J. Fluid Mech. (2009), *vol.* 634, *pp.* 113–135. © 2009 Cambridge University Press
doi:10.1017/S0022112009007794 Printed in the United Kingdom

Role of the Knudsen layer in determining surface reaction rates based on sticking coefficients

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(Received 4 December 2008 and in revised form 26 April 2009)

A theory on weakly rarefied low-Mach-number flows with surface reactions based on small sticking coefficients was formulated for a binary gas mixture with an irreversible surface reaction, and then extended to a multicomponent mixture with multi-step surface reactions for the situation when all chemically active species are small in concentration compared to a major inert species. Particular interest was placed on the interaction between the Knudsen layer and the surface reactions. Results show that the Knudsen layer modifies not only the incident flux of the molecules striking the surface but also the temperature-sensitive sticking coefficients, and consequently the surface reaction rates. The surface reactions in turn modify the flow structure in the Knudsen layer through the non-zero net flux at the surface. The rate expressions for the surface reactions based on sticking coefficients were derived, and the slip boundary conditions for the temperature and the species concentration suitable for application were established. The widely used Motz–Wise correction formula for the surface reaction rate was revised and the underlying assumptions leading to its derivation were shown to be inappropriate.

1. Introduction

Recent interests in materials synthesis and small-scale phenomena have rekindled research in slow rarefied flows (Cercignani 2005). For example, in flow processes involving low-pressure chemical vapour deposition (LPCVD), in which gas-phase materials are deposited on solid-phase substrates through surface reactions, the characteristic dimension of the flows could become comparable to the mean free path of the gas. As a consequence, the Knudsen number Kn, which measures the (inverse) ratio of these two dimensions, could be in the range of $10^{-3} < Kn < 10^{-1}$ in prevalent operational conditions, and as such renders the flows to be weakly rarefied. Consequently, it is necessary to include effects of gas rarefaction on the flow field as well as the surface reactions in the description of the flow and its control.

The study of rarefied flows generally requires kinetic description in terms of the distribution function of gas molecules and the Boltzmann equation which describes the evolution of the distribution function in space and time (Chapman & Cowling 1970; Cercignani 1975). For a weakly rarefied flow bounded by a surface, the flow is continuous except for the thin Knudsen layer next to the surface within which collision between the molecules is less frequent than that between the molecules and the surface. This causes the velocity distribution of the molecules in the Knudsen layer to be generally non-Maxwellian. In order to account for effects of the Knudsen

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layer, studies of weakly rarefied flows are conventionally based on the framework of continuum mechanics, but with appropriate boundary conditions, namely slip boundary conditions, applied at the surface. Consequently, identification of these boundary conditions is frequently the primary task in such studies, and has been extensively performed for non-reactive flows composed of simple gases (Albertoni, Cercignani & Gotusso 1963; Loyalka & Ferziger 1967, 1968; Siewert & Sharipov 2002) and gas mixtures (Ivchenko & Yalamov 1971; Loyalka 1971; Zharov 1972; Shen 1983; Ivchenko, Loyalka & Tompson 2007).

The presence of surface reactions further complicates the description of the weakly rarefied flows due to the intrinsic interaction between the Knudsen layer and the surface reactions. Specifically, the surface reactions affect the structure of the Knudsen layer through a non-trivial net mass flux at the surface, which in turn affects the slip boundary conditions. Conversely, the nature of the Knudsen layer also influences the surface reaction rates in that, while continuum description implies Maxwellian distribution of the gas molecules and thermal equilibrium between the surface and the gas molecules striking it, the surface reaction rates are fundamentally affected by the non-Maxwellian distribution of the molecules.

Studies of the interaction between the Knudsen layer and surface reactions usually rely on the specific surface reaction adopted. As a notable example of such studies, the evaporation and condensation occurring between a liquid surface and its vapour (or vapour–gas mixture) have been extensively studied as a special class of surface reactions (Pao 1971*a*,*b*; Sone 2006). Another important situation, investigated by Kogan & Makashev (1972), is that of a binary gas mixture undergoing the surface reaction $l_A A(s) \rightleftharpoons l_B B(s)$, in which $A(s)$ and $B(s)$ are adsorbates, and l_A and l_B the respective stoichiometric coefficients. This reaction is of fundamental interest as it simulates the rate-controlling reaction in Langmuir–Hinshelwood surface reaction kinetics (Kee, Coltrin & Glarborg 2003), in which the adsorbates are assumed to be in equilibrium with the corresponding gas molecules such that the reactions between the adsorbates are assumed to be relatively slow and rate controlling.

The present study considers another important situation, in which the surface reactions are described via the so called sticking coefficient (also known as the sticking probability), which is defined based on the facts that collisions between molecules and the surface are needed to initialize surface reactions, and that not all of the collisions result in reaction. Consequently, the sticking coefficient is the probability of a gas-surface collision resulting in a reaction such that the surface reaction rate can be expressed as the number flux of the molecules hitting on the surface times the sticking coefficient. Due to its simple and clear physical definition, the sticking coefficient formalism is widely used in practice to describe many elementary or semi-empirical surface reactions as long as they involve only one gaseous reactant (Kee *et al.* 2003).

In view of the above considerations, the present study aims to obtain reaction rate expressions for multicomponent gas mixtures with surface reactions based on sticking coefficients, and establish relevant slip boundary conditions. In the next section, we shall present further theoretical considerations of the problem, and consequently identify the appropriate theoretical approach and important factors for a satisfactory characterization of the problem. Mathematical formulation will then be given in succeeding sections, which are followed by the derivation of analytical results and their comparison with previous theoretical results.

2. Theoretical considerations

To identify the theoretical approach to the present problem, we first note that analyses have been conducted without actually solving the Boltzmann equation in the Knudsen layer (Scott 1973; Gupta, Scott & Moss 1985; Xu & Ju 2006). While these efforts are comparatively simple in the analysis, the formulations contain two conceptual difficulties as pointed out by Kogan (1969): the actual flow in the Knudsen layer is distorted by neglecting the variation of the distribution function across it, and the formulation becomes overspecified by introducing the slip boundary condition for pressure. Furthermore, we recognize that the solution of the Boltzmann equation in the Knudsen layer is crucial to the correct determination of the surface reaction rate because of the non-Maxwellian characteristics of the molecules incident on the surface. Consequently, a conceptually rigorous approach (Kogan & Makashev 1972) is adopted in the present study. Specifically, the Boltzmann equation is solved in the Knudsen layer and its solution is then asymptotically matched to the Chapman–Enskog solution (Chapman & Cowling 1970; Kogan 1969) external to it in order to determine the slip boundary conditions and the physical quantities in the Knudsen layer.

We next recognize that the solution of the Boltzmann equation in the Knudsen layer strongly depends on the specification of the kinetic boundary conditions that describe the interaction law between the molecules and the surface. The interaction law is usually expressed as the relation between the distribution functions of the incident and the reflected molecules. Among the various kinetic boundary conditions, the most widely used one is the non-drift Maxwellian distribution function (Kogan 1969), obtained by assuming that the molecules striking the surface reach thermal equilibrium with the surface and then are randomly emitted from it with no macroscopic velocity. The absence of a macroscopic velocity obviously underestimates the number flux of the reflected molecules and consequently affects the surface reaction rate, which can be also defined as the difference between the number flux of the molecules incident on the surface and that of the molecules reflected from it. The kinetic boundary condition was improved by Nocilla (1963) by introducing certain macroscopic velocity and temperature that are different from those of the surface in order to reconcile his experimental results (Nocilla 1961). In the present study, we shall therefore adopt Nocilla's kinetic boundary condition because it offers a more realistic description of the gas-surface interaction without substantially increasing the mathematical difficulty. It is also noted that a physically significant kinetic boundary condition model was proposed by Cercignani & Lampis (1971), although its application to the present problem is too challenging in mathematics.

Another important factor in the formulation is the modelling of the collision integrals in the Boltzmann equation for multicomponent mixtures. From the mathematical viewpoint, this is the main difficulty in solving the Boltzmann equation. The most widely used model for the collision integral of simple gases is the BGK model proposed by Welander (1954) and Bhatnagar, Gross & Krook (1954). Subsequently, various models were proposed for binary (Sirovich 1962; Hamel 1965; Boley & Yip 1972) and multicomponent mixtures (Garzó, Santos & Brey 1989; Andries, Aoki & Perthame 2002). For the present formulation we recognize that in many practical situations, such as those involving air as the oxidizer, a multicomponent mixture consists of a concentrationally dominant inert, with the chemically active species existing in dilute concentrations. The kinetics of such a mixture can therefore be approximated as one in which each chemically active species forms a binary mixture with the inert species and the behaviour of the binary mixture can be analysed independently of other binary systems. The total flux at the surface is then the sum of the fluxes of the binary mixtures.

In summary, it is recognized that directly solving the Boltzmann equation in the Knudsen layer with appropriate collision model and kinetic boundary condition is necessary to obtain the correct slip boundary conditions and surface reaction rates. As such, we shall first start with a binary mixture which constitutes the theoretical base for a multicomponent mixture. Following the approach of Kogan & Makashev (1972) and using Nocilla's model (Nocilla 1965) for the kinetic boundary condition, we shall derive a set of analytical solutions for velocity, temperature and species concentration, with constants to be determined from the surface reaction rates in § 3. The general expression of the surface reaction rate based on the sticking coefficient is then given and compared with previous theoretical results, in § 4. The slip boundary conditions for temperature and concentration, which are suitable for application, are given in § 5. The results based on binary mixtures are then extended to multicomponent mixtures, in § 6.

3. Solution of the Boltzmann equation in the Knudsen layer

Asymptotic analysis of weakly rarefied, low Mach number flows is well established by using the linearized Boltzmann equation and the linearized collision integral for simple gases (Kogan 1969; Cercignani 2005) and binary gas mixtures (Ivchenko & Yalamov 1971; Zharov 1972). It is also recognized that (Kogan & Makashev 1972) the asymptotic scheme is applicable to the situation when surface reactions are present, as long as the reaction rates are small so that the attendant net flux at the surface does not substantially affect the structure of the Knudsen layer. As a consequence, the present analysis can be unified with that of Kogan & Makashev (1972), albeit with the different surface reaction mechanism and the kinetic boundary condition at the surface.

3.1. *The Boltzmann equation for binary mixtures*

We consider the weakly rarefied flow of a binary mixture bounded by a solid surface. A coordinate system is so established that the steady planar flow only depends on the coordinates x and y which are parallel and normal to the surface, respectively. The Boltzmann equation in the absence of external force and with the Hamel's model (Hamel 1965) describing the collision integral is given by

$$\xi_{ix}\frac{\partial f_i}{\partial x}+\xi_{iy}\frac{\partial f_i}{\partial y}=A_{ii}n_i\left(f_{ii}^{\mathrm{M}}-f_i\right)+A_{ij}n_j\left(f_{ij}^{\mathrm{M}}-f_i\right), \tag{3.1}$$

where $i, j=1, 2$ and $i\neq j$ (similarly hereinafter), $f_i=f_i(x, y, \boldsymbol{\xi}_i)$ is the distribution function of the ith species of the binary mixture and f_{ii}^{M} and f_{ij}^{M} are the local Maxwellian distribution functions defined as

$$f_{ii}^{\mathrm{M}}=n_i\left(m_i/2\pi kT_i\right)^{3/2}\exp[-m_i(\boldsymbol{\xi}_i-\boldsymbol{U}_i)^2/2kT_i], \tag{3.2}$$

$$f_{ij}^{\mathrm{M}}=n_i(m_i/2\pi kT_{ij})^{3/2}\exp[-m_i(\boldsymbol{\xi}_i-\boldsymbol{U}_{ij})^2/2kT_{ij}], \tag{3.3}$$

in which k is the Boltzmann constant and all of the macroscopic hydrodynamic quantities, such as n_i, T_i, T_{ij}, $\boldsymbol{U}_i$ and $\boldsymbol{U}_{ij}$ are spatially dependent. m_i and $\boldsymbol{\xi}_i$ are respectively the mass and velocity of the ith molecule. n_i, U_i and T_i are respectively the number density, the mean velocity and the temperature of the ith species, defined as

$$n_i = \int f_i \, \mathrm{d}\boldsymbol{\xi}_i, \; \boldsymbol{U}_i = \frac{1}{n_i} \int \boldsymbol{\xi}_i f_i \, \mathrm{d}\boldsymbol{\xi}_i, \; T_i = \frac{1}{3kn_i} \int m_i(\boldsymbol{\xi}_i - \boldsymbol{U}_i)^2 f_i \, \mathrm{d}\boldsymbol{\xi}_i. \tag{3.4}$$

T_{ij} and $\boldsymbol{U}_{ij}$ are defined as $T_{ij} = T_i + 2\mu_i\mu_j(T_j - T_i) + m\mu_i\mu_j^2(\boldsymbol{U}_j - \boldsymbol{U}_i)^2/3k$, $\boldsymbol{U}_{ij} = \mu_i\boldsymbol{U}_i + \mu_j\boldsymbol{U}_j$, $\mu_i = m_i/m$, $\mu_j = m_j/m$, $m = m_i + m_j$. The term involving A_{ii} in (3.1) represents the self-collision between molecules of the same kind, with $1/(A_{ii}n_i)$ indicating the mean time between two successive collisions. Similarly, the term involving A_{ij} represents the cross collision between molecules of different kinds, with $1/(A_{ij}n_j)$ the corresponding mean collision time.

For a weakly rarefied flow bounded by a sold surface, there exists a Knudsen layer separating the surface and the external flow described by the outer, Chapman–Enskog solution of (3.1). Zharov (1972) gave the first two terms of this solution, corresponding to the Navier–Stokes equation of the external flow:

$$f_i^{(o)} = f_{i0}^{(o)} - \frac{f_{i0}^{(o)}}{R_i^{(o)}} \left\{ \begin{array}{l} \frac{mn^{(o)}R_i^{(o)}}{\rho^{(o)}n_i^{(o)}A_{12}} \boldsymbol{c}_i^{(o)} \cdot \boldsymbol{d}_i^{(o)} + \frac{m_i}{kT^{(o)}} \left[c_{il}^{(o)} c_{ir}^{(o)} - \frac{1}{3}\delta_{lr} \left(\boldsymbol{c}_i^{(o)}\right)^2 \right] \frac{\partial U_l^{(o)}}{\partial x_r} \\ + \left[\frac{m_i}{2kT^{(o)}} \left(\boldsymbol{c}_i^{(o)}\right)^2 - \frac{5}{2} \right] c_{ir}^{(o)} \frac{\partial \ln T^{(o)}}{\partial x_r} \end{array} \right\}, \tag{3.5}$$

where

$$f_{i0}^{(o)} = n_i^{(o)} \left(\frac{m_i}{2\pi kT^{(o)}} \right)^{3/2} \exp\left[-\frac{m_i}{2kT^{(o)}} \left(\boldsymbol{c}_i^{(o)}\right)^2 \right], \; R_i^{(o)} = A_{ii}n_i^{(o)} + A_{ij}n_j^{(o)}, \tag{3.6}$$

and we have used Einstein summation for the subscripts $l, r = 1, 2, 3$ and δ_{lr} to represent the delta function. The superscript (o) denotes the outer solution as well as the related macroscopic hydrodynamic quantities, which are functions of x and y and are defined as

$$n = n_i + n_j, \; \rho = m_i n_i + m_j n_j, \; T = (n_i T_i + n_j T_j)/n, \; p = nkT, \tag{3.7}$$

$$\boldsymbol{U} = (m_i n_i \boldsymbol{U}_i + m_j n_j \boldsymbol{U}_j)/\rho, \; \boldsymbol{d}_i = \nabla\left(\frac{n_i}{n}\right) + \left(\frac{n_i}{n} - \frac{m_i n_i}{\rho}\right)\frac{\nabla p}{p}, \boldsymbol{c}_i = \boldsymbol{\xi}_i - \boldsymbol{U}, \tag{3.8}$$

where n_i, $\boldsymbol{U}_i$ and T_i are the macroscopic variables to be determined. According to the Chapman–Enskog theory, the second term on the right-hand side of (3.5) is of $O(\epsilon|f_{i0}^{(o)}|)$, where ϵ is a perturbation parameter corresponding to the small Knudsen number of the weakly rarefied flow, and will be specified shortly.

Within the Knudsen layer, the Chapman–Enskog-type series solution is not valid. Instead, we shall seek an inner solution of (3.1) in the linearized form

$$f_i^{(i)} = f_i^R(1 + \varphi_i), \; \varphi_i = \varphi_i(x, y, \boldsymbol{\xi}_i) = O(\epsilon). \tag{3.9}$$

The superscript (i) denotes the inner solution and the related macroscopic hydrodynamics quantities. f_i^R is the local Maxwellian distribution function defined as

$$f_i^R = n_i^{(o)}(x, 0) \left[\frac{m_i}{2\pi kT^{(o)}(x, 0)} \right]^{3/2} \exp\left[-\frac{m_i \boldsymbol{\xi}_i^2}{2kT^{(o)}(x, 0)} \right]. \tag{3.10}$$

The superscript R is used to distinguish the local Maxwellian distribution (3.10) from (3.2) and (3.3). φ_i is the perturbed distribution function, satisfying $|\partial\varphi_i/\partial x| = O(\epsilon)$ and $|\partial\varphi_i/\partial y| = O(1)$, which imply that the distribution function varies more rapidly across the Knudsen layer than along it. Similarly, the number density and the temperature in the Knudsen layer can be linearized by

$$n_i^{(i)}(x, y) = n_i^{(o)}(x, 0)[1 + \nu_i(x, y)], \; T_i^{(i)}(x, y) = T^{(o)}(x, 0)[1 + \tau_i(x, y)], \tag{3.11}$$

where $\nu_i = O(\epsilon)$ and $\tau_i = O(\epsilon)$ are the perturbed number density and temperature, respectively.

By writing the inner solution in the form of (3.9)–(3.11), it is assumed that the distribution function inside the Knudsen layer is close to the Maxwellian distribution up to $O(\epsilon)$, even though it cannot be represented in a Chapman–Enskog series solution, and that the macroscopic quantities vary with $O(\epsilon)$ across the layer (Kogan 1969). It is noted that $n_i^{(o)}(x,0)$ and $T_i^{(o)}(x,0)$ do not represent any actual physical quantities at the surface, $y=0$, since the outer solution is only valid outside the Knudsen layer and cannot be extended to the surface. Nevertheless, these fictitious quantities are useful in that they reflect the effects of the Knudsen layer on the outer flow, and that they are the quantities that the outer flow feels from the surface. Accordingly, the Navier–Stokes equation subject to these quantities is able to provide proper description to the flow outside the Knudsen layer, and as such they constitute useful boundary conditions, namely, the slip boundary conditions. One of the primary objectives of the present study is to obtain these quantities.

We further look for a solution of φ_i in the form of separation of variables (Kogan 1969),

$$\varphi_i = \phi_i + \sqrt{h_{i0}}\xi_{ix}\psi_i, \tag{3.12}$$

which means that the heat and mass transfer aspects of the problem, corresponding to ϕ_i, are separated from those describing the tangential flow, corresponding to ψ_i. In the present study, we are interested in the heat and mass transfer that is directly related to the surface reactions. The problem of the pure tangential flow was studied by Zharov (1972), yielding the slip boundary condition for the tangential velocity.

Substituting (3.9) and (3.12) into (3.1), separating the terms without $\sqrt{h_{i0}}\xi_{ix}$ from those containing it, we have

$$v_{iy}\frac{\partial \phi_i}{\partial y_1} = -\phi_i + \nu_i + \left(\boldsymbol{v}_i^2 - \frac{3}{2}\right)\theta_i + 2v_{iy}W_i, \tag{3.13}$$

where

$$y_1 = y/\lambda,\ \boldsymbol{v}_i = \sqrt{h_{i0}}\,\boldsymbol{\xi}_i,\ \boldsymbol{u}_i = \sqrt{h_{i0}}\,\boldsymbol{U}_i,\ h_{i0} = m_i/2kT^{(o)}(x,0), \tag{3.14}$$

$$R_{i0} = A_{ii}n_i^{(o)}(x,0) + A_{ij}n_j^{(o)}(x,0),\ \beta_{i0} = A_{ij}n_j^{(o)}(x,0)/R_{i0}, \tag{3.15}$$

$$\theta_i = (1-2\beta_{i0}\mu_i\mu_j)\tau_i + 2\beta_{i0}\mu_i\mu_j\tau_j,\ W_i = (1-\beta_{i0}\mu_j)u_{iy}^{(i)} + \beta_{i0}\mu_j\sqrt{\mu_i/\mu_j}\,u_{jy}^{(i)}. \tag{3.16}$$

In deriving (3.13), we have assumed $|\boldsymbol{U}_i|/\epsilon \sim |\boldsymbol{\xi}_i| \sim |\boldsymbol{c}_i| \sim 1/\sqrt{h_{i0}}$, which physically means that the flow Mach number is assumed to be of the same order of the Knudsen number. Furthermore, by noting that $1/R_{i0}$ is of the order of the characteristic time between two successive molecular collisions, and hence $1/(R_{i0}\sqrt{h_{i0}})$ has the physical meaning of the mean free path of the gas molecules of the ith species, we further assume that the mean free paths of molecules of different species have the same value $\lambda = 1/(R_{i0}\sqrt{h_{i0}}) = 1/(R_{j0}\sqrt{h_{j0}})$. These two assumptions substantially simplify the problem studied in that we need to consider only one perturbation parameter in the present formation, namely the Knudsen number defined as $Kn = \lambda/L = \epsilon$, where L is the characteristic length of the flow.

3.2. *Integral equations for the perturbed macroscopic variables*

Two boundary conditions are needed to solve (3.13), with one specified at the surface, which is the inner boundary of the Knudsen layer, and the other specified at the outer boundary of the Knudsen layer in the asymptotic sense. At the surface, we apply

Nocilla's model of molecule-surface interaction (Nocilla 1961, 1963):

$$f_i^{(i)}(x, y=0, \xi_{iy}>0) = n_{ir}\left(\frac{m_i}{2\pi kT_r}\right)^{3/2}\exp\left[-\frac{m_i}{2kT_r}\left(\boldsymbol{\xi}_i - \boldsymbol{U}_i^r\right)^2\right], \tag{3.17}$$

which physically means that the reflected molecules of the ith species are Maxwellian-like in the velocity distribution. They have a non-zero macroscopic velocity $\boldsymbol{U}_i^r$ and their temperature T_r is different from the surface temperature. Similar to (3.11), we linearize n_{ir} and T_r as

$$n_{ir}(x) = n_i^{(o)}(x,0)[1+\nu_{ir}(x)], \;\; T_r(x) = T^{(o)}(x,0)[1+\tau_r(x)], \tag{3.18}$$

where $\nu_{ir} = O(\epsilon)$ and $\tau_r = O(\epsilon)$ are the perturbed number density and temperature of the reflected molecules at the surface, respectively. Substituting (3.17) and (3.18) into (3.9) and applying (3.12), we have

$$\varphi_i(x,0,v_{iy}>0) = \nu_{ir} + \left(\boldsymbol{v}_i^2 - 3/2\right)\tau_r + 2\boldsymbol{v}_i\cdot\boldsymbol{u}_i^r, \tag{3.19}$$

and hence

$$\phi_i(x,0,v_{iy}>0) = \nu_{ir} + \left(\boldsymbol{v}_i^2 - 3/2\right)\tau_r + 2v_{iy}u_{iy}^r, \tag{3.20}$$

which constitutes the inner boundary conditions for (3.13).

Nocilla's kinetic boundary condition (3.17) is essentially a three-parameter model, in which U_{ix}^r, U_{iy}^r and T_r need to be specified independently while n_{ir} is determined through species conservation at the surface. Following Nocilla (1961), we have the relation between the macroscopic (mean) velocity of the reflected and incident molecules:

$$U_{iy}^r(x) = -(1-\alpha_n)U_{iy}^{(i)}(x,0), \tag{3.21}$$

where α_n is the accommodation coefficient of the normal velocity and is assumed to be the same constant for molecules of all kinds. The accommodation coefficient α_τ of the tangential velocity U_{ix}^r does not affect the present problem, and therefore will not appear in the formulation. The energy accommodation coefficient α_e is introduced to implicitly determine T_r through $\alpha_e = (E_{ii} - E_{ir})/(E_{ii} - E_{iw})$, where E_{ii} and E_{ir} are, respectively, the energy carried by the incident and reflected molecules of the ith kind; E_{ir} is equal to E_{iw} when the reflected molecules are in thermal equilibrium with the surface.

According to (3.4), the perturbed macroscopic variables ν_i, τ_i and $u_{iy}^{(i)}$ appearing in (3.13) and (3.16) are certain integrals of φ_i, given by

$$\nu_i = \pi^{-\frac{3}{2}}\int e^{-\boldsymbol{v}_i^2}\varphi_i\,d\boldsymbol{v}_i, \;\; \tau_i = -\nu_i + \frac{2}{3}\pi^{-\frac{3}{2}}\int \boldsymbol{v}_i^2 e^{-\boldsymbol{v}_i^2}\varphi_i\,d\boldsymbol{v}_i, \;\; u_{iy}^{(i)} = \pi^{-\frac{3}{2}}\int v_{iy}e^{-\boldsymbol{v}_i^2}\varphi_i\,d\boldsymbol{v}_i, \tag{3.22}$$

and hence

$$\nu_i = \pi^{-\frac{3}{2}}\int e^{-\boldsymbol{v}_i^2}\phi_i\,d\boldsymbol{v}_i, \;\; \tau_i = -\nu_i + \frac{2}{3}\pi^{-\frac{3}{2}}\int \boldsymbol{v}_i^2 e^{-\boldsymbol{v}_i^2}\phi_i\,d\boldsymbol{v}_i, \;\; u_{iy}^{(i)} = \pi^{-\frac{3}{2}}\int v_{iy}e^{-\boldsymbol{v}_i^2}\phi_i\,d\boldsymbol{v}_i, \tag{3.23}$$

in which all integrations are defined in the entire velocity space, that is, the integration domain for each velocity component is $(-\infty, \infty)$.

Since (3.13) is essentially an integro–differential equation, to facilitate analytical solution we formally integrate it, subject to its inner boundary condition (3.20), to obtain

$$\begin{aligned}\phi_i(v_{iy} > 0) = &\int_0^{y_1} \left[\nu_i + \left(\boldsymbol{v}_i^2 - \frac{3}{2}\right)\theta_i + 2v_{iy}W_i\right]\frac{1}{v_{iy}}\exp\left(-\frac{y_1 - s}{v_{iy}}\right)\mathrm{d}s\\ &+ \left[\nu_{ir} + \left(\boldsymbol{v}_i^2 - \frac{3}{2}\right)\tau_r + 2v_{iy}u_{iy}^r\right]\exp\left(-\frac{y_1}{v_{iy}}\right),\\ \phi_i(v_{iy} < 0) = &\int_\infty^{y_1} \left[\nu_i + \left(\boldsymbol{v}_i^2 - \frac{3}{2}\right)\theta_i + 2v_{iy}W_i\right]\frac{1}{v_{iy}}\exp\left(-\frac{y_1 - s}{v_{iy}}\right)\mathrm{d}s,\end{aligned} \tag{3.24}$$

which when substituted into (3.23) yields

$$\sqrt{\pi}\,\nu_i = \left\{\begin{matrix} I_{-1} * \nu_i + \left(I_1 - \frac{1}{2}I_{-1}\right) * \theta_i - 2\left(W_i - u_{iy}^r\right)J_1(y_1)\\ + \nu_{ir}J_0(y_1) + \tau_r\left[J_2(y_1) - \frac{1}{2}J_0(y_1)\right]\end{matrix}\right\}, \tag{3.25}$$

$$\sqrt{\pi}\,\tau_i = \left\{\begin{matrix}\left(\frac{2}{3}I_1 - \frac{1}{3}I_{-1}\right) * \nu_i + \left(\frac{2}{3}I_3 - \frac{2}{3}I_1 + \frac{5}{6}I_{-1}\right) * \theta_i\\ -2\left(W_i - u_{iy}^r\right)\left[\frac{2}{3}J_3(y_1) - \frac{1}{3}J_1(y_1)\right] + \nu_{ir}\left[\frac{2}{3}J_2(y_1) - \frac{1}{3}J_0(y_1)\right]\\ + \tau_r\left[\frac{2}{3}J_4(y_1) - \frac{2}{3}J_2(y_1) + \frac{5}{6}J_0(y_1)\right]\end{matrix}\right\}, \tag{3.26}$$

where the special function $J_n(y_1)$ and the integral operator I_n (n is integer) are respectively defined by

$$J_n(y_1) = \int_0^\infty s^n \exp\left(-s^2 - \frac{y_1}{s}\right)\mathrm{d}s,\ \ I_n * f(y_1) = \int_0^\infty f(s)J_n(|y_1 - s|)\,\mathrm{d}s. \tag{3.27}$$

Selected properties of J_n and I_n, which have been repeatedly used to obtain (3.25) and (3.26), are listed in Appendix A. It is noted that (3.25) and (3.26) are the same as those derived by Kogan & Makashev (1972) except the terms containing u_{iy}^r, which are the consequence of using Nocilla's boundary condition.

The kinetic boundary condition at the outer boundary of the Knudsen layer can be obtained by asymptotically matching the outer solution (3.5) with the inner solution (3.9) (Zharov 1972):

$$\begin{aligned}\varphi_i(x, y_1 \to \infty) = &\ 2h_{i0}\boldsymbol{\xi}_i \cdot \boldsymbol{U}^{(o)}(x,0) + \lambda y_1\left[\begin{matrix}\left(\frac{\partial \ln n_i^{(o)}}{\partial y}\right)_{y=0} + \left(h_{i0}\boldsymbol{\xi}_i^2 - \frac{3}{2}\right)\left(\frac{\partial \ln T^{(o)}}{\partial y}\right)_{y=0}\\ + 2h_{i0}\boldsymbol{\xi}_i \cdot \left(\frac{\partial \ln \boldsymbol{U}^{(o)}}{\partial y}\right)_{y=0}\end{matrix}\right]\\ &- \frac{1}{R_{i0}}\left[\begin{matrix}\frac{mn^{(o)}(x,0)R_{i0}}{\rho^{(o)}(x,0)n_i^{(o)}(x,0)A_{12}}\boldsymbol{\xi}_i \cdot \boldsymbol{d}_i^{(o)}(x,0) + 2h_{i0}\left(\xi_{il}\xi_{ir} - \frac{1}{3}\delta_{lr}\boldsymbol{\xi}_i^2\right)\left(\frac{\partial U_l^{(o)}}{\partial x_r}\right)_{y=0}\\ + \left(h_{i0}\boldsymbol{\xi}_i^2 - \frac{5}{2}\right)\xi_{ir}\left(\frac{\partial \ln T^{(o)}}{\partial x_r}\right)_{y=0}\end{matrix}\right],\end{aligned}$$

which when substituted into (3.22) yields

$$\nu_i(\infty) = y_1\Phi_i,\ \ \tau_i(\infty) = y_1\Phi_0,\ \ \Phi_i = \lambda\left(\frac{\partial \ln n_i^{(o)}}{\partial y}\right)_{y=0},\ \ \Phi_0 = \lambda\left(\frac{\partial \ln T^{(o)}}{\partial y}\right)_{y=0}, \tag{3.28}$$

and

$$u_{iy}^{(i)}(x,\infty) = \sqrt{h_{i0}}U_y^{(o)}(x,0) - D_{i0}X_{i0}X_{j0}\sqrt{h_{i0}}\lambda^{-1}\Phi_{ij}, \tag{3.29}$$

where $X_{i0} = n_i^{(o)}(x,0)/n^{(o)}(x,0)$, $D_{i0} = m/[2\rho^{(o)}(x,0)X_{i0}A_{12}h_{i0}]$, $\Phi_{ij} = -\Phi_{ji} = \Phi_i - \Phi_j$. Since the flow studied is assumed to be of $O(\epsilon)$ Mach number, the pressure gradients along x and y directions can be neglected (Kogan 1969). Consequently, from the ideal gas law, we have

$$\Phi_0 = -X_{i0}\Phi_i - X_{j0}\Phi_j, \;\; \Phi_i = -\Phi_0 + X_{j0}\Phi_{ij}, \tag{3.30}$$

which will be used later.

We next recognize that, in the presence of surface reactions, the surface reaction rate Rc_i of the ith species is exactly its flow flux at the surface, which must be a constant cross the Knudsen layer (Kogan & Makashev 1972). Consequently, we have

$$Rc_i = n_i^{(i)}(x,0)U_{iy}^{(i)}(x,0) = n_i^{(i)}(x,y)U_{iy}^{(i)}(x,y) \sim \epsilon n_i^{(i)} c_i^{(i)}, \tag{3.31}$$

which is equivalent to the assumption that the sticking coefficient is of $O(\epsilon)$, as will be shown later. Since $n_i^{(i)}(x,y) = n^{(o)}(x,0) + O(\epsilon)$, the normal velocity $U_{iy}^{(i)}$ satisfies $\partial U_{iy}^{(i)}/\partial y = 0$ up to $O(\epsilon^2)$ in the Knudsen layer and hence $U_{iy}^{(i)}(x,y) = U_{iy}^{(i)}(x,\infty) + O(\epsilon^2)$. Consequently, it is not necessary to establish and solve the integral equation for $U_{iy}^{(i)}$, which can be obtained immediately once (3.25) and (3.26) are solved and the surface reaction rate is determined.

To involve surface reaction in the present mathematical formulation, we assume that the binary mixture studied consists of a chemically active species and a chemically inert species, which are respectively denoted by $i = 1$ and $i = 2$ for clarity. Since the normal velocity of the inert species vanishes in the Knudsen layer up to $O(\epsilon^2)$, we have

$$u_{2y}^{(i)}(x,\infty) = \sqrt{h_{20}}U_y^{(o)}(x,0) - D_{20}X_{20}X_{10}\sqrt{h_{20}}\lambda^{-1}\Phi_{21} = 0, \tag{3.32}$$

which leads to

$$U_y^{(o)}(x,0) = -D_{20}X_{10}X_{20}\lambda^{-1}\Phi_{12}. \tag{3.33}$$

Consequently, we have

$$u_{1y}^{(i)}(x,\infty) = \sqrt{h_{10}}U_y^{(o)}(x,0) - D_{10}X_{10}X_{20}\sqrt{h_{10}}\lambda^{-1}\Phi_{12} = -\sqrt{h_{10}}\lambda^{-1}D_{12}\Phi_{12}, \tag{3.34}$$

where $D_{12} = X_{10}X_{20}(D_{10} + D_{20}) = kT^{(o)}(x,0)/[A_{12}n^{(o)}(x,0)m\mu_1\mu_2]$ is the binary mass diffusivity affiliated with the Hamel's model (Hamel 1965).

Substituting (3.34) and (3.32) into (3.16) and applying (3.21), we have

$$\left(W_1 - u_{1y}^r\right)/\Phi_{12} = -(2 - \beta_{10}\mu_2 - \alpha_n)\sqrt{h_{10}}\lambda^{-1}D_{12}, \tag{3.35}$$

$$\left(W_2 - u_{2y}^r\right)/\Phi_{21} = \beta_{20}\mu_1\sqrt{\mu_2/\mu_1}\sqrt{h_{10}}\lambda^{-1}D_{12}. \tag{3.36}$$

It is noted that $(W_i - u_{iy}^r)/\Phi_{ij}$ is independent of the coordinate y and hence can be treated as constants when solving the integral equations (3.25) and (3.26). This result actually can be obtained for other surface reaction systems (Kogan & Makashev 1972) and therefore can be considered to be valid in general.

3.3. *Solutions of the perturbed macroscopic variables*

By observing (3.25) and (3.26) and the corresponding boundary conditions (3.28), we can seek solution in the form

$$\nu_i = G_{\nu_i}(y_1) + y_1\Phi_i + \nu_{ir}, \;\; \tau_i = G_{\tau_i}(y_1) + y_1\Phi_0 + \tau_r, \tag{3.37}$$

and hence

$$\theta_i = G_{\theta_i}(y_1) + y_1\Phi_0 + \tau_r, \;\; G_{\theta_i}(y_1) = (1 - 2\beta_{i0}\mu_i\mu_j)G_{\tau_i}(y_1) + 2\beta_{i0}\mu_i\mu_j G_{\tau_j}(y_1). \tag{3.38}$$

Consequently, we have

$$G_{\nu_i}(y_1) = \pi^{-\frac{1}{2}} \left\{ \begin{aligned} & I_{-1} * G_{\nu_i}(y_1) + \left(I_1 - \tfrac{1}{2} I_{-1}\right) * G_{\theta_i}(y_1) \\ & \quad + 2 w_i \varPhi_{ij} J_1(y_1) + \varPhi_0 \left[J_3(y_1) - \tfrac{3}{2} J_1(y_1)\right] \end{aligned} \right\}, \tag{3.39}$$

$$G_{\tau_i}(y_1) = \pi^{-\frac{1}{2}} \left\{ \begin{aligned} & \left(\tfrac{2}{3} I_1 - \tfrac{1}{3} I_{-1}\right) * G_{\nu_i}(y_1) + \left(\tfrac{2}{3} I_3 - \tfrac{2}{3} I_1 + \tfrac{5}{6} I_{-1}\right) * G_{\theta_i}(y_1) \\ & \quad + 2 w_i \varPhi_{ij} \left[\tfrac{2}{3} J_3(y_1) - \tfrac{1}{3} J_1(y_1)\right] \\ & \quad + \varPhi_0 \left[\tfrac{2}{3} J_5(y_1) - \tfrac{4}{3} J_3(y_1) + \tfrac{7}{6} J_1(y_1)\right] \end{aligned} \right\}, \tag{3.40}$$

subject to the boundary conditions

$$G(\infty) = -\nu_{ir}, \; G(\infty) = -\tau_r. \tag{3.41}$$

The constant w_i in (3.39) and (3.40) is given by

$$w_i = X_{j0}/2 - \left(W_i - u^r_{iy}\right)/\varPhi_{ij}, \tag{3.42}$$

which is independent of the coordinate y and is treated as constant, as discussed in the last section.

Noting the symmetry of (3.39) and (3.40) with respect to $\varPhi_0$ and $\varPhi_{ij}$, we further assume

$$G_{\nu_i}(y_1) = -g_\nu(y_1)\,\varPhi_0 + 2h_{\nu_i}(y_1)\,w_i \varPhi_{ij}, \tag{3.43}$$

$$G_{\tau_i}(y_1) = -g_\tau(y_1)\,\varPhi_0 + 2h_{\tau_i}(y_1)\,w_i \varPhi_{ij}, \tag{3.44}$$

$$G_{\theta_i}(y_1) = -g_\theta(y_1)\,\varPhi_0 + 2h_{\theta_i}(y_1)\,w_i \varPhi_{ij}, \tag{3.45}$$

in which

$$g_\theta = g_\tau, \; h_{\tau_i} = h_{\theta_i} + \delta_i[h_{\theta_i} + (w_j/w_i) h_{\theta_j}], \; \delta_i = 2\beta_{i0}\mu_i\mu_j/[1 - 2(\beta_{i0} + \beta_{j0})\mu_i\mu_j]. \tag{3.46}$$

Consequently, a set of integral equations for g_ν, g_θ, h_{ν_i} and h_{θ_i} are obtained as follows:

$$g_\nu = L_1 * g_\nu + M_1 * g_\theta - Y_1, \; g_\theta = L_2 * g_\nu + M_2 * g_\theta - Y_2, \tag{3.47}$$

$$h_{\nu_i} = L_1 * h_{\nu_i} + M_1 * h_{\theta_i} + X_1, \; h_{\theta_i} = L_2 * h_{\nu_i} + M_2 * h_{\theta_i} - \delta_i[h_{\theta_i} + (w_j/w_i) h_{\theta_j}] + X_2, \tag{3.48}$$

where L_1, L_2, M_1 and M_2 are the integral operators defined as $L_1 = \pi^{-\frac{1}{2}} I_{-1}$, $L_2 = \pi^{-\frac{1}{2}}(2I_1 - I_{-1})/3$, $M_1 = \pi^{-\frac{1}{2}}(2I_1 - I_{-1})/2$, $M_2 = \pi^{-\frac{1}{2}}(4I_3 - 4I_1 + 5I_{-1})/6$. X_1, X_2, Y_1 and Y_2 are functions of y_1, defined as $X_1 = \pi^{-\frac{1}{2}} J_1(y_1)$, $X_2 = \pi^{-\frac{1}{2}}[2J_3(y_1) - J_1(y_1)]/3$, $Y_1 = \pi^{-\frac{1}{2}}[2J_3(y_1) - 3J_1(y_1)]/2$, $Y_2 = \pi^{-\frac{1}{2}}[4J_5(y_1) - 8J_3(y_1) + 7J_1(y_1)]/6$.

By writing h_{ν_i} and h_{θ_i} in the separation form

$$h_{\nu_i}(y_1) = \frac{\delta_i(w_i + w_j)}{w_i(\delta_i + \delta_j)} q_\nu(y_1) + \frac{\delta_j w_i - \delta_i w_j}{w_i(\delta_i + \delta_j)} h_\nu(y_1), \tag{3.49}$$

$$h_{\theta_i}(y_1) = \frac{\delta_i(w_i + w_j)}{w_i(\delta_i + \delta_j)} q_\theta(y_1) + \frac{\delta_j w_i - \delta_i w_j}{w_i(\delta_i + \delta_j)} h_\theta(y_1), \tag{3.50}$$

equation (3.48) can be transformed into

$$h_\nu = L_1 * h_\nu + M_1 * h_\theta + X_1, \; h_\theta = L_2 * h_\nu + M_2 * h_\theta + X_2, \tag{3.51}$$

$$q_\nu = L_1 * q_\nu + M_1 * q_\theta + X_1, \; (1 + \delta_i + \delta_j) q_\theta = L_2 * q_\nu + M_2 * q_\theta + X_2. \tag{3.52}$$

We have therefore obtained a series of integral equations (3.47), (3.51) and (3.52), which are exactly the same as those derived by Kogan & Makashev (1972), even though the different surface reaction model and the kinetic boundary condition at the surface are used in their analysis. For the purpose of establishing the slip boundary conditions, only solutions of the integral equations at $y_1 = \infty$ are needed, which are given in Kogan & Makashev (1972): $g_\nu(\infty) = 0.68, g_\tau(\infty) = -1.25; h_\nu(\infty) = 0.82, h_\theta(\infty) = 0.22; q_\theta(\infty) = 0;$ $\delta_i + \delta_j = 0.1 : q_\nu(\infty) = 0.950; \delta_i + \delta_j = 0.5 : q_\nu(\infty) = 0.976;$ $\delta_i + \delta_j = 2.5 : q_\nu(\infty) = 0.978; \delta_i + \delta_j = 12.5 : q_\nu(\infty) = 0.978.$ In the present problem, to calculate the surface reaction rate, we also need the solutions at $y_1 = 0$, as will be shown in the next section. Accordingly, the integral equations (3.47), (3.51) and (3.52) are numerically solved (see appendix B) to give the following results: $g_\nu(0) = 0.39, g_\tau(0) = -0.77, h_\nu(0) = 0.62, h_\theta(0) = 0.17;$ $\delta_i + \delta_j = 0.1 : q_\nu(0) = 0.634, q_\theta(0) = 0.129; \delta_i + \delta_j = 0.5 : q_\nu(0) = 0.646, q_\theta(0) = 0.072;$ $\delta_i + \delta_j = 2.5 : q_\nu(0) = 0.655, q_\theta(0) = 0.028; \delta_i + \delta_j = 12.5 : q_\nu(0) = 0.658, q_\theta(0) = 0.007.$

Consequently, from (3.41), we have

$$\nu_{ir} = -G_{\nu_i}(\infty) = g_\nu(\infty)\,\Phi_0 - 2\left[q_\nu(\infty)\frac{\delta_i(w_i + w_j)}{\delta_i + \delta_j} + h_\nu(\infty)\frac{\delta_j w_i - \delta_i w_j}{\delta_i + \delta_j}\right]\Phi_{ij}, \quad (3.53)$$

and

$$\tau_r = -G_{\tau_i}(\infty) = g_\tau(\infty)\Phi_0 - 2h_\theta(\infty)\frac{\delta_j w_i - \delta_i w_j}{\delta_i + \delta_j}\Phi_{ij}. \quad (3.54)$$

Equation (3.54) is invariant when exchanging the index i and j, as it should be since it represents the perturbed temperature of the binary mixture. Similarly, from (3.37), we have

$$\nu_i(x,0) - \nu_{ir} = G_{\nu_i}(0) = -g_\nu(0)\,\Phi_0 + 2\left[q_\nu(0)\frac{\delta_i(w_i + w_j)}{\delta_i + \delta_j} + h_\nu(0)\frac{\delta_j w_i - \delta_i w_j}{\delta_i + \delta_j}\right]\Phi_{ij}, \quad (3.55)$$

and

$$\begin{aligned}\tau_i(x,0) - \tau_r &= G_{\tau_i}(0)\\ &= -g_\tau(0)\Phi_0 + 2\left\{q_\theta(0)\frac{(w_i + w_j)\delta_i(1 + \delta_i + \delta_j)}{\delta_i + \delta_j} + h_\theta(0)\frac{\delta_j w_i - \delta_i w_j}{\delta_i + \delta_j}\right\}\Phi_{ij}.\end{aligned} \quad (3.56)$$

Based on the above results, we can express the slip concentration and the slip temperature as

$$n_i^{(o)}(x,0) = n_{ir}(1 - \nu_{ir}), \;\; T^{(o)}(x,0) = T_r(1 - \tau_r). \quad (3.57)$$

To calculate the surface reaction rate, we also need to express the concentration and temperature of the gas molecules at the surface, given by

$$n_i^{(i)}(x,0) = n_i^{(o)}(x,0)[1 + \nu_i(x,0)] = n_{ir}[1 + \nu_i(x,0) - \nu_{ir}] + O(\epsilon^2), \quad (3.58)$$

$$T_i^{(i)}(x,0) = T^{(o)}(x,0)[1 + \tau_i(x,0)] = T_r[1 + \tau_i(x,0) - \tau_r] + O(\epsilon^2). \quad (3.59)$$

4. Surface reaction rate based on sticking coefficients

Although chemical kinetics of surface reactions is complicated in nature and is far from completely understood, it is clear that collisions between gas molecules and a surface is needed to initiate a reaction. Consequently, a collision theory of surface reaction rate can be established, similar to that of gas-phase reactions. Specifically, the surface reaction rate is defined as the number flux of the molecules hitting the surface times a sticking coefficient, which is the probability that a collision results in a reaction and has a value between zero and unity.

In this section, we consider a simple one-step irreversible surface reaction

$$M_i(g) \rightarrow M_i(s), \tag{4.1}$$

where g and s denote the gas phase and surface phase, respectively. According to definition, the surface reaction rate of M_i is given by

$$R_{ci} = \kappa J_i^{(-)}, \tag{4.2}$$

where the sticking coefficient κ has the same order of ϵ in the present assumption of small surface reaction rate, and $J_i^{(-)}$ is the number flux of incident M_i striking the surface, defined as

$$J_i^{(-)} = -\int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}<0} f_i^{(i)}(x, y, \boldsymbol{\xi}_i)(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i. \tag{4.3}$$

Assuming that the incident molecules striking the surface follow the Maxwellian distribution function and are in thermal equilibrium with the surface, the surface reaction rate is usually given by:

$$R_{ci} = \kappa J_{iw} = \kappa n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}}, \tag{4.4}$$

where T_w is the surface temperature and n_{iw} (similar to n_{ir}) can be determined through species conservation at the surface. However, as discussed above, this assumption and hence (4.4) is not correct when a Knudsen layer is present at the surface and as such the distribution function of the molecules striking the surface is generally non-Maxwellian.

A correction to (4.4), taking into account the effect of the non-Maxwellian distribution of molecules in the Knudsen layer, can be obtained by applying (3.9) and (3.19) in (4.3):

$$\begin{aligned} J_i^{(-)} &= -\int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}<0} f_i^R(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i - \int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}<0} f_i^R \varphi_i(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i \\ &= -\int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}<0} f_i^R(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i - \int f_i^R \varphi_i(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i + \int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}>0} f_i^R \varphi_i(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i \\ &= J_{i0}\left(1 + \nu_{ir} + \sqrt{\pi} u_{iy}^r - 2\sqrt{\pi} u_{iy}^{(i)}\right), \end{aligned} \tag{4.5}$$

where

$$J_{i0} = -\int_{\boldsymbol{\xi}_i \cdot \boldsymbol{n}<0} f_i^R(\boldsymbol{\xi}_i \cdot \boldsymbol{n})\, \mathrm{d}\boldsymbol{\xi}_i = n_i^{(o)}(x, 0)\sqrt{\frac{kT^{(o)}(x, 0)}{2\pi m_i}}. \tag{4.6}$$

Consequently, the corrected surface reaction rate is

$$R_{ci} = \kappa J_{i0}\left[1 + \nu_{ir} + \sqrt{\pi} u_{iy}^r - 2\sqrt{\pi} u_{iy}^{(i)}\right] = \kappa J_{i0}\left[1 + \nu_{ir} - (3 - \alpha_n)\sqrt{\pi} u_{iy}^{(i)}\right], \tag{4.7}$$

with the use of (3.21). On the other hand, from (3.31), we have

$$R_{ci} = -n_i^{(o)}(x, 0) U_{iy}^{(i)}(x)[1 + \nu_i(x, 0)] = -2\sqrt{\pi} J_{i0} u_{iy}^{(i)}(x)[1 + \nu_i(x, 0)]. \tag{4.8}$$

Considering (4.7) and (4.8) together and using (3.21), we have

$$R_{ci} = \frac{\kappa}{1 - \kappa \frac{3-\alpha_n}{2} \frac{1}{1+\nu_i(x,0)}} J_{i0}(1 + \nu_{ir}) = \frac{\kappa}{1 - \kappa \frac{3-\alpha_n}{2}} J_{i0}(1 + \nu_{ir}) + O(\epsilon^3), \tag{4.9}$$

which gives a general expression for the surface reaction rate of (4.1).

To compare the present result with those previously reported by other investigators, we apply (3.57) in (4.9), assuming hereafter that the energy accommodation coefficient is $\alpha_e = 1$, which means $T_r = T_w$, and neglecting the temperature and concentration gradients. We thus have

$$R_{ci} = \frac{\kappa}{1 - \kappa\frac{3-\alpha_n}{2}} n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}}, \tag{4.10}$$

which has the correction factor $1 - \kappa(3 - \alpha_n)/2$ relying on the sticking coefficient κ and the accommodation coefficient α_n for the normal velocity, as compared with (4.4).

Two important limiting results can be obtained from (4.10). For diffusive reflection, $\alpha_n = 1$ and $U_{iy}^r = 0$, we have

$$R_{ci} = \frac{\kappa}{1 - \kappa} n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}}, \tag{4.11}$$

while for specular reflection, $\alpha_n = 0$ and $U_{iy}^r = -U_{iy}^{(i)}$, we have

$$R_{ci} = \frac{\kappa}{1 - 3\kappa/2} n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}}. \tag{4.12}$$

Neither of them agrees with the widely used formula given by Motz & Wise (1960):

$$R_{ci} = \frac{\kappa}{1 - \kappa/2} n_{iw} \sqrt{\frac{kT_w}{2\pi m_i}}, \tag{4.13}$$

which can however be obtained from (4.10) by setting the unreasonable value of $\alpha_n = 2$, which is equivalent to $U_{iy}^r = U_{iy}^{(i)}$.

To resolve this discrepancy and in view of the extensive adoption of the Motz–Wise formula, we re-examine Motz & Wise's derivation as follows (also see Dorsman & Kleijn 2007). They first derived the number fluxes of the molecules by applying Meyer's theory on diffusion (Jean 1925), in which the distribution function of the ith kind molecules was assumed to be locally Maxwellian and given by

$$f_i = n_i \left(\frac{m_i}{2\pi kT}\right)^{\frac{3}{2}} \exp\left\{-\frac{m_i}{2kT}\left[u_i^2 + v_i^2 + (w_i - w)^2\right]\right\}, \tag{4.14}$$

and $|w| \ll |c_i|$, in which w is the mean particle transport velocity and c_i the mean random velocity of species i (Motz & Wise 1960). Accordingly, the number fluxes of the ith kind molecules, which cross the plane $z = z_0$ in the direction of increasing z and decreasing z, are given by

$$J_i^+ = \left(\frac{m_i}{2\pi kT}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty}\int_0^{\infty}\int_{-\infty}^{\infty} n_i^+ \exp\left\{-\frac{m_i}{2kT}\left[u_i^2 + v_i^2 + (w_i - w)^2\right]\right\} w_i \,\mathrm{d}u_i \,\mathrm{d}v_i \,\mathrm{d}w_i, \tag{4.15}$$

$$J_i^- = \left(\frac{m_i}{2\pi kT}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty}\int_{-\infty}^{0}\int_{-\infty}^{\infty} n_i^- \exp\left\{-\frac{m_i}{2kT}\left[u_i^2 + v_i^2 + (w_i - w)^2\right]\right\} w_i \,\mathrm{d}u_i \,\mathrm{d}v_i \,\mathrm{d}w_i. \tag{4.16}$$

Since n_i varies along z, a phenomenological model accounting for this variation is given by

$$n_i^{\pm} = n_i(z_0) \mp \lambda \frac{w_i}{c_i} \left(\frac{\partial n_i}{\partial z} \right)_{z_0}, \tag{4.17}$$

which leads to

$$J_i^{\pm} = \frac{1}{2} n_i \left(\frac{1}{2} c_i \pm w \right) \mp \frac{1}{6} \lambda \left(\frac{\partial n_i}{\partial z} \right)_{z_0} c_i. \tag{4.18}$$

Finally, they set the plane $z = z_0$ at the surface and obtained

$$\begin{aligned} R_{ci} = \kappa J_i^- &= \kappa \left\{ \frac{1}{4} n_i c_i - \left[\frac{1}{2} n_i w - \frac{1}{6} \lambda \left(\frac{\partial n_i}{\partial z} \right)_{z_0} c_i \right] \right\} \\ &= \kappa \left[\frac{1}{4} n_i c_i + \frac{1}{2} (J_i^- - J_i^+) \right] = \kappa \left(\frac{1}{4} n_i c_i + \frac{1}{2} R_{ci} \right), \end{aligned} \tag{4.19}$$

and hence

$$R_{ci} = \frac{\kappa}{1 - \kappa/2} \frac{1}{4} n_i c_i = \frac{\kappa}{1 - \kappa/2} n_i \sqrt{\frac{kT}{2\pi m_i}}. \tag{4.20}$$

It is readily seen that, even if we could neglect the effects of the Knudsen layer on the molecular fluxes and accordingly express the incident molecular flux by (4.16), it is not correct to express the reflected molecular flux by (4.15). 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, as shown in Nocilla's experiment and theory (Nocilla 1961, 1963). Furthermore, even for the special case of specular reflection, the magnitude of the normal velocity remains the same but its sign changes. In fact, the expression (4.18) is only valid in the flow region outside the Knudsen layer. To obtain the correct expression for the flux of reflected molecules from the surface, the molecule-surface interaction law must be applied. Consequently, the general expression (4.9) or its simplified form (4.10) should be used.

So far the sticking coefficient is assumed to be a given constant in our discussion on the surface reaction rate. Actually, it is usually very temperature sensitive, being described by the Arrhenius law (Kee *et al.* 2003):

$$\kappa \sim \exp\left(-\frac{E_s}{kT_m} \right), \tag{4.21}$$

in which E_s is the activation energy of the surface reaction and T_m the temperature of the molecules striking the surface (Ceyer 1990). In many previous studies, the surface temperature T_w is used to replace T_m in (4.21) based on the assumption that the molecules are in thermal equilibrium with the surface. This is obviously not correct when there is a Knudsen layer attached to the surface, so that T_m is generally different from T_w, because of the non-equilibrium between the molecules in the Knudsen layer and the surface. Hu & Glumac (2002) accounted for the temperature jump (or slip) effect on the surface reaction rate by using $T_m = T^{(o)}(x, 0) = T_w(1 - \tau_r)$, $\tau_r = O(\epsilon)$, as shown in (3.57), in the Arrhenius factor, and showed that the surface reaction rates based on $T^{(o)}(x, 0)$ can be a few times different from that based on T_w:

$$\kappa \sim \exp\left[-\frac{E_s}{kT_w(1 - \tau_r)} \right] = \exp\left(-\frac{E_s}{kT_w} \tau_r \right) \exp\left(-\frac{E_s}{kT_w} \right), \tag{4.22}$$

since the scaled activation energy E_s/kT_w is usually much larger than unity and hence $\exp(-E_s\tau_r/kT_w)$ can be up to $O(1)$.

We note however that, according to definition, $T_m = T_i^{(i)}(x, 0)$ is generally neither the surface temperature nor the slip temperature. Moreover, the difference between any two of these three temperatures is of the order of the Knudsen number. Consequently, by using (3.59), we have

$$\kappa \sim \exp\left\{-\frac{E_s}{kT_w[1+\tau_i(x,0)-\tau_r]}\right\} = \exp\left\{\frac{E_s}{kT_w}[\tau_i(x,0)-\tau_r]\right\}\exp\left(-\frac{E_s}{kT_w}\right). \tag{4.23}$$

Since $\tau_r - \tau_i(x, 0)$ always has the same sign as that of τ_r but is smaller in magnitude, as can be easily seen in (3.54) and (3.56), the effect of the Knudsen layer on the sticking coefficient, which can still be up to $O(1)$, is overestimated in (4.22).

5. Slip boundary conditions for temperature and concentration

In § 3 and § 4, we obtained a set of solutions of the Boltzmann equation and the corresponding slip boundary conditions, namely (3.57), (3.53) and (3.54), with the constant w_i to be determined by applying specific surface reactions, for example, (3.42), (3.35) and (3.36), as well as the constant δ_i related to the physical properties of molecules. In this section, we shall apply these solutions to some binary mixture systems of interest, with emphasis on obtaining the simplified and readily applied slip boundary conditions.

We first consider the situation where there is no surface reaction, implying $u_{iy}^{(i)} = 0$ for both species in the binary mixture. Accordingly, from (3.34), we have

$$\Phi_{ij} = \Phi_i - \Phi_j = \lambda\left(\frac{\partial \ln n_i^{(o)}}{\partial y} - \frac{\partial \ln n_j^{(o)}}{\partial y}\right)_{y=0} = 0. \tag{5.1}$$

It is noted that, in many problems of chemically reacting flows, the mass fraction $Y_i = \rho_i/\rho$ is frequently used to replace the molar fraction $X_i = n_i/n$ for the reason that, while chemical reaction is a mole-based process, implying the use of X_i, convection is a mass-based process, implying the use of Y_i (Law 2006). Consequently, for binary mixtures, we have

$$\frac{\partial \ln n_i^{(o)}}{\partial y} - \frac{\partial \ln n_j^{(o)}}{\partial y} = \frac{1}{X_iX_j}\frac{\partial X_i^{(o)}}{\partial y} = \frac{1}{Y_iY_j}\frac{\partial Y_i^{(o)}}{\partial y}, \tag{5.2}$$

and then the boundary conditions

$$\left(\frac{\partial X_i^{(o)}}{\partial y}\right)_{y=0} = 0 \text{ or } \left(\frac{\partial Y_i^{(o)}}{\partial y}\right)_{y=0} = 0, \tag{5.3}$$

which are valid for weakly rarefied binary mixtures in the absence of surface reactions and were derived by Gupta *et al.* (1985). The slip boundary condition for temperature can be obtained from (3.54), (3.57) and (5.1):

$$T^{(o)}(x,0) = T_w\left[1 - g_\tau(\infty)\Phi_0\right] = T_w\left[1 + 1.25Kn\left(\frac{\partial \ln T^{(o)}}{\partial y_1}\right)_{y_1=0}\right]. \tag{5.4}$$

We next consider the situation where there exists a surface reaction involving a reacting species 1 and an inert species 2, as we studied in § 3. For species 1, we consider (3.34), (4.8) and (4.9) together and have

$$-u_{1y}^{(i)} = \sqrt{h_{10}}\lambda^{-1}D_{12}\Phi_{12} = \frac{R_{c1}}{2\sqrt{\pi}J_{10}[1+\nu_1(x,0)]} = \frac{1}{2\sqrt{\pi}}\frac{\kappa[1+\nu_{1r}-\nu_1(x,0)]}{1-\kappa(3-\alpha_n)/2}. \tag{5.5}$$

Applying (5.2) to (5.5), we obtain the slip boundary condition for the mass fraction Y_i,

$$\begin{aligned} Y_1^{(o)}(x,0) &= \sqrt{h_{i0}}D_{12}\frac{1}{Y_2^{(o)}}\left(\frac{\partial Y_1^{(o)}}{\partial y}\right)_{y=0} 2\sqrt{\pi}\frac{1-\kappa(3-\alpha_n)/2}{\kappa[1+\nu_{1r}-\nu_1(x,0)]} \\ &= \left[\frac{2-\kappa(3-\alpha_n)}{2\kappa}\right][1+\nu_1(x,0)-\nu_{1r}]\sqrt{\frac{2\pi m_1}{kT^{(o)}(x,0)}}\frac{D_{12}}{1-Y_1^{(o)}}\left(\frac{\partial Y_1^{(o)}}{\partial y}\right)_{y=0}. \end{aligned} \tag{5.6}$$

A similar result was given by Gupta *et al.* (1985) as

$$C_A^s = \frac{2-\gamma_A}{2\gamma_A}\sqrt{\frac{2\pi m_A}{kT_s}}D_{AM}^s\left(\frac{\partial C_A}{\partial y}\right)_s, \tag{5.7}$$

where the mass fraction of the atom species A is denoted by C_A, γ_A is the recombination coefficient and D_{AM} the mass diffusivity of the atom A with respect to its molecules.

Compared with (5.7), (5.6) shows effects of various factors on the slip concentration $Y_1^{(o)}(x,0)$ in a general, albeit complicated manner. Specifically, $Y_1^{(o)}(x,0)$ depends not only on its gradient but also the temperature gradient through the slip temperature $T^{(o)}(x,0)$. The surface reaction affects $Y_i^{(o)}(x,0)$ through both the correction formula $2-\kappa(3-\alpha_n)$, replacing that of Motz–Wise, and the influence factor $\nu_1(x,0)-\nu_{1r}$ due to the non-equilibrium distribution of molecules in the Knudsen layer. For species 2, the boundary condition for $Y_2^{(o)}$ is simply given by $Y_2^{(o)}=1-Y_1^{(o)}$.

The slip boundary condition for temperature is obtained from (3.57) and (3.54):

$$\begin{aligned} &T^{(o)}(x,0) \\ &= T_w\left[1+1.25Kn\left(\frac{\partial \ln T^{(o)}}{\partial y_1}\right)_{y_1=0}+0.44Kn\frac{\delta_j w_i-\delta_i w_j}{\delta_i+\delta_j}\frac{1}{Y_i^{(o)}Y_j^{(o)}}\left(\frac{\partial Y_i^{(o)}}{\partial y_1}\right)_{y_1=0}\right], \end{aligned} \tag{5.8}$$

which is invariant by exchanging i and j. This result shows that $T^{(o)}(x,0)$ depends not only on its gradient but also on the concentration gradient as well as the physical properties of the species through the factor $(\delta_j w_i-\delta_i w_j)/(\delta_i+\delta_j)$, which renders (5.8) different from the similar boundary condition derived by Kogan & Makashev (1972) for other surface reaction system.

To facilitate application, we shall make some simplifications to the slip boundary conditions, especially to the local constants w_i and δ_i. We assume that the two species have the same molecular mass $m_1=m_2$, which implies $\mu_1=\mu_2=1/2$; the same characteristic collisional constant A_{ij}, namely, $A_{11}=A_{22}=A_{12}=A_{21}$; and hence $\sqrt{h_{i0}}\lambda^{-1}D_{12}=1$. We then have $\delta_i=\beta_{i0}=X_j^{(o)}$, $(i,j=1,2)$; $w_1=2-\alpha_n$, $w_2=0$, which yield

$$\frac{\delta_i(w_i+w_j)}{\delta_i+\delta_j} = X_j^{(o)}(2-\alpha_n), \quad \frac{(w_i+w_j)\delta_i(1+\delta_i+\delta_j)]}{\delta_i+\delta_j} = 2(2-\alpha_n)X_j^{(o)}, \tag{5.9}$$

$$\frac{\delta_2 w_1-\delta_1 w_2}{\delta_1+\delta_2} = X_1^{(o)}(2-\alpha_n), \quad \frac{\delta_1 w_2-\delta_2 w_1}{\delta_1+\delta_2} = -X_1^{(o)}(2-\alpha_n), \tag{5.10}$$

in which the molar fraction $X_i^{(o)}$ can be replaced by the mass fraction $Y_i^{(o)}$ since the molecular masses are assumed to be the same. It is noted that the above approximation implies $\delta_i + \delta_j = 1$, and we have $q_\nu(\infty) \approx 0.98$, $q_\nu(0) \approx 0.65$ and $q_\theta(0) \approx 0.06$ by interpolation. Furthermore, we note that $Y_2^{(o)} = 1 - Y_1^{(o)}$ can be approximated by unity only when $Y_1^{(o)} \ll 1$, which is the prevalent situation for mixtures with a dominant inert species and shall be used to extend the present results to multicomponent mixtures, considered in the next section.

6. Extension to multicomponent mixtures

In § 4 and § 5, we studied binary gas mixtures in which the two species have arbitrary mass (molar) ratio, with one of them undergoing a one-step irreversible reaction at the surface while the other is chemically inert. In many problems, the number of gas-phase species is more than two and their surface reactions are usually multi-step and reversible. It is therefore of practical interest to extend the results based on binary mixtures to multicomponent and multi-step reaction systems.

As mentioned in § 1, rigorous mathematical treatment of the Boltzmann equation for a multicomponent mixture is extremely difficult due to the lack of mathematically tractable models for the collision integrals. Fortunately, in many practical reaction systems, there exists a major inert species, such as nitrogen in the air, so that the other chemically active species exist in small concentrations. Consequently the present problem can be substantially simplified as follows. We assume that each chemically active species together with the major inert species constitutes a pseudo binary system, whose behaviour is unaffected by those of the other species. All the species are considered only when calculating the total flow flux at the surface.

We next recognize that a realistic surface reaction usually consists of some subprocesses, for example, the adsorption of gas molecules to form adsorbates, the reaction between adsorbates, and the desorption of the products. Each of these processes has its own rate so that the overall surface reaction rate depends on each process in a complicated manner. In general, analytical expressions of the overall surface reaction rate can be obtained only for some special cases, for which there exists a rate-controlling (limiting) process (Szekely, Evans & Sohn 1976). For a general surface reaction system, the reaction rate of each species must be solved numerically with the given reaction mechanism and the relevant reaction rate constants. A general surface kinetics formalism involving K surface reactions and I species can be expressed as (Coltrin *et al.* 1996),

$$\sum_{i=1}^{I} \nu'_{i,k} M_i \underset{k_{b,k}}{\overset{k_{f,k}}{\rightleftharpoons}} \sum_{i=1}^{I} \nu''_{i,k} M_i \qquad (k = 1, 2, \ldots, K), \tag{6.1}$$

where $\nu'_{i,k}$ and $\nu''_{i,k}$ are respectively the stoichiometric coefficients of the ith species M_i in the kth reaction as a reactant and a product, and $k_{f,k}$ and $k_{b,k}$ are the forward and backward reaction rate constants, respectively. Adsorption and desorption are considered as special reactions since a gas-phase species and its adsorbate can be regarded as different species.

To extend the sticking coefficient formalism to multi-step reactions, we consider a special case of (6.1):

$$a_k A_k(g) + \sum_{i=1}^{I-1} \nu'_{i,k} M_{i,k}(s) \underset{\kappa_{B_k}}{\overset{\kappa_{A_k}}{\rightleftharpoons}} b_k B_k(g) + \sum_{i=1}^{I-1} \nu''_{i,k} M_{i,k}(s), \tag{6.2}$$

in which A_k and B_k are respectively the only gas-phase reactant in the forward and backward reactions of the kth reversible reaction, and κ_{A_k} and κ_{B_k} are their sticking coefficients, which can be calculated through the relations (Kee *et al.* 2003)

$$k_{f,k} = \frac{\kappa_{A_k}}{(\Gamma_{tot})^m}\sqrt{\frac{kT}{2\pi W_{A_k}}}, \quad k_{b,k} = \frac{\kappa_{B_k}}{(\Gamma_{tot})^m}\sqrt{\frac{kT}{2\pi W_{B_k}}}, \tag{6.3}$$

where Γ_{tot} is the total surface site concentration, m the sum of stoichiometric coefficients of all of the surface reactants $M_{i,k}(s)$, and $W_{A_k}(W_{B_k})$ the molecular weight of $A_k(B_k)$.

Rigorously speaking, (6.2) is only applicable to those surface reactions in which only one gas molecule acts as the reactant species. Fortunately, this condition is satisfied for many surface processes, except those occurring among adsorbates. Nevertheless, these reactions among the adsorbates influence the gas-phase species indirectly through Γ_{tot} and therefore are assumed not to appear explicitly in the formulation. It is noted that we have included more than one surface species on both sides of (6.2) so that it can be used to represent many empirical and semi-empirical mechanisms, and as such it is not necessarily an elementary surface reaction.

Based on the above considerations, it is straightforward to extend the results obtained in § 4 to the multicomponent system consisting of (6.2). By applying (4.7), we have the net reaction rate of species A in the kth reversible reaction

$$R_{A_k} = \kappa_{A_k} J_{A0}\left[1 + \nu_{Ar} - (3-\alpha_n)\sqrt{\pi}u_{Ay}^{(i)}\right] - \frac{a_k}{b_k}\kappa_{B_k} J_{B0}\left[1 + \nu_{Br} - (3-\alpha_n)\sqrt{\pi}u_{By}^{(i)}\right], \tag{6.4}$$

in which we have assumed that all accommodation coefficients α_n have the same value. J_{A0} and J_{B0} are given by replacing i in (4.6) with A and B, respectively. By the same token, ν_{Ar} and ν_{Br} are given by (3.53). Similar to (4.8), we have

$$R_A = \sum_{\text{all } A} R_{A_k} = -2\sqrt{\pi}J_{A0}u_{Ay}^{(i)}[1 + \nu_A(x,0)], \tag{6.5}$$

$$R_B = \sum_{\text{all } B} R_{B_k} = -2\sqrt{\pi}J_{B0}u_{By}^{(i)}[1 + \nu_B(x,0)], \tag{6.6}$$

in which the total reaction rate of species $A(B)$ is given by summing over all $R_{A_k}(R_{B_k})$ for all reactions containing $A(B)$. $\nu_A(x,0)$ and $\nu_B(x,0)$ are given by obtaining $\nu_i(x,0)$ by considering together (3.55) and (3.53) and then replacing i in $\nu_i(x,0)$ with A and B, respectively. Considering (6.4) and (6.5) together, we have

$$\begin{aligned} R_{A_k} = {} & \kappa_{A_k} J_{A0}(1 + \nu_{Ar}) - \frac{a_k}{b_k}\kappa_{B_k} J_{B0}(1 + \nu_{Br}) \\ & + \frac{3-\alpha_n}{2}\left[\kappa_{A_k}\frac{R_A}{1 + \nu_A(x,0)} - \frac{a_k}{b_k}\kappa_{B_k}\frac{R_B}{1 + \nu_B(x,0)}\right]. \end{aligned} \tag{6.7}$$

Similar expressions can be obtained for B and other chemically active species. Consequently, we obtain a set of simultaneous linear equations consisting of all R_{A_k} and R_{B_k}, which in principle can be solved analytically to obtain their explicit expressions. Once $R_A(R_B)$ and therefore $u_{Ay}^{(i)}(u_{By}^{(i)})$ are obtained, we can replace $u_{iy}^{(i)}$ in (5.5) by it to establish the slip boundary conditions for the mass fraction $Y_A(Y_B)$ and the temperature, as was shown earlier.

7. Conclusions and discussion

In the present study we have formulated a theory on the effects of the Knudsen layer on surface reactions for situations where the weakly rarefied flow consists of a binary gas mixture with an irreversible surface reaction based on a small sticking coefficient. Furthermore, this theory has also been extended to flows consisting of a multicomponent mixture with multi-step surface reactions. The corresponding reaction rate expressions and the slip boundary conditions have been established for these situations.

The study further shows that the application of Nocilla's model for gas-surface interaction is essential, and that it clarifies the misconception embedded in the formulation leading to the widely used, albeit incorrect, Motz–Wise formula for surface reaction rates. The magnitude of the relative error introduced by using Motz–Wise formula is proportional to the Knudsen number, which is of the same order of the sticking coefficient, as indicated in (4.9). Furthermore, the rigorous mathematical solution of the Boltzmann equation in the Knudsen layer enables us to distinguish the difference between the surface temperature, the slip temperature and the temperature of the molecules striking the surface, and thereby clarify the role of the Knudsen layer in modifying the temperature-sensitive sticking coefficient. The magnitude of such a modification can be up to $O(1)$, depending on the activation energy of the surface reaction, the surface temperature and the Knudsen number, as indicated in (4.23).

The present study is based on the assumption of small sticking coefficient and flow Mach number, which together allow us to linearize the Boltzmann equation and facilitate analytical solutions. For situations of strong surface reactions, as for example in the case of strong vapour condensation causing the so-called condensation shock (Kogan 1973), the sticking coefficient κ is close to unity and the linearization assumption is not valid any more (Kogan & Makashev 1971). It is of interest to extend the present theory to such situations of strong surface reactions.

This research was supported by the US Air Force Office of Scientific Research under the technical monitoring of Dr Michael R. Berman.

Appendix A. Selected properties of $J_n(x)$

The special function $J_n(x)$ was studied by, for example, Laporte (1937), Abramowitz (1953) and Welander (1954). The following are some useful integration results of $J_n(x)$:

$$\int_0^{y_1} J_n(y_1 - s)\,\mathrm{d}s = J_{n+1}(0) - J_{n+1}(y_1), \quad \int_{y_1}^{\infty} J_n(s - y_1)\,\mathrm{d}s = J_{n+1}(0), \tag{A 1}$$

$$\int_0^{y_1} s J_n(y_1 - s)\,\mathrm{d}s = J_{n+2}(y_1) - J_{n+2}(0) + y_1 J_{n+1}(0), \tag{A 2}$$

$$\int_{y_1}^{\infty} s J_n(s - y_1)\,\mathrm{d}s = J_{n+2}(0) + y_1 J_{n+1}(0), \tag{A 3}$$

where $J_n(0)$ (n is integer) is given by

$$J_n(0) = \begin{cases} \sqrt{\pi}/2 & n = 0 \\ (m-1)!/2 & n = 2m-1 \\ 1\cdot 3\cdots(2m-1)\sqrt{\pi}/2^{m+1} & n = 2m \end{cases} \quad (m = 1, 2, \ldots), \tag{A 4}$$

while $J_n(\infty) = 0$ for all n.

Consequently, we have

$$I_n * 1 = \int_0^\infty J_n(|y_1 - s|)\,\mathrm{d}s = 2J_{n+1}(0) - J_{n+1}(y_1), \tag{A 5}$$

for example, $I_{-1} * 1 = \sqrt{\pi} - J_0(y_1)$ and $I_1 * 1 = \sqrt{\pi}/2 - J_2(y_1)$, and

$$I_n * y_1 = \int_0^\infty s J_n(|y_1 - s|)\,\mathrm{d}s = 2y_1 J_{n+1}(0) + J_{n+2}(y_1), \tag{A 6}$$

for example, $I_{-1} * y_1 = \sqrt{\pi}\, y_1 + J_1(y_1)$, $I_1 * y_1 = \sqrt{\pi}\, y_1/2 + J_3(y_1)$ and $I_3 * y_1 = 3\sqrt{\pi}\, y_1/4 + J_5(y_1)$.

There are two useful two-fold integrals:

$$\int_0^{y_1}\int_0^{y_1'} g(s)J_0(y_1' - s)\,\mathrm{d}s\,\mathrm{d}y_1' = -\int_0^{y_1} g(s)J_1(y_1 - s)\,\mathrm{d}s + J_1(0)\int_0^{y_1} g(s)\,\mathrm{d}s, \tag{A 7}$$

$$\int_0^{y_1}\int_{y_1'}^{\infty} g(s)J_0(s - y_1')\,\mathrm{d}s\,\mathrm{d}y_1' = \int_{y_1}^{\infty} g(s)J_1(s - y_1)\mathrm{d}s + J_1(0)\int_0^{y_1} g(s)\,\mathrm{d}s. \tag{A 8}$$

Appendix B. Numerical solution of the integral equations system (3.47), (3.51) and (3.52)

The Wiener–Hopf method is generally used to solve the Fredholm-type integral equations with semi-infinite integration limits (Polyanin & Manzhirov 1998). Standard albeit involved solution procedures are required. The disadvantage of this method is that it is difficult to be extended to integral equations consisting of two or more unknown variables, such as (3.47), (3.51) and (3.52). Consequently an approximate method is used instead to obtain numerical results, with reasonable accuracy.

We recognize that the integral kernels in these equations consist of the special functions $J_n(x)$, which is a monotonic function decreasing rapidly with increasing x, and that the unknown variables are all bounded functions in $[0, \infty)$. Since our purpose is to find the solutions of (3.47), (3.51) and (3.52) at $y_1 = 0$, we can use $\int_0^L J_n(|y_1 - s|)f(s)\,\mathrm{d}s$ to replace $\int_0^\infty J_n(|y_1 - s|)f(s)\,\mathrm{d}s$ in the integral equations with satisfactory accuracy as long as L is large enough. Consequently, we transform the singular integral equations defined within a semi-infinite domain into regular ones defined within the finite length domain.

Following Cercignani & Daneri (1963) and using (3.47) as an example to explain our numerical method, we have the discrete integral equations with constant step size $\delta = L/N$, as follows

$$\begin{aligned} g_\nu\,[(n-1/2)\delta] = {} & \sum_{m=1}^{N}\left\{\int_{(m-1)\delta}^{m\delta} L_1[(n-1/2)\delta, s]\,\mathrm{d}s\right\} g_\nu[(m-1/2)\delta] \\ & + \sum_{m=1}^{N}\left\{\int_{(m-1)\delta}^{m\delta} M_1[(n-1/2)\delta, s]\,\mathrm{d}s\right\} g_\theta[(m-1/2)\delta] \\ & - Y_1[(n-1/2)\delta], \quad n = 1, 2, \ldots, N, \end{aligned} \tag{B 1}$$

$$\begin{aligned} g_\theta\,[(n-1/2)\delta] = {} & \sum_{m=1}^{N}\left\{\int_{(m-1)\delta}^{m\delta} L_2[(n-1/2)\delta, s]\;\mathrm{d}s\right\} g_\nu[(m-1/2)\delta] \\ & + \sum_{m=1}^{N}\left\{\int_{(m-1)\delta}^{m\delta} M_2[(n-1/2)\delta, s]\;\mathrm{d}s\right\} g_\theta[(m-1/2)\delta] \\ & - Y_2[(n-1/2)\delta], \quad n = 1, 2, \ldots, N, \end{aligned} \tag{B 2}$$

where we have used $L_1(y_1, s)$, $L_2(y_1, s)$, $M_1(y_1, s)$ and $M_1(y_1, s)$ to represent the integral kernels in the corresponding operators. The terms in the brackets in (B 1) and (B 2) consist of the integral (n is integer):

$$\int_{(j-1)\delta}^{j\delta} J_n[|(i-1/2)\delta - s|]\,\mathrm{d}s = \begin{cases} 2J_{n+1}(0) - 2J_{n+1}(\delta/2), \ i = j, \\ \\ J_{n+1}[|i-j|\delta - \delta/2] - J_{n+1}[|i-j|\delta + \delta/2], \ i \neq j. \end{cases} \tag{B 3}$$

Consequently, we have the following simultaneous matrix equations

$$\boldsymbol{g}_\nu = \boldsymbol{L}_1 \boldsymbol{g}_\nu + \boldsymbol{M}_1 \boldsymbol{g}_\theta - \boldsymbol{Y}_1, \tag{B 4}$$

$$\boldsymbol{g}_\theta = \boldsymbol{L}_2 \boldsymbol{g}_\nu + \boldsymbol{M}_2 \boldsymbol{g}_\theta - \boldsymbol{Y}_2, \tag{B 5}$$

in which the unknown vector $\boldsymbol{g}_\nu$ and the constant vector $\boldsymbol{Y}_1$ are respectively given by

$$\boldsymbol{g}_\nu = \left[g_\nu\left(\frac{1}{2}\delta\right), g_\nu\left(\frac{3}{2}\delta\right), g_\nu\left(\frac{5}{2}\delta\right), \dots g_\nu\left(n\delta - \frac{1}{2}\delta\right)\right]^T, \tag{B 6}$$

$$\boldsymbol{Y}_1 = \left[Y_1\left(\frac{1}{2}\delta\right), Y_1\left(\frac{3}{2}\delta\right), Y_1\left(\frac{5}{2}\delta\right), \dots Y_1\left(n\delta - \frac{1}{2}\delta\right)\right]^T, \tag{B 7}$$

where $\boldsymbol{L}_1$ is an $N \times N$ constant matrix consisting of elements like $\int_{(m-1)\delta}^{m\delta} L_1[(n - 1/2)\delta, s]\mathrm{d}s$. Similarly, we have other vectors $\boldsymbol{g}_\theta$ and $\boldsymbol{Y}_2$ as well as the constant matrices $\boldsymbol{L}_2$, $\boldsymbol{M}_1$ and $\boldsymbol{M}_2$. Solving (B 4) and (B 5), we obtain the solutions for g_ν and g_ν in terms of their discrete points in $[0, L]$. It is found that very coarse mesh grids with $L \geqslant 10$ and $\delta \leqslant 0.05$ are good enough to yield satisfactory numerical results. The following are the final numerical results of the unknown variables at $y_1 = 0$:

$$g_\nu(0) = 0.39, \ g_\tau(0) = -0.77. \tag{B 8}$$

Similarly, for (3.51) and (3.52), we have

$$h_\nu(0) = 0.62, \ h_\theta(0) = 0.17; \tag{B 9}$$

and

$$\delta_i + \delta_j = 0.1 : q_\nu(0) = 0.634, \ q_\theta(0) = 0.129; \tag{B 10}$$

$$\delta_i + \delta_j = 0.5 : q_\nu(0) = 0.646, \ q_\theta(0) = 0.072; \tag{B 11}$$

$$\delta_i + \delta_j = 2.5 : q_\nu(0) = 0.655, \ q_\theta(0) = 0.028; \tag{B 12}$$

$$\delta_i + \delta_j = 12.5 : q_\nu(0) = 0.658, \ q_\theta(0) = 0.007. \tag{B 13}$$

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