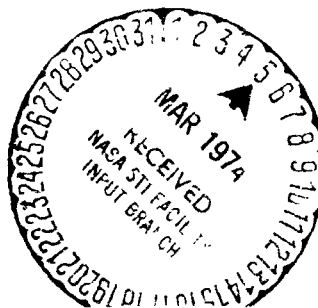NASA TECHNICAL MEMORANDUM

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WALL BOUNDARY EQUATIONS WITH SLIP

AND CATALYSIS FOR MULTICOMPONENT,

NONEQUILIBRIUM GAS FLOWS

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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16. Abstract

Boundary equations obtained for a low Reynolds number, high enthalpy gas flow in regions of velocity slip and temperature jump are presented. The formulation treats, through a first-order distribution function used to include multicomponent diffusion, a multicomponent gas mixture that may be in nonequilibrium with finite-rate catalytic recombination occurring on the wall. In the boundary equations, which are obtained for use in flow-field calculations applicable to low-density flow regimes, a simplified gas/wall interaction is assumed wherein individual atoms or molecules either reflect specularly off the wall or stick and are fully accommodated. Fluxes in terms of evaluated integrals over the distribution function and integrals necessary for determining fluxes are given.

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CONTENTS

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FIGURES

WALL BOUNDARY EQUATIONS WITH SLIP AND CATALYSIS

FOR MULTICOMPONENT, NONEQUILIBRIUM GAS FLOWS

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SUMMARY

Boundary equations are obtained for a low Reynolds number, high enthalpy gas flow where velocity slip and temperature jump are important. The formulation treats a multicomponent gas mixture that may be in nonequilibrium with finite-rate catalytic reactions occurring on the wall. A first-order distribution function is used to include multicomponent diffusion. A simplified gas/wall interaction is assumed where individual atoms or molecules either reflect specularly off the wall or stick and are fully accommodated. The boundary equations are obtained for use in flow-field calculations such as finite-difference time-dependent methods or other methods that are applicable to low-density flow regimes.

INTRODUCTION

The interaction between a high enthalpy, low Reynolds number gas flow and a relatively cold surface can be significantly influenced by the characteristics of the surface. This interaction establishes boundary properties for the gas flow and can influence the overall flow field. Surface characteristics are important, for example, in the high altitude, low Reynolds number flight regime for prediction of Space Shuttle orbiter entry heating and for interpreting data obtained in ground tests of spacecraft entry thermal protection systems.

In low Reynolds number hypersonic flows such as at high altitudes or in low-density arc-heated wind tunnels, the boundary condition assumptions that are adequate for the higher Reynolds number regimes may no longer be adequate for describing the flow parameters at a wall (solid boundary). Specifically, the density at the wall is sufficiently low that the velocity and temperature of the wall are no longer the same as those of the gas immediately adjacent to the wall. These phenomena are referred to as velocity slip and temperature jump.

Figure 1 is a plot of stagnation pressure as a function of total enthalpy showing typical entry trajectories for the Space Shuttle and Apollo vehicles. Regions where arc-heated wind tunnels typically operate for simulating entry heating and the approximate region in which slip effects become important are also shown. It can be seen that there is a region of the shuttle trajectory in which slip may have some significant effect on the boundary conditions. Moreover, there is a large region of a typical arc-tunnel operating map for which slip is significant.

For a real, chemically reacting gas, it is necessary to formulate a boundary description in which the pressure and species concentration also "jump" at the wall because of rarefaction effects and chemical reactions on the surface. This report is concerned specifically with catalytic recombination reactions on the surface.

As the density decreases, the continuum flow equations that adequately describe higher density flow are no longer adequate close to the wall because the mean free path becomes long compared to characteristic lengths associated with significant changes in macroscopic flow properties. The flow in a region next to the wall having a thickness on the order of a mean free path (the Knudsen layer) cannot be described by the Navier-Stokes description (ref. 1). Gradients near the wall cause the velocity distribution function to deviate significantly from equilibrium. Rigorously, one should calculate the flow using the Boltzmann equation because there are not sufficient collisions between the gas molecules for the Navier-Stokes approximation to be valid. The solution to the Boltzmann equation in the Knudsen layer with suitable kinetic boundary conditions at the wall must then be matched to the solution of the Navier-Stokes equations in the bulk flow. The laws governing the interaction of the gas with the surface influence the boundary conditions and must be taken into account. This procedure can be done simply through the use of accommodation coefficients.

Without actually solving the Boltzmann equation in the Knudsen layer, it is possible to find an approximate Navier-Stokes solution to the flow in the Knudsen layer using suitable slip conditions (refs. 2 and 3). Patterson (ref. 2) obtained a Navier-Stokes type solution to the Boltzmann equation that was of the form of the equilibrium velocity distribution function times a power series in the three-dimensional velocity space.

$$f(\vec{v}) = f^{o}(\vec{v})\left(1 + a_i v_i + \frac{1}{2} a_{ij} v_i v_j + \frac{1}{6} a_{ijk} v_i v_j v_k\right) \qquad (1)$$

where $f(\vec{v})$ is the velocity distribution function; $f^{o}(\vec{v})$ is the equilibrium velocity distribution function; a_i, a_{ij}, and a_{ijk} are

coefficients of the distribution function; and v_i, v_j, and v_k are velocity vector components. (Summation convention is used here.) Patterson obtained the coefficients in terms of gradients of the macroscopic variables. To obtain the slip relations, he assumed a fully accommodating surface (diffuse reflections) and equated the net fluxes of mass, momentum, and energy to the difference between the incident and reflected fluxes, respectively. Shidlovskiy (ref. 3) performed essentially the same type of calculation except that he allowed for a non-fully accommodating surface (specular and diffuse reflection). In both of these treatments, a single-species gas was assumed.

Flow-field and boundary-layer calculations have been made that incorporate limited combinations of the boundary conditions considered in this report. Treatments of slip effects can be found in references 1 to 3. Davis (ref. 4) included first-order slip effects in temperature and velocity for his reacting binary mixture flow past a blunt body. This included calculations for catalycity limits of zero and infinity. Inger (ref. 5) included a variable catalytic wall-boundary condition for stagnation point, nonequilibrium flow of a binary gas past a sphere. He assumed the following: (1) a constant Prandtl number, Schmidt number, density viscosity product, and specific heat across the shock layer; (2) negligible thermal diffusion; (3) a thin shock layer model; and (4) no slip at the wall, but slip at the shock wave. Blottner (ref. 6) used a finite-difference method to investigate the viscous shock layer at the stagnation point of a blunt body. An air gas model was used with finite reaction rates and transport properties based on Yun and Mason (ref. 7) and Yos (ref. 8). Blottner did not consider slip, and he assumed a fully catalytic body. Blottner reviewed the literature relative to blunt-body flow problems (ref. 6).

No one has included the effects of slip, multicomponent diffusion, and wall catalycity in a single-flow-field problem. In this report, boundary relations that incorporate all of these effects for application to flow-field calculations are derived. Boundary conditions for the temperature, velocity, pressure, and species concentrations are obtained for a multicomponent mixture at a wall of arbitrary catalycity. To be general enough for low-density continuum flows, slip is also considered herein.

SYMBOLS

$\vec{A}_i, \overleftrightarrow{B}_i, \vec{C}_i^{(j)}$	coefficients of the distribution function for ith species
a_i, a_{ij}, a_{ijk}	coefficients of the distribution function

4

$a_{i0}, a_{i1}, b_{i0}, c_{i0}{}^{(j)}$	distribution function coefficients defined in reference 9 for ith species
b	impact parameter
c_i	mass fraction of species i
D_{ij}	diffusion coefficient
$D_i{}^T$	thermal diffusion coefficient
$\vec{d}_j$	diffusion vector of jth species
E	net energy flux from translational energy
$\mathcal{E}$	energy flux from translational energy
F	net general flux
$\mathcal{F}$	general flux
f_i	distribution function of ith species
f_i^o	equilibrium distribution function of ith species
g	initial relative speed during a collision
$I, \mathcal{I}$	component terms in integration over distribution function
k	Boltzmann constant
k_w	wall catalytic rate constant
ℓ	order of surface recombination reaction
M	net mass flux
$\mathcal{M}$	mass flux
m_i	mass of ith species
n	number density

P	net momentum flux
p	momentum flux
p	pressure
$Q^{(\ell)}$	collision cross section
$Q_{ij}, R_i^{(h)}$	factors in the Sonine polynomial expansion pertaining to mass fluxes or species defined in appendix A
$\tilde{Q}_{ij}^{00}, \tilde{Q}_{ij}^{01}, \tilde{Q}_{ij}^{10}, \tilde{Q}_{ij}^{11}, R_{im}$	factors in the Sonine polynomial expansion pertaining to temperature gradient defined in appendix A
Q_{ij}^{00}, R_{i0}	factors in the Sonine polynomial expansion pertaining to velocity gradient defined in appendix A
r	separation distance of atoms during collision
r_m	distance of closest approach
T	temperature
t	time
$\overleftrightarrow{U}$	unit tensor
$\vec{V}_i$	thermal velocity
$\overleftrightarrow{\vec{V}}_i$	diffusion velocity
$\vec{v}$	velocity
$\vec{v}_0$	bulk velocity
$\vec{W}$	dimensionless velocity $= \sqrt{\dfrac{m_i}{2kT}}\, \vec{V}$

6

$\dot{w}_i$	rate of mass production in volume eleme˙ of ith species
α	energy accommodation coefficient
γ	dimensionless relative velocity in collision, used in appendix A
γ	recombination coefficient
δ_{ij}	Kronecker delta
η	viscosity
θ	fraction of incident atoms that are diffusely reflected
θ'	fraction of incident atoms that stick
μ	reduced mass
ρ	density
Φ	perturbation part of distribution function
$\phi(r)$	interaction potential
$\phi(\vec{V})$	a general property
$\chi(g,b)$	collision deflection angle
$\Omega_{ij}^{(s,\ell)}$	collision integrals

Affixes:

h,i,j	species indexes
s	property at edge of Knudsen layer
w	wall property

Subscripts:

a	atomic species
i,j,k	vector component indexes
x,y,z	component directions
y	normal component
$\|$,x,z	tangential components

Superscripts:

q,ℓ,m,n	exponents used in flux integrals defined in equation (C1)
s,ℓ	indexes appearing in collision integral
↓	incident flux
↑	specularly reflected flux

ANALYSIS

The approach to the slip boundary condition problem follows closely that of Shidlovskiy (ref. 3), although additional factors are included herein to account for wall reactions. The slip conditions are taken across the Knudsen layer, which is on the order of one mean free path in thickness. In figure 2, the Knudsen layer and the jump in temperature T are shown. The jump is treated as discontinuous across an arbitrarily thin Knudsen layer, and no account is taken of variations of the velocity distribution through the Knudsen layer as would be required by the more rigorous approach of Kogan (ref. 1). It is assumed here that the distribution function near the wall can be described to first-order accuracy by the so-called Navier-Stokes approximation as used by Shidlovskiy. The use in this report of a Chapman-Enskog type distribution function for a multicomponent mixture obtained by the variational method of Hirschfelder, Curtiss, and Bird (ref. 9), however, is a deviation from the procedures of Shidlovskiy. The advantage of this usage lies in the fact that the Chapman-Enskog distribution function accounts for diffusion.

The interaction model does not distinguish between energy accommodation α and momentum accommodation θ. For many materials, α and θ

8

are nearly equal and have values close to unity; therefore, only a number accommodation is considered. By this, it is assumed that the gas atoms (molecules) interact with the wall as follows: each atom either reflects specularly (is not accommodated at all) or sticks to the wall (is fully accommodated). The fraction that sticks is called θ'. Of those atoms that stick, a certain number react with other gas atoms on the wall (usually by recombination). The fraction of incident atoms that reacts (recombines) is called γ. Those that do not react leave the wall fully accommodated to the wall temperature. This process will be called diffuse reflection in this report. The fraction of incident atoms that is diffusely reflected is θ. This interaction model is considered to be adequate because the data required for a more detailed model are very limited. The change in internal energy of the reflecting molecules, such as vibrational and electronic excitation, is neglected.

The Distribution Functions

As stated previously, the velocity distribution functions used here are those for multicomponent mixtures

$$f_i(\vec{V}) = f_i^o(\vec{V})\left[1 + \Phi_i(\vec{V})\right] \qquad (2)$$

where

$$\Phi_i(\vec{V}) = -\vec{A}_i \cdot \ln T - \overset{\leftrightarrow}{B}_i : \nabla \vec{v}_0 + n\sum_j \vec{C}_i^{(j)} \cdot \vec{d}_j \qquad (3)$$

The Maxwellian velocity distribution for the ith species is $f_i^o(\vec{V})$. The coefficients $\vec{A}_i$, $\overset{\leftrightarrow}{B}_i$, and $\vec{C}_i^{(j)}$ are functions of the dimensionless velocity $\vec{W}_i = \sqrt{m_i/(2kT)}\vec{V}_i$ and may be defined as

$$\vec{A}_i = \left[a_{i0} + a_{i1}\left(\frac{5}{2} - W_i^2\right)\right]\vec{W}_i \qquad (4)$$

$$\overset{\leftrightarrow}{B}_i = b_{i0}\left(\vec{W}_i\vec{W}_i - \frac{1}{3}W_i^2\overset{\leftrightarrow}{U}\right) \qquad (5)$$

$$\vec{C}_i^{(1)} = c_{i0}^{(j)} \vec{W}_i \qquad (6)$$

where a_{i0}, a_{i1}, b_{i0}, and $c_{i0}^{(j)}$ are constants determined from the Hirschfelder, Curtiss, and Bird (ref. 9) variation problem in the first approximation for a mixture and $\overleftrightarrow{U}$ is the unit tensor. These constants are functions of the collision integrals and are related to the transport properties. See appendix A for the explicit form of these constants.

The vector $\vec{d}_j$ is related to the diffusion velocity of the jth species in the mixture and is defined as

$$\vec{d}_j = \nabla\left(\frac{n_j}{n}\right) + \left(\frac{n_j}{n} - \frac{n_j m_j}{\rho}\right)\nabla \ln p \qquad (7)$$

where n_j and m_j are, respectively, the number density and mass of the jth species, n is the total number density $n = \sum_j n_j$, ρ is the total mass density $\rho = \sum_j n_j m_j$, and p is the total pressure $p = \sum_j p_j$.

The total mass averaged velocity $\vec{v}_0 = 1/\rho \sum_j n_j m_j \vec{v}_j$ where $\vec{v}_j$ is the total velocity $\vec{v}_j = \vec{v}_0 + \vec{V}_j$ of the jth species averaged over the distribution function and $\vec{V}_j$ is the thermal velocity.

The Balance Equations

To obtain the slip relations at a wall, it is necessary to consider the balance of normal fluxes of mass, momentum, and energy at the wall for each species. The net flux equals the difference between the incident flux and the outgoing flux at the wall. In the following equations, the net flux will be denoted by an uppercase block letter and the incident and outgoing fluxes by uppercase script letters. An upward arrow denotes flux caused by specularly reflected particles, and a downward arrow denotes incident fluxes. A superscript w denotes outward fluxes of wall-accommodated particles.

10

Consider a property $\phi(\vec{V})$ such as mass, momentum, and energy, and the normal flux of that property across the surface

$$F \equiv \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} v_y \phi(\vec{V}) f_s(\vec{V})\ d^3v \tag{8}$$

is the net flux of $\phi(\vec{V})$. A Cartesian coordinate system is used, and the direction normal to the surface is y. The distribution function $f_s(\vec{V})$ is that just outside the wall on the outer surface of the Knudsen layer.

$$F^{\downarrow} \equiv \int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{0}\int\limits_{-\infty}^{\infty} v_y \phi(\vec{V}) f_s^{\downarrow}(\vec{V})\ d^3v \tag{9}$$

is the incident flux.

$$F^{\uparrow} \equiv \int\limits_{-\infty}^{\infty}\int\limits_{0}^{\infty}\int\limits_{-\infty}^{\infty} v_y \phi(\vec{V}) f_s^{\uparrow}(\vec{V})\ d^3v \tag{10}$$

is proportional to the specularly reflected flux.

$$F^{W} \equiv \int\limits_{-\infty}^{\infty}\int\limits_{0}^{\infty}\int\limits_{-\infty}^{\infty} v_y \phi(\vec{V}) f_w(\vec{V})\ d^3v \tag{11}$$

is proportional to the diffusely reflected flux. These fluxes are shown schematically in figure 2. The distribution function $f_w(\vec{V})$ is that of a gas at equilibrium with the wall temperature. The distribution function $f_s^{\uparrow}(V_x, V_y, V_z) = f_s^{\downarrow}(V_x, -V_y, V_z)$ because the sign of V_y

changes upon reflection. If $\phi(\vec{V})$ is the mass, then the normal mass-flux balance at the wall is: net mass flux equals incident mass flux, leaving mass flux. For atomic species

$$M_i = M_i^\downarrow + \left(1 - \theta_i'\right)M_i^\uparrow + \left(\theta_i' - \gamma\right)M_i^W \tag{12}$$

Because it is assumed atoms are being consumed at the wall by catalytic recombination, the net mass flux $M_i \neq 0$. The first term on the right is the mass flux of incident particles, the second term is the flux of particles specularly reflected, and the last term is the mass flux of particles diffusely reflected (those that stick minus those that recombine).

Relations similar to equation (12) for the fluxes normal to the surface of the normal component of momentum, the tangential component of momentum, and the energy, respectively, are obtained as follows.

$$\sum_i P_{iy} = \sum_i P_{iy}^\downarrow + \sum_i \left(1 - \theta_i'\right)P_{iy}^\uparrow + \sum_i \left(\theta_i' - \gamma\right)P_{iy}^W \tag{13}$$

$$\sum_i P_{i||} = \sum_i P_{i||}^\downarrow + \sum_i \left(1 - \theta_i'\right)P_{i||}^\uparrow + \sum_i \left(\theta_i' - \gamma\right)P_{i||}^W \tag{14}$$

$$\sum_i E_i = \sum_i E_i^\downarrow + \sum_i \left(1 - \theta_i'\right)E_i^\uparrow + \sum_i \left(\theta_i' - \gamma\right)E_i^W = E \tag{15}$$

By evaluating the integrals represented by equations (9), (10), and (11), it can be shown that $M_i^\downarrow = -M_i^\uparrow$, $P_{i||}^\uparrow = -P_{i||}^\downarrow$, $E_i^\uparrow = -E_i^\downarrow$, $P_{i||}^W = 0$, and $P_{iy}^\downarrow = P_{iy}^\uparrow$. Equations (12) to (15) then can be reduced to

$$M_i = \theta_i' M_i^\downarrow + \left(\theta_i' - \gamma\right)M_i^W \tag{16}$$

$$\sum_i P_{iy} = \sum_i \left(2 - \theta_i'\right) P_{iy}^{\downarrow} + \sum_i \left(\theta_i' - \gamma\right) P_{iy}^{W} = p^s \qquad (17)$$

$$\sum_i P_{i||} = \sum_i \theta_i' P_{i||}^{\downarrow} \qquad (18)$$

$$\sum_i E_i = \sum_i \theta_i' E_i^{\downarrow} + \sum_i \left(\theta_i' - \gamma\right) E_i^{W} = E \qquad (19)$$

The flux balance equations can be expressed in terms of the flux integrals to obtain the following, in which k is the Boltzmann constant.

Mass of species i:

$$\frac{m_i n_i^{\,s}}{\pi^{\frac{3}{2}}} \left(\frac{2kT}{m_i}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y e^{-W^2}\left[1 + \phi_s(\vec{W})\right] d^3W$$

$$= \theta_i' \frac{m_i n_i^{\,s}}{\pi^{\frac{3}{2}}} \left(\frac{2kT_s}{m_i}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} W_y e^{-W^2}\left[1 + \phi_s(\vec{W})\right] d^3W$$

$$+ \left(\theta_i' - \gamma\right)\frac{m_i n_i^{\,W}}{\pi^{\frac{3}{2}}} \left(\frac{2kT_w}{m_i}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{-\infty}^{\infty} W_y e^{-W^2} d^3W$$

$$(20)$$

Normal momentum:

$$\sum_i m_i n_i {}^s \left(\frac{2kT_s}{m_i}\right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y{}^2 e^{-W^2}\left[1 + \phi_s(\vec{W})\right] \, d^3W$$

$$= \sum_i \left(2 - \theta_i'\right) m_i n_i {}^s \left(\frac{2kT}{m_i}\right) \int_{-\infty}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} W_y{}^2 e^{-W^2}\left[1 + \phi_s(\vec{W})\right] \, d^3W$$

$$+ \sum_i \left(\theta_i' - \gamma\right) m_i n_i {}^w \left(\frac{2kT_w}{m_i}\right) \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{-\infty}^{\infty} W_y{}^2 e^{-W^2} \, d^3W \qquad (21)$$

Tangential momentums:

$$\sum_i m_i n_i {}^s \left(\frac{2kT_s}{m_i}\right) \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y \left(W_{||} + w_{0||}\right) e^{-W^2}\left[1 + \phi_s(\vec{W})\right] \, d^3W$$

$$= \theta_i' \sum_i m_i n_i {}^s \left(\frac{2kT_s}{m_i}\right) \int_{-\infty}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} W_y \left(W_{||} + w_{0||}\right) e^{-W^2}\left[1 + \phi_s(\vec{W})\right] \, d^3W$$

$$(22)$$

14

Energy:

$$\sum_i \frac{m_i n_i^s}{2}\left(\frac{2kT_s}{m_i}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y e^{-W^2}\left[1 + \phi_s(\vec{W})\right]\left[\left(W_x + w_{0x}\right)^2 + W_y^2\right.$$

$$+ \left.\left(W_z + w_{0z}\right)^2\right] d^3W = \sum_i \theta_i' \frac{m_i n_i^s}{2}\left(\frac{2kT_s}{m_i}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty}\int_{-\infty}^{0}\int_{-\infty}^{\infty} W_y e^{-W^2}\left[1 + \phi_s(\vec{W})\right]$$

$$\cdot \left[\left(W_x + w_{0x}\right)^2 + W_y^2 + \left(W_z + w_{0z}\right)^2\right] d^3W + \sum_i \left(\theta_i' - \gamma\right)\frac{m_i n_i^w}{2}\left(\frac{2kT_w}{m_i}\right)^{\frac{3}{2}}$$

$$\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{-\infty}^{\infty} W_y W^2 e^{-W^2} d^3W$$

$$(23)$$

The wall number density n_i^w is defined following the convention of Shidlovskiy (ref. 3) such that the factor $(\theta' - \gamma)$ appears in the last terms of the preceding equations.

The Slip Equations

When the integrals in equations (20) to (23) are evaluated and after the terms have been rearranged, the following relations for the slip quantities are obtained. All accommodation coefficients θ_i' are equal to θ'.

Concentration slip (single species):

$$\frac{n_i^w}{n_i^s}\left(\frac{T_w}{T_s}\right)^{\frac{1}{2}} = \frac{\theta_i'}{\theta_i' - \gamma}\left[1 + \frac{b_{i0}}{6}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right)\right]_s$$

$$- \frac{\sqrt{\pi}}{2}\left(\frac{2 - \theta_i'}{\theta_i' - \gamma}\right)\left[\frac{\partial \ln T}{\partial y} a_{i0} - n\sum_j c_i^{(j)} d_{jy}\right]_s \qquad (24)$$

Pressure slip:

$$p_s = \frac{\frac{\theta' n}{3}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right) + k\frac{\partial T}{\partial y}\frac{2 - \theta'}{\sqrt{\pi}}\sum\left(a_{i0} + a_{i1}\right)n_i + \theta' p^w - \sum \gamma p_i^w}{\frac{\theta'}{2} + \frac{1}{\sqrt{\pi}}\sum_i n_i \sum_j c_{i0}^{(j)} d_{jy}}$$

$$(25)$$

The viscosity $\eta = \frac{1}{2} kT \sum_i n_i b_{i0}.$

Velocity slip:

$$v_{0x} = \frac{1}{\sum_i\left(\frac{m_i}{2kT_s}\right)^{\frac{1}{2}} p_i^s}\left\{\sqrt{\pi}\frac{2 - \theta'}{2\theta'}\eta\left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x}\right)_s\right.$$

$$\left. + \sum_i \frac{p_i^s}{2}\left[\frac{\partial \ln T}{\partial x}\left(a_{i0} - a_{i1}\right) - n\sum_j c_{i0}^{(j)} d_{jx}\right]_s\right\}$$

$$(26)$$

$$v_{Oz} = \cfrac{1}{\displaystyle\sum_i \left(\frac{m_i}{2kT_s}\right)^{\frac{1}{2}} p_i^{\ s}} \left\{ \sqrt{\pi}\ \frac{2-\theta'}{2\theta'}\ \eta\left(\frac{\partial v_{Ox}}{\partial y} + \frac{\partial v_{Oy}}{\partial x}\right)_s \right.$$

$$\left. + \sum_i \frac{p_i^{\ s}}{2}\left[\frac{\partial \ln T}{\partial x}\left(a_{i0} - a_{i1}\right) - n\sum_j c_{ic}^{\ (j)} d_{jz}\right]_s \right\}$$

<div align="right">(27)</div>

Temperature slip:

$$\left(2kT_s\right)^{\frac{3}{2}} = \cfrac{-2\sqrt{\pi}\left(\dfrac{2-\theta'}{2\theta'}\right)\vec{E}\cdot\hat{n} + \left(2kT_w\right)^{\frac{3}{2}} \displaystyle\sum_i \left(\dfrac{\theta_i' - \gamma}{\theta'}\right)\dfrac{n_i^{\ w}}{\sqrt{m_i}}}{\displaystyle\sum_i \dfrac{n_i^{\ s}}{\sqrt{m_i}} + \dfrac{1}{4}\sum_i \dfrac{1}{\sqrt{m_i}}\ n_i b_{i0}\left(\dfrac{\partial v_{Ox}}{\partial x} + \dfrac{\partial v_{Oz}}{\partial z} - 2\dfrac{\partial v_{Oy}}{\partial y}\right)}$$

<div align="right">(28)</div>

The net energy flux $\vec{E}$ is defined in appendix B. See appendix C for the integrals necessary for determining fluxes.

<div align="center">

The Relation Between Catalytic Recombination
Coefficient γ and Rate Constant k_w

</div>

Using the results obtained for concentration slip, an unresolved conflict in the literature may be resolved. The relation between the recombination coefficient γ and the rate constant k_w will be obtained. Two expressions have frequently appeared in the literature for first-order recombination. One is

$$k_w = \gamma\sqrt{\frac{kT_w}{2\pi m_i}}$$

<div align="right">(29)</div>

(e.g., refs. 10 and 11), and the other is

$$k_w = \frac{2\gamma}{2 - \gamma}\sqrt{\frac{kT_w}{2\pi m_i}} \tag{30}$$

(e.g., ref. 12). The purported difference (ref. 10) between these two expressions stems from inclusion of the diffusion velocity in the derivation of equation (30).

These relations can be obtained by using the flux and slip equations given previously in this report. The net mass flux of atoms to the surface is given by

$$M_i = M_i^{\downarrow}\gamma \tag{31}$$

This is equated to the expression defining the catalytic rate constant k_w. The rate of consumption of atoms at the wall from surface recombination is

$$M_i = \gamma M_i^{\downarrow} = k_w\left(n_i{}^w m_i\right)^{\ell} \tag{32}$$

where ℓ is the order of the surface recombination reaction. For a first-order reaction $\ell = 1$, therefore

$$M_i = -k_w n_i{}^w m_i \tag{33}$$

The minus sign indicates that the flux is in the direction opposite to the outward surface normal. Substituting the expression for the mass fluxes (eqs. (B1) and (B2)) into equation (31) obtains the relation

$$-\frac{1}{T}\frac{\partial T}{\partial y}\,a_{10} + n\sum_{j}c_{10}{}^{(j)}d_{jy} = -\left(\frac{2\gamma}{2 - \gamma}\right)\left[\frac{1}{\sqrt{\pi}} + \frac{b_{10}}{6\sqrt{\pi}}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_z}{\partial z} - 2\,\frac{\partial v_{0y}}{\partial y}\right)\right]$$

$$\tag{34}$$

18

Substituting the expression for the net mass flux (eq. (B1)) into equation (32), then

$$\frac{m_i n_i{}^s}{2}\left(\frac{2kT_s}{m_i}\right)^{\frac{1}{2}}\left[-\frac{1}{T}\frac{\partial T}{\partial y}a_{i0} + n\sum_j c_{i0}{}^{(j)}d_{jy}\right] = -k_w n_i{}^w m_i \qquad (35)$$

Substituting equations (34) and (35) and solving for k_w, then

$$k_w = \frac{n_i{}^s}{n_i{}^w}\left(\frac{kT_s}{2\pi m_i}\right)^{\frac{1}{2}}\frac{2\gamma}{2-\gamma}\left[1 + \frac{b_{i0}}{6}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right)\right]_s \qquad (36)$$

If slip and shear are neglected, then this expression reduces to equation (30). However, if the species density slip equation (eq. (24)) is substituted in equation (36), the expression

$$k_w = \gamma\left(\frac{kT_w}{2\pi m_i}\right)^{\frac{1}{2}} \qquad (37)$$

is obtained with no simplifying assumptions. It can be seen that by neglecting slip but including diffusion, one obtains the usual form for the relation between k_w and γ (eq. (30)) when diffusion is included. However, when both diffusion and slip are considered, then the simple form (eq. (29)) is obtained. Therefore, the latter form (eq. (29)) is to be preferred because it is more general. These expressions imply that k_w never approaches infinity; that is, there is an upper bound on the rate constant which is controlled by the thermal velocity at the wall. However, it is sometimes convenient to assume $k_w \to \infty$ to simplify the boundary equations for fully catalytic cases.

The Species Boundary Equations

To obtain the boundary condition for species concentrations at the wall, one may begin with the species continuity equation.

$$\frac{\partial \rho c_i}{\partial t} + \nabla \cdot \left[\rho c_i \left(\vec{v}_0 + \vec{\overline{V}}_i \right) \right] = \dot{w}_i \qquad (38)$$

where c_i is the mass fraction of the ith species, t is time, and $\dot{w}_i$ is the ith species volume production term. Although the problems to which the boundary conditions will be applied may be time dependent, it is assumed that the solutions to be reached are steady state. Then, the time-dependent terms of equation (38) go to zero. In addition, on the wall, the species volume production term $\dot{w}_i$ vanishes. Therefore, the term in brackets is a constant vector.

The normal (y) component is then the net species flux to the surface, which has been defined previously.

$$\rho c_i {}^s\overline{V}_y = \rho_w c_i {}^w k_w \qquad (39)$$

The normal bulk velocity v_{0y} is zero at the wall. The preceding is the same as the expression obtained in equation (35) for the net species flux to the wall.

$$-M_i = n_i {}^s m_i \overline{V}_y = \rho_w c_i {}^w k_w = n_i {}^w m_i k_w \qquad (40)$$

By expressing $c_{i0}{}^{(j)}$ in terms of the diffusion coefficient D_{ij} and in terms of the thermal diffusion coefficient $D_i{}^T$ (ref. 9, p. 479), then

$$\frac{\partial \ln T}{\partial y} D_i{}^T - \sum_j \frac{n^2 m_i m_i}{\rho} D_{ij} \left[\frac{\partial \left(\frac{n_i}{n} \right)}{\partial y} + \left(\frac{n_i}{n} - \frac{n_i m_i}{\rho} \right) \frac{\partial \ln p}{\partial y} \right] = k_w n_i {}^w m_i \qquad (41)$$

If all gradients except the concentration gradient are neglected and if a binary gas is assumed, then equation (41) reduces to

$$\frac{n^2 m_2 m_1}{\rho} D_{12} \frac{\partial\left(\frac{n_2}{n}\right)}{\partial y} = k_w n_1^w m_1 \tag{42}$$

In terms of the mass fraction of species 1 and neglecting slip, then

$$\rho D_{12} \frac{\partial c_1}{\partial y} = k_w c_1 \rho \tag{43}$$

where $c_1 = (n_1 m_1)/\rho$. The relation

$$\frac{\partial\left(\frac{n_2}{n}\right)}{\partial y} = -\frac{\partial\left(\frac{n_1}{n}\right)}{\partial y} \tag{44}$$

was used here. Equation (43) is the form of the atom boundary condition usually employed in flow-field calculations for binary mixtures. Equation (41) is the more general boundary condition to be used with slip, gradients in T and p, and multicomponent mixtures.

It may be more convenient to express equation (41) in terms of n_i^s and γ rather than n_i^w and k_w. Equation (31) is solved to obtain

$$n_i^s = \frac{-\frac{2-\gamma}{2\gamma}\left(\frac{2\pi m_i}{kT_s}\right)^{\frac{1}{2}} \frac{M_i}{m_i}}{1 + \frac{b_{10}}{6}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right)} \tag{45}$$

DISCUSSION

From the results obtained in the previous section, the wall boundary
conditions can be calculated for a multicomponent gas reacting catalyti-
cally on the surface, with slip and temperature jump. Equations (24)
to (28) and (45) form a coupled set of boundary conditions to be used
with flow-field calculations. However, i   y not be necessary to use
the pressure slip equation. A constant   rature boundary condition
is a natural stipulation for these equat..   nowever, for an adiabatic
wall boundary equation, the equation for   transfer at the wall must
be set equal to zero, thus adding an additional simultaneous equation to
the set. The wall temperature is then not given as a boundary condition.
Because the accommodation coefficient θ' is based on the rather crude
model that either a molecule is not accommodated or is fully accommodated,
and because for many gas/surface interactions the coefficients are nearly
equal to unity, it is convenient to assign the accommodation coefficient
the value unity. If the gas/solid interaction law is known with suffi-
cient accuracy, it would be more appropriate to reformulate the balance
equations taking these known accommodation coefficients into account.
It may be necessary to define individual momentum accommodation coeffi-
cients for both tangential and normal momentum accommodation. Rigorously,
the accommodation coefficients may be functions of velocity and should
be included in the integrals over the distribution functions.

To assess the importance of various terms in the general boundary
equations will require a systematic study in which the flow properties
and boundary conditions are varied. In many cases, the equations may
be simplified by choosing appropriate transport property approximations
or by neglecting various terms in the equations. Coupling of these
equations with a time-dependent technique such as that of C. P. Li
(ref. 13) would yield a good calculational procedure to investigate the
influence of the boundary conditions on the heat transfer and flow.
Such a procedure should also provide a set of more realistic boundary
conditions for low Reynolds number hypersonic flows.

22

CONCLUSIONS AND RECOMMENDATIONS

The equations describing the boundary conditions for a multicomponent, nonequilibrium gas reacting catalytically on a surface with temperature jump and slip are derived on the basis of a simplified gas/surface interaction model. These equations form a simultaneous set which must be coupled with a flow-field calculation. The equations may be used with various calculational techniques in an iterative fashion. They are convenient for a time-dependent numerical flow-field calculation technique where the time dependence of the boundary properties is not of interest. As the flow-field solution approaches steady state, the boundary properties approach those given by the boundary constraints determined by the flow and the boundary conditions

To assess the importance of various terms in those general boundary equations, a systematic study should be conducted in which the flow properties and boundary conditions are varied. Coupling of these equations with a time-dependent technique would yield a good calculational procedure to investigate the influence of the boundary conditions on the heat transfer and flow; it should also provide a set of more realistic boundary conditions for low Reynolds number hypersonic flows.

Lyndon B. Johnson Space Center
    National Aeronautics and Space Administration
        Houston, Texas, December 18, 1973
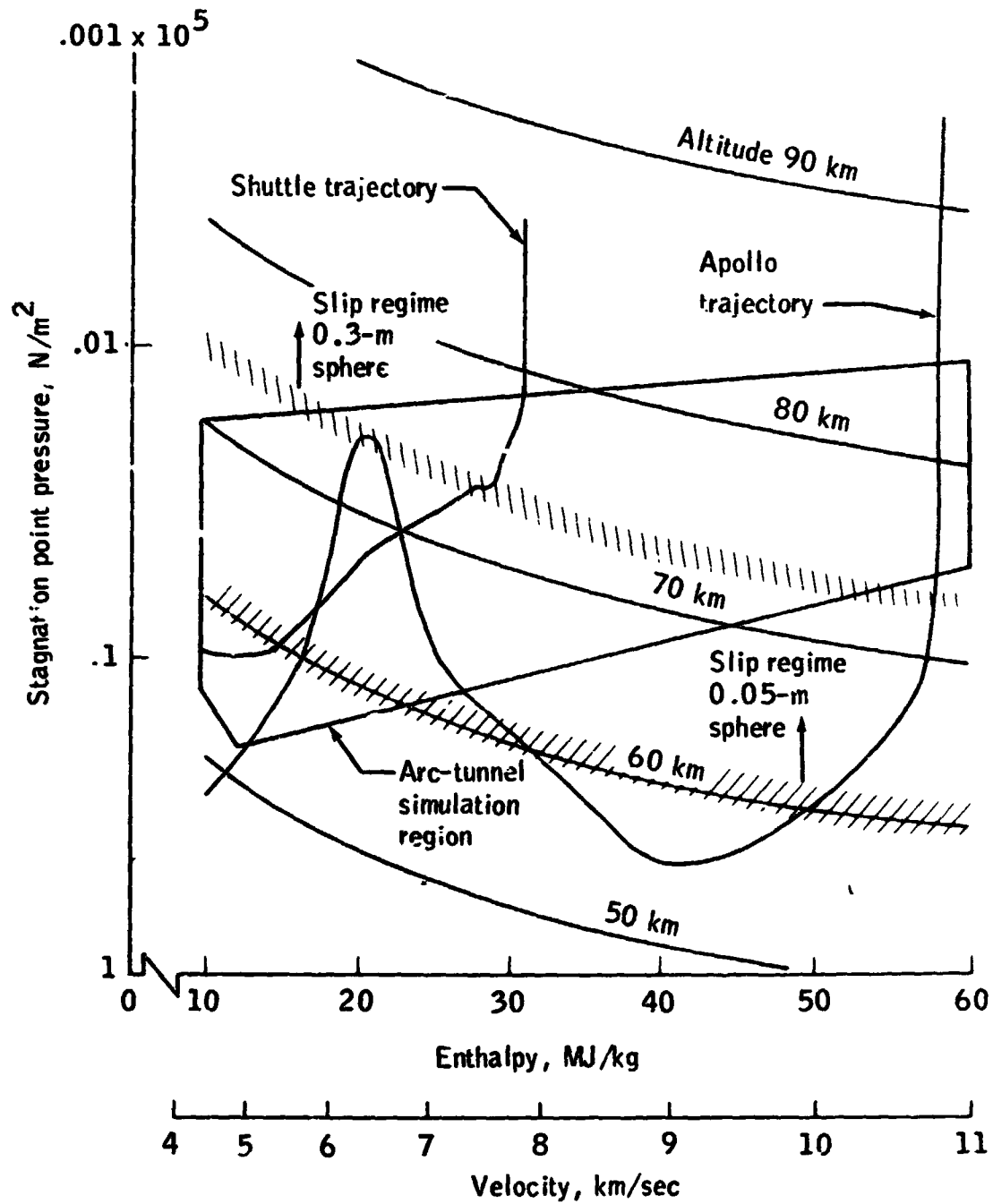   986-15-31-07-72

Figure 1.- Plot of stagnation pressure as a function of enthalpy showing Space Shuttle and Apollo trajectories with typical arc-jet operating ranges where slip flow begins for a 0.3-meter-radius and a 0.05-meter-radius sphere are denoted. The range is typical of arc-jet test models.

F^i = incident flux

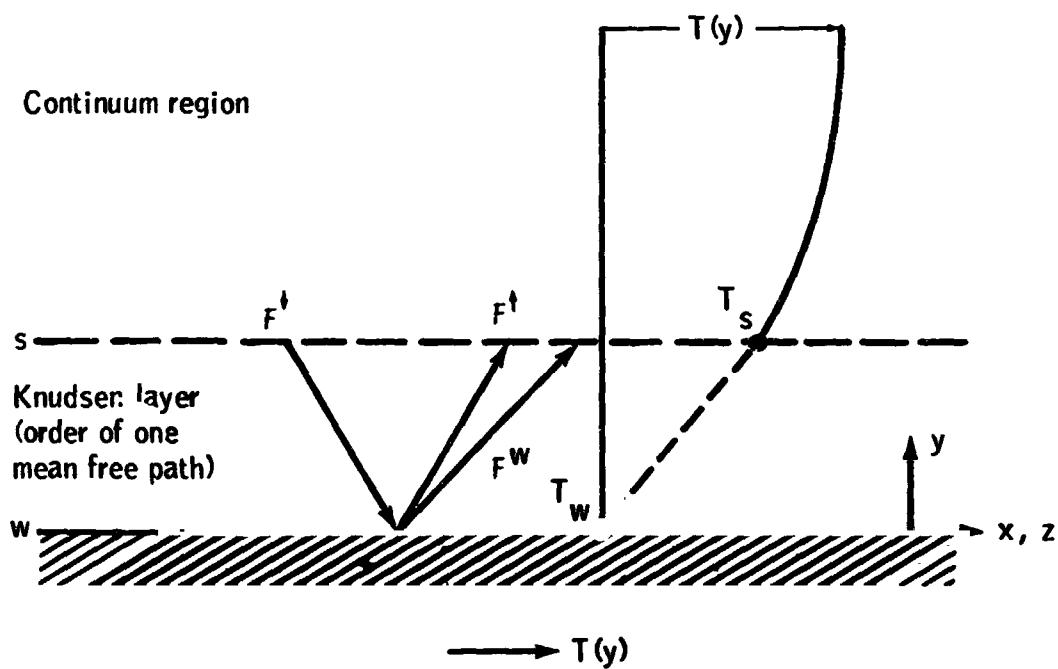F^i = specularly reflected flux

F^w = diffusely reflected flux

Figure 2.— Diagram of the Knudsen layer showing general fluxes and
coordinate axes. The temperature as a function of normal distance
is schematically overlayed.

APPENDIX A

CONSTANTS APPEARING IN THE DISTRIBUTION FUNCTION

The general velocity distribution function for one species of a multicomponent gas is given in Hirschfelder, Curtiss, and Bird (ref. 9) as

$$f_i(\vec{v}) = f_i^0(\vec{v})\left[1 + \phi_i(\vec{V})\right] \tag{A1}$$

In the section entitled "Analysis," it was shown that

$$\phi_i\left(\vec{V}_i\right) = -\left[a_{i0} + a_{i1}\left(\frac{5}{2} - W_i^2\right)\right]\vec{W}_i \cdot \nabla \ln T + n\sum_j c_{i0}^{(j)}\vec{W}_i \cdot \vec{d}_j$$
$$- b_{i0}\left(\vec{W}_i\vec{W}_i - \frac{1}{3}W_i^2\overset{\leftrightarrow}{U}\right) : \nabla\vec{v}_0 \tag{A2}$$

where $\vec{W}_i = \sqrt{m_i/(2kT)}\,\vec{V}_i$. This distribution function is a first-order approximation sometimes called the Navier-Stokes approximation. The coefficients a_{i0}, a_{i1}, b_{i0}, and c_{i0} are found by a variational technique in which they are solutions to sets of simultaneous equations (ref. 9). This appendix expresses the coefficients in terms of solutions to these sets of equations. These solutions are expressed in terms of the collision integrals $\Omega_{ij}^{(s,\ell)}$.

$$\Omega_{ij}^{(s,\ell)} = \sqrt{\frac{kT}{2\pi\mu}} \int_0^\infty e^{-\gamma^2}\gamma^{2s+3}Q^{(\ell)}(g)\,d\gamma \tag{A3}$$

where μ is the reduced mass of the colliding particles i and j, γ is the dimensionless relative velocity in collision ($\gamma^2 = \mu g^2/kT$), and g is the initial relative speed.

$$Q^{(\ell)} = 2\pi \int_0^\infty \left(1 - \cos^\ell \chi\right) b \; db \qquad (A4)$$

is the collision cross section at collision deflection angle

$$\chi(g,b) = \pi - 2b \int_{r_m}^\infty \left(1 - \frac{b^2}{r^2} - \frac{2\phi(r)}{\mu g^2}\right)^{-\frac{1}{2}} r^{-2} \; dr \qquad (A5)$$

where $\phi(r)$ is the interaction potential, b is the impact parameter, and r_m is the distance of closest approach. The collision integrals have been evaluated for a number of interacting species as a function of temperature and are available from several sources (e.g., refs. 8 and 14).

The solutions to the variational problem are from reference 9 where simultaneous equations are to be solved. The coefficients of the diffusion terms in the distribution function are

$$\sum_j Q_{ij} c_{j0}^{(h)} = -R_i^{(h)} \qquad (A6)$$

where

$$Q_{ij} = \sum_\ell \frac{n_\ell m_\ell}{(m_i + m_\ell)\sqrt{m_j}} \left[m_i n_i \left(\delta_{ij} - \delta_{j\ell}\right) - n_j m_j \left(1 - \delta_{i\ell}\right) \right] \Omega_{i\ell}^{(1,1)} \qquad (A7)$$

$$R_i^{(h)} = \left(1 - \delta_{ih}\right) \frac{3}{16} \sqrt{2kT} \qquad (A8)$$

The set of simultaneous equations for the coefficients of the temperature gradient terms in the distribution function is

$$\sum_j \sum_{m'=0}^{1} \tilde{Q}_{ij}^{mm'} a_{jm'} = R_{im} \qquad m', m \in \{0,1\} \qquad (A9)$$

where

$$\tilde{Q}_{ij}^{00} = 8 \sum_k \frac{n_k m}{\sqrt{m_i m_j}\left(m_i + m_k\right)}\left[n_i m_i \left(\delta_{ij} - \delta_{jk}\right) - n_j m_j \left(1 - \delta_{ik}\right)\right] \Omega_{ik}^{(1,1)} \qquad (A10)$$

$$\tilde{Q}_{ij}^{01} = -8\left(\frac{m_i}{m_j}\right)^{\frac{3}{2}} \sum_k \frac{n_i n_k m_k^2}{\left(m_i + m_k\right)^2}\left(\delta_{ij} - \delta_{kj}\right)\left[\Omega_{ik}^{(1,2)} - \frac{5}{2}\,\Omega_{ik}^{(1,1)}\right] \qquad (A11)$$

$$\tilde{Q}_{ij}^{10} = \frac{m_j}{m_i}\,\tilde{Q}_{ij}^{01} \qquad (A12)$$

$$\tilde{Q}_{ij}^{11} = 8\left(\frac{m_i}{m_j}\right)^{\frac{3}{2}} \sum_k \frac{n_i n_k m_k}{\left(m_i + m_k\right)^3}\left\{\left(\delta_{ij} - \delta_{ik}\right)\left[\frac{5}{4}\left(6m_j^2 + 5m_k^2\right)\Omega_{ik}^{(1,1)}\right.\right.$$

$$\left.\left. - 5m_k^2 \Omega_{ik}^{(1,2)} + m_k^2 \Omega_{ik}^{(1,3)}\right] + \left(\delta_{ij} + \delta_{jk}\right) 2m_j m_k \Omega_{ik}^{(2,2)}\right\} \qquad (A13)$$

and

$$R_{im} = -\delta_{mi} \frac{15}{4} n_i \sqrt{\frac{2kT}{m_i}} \qquad (A14)$$

The set of simultaneous equations for the coefficients of the velocity gradient terms in the distribution function is

$$\sum_j Q_{ij}^{00} b_{j0} = -R_{i0} \tag{A15}$$

where

$$Q_{ij}^{00} = \frac{16}{15} \frac{m_i}{m_j} \sum_k \frac{n_\ell m_\ell}{\left(m_i + m_\ell\right)^2} \left[5m_j \left(\delta_{ij} - \delta_{i\ell} \right) \Omega_{i\ell}^{(1,1)} \right.$$

$$\left. + \frac{3}{2} m_\ell \left(\delta_{ij} + \delta_{j\ell} \right) \Omega_{i\ell}^{(2,2)} \right] \tag{A16}$$

and

$$R_{i0} = -5n_i \tag{A17}$$

APPENDIX B

FLUXES IN TERMS OF EVALUATED INTEGRALS OVER

THE DISTRIBUTION FUNCTION

The fluxes of a property $\phi(\vec{V})$ and the form of the distribution function $f(\vec{V})$ are defined and described in the section entitled "Analysis." This appendix is a compilation of the forms of these fluxes that have been integrated over the distribution functions.

MASS FLUXES OF SPECIES

Net

$$M_i = \frac{m_i n_i^s}{2}\left(\frac{2kT_s}{m_i}\right)^{\frac{1}{2}}\left[-\frac{\partial \ln T}{\partial y}a_{i0} + n\sum_j c_{i0}^{(j)}d_{jy}\right]_s \tag{B1}$$

Incident

$$M_i^{\downarrow} = -\frac{m_i n_i^s}{2\sqrt{\pi}}\left(\frac{2kT_s}{m_i}\right)^{\frac{1}{2}}\left[1 + \frac{b_{i0}}{6}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right)\right.$$
$$\left. + \frac{\sqrt{\pi}}{2}\frac{\partial \ln T}{\partial y}a_{i0} \frac{\sqrt{\pi n}}{2}\sum_j c_{i0}^{(j)}d_{jy}\right]_s \tag{B2}$$

Specularly Reflected

$$M_i^{\uparrow} = -M_i^{\downarrow} \tag{B3}$$

30

Diffusely Reflected

$$M_i^{\ w} = \frac{m_i n_i^{\ w}}{2\sqrt{\pi}} \left(\frac{2kT_w}{m_i}\right)^{\frac{1}{2}} \tag{B4}$$

NORMAL MOMENTUM FLUX

Net

$$P_{iy} = p_i^{\ s}\left[1 + \frac{b_{i0}}{3}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right)\right]_s \tag{B5}$$

Incident and Specularly Reflected

$$P_{iy}^{\downarrow} = P_{iy}^{\uparrow} = p_i^{\ s}\left[\frac{1}{2} + \frac{b_{i0}}{6}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - \frac{\partial v_{0y}}{\partial y}\right)\right.$$
$$\left. + \frac{1}{\sqrt{\pi}}\frac{\partial \ln T}{\partial y}\left(a_{i0} - \frac{1}{2}a_{i1}\right) - \frac{n}{\sqrt{\pi}}\sum_j c_{i0}^{\ (j)}d_{jy}\right]_s \tag{B6}$$

Diffusely Reflected

$$P_{iy}^{\ w} = \frac{1}{2}p_i^{\ w} \tag{B7}$$

TANGENTIAL MOMENTUM FLUX

Net

$$P_{ix} = -p_i{}^s \frac{b_{i0}}{2}\left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x}\right)_s \qquad (B8)$$

$$P_{iz} = -p_i{}^s \frac{b_{i0}}{2}\left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z}\right)_s \qquad (B9)$$

Incident

$$P_{ix}^{\downarrow} = \frac{1}{\sqrt{\pi}} p_i{}^s \left[-w_{0x} - \frac{\sqrt{\pi}b_{i0}}{4}\left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x}\right)\right.$$

$$\left. + \frac{1}{2}\frac{\partial \ln T}{\partial x}\left(a_{i0} - \frac{1}{2}a_{i1}\right) - \frac{n}{2}\sum_j c_{i0}{}^{(j)}d_{jx}\right]_s \qquad (B10)$$

$$P_{iz}^{\downarrow} = \frac{1}{\sqrt{\pi}} p_i{}^s \left[-w_{0z} - \frac{\sqrt{\pi}b_{i0}}{4}\left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z}\right)\right.$$

$$\left. + \frac{1}{2}\frac{\partial \ln T}{\partial x}\left(a_{i0} - \frac{1}{2}a_{i1}\right) - \frac{n}{2}\sum_j c_{i0}{}^{(j)}d_{jz}\right]_s \qquad (B11)$$

Diffusely Reflected

$$P_{ix}{}^w = P_{iz}{}^w = 0 \qquad (B12)$$

ENERGY FLUX

Net

$$E_i = \frac{5}{8} m_i n_i{}^s \left(\frac{2kT_s}{m_i}\right)^{\frac{3}{2}} \left[-\frac{\partial \ln T}{\partial y}\left(a_{i0} - a_{i1}\right) + n\sum_j c_{i0}{}^{(j)} d_{jy} \right]_s \tag{B13}$$

Incident

$$E_i^{\downarrow} = -\frac{m_i n_i{}^s}{2\sqrt{\pi}}\left(\frac{2kT_s}{m_i}\right)^{\frac{3}{2}} \left\{ 1 + \frac{b_{i0}}{4}\left(\frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2\frac{\partial v_{0y}}{\partial y}\right) \right.$$

$$\left. + \frac{5}{8}\pi^{\frac{1}{2}}\left[\frac{\partial \ln T}{\partial y}\left(a_{i0} - a_{i1}\right) - \sum_j nc_{i0}{}^{(j)} d_{jy}\right] \right\}_s \tag{B14}$$

Specularly Reflected

$$E_i^{\uparrow} = -E_i^{\downarrow} \tag{B15}$$

Diffusely Reflected

$$E_i^{\,w} = \frac{m_i n_i{}^w}{2\sqrt{\pi}}\left(\frac{2kT_w}{m_i}\right)^{\frac{3}{2}} \tag{B16}$$

APPENDIX C

INTEGRALS NECESSARY FOR DETERMINING FLUXES

The normal fluxes of mass, momentum, and energy are defined in terms of integrals over the velocity distribution function. These integrals consist of terms that are various velocity moments of the distribution function for the nonuniform, multicomponent gas and that are expressed in terms of the general expressions

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dW_x \, dW_y \, dW_z \, W^q W_x^{\ell} W_y^{m} W_z^{n} e^{-W^2} \qquad (C1)$$

for the net fluxes, where q, ℓ, m, and n are exponents having values 0, 1, or 2 and $W^2 = W_x^2 + W_y^2 + W_z^2$,

$$I^{\downarrow} = \int_{-\infty}^{\infty} \int_{-\infty}^{0} \int_{-\infty}^{\infty} dW_x \, dW_y \, dW_z \, W^q W_x^{\ell} W_y^{m} W_z^{n} e^{-W^2} \qquad (C2)$$

for the incident fluxes, and

$$I^{\uparrow} = \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{-\infty}^{\infty} dW_x \, dW_y \, dW_z \, W^q W_x^{\ell} W_y^{m} W_z^{n} e^{-W^2} \qquad (C3)$$

34

for the specularly reflected fluxes. Specifically, these integrals are
the following.

<div align="center">

INTEGRALS OF THE ENTIRE VELOCITY SPACE
(NET QUANTITIES)

</div>

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y e^{-W^2}\, d^3W = 0$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y W_i e^{-W^2}\, d^3W = 0 \qquad i \neq y$$

$$= \frac{1}{2}\pi^{\frac{3}{2}} \qquad i = y$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y W^2 e^{-W^2}\, d^3W = 0$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y W_i W_j e^{-W^2}\, d^3W = 0$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y W_i W^2 e^{-W^2}\, d^3W = 0 \qquad i \neq y$$

$$= \frac{5}{4}\pi^{\frac{3}{2}} \qquad i = y$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y^2 W_i^2 e^{-W^2}\, d^3W = \frac{1}{4}\pi^{\frac{3}{2}} \qquad i \neq y$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y^2 W_i W_j e^{-W^2}\, d^3W = 0 \qquad i \neq j$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y^4 e^{-W^2}\, d^3W = \frac{3}{4}\pi^{3}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y^2 W_i W_j^2 e^{-W^2}\, d^3W = 0$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y^2 W_i W^2\, d^3W e^{-W^2} = 0$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} W_y W_i W_j W^2 e^{-W^2}\, d^3W = 0$$

(C4)

INTEGRALS OVER THE LOWER HALF SPACE (INCIDENT QUANTITIES)

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y e^{-w^2}\, d^3w = -\frac{\pi}{2}$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w_i e^{-w^2}\, d^3w = 0 \qquad i \neq y$$

$$= \frac{1}{4}\pi^{\frac{3}{2}} \qquad i = y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w^2 e^{-w^2}\, d^3w = -\pi$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w_i w_j e^{-w^2}\, d^3w = 0 \qquad i \neq j$$

$$= -\frac{\pi}{4} \qquad i = j \neq y$$

$$= -\frac{\pi}{2} \qquad i = j = y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w_i w^2 e^{-w^2}\, d^3w = 0 \qquad i \neq y$$

$$= \frac{5}{8}\pi^{\frac{3}{2}} \qquad i = y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y^2 w_i w_j e^{-w^2}\, d^3w = 0 \qquad i \neq j,\ i\ \text{or}\ j \neq y$$

$$= \frac{1}{8}\pi^{\frac{3}{2}} \qquad i = j \neq y$$

$$= \frac{3}{8}\pi^{\frac{3}{2}} \qquad i = j = y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y^2 w_i w^2 e^{-w^2}\, d^3w = 0 \qquad i \neq y$$

$$= -\frac{3}{2}\pi \qquad i = y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w_i^2 w^2 e^{-w^2}\, d^3w = -\frac{3\pi}{4} \qquad i \neq y$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w^4 e^{-w^2}\, d^3w = -3\pi$$

$$\int\!\!\int_{-\infty}^{0}\!\!\int w_y w_i w^4 e^{-w^2}\, d^3w = 0 \qquad i \neq y$$

$$= \frac{35}{16}\pi^{\frac{3}{2}} \qquad i = y$$

(C5)

INTEGRALS OVER THE UPPER HALF SPACE (SPECULAR REFLECTION)

Integrals over the upper half space (specular reflection) are the same as those over the lower half space except for the following.

$$\int\int\int w_y e^{-w^2}\, d^3w = +\frac{\pi}{2}$$

$$-\int\int\int w_y^2 e^{-w^2}\, d^3w = -\frac{\pi^{3/2}}{4}$$

$$\int\int\int w_y w^2 e^{-w^2}\, d^3w = +\pi$$

$$\int\int\int w_y w_i^2 e^{-w^2}\, d^3w = \frac{\pi}{4} \qquad i \neq y$$

$$\int\int\int w_y(-w_y)w^2 e^{-w^2}\, d^3w = -\frac{5}{8}\pi^{3/2}$$

$$\int\int\int w_y w_y w_i^2 e^{-w^2}\, d^3w = -\frac{1}{8}\pi^{3/2} \qquad i \neq y$$

$$\int\int\int w_y w_i w^2 e^{-w^2}\, d^3w = \frac{\pi}{4} \qquad i \neq y$$

$$\int\int\int w_y w_i^2 w^2 e^{-w^2}\, d^3w = \frac{3\pi}{4} \qquad i \neq y$$

$$\int\int\int w_y(-w_y)^2 e^{-w^2}\, d^3w = \frac{1}{2}\pi^{3/2}$$

$$\int\int\int w_y(-w_y)w^2 e^{-w^2}\, d^3w = -\frac{5}{4}\pi^{3/2}$$

$$\int\int\int w_y w^4 e^{-w^2}\, d^3w = 3\pi$$

$$\int\int\int w_y(-w_y)^2 w^2 e^{-w^2}\, d^3w = \frac{3\pi}{2}$$

$$\int\int\int w_y(-w_y)w^4 e^{-w^2}\, d^3w = -\frac{35}{16}\pi^{3/2}$$

(C6)

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