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# Role of the Knudsen Layer in Determining Surface Reaction Rates Based on Sticking Coefficients

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Recent studies on catalytic micro-combustors and LPCVD (Low-pressure Chemical Vapor Deposition) have shown the necessity to include effects of the Knudsen layer on surface reactions. In the present work, a weakly rarefied flow of a binary gas mixture with surface reactions was analyzed by using Hamel's model of the Boltzmann equation and Nocilla's model of molecule-wall interaction. Particular interest was placed on the interaction between the Knudsen layer and surface reactions. The theoretical results show that the Knudsen layer modifies the incident flux of the molecules striking the surface and consequently the surface reaction rate, while the surface reactions in turn modify the flow structure in the Knudsen layer through the non-zero net flux at the surface. A general rate expression for a one-step surface reaction based on the sticking coefficient was obtained and can be readily extended to more complex surface reaction mechanisms. The assumptions underlying the widely-used Motz-Wise correction formula for surface reaction rate are discussed.

## **1. Introduction**

Recent studies [1-3] on catalytic micro-combustors and LPCVD (Low-pressure Chemical Vapor Deposition) have shown that, as the characteristic length, which is the minimum diameter of the micro-combustor or the boundary layer thickness of the flow in LPCVD reactors, becomes comparable to the mean free path of the molecules, it is necessary to include the effects of gas rarefaction on the flow fields and surface reactions. The magnitude of the influence is determined by the degree of the rarefaction which is characterized by the Knudsen number,  $Kn$ , defined as the ratio of the mean free path to the characteristic length. In the present study, we consider the situation of small  $Kn$ , i.e. weakly rarefied flows, which is typical of the flow regime in the above applications. In general, for a weakly rarefied flow, almost the entire flow field can be described by hydrodynamic equations except a thin Knudsen layer immediately close to the wall (e.g. catalytic walls or CVD substrates) [4]. Despite its small thickness, which is of the order of the mean free path, the Knudsen layer plays an important role in determining the surface reaction rates. The reason is that, in many hydrodynamic problems in the presence of surface reactions, the reaction rates are determined based on the assumption that the gas molecules striking the wall have a Maxwellian distribution. However, the Knudsen layer causes deviation of the distribution from the equilibrium Maxwellian distribution [5, 6]. Therefore, the non-Maxwellian distribution of gas molecules at the wall should be taken into account. The present paper aims to derive a correction expression for surface reaction rates by considering the effects of the Knudsen layer. We start with a weakly rarefied flow of a binary gas mixture with surface reactions. The non-Maxwellian distribution function of the gas molecules in the Knudsen layer is obtained by solving the Boltzmann equation. The surface reaction rates are expressed by using the sticking coefficient

which accounts for the probability that a collision between the molecules and the wall results in a reaction. A general rate expression for a one-step surface reaction based on the sticking coefficient is subsequently derived. The assumptions underlying the widely used Motz-Wise correction formula for surface reaction rate are discussed.

## 2. Formulation

We consider the boundary value problem of a steady, planar, rarefied flow of a binary gas mixture in the Knudsen layer, in the absence of external forces. A coordinate system is so established that the flow only depends on the coordinates  $x$  and  $y$  which are respectively parallel and normal to the wall. A model Boltzmann equation [7] for this problem can be written as

$$\xi_{ix} \frac{\partial f_i}{\partial x} + \xi_{iy} \frac{\partial f_i}{\partial y} = A_{ii} n_i (f_{ii}^M - f_i) + A_{ij} n_j (f_{ij}^M - f_i) \quad (1)$$

$$f_{ii}^M = n_i \left( \frac{m_i}{2\pi k T_i} \right)^{3/2} \exp \left[ -\frac{m_i}{2k T_i} (\xi_i - \mathbf{U}_i)^2 \right], f_{ij}^M = n_j \left( \frac{m_j}{2\pi k T_j} \right)^{3/2} \exp \left[ -\frac{m_j}{2k T_j} (\xi_j - \mathbf{U}_j)^2 \right] \quad (2)$$

Here,  $f_i$  ( $i, j = 1, 2$ ) is the distribution function of the  $i$ -th component of the gas mixture.  $f_{ii}^M$  and  $f_{ij}^M$  ( $i \neq j$ ) are local Maxwellian distribution functions in which all of the macroscopic hydrodynamic quantities have spatial dependence.  $k$  is the Boltzmann constant.  $m_i$ ,  $\xi_i$ ,  $n_i$ ,  $\mathbf{U}_i$  and  $T_i$  are respectively the mass of a molecule, the molecular velocity, the number density, the mean velocity and the temperature of the  $i$ -th component of the gas mixture. They are defined by  $n_i = \int f_i d\xi_i$ ,  $\mathbf{U}_i = n_i^{-1} \int \xi_i f_i d\xi_i$  and  $T_i = (3kn_i)^{-1} \int m_i (\xi_i - \mathbf{U}_i)^2 f_i d\xi_i$ .  $T_{ij}$  and  $\mathbf{U}_{ij}$  are given by  $T_{ij} = T_i + 2\mu_i \mu_j (T_j - T_i) + m \mu_i \mu_j^2 (\mathbf{U}_j - \mathbf{U}_i)^2$  and  $\mathbf{U}_{ij} = \mu_i \mathbf{U}_i + \mu_j \mathbf{U}_j$ , where  $\mu_i = m_i / m$  ( $i = 1, 2$ ) and  $m = m_i + m_j$ .  $A_{ii}$  and  $A_{ij}$  are constants characterizing the cross sections of molecular collision.

Outside the Knudsen layer, we assume a series solution of the model equation (1) by using the Chapman-Enskog theory [8]. The solution with an  $O(\varepsilon^2)$  accuracy ( $\varepsilon = Kn$  is a perturbation parameter in the present problem) is given by [9]

$$f_i^{(o)} = f_{i0}^{(o)} + f_{i1}^{(o)} \quad (3)$$

$$f_{i0}^{(o)} = n_i^{(o)} \left( \frac{m_i}{2\pi k T^{(o)}} \right)^{3/2} \exp \left[ -\frac{m_i}{2k T^{(o)}} (\mathbf{c}_i^{(o)})^2 \right] \quad (4)$$

$$f_{i1}^{(o)} = -\frac{f_{i0}^{(o)}}{R_i^{(o)}} \left\{ \begin{aligned} & \frac{mn^{(o)} R_i^{(o)}}{\rho^{(o)} n_i^{(o)} A_{12}} \mathbf{c}_i^{(o)} \cdot \mathbf{d}_i^{(o)} + \frac{m}{k T^{(o)}} \left[ c_{il}^{(o)} c_{ir}^{(o)} - \frac{1}{3} \delta_{lr} (\mathbf{c}_i^{(o)})^2 \right] \frac{\partial U_l^{(o)}}{\partial x_r} \\ & + \left[ \frac{m_i}{2k T^{(o)}} (\mathbf{c}_i^{(o)})^2 - \frac{5}{2} \right] c_{ir}^{(o)} \frac{\partial \ln T_l^{(o)}}{\partial x_r} \end{aligned} \right\}$$

Here we use the superscript  $o$  to indicate the solution and the hydrodynamic quantities appearing in it. All the symbols in (3) and (4) are the conventional ones. Inside the Knudsen layer, we can look for a solution of (1) in the form [4]

$$f_i^{(i)} = n_i^{(o)}(x, 0) \left( \frac{m_i}{2\pi k T^{(o)}(x, 0)} \right)^{3/2} \exp \left[ -\frac{m_i \xi_i^2}{2k T^{(o)}(x, 0)} \right] (1 + \varphi_i), \varphi_i = O(\varepsilon) \quad (5)$$

and

$$\begin{aligned} n_i^{(i)}(x, y) &= n_i^{(o)}(x, 0)[1 + v_i(x, y)], v_i = O(\varepsilon) \\ T_i^{(i)}(x, y) &= T_i^{(o)}(x, 0)[1 + \tau_i(x, y)], \tau_i = O(\varepsilon) \end{aligned} \quad (6)$$

Here we use the superscript  $i$  to indicate the solution in the Knudsen layer.  $v_i$  and  $\tau_i$  are respectively the perturbation to the number density and the temperature. Substituting (5) and (6) into (1), we can obtain a linearized equation for the perturbation distribution function  $\varphi_i$ .

Two kinetic boundary conditions are needed to solve the linearized Boltzmann equation of  $\varphi_i$ . One is specified at the wall (the inner boundary of the Knudsen layer) and is obtained by applying the Nocilla's model [11, 12] for the interaction between molecules and wall. The other one is specified at the outer boundary of the Knudsen layer and is obtained by asymptotically matching the outer (3) and the inner (5) solutions in the inner coordinates.

### 3. Surface Reaction Rates Based on Sticking Coefficients

We consider a simple one-step irreversible surface reaction



where  $M_i$  denotes the  $i$ -th component of the gas mixture, and  $g$  and  $s$  respectively denotes gas phase and surface phase. Based on the sticking coefficient formulation, the surface reaction rate of (7) is defined as [5, 6 and 12]

$$Rc_i = \kappa J_i^{(-)} = -\kappa \int_{\xi_i \cdot \mathbf{n} < 0} f_i(\xi_i \cdot \mathbf{n}) d\xi_i \quad (8)$$

where  $\kappa$  is the sticking coefficient and  $J_i^{(-)}$  is the number flux of the incident molecules of the  $i$ -th kind. In previous studies, the incident molecules are assumed to be in equilibrium with the surface and have the Maxwellian distribution. So, the surface reaction rate is given by

$$Rc_i = \kappa J_w^{(-)} = \kappa n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}} = \frac{1}{4} \kappa n_{iw} \bar{c}_i \quad (9)$$

where  $T_w$  is the wall temperature;  $n_{iw}$  and  $\bar{c}_i$  are respectively the number density and mean molecular velocity of the  $i$ -th kind molecule at the wall. Since the distribution of incident molecules is non-Maxwellian due to the existence of the Knudsen layer, a correction expression for the surface reaction rate can be obtained by using the solution of the Boltzmann equation (1) in the Knudsen layer, and is given by

$$Rc_i = \frac{\kappa}{1 - \kappa \left[ \frac{3 - \alpha_n}{2} - \frac{0.82}{\sqrt{\pi}} \alpha_n \right]} J_{i0} \left[ 1 - 1.25 \lambda \left( \frac{\partial \ln T^{(o)}}{\partial y} \right)_{y=0} \right] \quad (10)$$

where

$$J_{i0} = n_i^{(o)}(x, 0) \sqrt{kT^{(o)}(x, 0) / 2\pi m_i} = \frac{1}{4} n_i^{(o)}(x, 0) \bar{c}_i^{(o)}(x, 0) \quad (11)$$

and  $\alpha_n$  is the normal momentum accommodation coefficient appearing in Nocilla's model [10, 11].  $\lambda$  is the mean free path. The correction expression shows that the reaction rate depends not only on the number density and temperature of the molecules at the wall, but also on the temperature gradient at the wall as well as other parameters characterizing the Knudsen layer. Furthermore, we found that, even by neglecting the temperature gradient and assuming specular reflection of the molecules ( $\alpha_n = 0$ ) in (10), the widely-used Motz-Wise correction formula for the surface reaction rate [12-14]:

$$Rc_i = \frac{\kappa}{1 - \kappa/2} J_{i0} \quad (12)$$

is still not recovered. To explain the difference, we note that (12) was derived with the use of Meyer's theory on diffusion [14], for which the distribution functions of the incident molecules and reflected molecules are assumed to be locally Maxwellian with a macroscopic velocity at every point, and are given by

$$f = n_i \left( \frac{m_i}{2\pi kT} \right)^{3/2} \exp \left\{ -\frac{m_i}{2kT} [u^2 + v^2 + (w - w_0)^2] \right\} \quad (13)$$

It is, however, not correct to express the distribution of reflected molecules by (13) even though it is locally Maxwellian. The reason is that the normal component of the macroscopic velocity of the reflected molecules from the surface is not equal to that of the incident molecules towards the surface. For a specular reflection, the magnitude of the normal velocity is the same, but the sign changes. As such, while expression (13) is valid at any point in the flow region outside the Knudsen layer, it fails to hold at the wall, at which the kinetic boundary condition must be applied to obtain the correct expression for the reflected flux.

Although (10) is only applicable for binary mixtures with the surface reaction mechanism (7), it is readily extended to more complex surface reaction mechanisms for which the multicomponent mixture has a major chemically inert species so that the other chemically active species exist in dilute concentrations. The resulting correction formula for the surface reaction rate can be applied in numerical simulation codes and be solved simultaneously with flow fields.

## References

- [1] Xu, B. & Ju, Y. 2005 Concentration slip and its impact on heterogeneous combustion in a micro-scale chemical reactor. *Chem. Eng. Sci.* **60**, 3561—3572.
- [2] Hu, T. and Glumac, N. 2002 The Effects of Temperature Jump on CVD Modeling. *Chemical Vap. Deposition.* **8**, No. 5. p. 205.
- [3] Sakiyama, Y., Takagi, S. & Matsumoto, Y. 2001 Full simulation of silicon chemical vapor deposition process. *Rarefied Gas Dynamics: 22nd International Symposium*, edited by T. J. Bartel and M. A. Gallis.
- [4] Kogan, M. N. 1969 *Rarefied Gas Dynamics*. Plenum Press.
- [5] Kogan, M. N. & Makashev, N. K. 1971 Role of the Knudsen layer in the theory of heterogeneous reactions and in flows with surface reactions. *Fluid Dynamics* **6**, 913—920.
- [6] Kogan, M. N. & Makashev, N. K. 1972 Boundary conditions for flows with chemical reaction occurring on a surface. *Fluid Dynamics* **7**, 116—125.
- [7] Hamel, B. B. 1965 Kinetic model for binary gas mixtures. *Phys. Fluids* **8**, 418—425.
- [8] Chapman, S. & Cowling, T. G. 1970 *The Mathematical Theory of Non-Uniform Gases*. 3rd Edn. Cambridge University Press.
- [9] Zharov, V. A. 1972 Determination of the slippage rate for a binary mixture of gases. *Fluid Dynamics* **7**, 274—279.
- [10] Nocilla, S. 1961 On the interaction between stream and body in free-molecule flow. In *Rarefied Gas Dynamics: 2nd International Symposium* (ed. L. Talbot). 169-207.
- [11] Nocilla, S. 1963 The surface re-emission law in free molecule flow. In *Rarefied Gas Dynamics: 3rd International Symposium* (ed. J. A. Laurmann). 327-346.
- [12] Kee, R. J., Coltrin, M. E. & Glarborg, P. 2003 *Chemically Reacting Flow: Theory and Practice*. Wiley.
- [13] Motz, H. & Wise, H. 1960 Diffusion and heterogeneous reaction. III. Atom recombination at a catalytic boundary. *J. Chem. Phys.* **32**, 1893—1894.
- [14] Jeans, J. H. 1925 *The Dynamical Theory of Gases*. Cambridge University Press.