, the Damköhler number can be defined as

$$
D_a = \frac{H B c}{\kappa / c_p} A e^{\frac{E_s}{RT_{max}}}
$$

The Damköhler number defined in Eq. 21 represents the ratio of the characteristic time of diffusion to the reaction. A unity Damköhler number implies equal rates of surface reaction and fuel mass transport due to diffusion. The activation energy $E_s$ is 4.62 kcal/mole. To investigate the impact of concentration slip on the coupling between transport and the catalytic reaction in a wide range of time scales of interest, $Da$ is varied from 0.1 to 5 in this study.
At the inlet, the velocity, temperature and species concentrations are assumed to be uniform. At the outlet, zero gradient boundary conditions are employed for all the variables. In our simulations, the length of the channel is at least five times longer than the width. In typical catalytic surface reactions, the reaction temperature is usually less than 1000 K. As a result, the surface reaction dominates over the gas phase reaction due to its low activation energy. When the pressure is very low or the channel is very narrow, the wall temperature will not increase too much because the chemical heat release from the surface reaction is very small compared with the heat capacity of the wall. Therefore, the wall temperature can be assumed to be constant. At the solid-gas interface, the slip boundary concentrations for the velocity, temperature and species concentrations are applied. This is necessary as long as the Kn number is large enough ($Kn > 0.01$). For the present channel width (0.25~1 mm) and pressure (100 Pa), the Kn number range is from 0.03~0.15.

The computation domain is the upper half channel and the problem is solved with the SIMPLE method. Non-uniform 40×150 mesh grids are used and the grid width near the inlet and the wall is much smaller than that near the outlet and the center line in order to capture the steep gradients of temperature and concentration. The effect of mesh size is studied by decreasing the cell width. The mesh size is chosen in such a way that a further decrease in the cell width does not change the numerical results. In our problem, the wall temperature $T_w$ is fixed at a typical catalytic reaction temperature (700 K). In our figures, the species concentration is nondimensionalized by the inlet parameter and the length is nondimensionalized by the channel width. The N-S equations as well as the mass and species conservation equations are solved using the SIMPLE method.

**Results and discussion**
In our simulations, the inlet velocity is fixed at 0.35 m/s and the pressure is varied from 200 to 1000 Pa. The resulting Peclet number of the flow, which is a measure of the relative rates of convective to diffusive transports, varies from $5 \times 10^{-3}$ to $2 \times 10^{-2}$. At first, the velocity slip effect is numerically investigated. Our results show that although the velocity slip will significantly affect the flow field, it has very little influence on the species concentration and temperature distribution because the convective transport is much slower than the diffusive transport for small Peclet numbers. Therefore, in the following study even though all the three slip conditions (velocity, temperature, and concentration) are considered, focus will be placed on the impact of temperature and concentration slips on the rate of catalytic reaction.

Figure 6 shows the temperature contours near the inlet of the channel with and without the slip effects (velocity, temperature, and concentration) at a $Kn$ of 0.14. It is shown that the slip effects dramatically decrease the heat transfer between the gas and wall. It is clearly seen that in the slip case, because of the temperature slip, the increase of gas temperature near the wall becomes much slower (Fig. 6b) than in the non-slip case (Fig. 6a). Note that in order to isolate the slip effects on the catalytic reaction from the effect of wall heat transfer, in our simulation, the temperature of the catalytic surface is fixed at 700 K. Therefore, the temperature jump will not affect the surface reaction rate through the Arrhenius law. However, in the case when the wall temperature is not fixed and the thermal diffusivity and thermal inertia of the wall are small, this temperature jump will lead to a very large departure of the reaction rate from the non-slip model.

In order to understand the impact of temperature and species concentration slips on the surface reaction rates, numerical simulations are conducted at various inlet gas temperatures. Figures 7, 8 and 9 show the distributions of the surface reaction rates along the channel, respectively, at three typical gas inlet temperatures (300 K, 600 K, and 1000 K). The dash-dot lines represent the results without any slip effects; the dotted lines are the results with only
temperature slip; and the solid lines are those with both temperature and species concentration slip. It is seen that in all three cases the slip effect causes a decrease in reaction rates along the flow direction. Moreover, the reductions of the reaction rate and the effect of temperature slip on the reaction rate are strongly dependent on the initial gas temperature.

For inlet gas temperatures of 300 K and 600 K, which are below the wall temperature, Figs. 7 and 8 show that the temperature slip model yields a higher reaction rate than the non-slip model. This is because the temperature slip slows down the increase of the gas temperature near the wall and thus increases the diffusion flux of the reactants to the catalytic surface via the increase of molecular number density.

On the other hand, when the inlet gas temperature is higher than the wall temperature, Fig. 9 shows that the temperature slip model yields a decrease of the reaction rate compared to Figs 7 and 8. This is because the temperature slip slows down the cool down of the gas mixture near the wall and thus reduces the diffusion flux of reactant to the catalytic surface due to the decrease of the molecular number density. Therefore, it can be concluded that the temperature slip effect on catalytic reaction is highly dependent on the temperature difference between the mixture and wall temperature.

However, it is interesting to note that when both the temperature and concentration slips are considered, independent of the temperature difference between the wall and the mixture, the predicted reaction rate is always smaller than that predicted by the non-slip model. This is because the concentration slip always tends to decrease the number densities of the reactants on the catalytic wall (see Eq.6) and the role of temperature slip is only to modify the magnitude of the concentration slip effect. Therefore, it should be pointed out that numerical simulations with only temperature slip effect may lead to misleading conclusions in the rarefied gas effect on catalytic reactions in micro chemical reactors. Furthermore, at a low gas temperature (300 K), Fig.
7 shows that there exists a non-monotonic reaction rate distribution near the channel entrance. This non-monotonic phenomenon is not predicted by the temperature slip model. It is a direct result of the competition between the diffusion transport and the reaction consumption of the reaction. A detailed explanation will be given later in the discussion of the Damköhler number effect.

The Knudsen number effect on the species number density slip is shown in Fig. 10. It is seen that the mole concentration slip increases with the increase of Knudsen number. At $Kn$ number of 0.1, it is seen that the mole concentration slip is very significant (up to 50%) near the entrance of the channel where the surface reaction rate is very large. As the reaction proceeds, the reactants are consumed and their concentrations decrease. As a result, the reaction rate decreases significantly due to the depletion of the reactants and the diffusion rate becomes faster when compared to the reaction rate. The diffusion renders more uniform concentration profiles and the concentration slip dramatically decreases along the channel.

Figure 11 shows the slip effect on the surface reaction rate at different Damköhler numbers. The results show that the slip effect becomes increasingly significant when Damköhler number is larger than unity. As is shown in Eq.15, the magnitude of the slip effect is proportional to the gradients of species concentrations and temperature. When the Damköhler number is large, the reaction process is diffusion controlled and a faster surface reaction will cause a larger concentration gradient and thus a larger slip effect. On the other hand, if the Damköhler number is small, the problem becomes reaction controlled. As a result, the relatively faster diffusion process yields a more uniform distribution of temperature and species near the reaction surface. Therefore, the slip effect becomes smaller at small Damköhler numbers. In practical applications, depending on the reactors working condition, the system Damköhler number can be either greater or less than unity.
Since the Damköhler number is a measure of the reaction rate, the surface reaction rate will continue to increase if we increase the Damköhler number. As the Damköhler number is increased from 0.1 to 5, Fig. 11 shows that both the slip model and the non-slip model show a monotonic increase of the reaction rates. However, if we further increase the Damköhler number to 10, the reaction rate will be dominated by diffusion transport. Fig.11 shows that a non-monotonic distribution of the reaction rate appears near the entrance of the reaction channel. This phenomenon is similar to the monotonic reaction rate distribution in Fig. 7. Therefore, the non-monotonic reaction rate distributions shown in Fig. 7 is actually caused by the competition between chemical reaction and species diffusion represented by the Damköhler number. A large Damköhler number yields a non-monotonic distribution and a small Damköhler number leads to a monotonic distribution. It is clearly shown that, for the inlet gas temperature of 1000 K, a monotonic distribution of the surface reaction rate in Fig. 9 will shift to a non-monotonic distribution in Fig. 12 only by increasing the Damköhler number from 2 to 3.

Figure 12 shows the reaction rate distribution similar to Fig.9 by only increasing the Damköhler number from 2 to 3. It is seen that the reaction process can be divided into three regimes. Regime I (A-B) shows a rapid drop of the reaction rate; in regime II (B-C), the reaction rate increases slowly while in regime III (C-D) it continues to decrease slowly. The nondimensional oxygen mole concentration profiles at different locations are shown in Fig. 13. Fig. 13a corresponds to location A on the distribution of the surface reaction rate in Fig. 12. The solid lines are the results without any slip effects and dashed ones are the results of slip effects. It is seen that the slip effects can dramatically change the species distribution. Even though the gas phase concentration with slip effect is higher than that without slip effect, the concentration at the wall is lower when slip effect is considered. This is caused by the slip of the concentration at the surface. This result also explains why the surface reaction rate is lower even when the gas phase
molar concentrations of the reactants are higher in the slip case. At the inlet of the channel, the species concentrations are very uniform and there is no concentration slip caused by the concentration gradients. The number densities of the reactants at the wall are large and the reaction is faster than the diffusion. The fast reaction quickly depletes the reactants near the wall but the reactant concentrations far away from the wall remain almost unchanged. Thus, the concentration gradients build up near the wall (Fig. 13a). As a result, the number densities of the reactants decrease quickly due to the concentration slip until point B (Fig. 13b). At location B, both the reaction rate and the number densities of the reactants reach their minimum and the diffusion reaches its maximum due to the large gradients of the species. Now the diffusion is faster than the reaction. This means that the local Damköhler number becomes small. The diffusion can now bring more reactants to the wall than the reaction can consume, causing a slow increase of the number densities of the reactants. At the same time, the surface reaction rate increases and the gradients of the species as well as the diffusion decrease until at location C (Fig. 13c) where the surface reaction rate stops increasing. After location C, the decrease of the concentration slip will not increase the number densities at the wall because the overall species concentration in the reactor is decreasing due to the reaction.

In the non-slip case, the concentration profiles are quite different from those of the slip case. In Fig. 13a, the oxygen number density is increasing towards the wall. This is actually caused by the cooling effect of the wall. The cooling effect tends to increase the number density while the reaction intends to decrease it. In the non-slip case, the temperature gradient is much larger near the inlet of the channel than in the slip case, which is shown in Fig. 6. Therefore, initially the cooling effect of the wall dominates in the non-slip case. After location B (Fig. 13b), the surface reaction dominates and the oxygen number density begins to decrease towards the wall. At location D (Fig. 13d), we can see that the overall concentration in the slip case is higher than that
in the non-slip case, which is a direct result of the decreased reaction rate due to the slip effects.

CONCLUSIONS

A slip model for species concentration was developed to consider the rarefied gas effect at the boundary in microscale reactors and nanoscale structures. The model showed that slip effect was proportional to the Knudsen number. The comparison with DSMC results showed that the present slip model could offer reasonable prediction of the slip effect within the range of the slip regime ($Kn$ between 0.1 and 0.01). Numerical simulations of the two-dimensional micro channel catalytic surface reactor showed that the species concentration slip reduced the species transport between the wall and the gas, and thus dramatically decreases the surface reaction rate. This reduction became more profound at large Knudsen numbers. The results also demonstrated that the impact of slip effects on catalytic reaction strongly depended on the Damköhler number of the reaction system, in particular at large Damköhler numbers. Moreover, a non-monotonic distribution of the reaction rate at large Damköhler numbers was found. Furthermore, the results showed that the net effect of temperature slip on catalytic reaction depended on the temperature difference between the wall and the gas mixture. An accurate prediction of the rarefied gas effect on catalytic reaction in microscale reactors needs to consider temperature slip together with concentration slip. Detailed catalytic reaction mechanisms need to be emphasized in future studies.

ACKNOWLEDGEMENT

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REFERENCE


Figure Captions

Table 1: Parameters used in DSMC simulations.
Fig. 1 Concentration profile within the Knudsen layer
Fig. 2 Schematic of the pure diffusion problem
Fig. 3 Species concentration profiles for $Kn=0.01$
Fig. 4 Species concentration profiles for $Kn=0.1$
Fig. 5 Schematic of the micro channel reactor
Fig. 6 (a) Temperature contours without slip effects ($Kn=0.14$)
Fig. 6 (b) Temperature contours with slip effects ($Kn=0.14$)
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Fig. 8 Surface reaction rate along the channel ($T_{in}=600K$, $Da=5$, $Kn=0.1$)
Fig. 9 Surface reaction rate along the channel ($T_{in}=1000K$, $Da=2$, $Kn=0.1$)
Fig. 10 Mole concentration slip of oxygen along the channel at $Da=5$, $T_{in}=600K$
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Fig. 12 Surface reaction rate along the channel ($T_{in}=1000K$, $Da=3$, $Kn=0.1$)
Fig. 13 Distributions of oxygen mole concentration at different positions at $Kn=0.1$, $Da=3$, $T_{in}=1000K$
### Table 1: Parameters used in DSMC simulations

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Boundary Knudsen Layer

Fig. 1
Fig. 3
Fig. 4

- DSMC
- Slip Model

Graph showing the ratio of density $n/n_0$ versus $y^*$.
$U_e, T_e, P_0$
$CO_2+N_2+H_2O$

Fig. 5
Fig. 6
\( T_{in} = 300K \)
\( Da = 5 \)

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**Fig. 7**
\( \omega_s \)

Fig. 8

- No slip
- Temperature slip
- Temperature and species slip

\( T_{in} = 600K \)

\( Da = 5 \)
Fig. 9

- No slip
- Temperature slip
- Temperature and species slip

$T_{in} = 1000K$

$Da = 2$
what does it mean? $Da=?$, $T=?$, title

Fig. 10
Fig. 11
Fig. 12  (ABCD too small, ws dot, title)
Fig. 13 (line is too thin, letters are too small)