

Chemical Nonequilibrium Boundary Layer

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The nonequilibrium boundary layer is considered as a binary mixture of atoms and molecules with finite rates of dissociation and recombination. To obtain accurate solutions to the partial differential equations for this type of flow without any necessary simplifying assumptions, an implicit finite-difference scheme is developed for solving these equations with a digital computer. Accurate solutions to the nonequilibrium boundary-layer equations have been obtained in a reasonable amount of computer time and are presented for a flat plate, cone, and hemisphere cylinder. The results show that the nonequilibrium boundary-layer temperature and composition can be considerably different from local equilibrium and frozen results. For a cone at 21,000 fps and 100,000 ft alt, the computations show that, at 60 ft from the tip, the flow has not reached equilibrium.

Nomenclature

A_n, B_n, C_n, D_n	= coefficient matrices in the difference equation (A4)
c_i	= mass fraction of species i , ρ_i/ρ
c_f	= local skin-friction coefficient, $2\tau_b/(\rho r u_e^2)$
c_{p_i}	= specific heat at constant pressure of species i , $\text{ft}^2/\text{sec}^2 \text{ } ^\circ\text{R}$
\bar{c}_p	= specific heat at constant pressure of the mixture $\sum_i c_i c_{p_i}$, $\text{ft}^2/\text{sec}^2 \text{ } ^\circ\text{R}$
\mathcal{D}_{ij}	= binary diffusion coefficients, ft^2/sec
D_i^T	= thermal diffusion coefficient, $\text{lb sec}/\text{ft}$
f'	= velocity ratio, u/u_e
h	= enthalpy, $\sum_i c_i h_i$, ft^2/sec^2
h_i	= enthalpy of species i , ft^2/sec^2
k	= thermal conductivity of mixture, $\text{lb}/\text{sec } ^\circ\text{R}$
l	= density-viscosity product, $\rho u/(\rho \mu)_r$
Le	= Lewis-Semenov number, $\bar{c}_p \mathcal{D}_{ij}/k$
Le^T	= thermal Lewis-Semenov number, $\bar{c}_p D_i^T/k$
\bar{M}	= molecular weight of the mixture, $1/(\sum_i c_i/M_i)$, $\text{lb}/\text{lb-mole}$
M_i	= molecular weight of species i , $\text{lb}/\text{lb-mole}$
Nu	= Nusselt number
Pr	= Prandtl number, $\bar{c}_p \mu/k$
p	= pressure, psf
R	= universal gas constant, $\text{lb ft}^2/(\text{lb-mole sec}^2 \text{ } ^\circ\text{R})$
Re_{x_r}	= Reynolds number based on distance along body and reference conditions, $\rho_r u_{e,r} x_r/\mu_r$
r	= distance from axis in axisymmetric problems, ft
T	= temperature, $^\circ\text{R}$
u, v	= velocity components tangential and normal to body surface, fps
V	= transformed normal velocity
w_i	= mass rate of formation of species i , $\text{lb sec}^2/\text{ft}^4 \text{ sec}$
w_n	= vector for dependent variables
x	= distance along surface from leading edge or stagnation point, ft
y	= distance along normal from surface, ft
β	= pressure gradient parameter
δ^*	= displacement thickness, ft
η	= transformed y coordinate
ξ	= transformed x coordinate, $\text{lb}^2 \text{ sec}^2/\text{ft}^{2(2-j)}$

$\Delta\eta, \Delta\xi$	= step sizes in transformed coordinates
θ	= temperature ratio, T/T_e
μ	= viscosity, $\text{lb sec}/\text{ft}^2$
ρ	= density, $\text{lb sec}^2/\text{ft}^4$
ρ_i	= density of species i , $\text{lb sec}^2/\text{ft}^4$
τ	= shear stress, psf

Subscripts

A	= atom
b	= conditions at body surface
e	= conditions at outer edge of boundary layer
m	= designation of mesh point in ξ direction, $\xi = (m-1)\Delta\xi$
n	= designation of mesh point in η direction, $\eta = (n-1)\Delta\eta$
M	= molecule
r	= quantities evaluated at some reference condition
s	= conditions at stagnation point or leading edge
∞	= freestream conditions

I. Introduction

FOR a complete investigation of the boundary layer on bodies at hypersonic velocities, it is necessary to consider chemical reactions in the flow. With finite chemical reaction rates that allow nonequilibrium flow, the boundary-layer equations can only be reduced to ordinary differential equations at the stagnation point of a blunt body. The stagnation problem with a binary mixture has been considered by Fay and Riddell,¹ whereas air with several species has been investigated by Moore and Pallone.² The flow away from the stagnation point and along bodies has been considered only with approximate procedures. Chung and Anderson^{3,4} have used an integral method to obtain the boundary-layer flow on an adiabatic and noncatalytic flat plate and around a noncatalytic sphere-cone with specified wall temperature. In the first example, the fluid was taken as oxygen atoms and molecules whereas for the latter case, oxygen atoms and nitrogen atoms and molecules are employed for the gas model. Rae⁵ has obtained the nonequilibrium boundary layer of a diatomic gas near the leading edge of a flat plate by employing a double expansion in terms of the distance along the surface and the atom mass fraction. Additional assumptions have been used, such as Prandtl and Lewis number equal to one, in the foregoing papers.

The ideal of local similarity has been employed by Levinsky and Brainerd⁶ to obtain the nonequilibrium boundary layer for a five species air model along a nozzle. This procedure can give reasonable results for equilibrium and frozen boundary layers, as shown by Lees,⁷ Kemp, Rose, and Detra,⁸ and Moore.⁹ No complete investigation of the validity of local similarity for nonequilibrium boundary layers has been per-

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formed; however, reasonable results are obtained for a flat-plate flow as shown by Blottner.¹⁰ Even if similar solutions are sufficiently precise, they are difficult to obtain, since accurate initial estimates are required for the boundary conditions that are being iterated. Hence, a large amount of time and effort is required to acquire the solution with this procedure.

For the present analysis, the gas in the nonequilibrium boundary layer is taken as a binary mixture of atoms and molecules with finite rates of dissociation and recombination. To obtain accurate solutions of these partial differential equations without any necessary simplifying assumptions, an implicit finite-difference scheme is developed for solving these equations. This method is similar to the procedure investigated by Flügge-Lotz and Blottner.¹¹ The important difference between the present approach and that of Ref. 11 is the manner in which the boundary-layer equations are transformed before the finite difference approximation is made. The coordinate normal to the wall is stretched in such a way that the boundary layer is of nearly uniform thickness in the transformed plane. This procedure allows solution of the boundary-layer equations from the stagnation point or from a leading edge with similar solutions as initial profiles. Also, this method permits larger steps to be taken along the body, since the profiles do not change rapidly in the transformed coordinates.

The boundary conditions at the outer edge of the boundary layer are obtained from the inviscid flow along the body. With the pressure distribution assumed known along the body, a set of ordinary differential equations which govern this flow, are solved to obtain the velocity, temperature, and atom mass fraction at the edge of the boundary layer. The following boundary conditions at the wall are considered: zero normal and tangential velocities, specified wall temperature or zero heat transfer, and catalytic or noncatalytic wall.

The boundary-layer flow on an insulated and noncatalytic flat plate has been obtained and is compared with the results of Chung and Anderson³ and Rae.⁵ The boundary layer on a flat plate with specified wall temperature and catalytic wall has also been considered. Calculations for a hemisphere-cylinder and a cone at various altitudes are presented.

II. Method of Analysis

A. System of Equations

The boundary-layer equations for a chemically reacting binary mixture of atoms and molecules are as follows:

Continuity

$$\frac{\partial}{\partial x}(\rho u r_b^j) + \frac{\partial}{\partial y}(\rho v r_b^j) = 0 \quad (1a)$$

Momentum

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = -\frac{dp_e}{dx} + \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right) \quad (1b)$$

Energy

$$\begin{aligned} \bar{c}_p \rho u \frac{\partial T}{\partial x} + \bar{c}_p \rho v \frac{\partial T}{\partial y} &= u \frac{dp_e}{dx} + \mu \left(\frac{\partial u}{\partial y}\right)^2 + \\ &\frac{\partial}{\partial y}\left(k \frac{\partial T}{\partial y}\right) - \sum_i \dot{w}_i h_i + \sum_i \left[c_{pi} \left(\rho \mathfrak{D}_{ij} \frac{\partial c_i}{\partial y} + \right. \right. \\ &\left. \left. \frac{D_i^T}{T} \frac{\partial T}{\partial y} \right) \right] \frac{\partial T}{\partial y} \quad (1c) \end{aligned}$$

Conservation of Species

$$\rho u \frac{\partial c_i}{\partial x} + \rho v \frac{\partial c_i}{\partial y} = \frac{\partial}{\partial y}\left(\rho \mathfrak{D}_{ij} \frac{\partial c_i}{\partial y} + \frac{D_i^T}{T} \frac{\partial T}{\partial y}\right) + \dot{w}_i \quad (1d)$$

For two-dimensional flow, $j = 0$, and for axisymmetric flow,

$j = 1$. To complete the foregoing relations, the equation of state

$$p = (R/\bar{M})\rho T \quad (2)$$

where

$$\bar{M} = 1/(\sum_i c_i/M_i)$$

is required. This equation assumes that the gas consists of a mixture of chemically reacting perfect gases. Since the pressure change across the boundary layer is negligibly small, the equation of state becomes

$$\rho/\rho_e = \bar{M}T_e/(\bar{M}_e T) \quad (3)$$

To obtain smoother profiles across the boundary layer which are more readily approximated numerically, and to have the equations in a form compatible with similar solutions, the boundary-layer equations are transformed with the Mangler and Howarth-Dorodnitsyn transformation:

$$\xi(x) = \int_0^x (\rho\mu)_{\infty} r_b^{2j} dx \quad \eta(x,y) = \frac{u_e r_b^j}{(2\xi)^{1/2}} \int_0^y \rho dy \quad (4a)$$

Then

$$\begin{aligned} \frac{\partial}{\partial x} &= (\rho\mu)_{\infty} r_b^{2j} \frac{\partial}{\partial \xi} + \frac{\partial \eta}{\partial x} \frac{\partial}{\partial \eta} \\ \frac{\partial}{\partial y} &= \frac{\rho u_e r_b^j}{(2\xi)^{1/2}} \frac{\partial}{\partial \eta} \end{aligned} \quad (4b)$$

Also, since we are considering a binary mixture of atoms and molecules, the following relations exist:

$$\sum_i c_i = c_A + c_M = 1 \quad (5a)$$

$$\sum_i \dot{w}_i = \dot{w}_A + \dot{w}_M = 0 \quad (5b)$$

$$Le = Le_{AM} = Le_{MA} \quad (5c)$$

$$Le^T = Le_A^T = -Le_M^T \quad (5d)$$

$$\bar{c}_p = \sum_i c_i \bar{c}_{pi} = c_A(\bar{c}_{pA} - \bar{c}_{pM}) + \bar{c}_{pM} \quad (5e)$$

When the foregoing relations (4) and (5) are used with Eqs. (1), the boundary-layer equations become

$$2\xi \frac{\partial f'}{\partial \xi} + \frac{\partial V}{\partial \eta} + f' = 0 \quad (6a)$$

$$2\xi f' \frac{\partial f'}{\partial \xi} + V \frac{\partial f'}{\partial \eta} = \beta \left[\frac{\bar{M}_e}{\bar{M}} \theta - (f')^2 \right] + \frac{\partial}{\partial \eta} \left(l \frac{\partial f'}{\partial \eta} \right) \quad (6b)$$

$$\begin{aligned} 2\xi f' \bar{c}_p \frac{\partial \theta}{\partial \xi} + \bar{c}_p V \frac{\partial \theta}{\partial \eta} &= \frac{u_e^2}{T_e} \left[l \left(\frac{\partial f'}{\partial \eta} \right)^2 - \beta \frac{\bar{M}_e}{\bar{M}} f' \theta \right] + \\ &\frac{\partial}{\partial \eta} \left(l \bar{c}_p \frac{\partial \theta}{\partial \eta} \right) - \frac{\beta \dot{w}_A (h_A - h_M)}{\rho T_e du_e/dx} + (c_{pA} - c_{pM}) \frac{l}{Pr} \times \\ &\left(Le \frac{\partial c_A}{\partial \eta} + \frac{Le^T}{\theta} \frac{\partial \theta}{\partial \eta} \right) \frac{\partial \theta}{\partial \eta} - 2\xi \bar{c}_p \frac{f' \theta}{T_e} \frac{dT_e}{d\xi} \quad (6c) \end{aligned}$$

$$\begin{aligned} 2\xi f' \frac{\partial c_A}{\partial \xi} + V \frac{\partial c_A}{\partial \eta} &= \frac{\beta \dot{w}_A}{\rho du_e/dx} + \\ &\frac{\partial}{\partial \eta} \left[\frac{l}{Pr} \left(Le \frac{\partial c_A}{\partial \eta} + \frac{Le^T}{\theta} \frac{\partial \theta}{\partial \eta} \right) \right] \quad (6d) \end{aligned}$$

where

$$V = \frac{2\xi}{(\rho\mu)_{\infty} r_b^{2j}} \left(f' \frac{\partial \eta}{\partial x} + \frac{\rho v r_b^j}{(2\xi)^{1/2}} \right) \quad (7a)$$

$$\beta = \frac{2\xi}{u_e} \frac{du_e}{d\xi} \quad (7b)$$

For the boundary conditions, it is assumed that no slip occurs

at the wall, temperature or heat transfer at the body is given, and the wall is catalytic or noncatalytic. The boundary conditions for the foregoing boundary-layer equations are as follows:

At the body

$$f'(\xi, 0) = 0 \quad (8a)$$

$$V(\xi, 0) = (2\xi)^{1/2}(\rho v)_b / [(\rho\mu)_r u_e r_b^j] \quad (8b)$$

with specified temperature

$$\theta(\xi, 0) = \theta_b(\xi)$$

or specified heat transfer

$$\left. \frac{\partial \theta}{\partial \eta} \right|_b = \left[\frac{[q(2\xi)^{1/2}/\rho u_e r_b^j] - (h_M - h_A)(\mu/Pr)Le(\partial c_A/\partial \eta)}{-kT_e + (h_M - h_A)(\mu/Pr)(LeT/\theta)} \right]_b \quad (8c)$$

and with catalytic wall

$$c_A(\xi, 0) = c_{Aeq}(\theta_b, p_e) \quad (8d)$$

or with noncatalytic wall

$$\left. \frac{\partial c_A}{\partial \eta} \right|_b = 0 \quad (8e)$$

At the outer edge

$$f'(\xi, \eta_e) = 1 \quad \theta(\xi, \eta_e) = 1 \quad c_A(\xi, \eta_e) = c_{Ae}(\xi) \quad (9)$$

When there is no injection of fluid at the wall, $V(\xi, 0) = 0$. The velocity, temperature, and mass fraction of atoms at the outer edge of the boundary layer are determined from the inviscid flow problem.

To obtain the solution of the foregoing boundary-layer equations (6) with boundary conditions (8) an implicit finite-difference scheme is employed as described in the Appendix.

B. Initial Profiles

As indicated previously, initial profiles are required for the finite-difference solution. At the stagnation point or leading edge of a sharp body, as $\xi \rightarrow 0$ the continuity equation (6a) becomes

$$(\partial V/\partial \eta) + f' = 0 \quad (10)$$

The mathematical difficulties of the singular point at $\xi = 0$ for a flat plate can be circumvented by having ξ a very small number slightly greater than zero.

If we define

$$f = \int_0^\eta f' d\eta \quad (11)$$

then $V = -f$ from Eq. (10). With this relation and $\xi \rightarrow 0$, the boundary-layer equations (6b–6d) become ordinary differential equations with two-point boundary conditions. These equations are solved using the usual iteration techniques employed for similar solutions of the boundary-layer equations.

C. Exterior Flow

The exterior flow at the edge of the boundary layer is obtained from the inviscid nonequilibrium flow at the surface of the body. As the pressure on a body is not affected significantly by the flow being in nonequilibrium and is usually easy to estimate, the pressure distribution is assumed known. The ordinary differential equations that govern the flow at the body in terms of the pressure distribution are

$$\frac{du_e}{dx} = -\frac{1}{\rho_e u_e} \frac{dp_e}{dx} \quad (12a)$$

$$\frac{dT_e}{dx} = \frac{1}{\bar{c}_{pe}\rho_e} \frac{dp_e}{dx} - \dot{w}_A \frac{(h_A - h_M)}{\bar{c}_{ve}\rho_e u_e} \quad (12b)$$

$$\frac{dc_{Ae}}{dx} = \frac{\dot{w}_A}{\rho_e u_e} \quad (12c)$$

Once the pressure distribution on the body is known, which is preferably obtained from the nonequilibrium flow field solutions, the remaining quantities at the edge of the boundary layer can then be obtained from Eqs. (12). Even if the nonequilibrium inviscid flow is known, this procedure is preferred to inputting all the necessary quantities. The boundary conditions for Eqs. (12), for example, at the stagnation point, are

$$u_e(0) = 0 \quad (13a)$$

$$T_e(0) = T_{es} \quad (13b)$$

$$c_{Ae}(0) = c_{Aes} \text{ (equilibrium concentration of atoms at temperature } T_{es}) \quad (13c)$$

For other types of bodies these three quantities with the appropriate values are required. Since the quantities at the edge of the boundary layer are required as a function of ξ , the differential equation

$$d\xi/dx = (\rho\mu)_r u_e r_b^{2j} \quad (14)$$

is solved along with the exterior flow equations (12) to give the desired relation between ξ and x . As the exterior flow quantities u_e , T_e , and c_{Ae} are required at $(m + \frac{1}{2})$ in the transformed plane, and the step-size can change, the following relation for the step size is employed to obtain the results at the desired location:

$$\Delta x_{m+1/2} = \frac{1}{2}(\Delta x_{m-1/2} + \Delta x_{m+1/2}) \quad (15)$$

For the first step, $\Delta x_{m-1/2}$ is zero, and $\Delta x_{m+1/2}$ is the desired step size. If the step size is changed, the new step size is $\Delta x_{m+1/2}$. The relation

$$\Delta \xi_{m+1/2} = 2(\xi_{m+1/2} - \xi_{m-1/2} - \frac{1}{2}\Delta \xi_{m-1/2}) \quad (16)$$

is employed to obtain the step size in the transformed plane.

To start the solution of Eq. (12) at the stagnation point, certain quantities on the right side of these equations are of an indeterminate form numerically. However, it can be shown that, at $x = 0$,

$$\left(\frac{1}{u_e} \frac{dp_e}{dx} \right)_s = -\frac{1}{R_N} [2(p_{es} - p_\infty)\rho_{es}]^{1/2} \text{ (Newtonian flow)} \quad (17a)$$

$$(\dot{w}_A/u_e)_s = 0 \quad (17b)$$

For other types of bodies this type of problem does not occur.

D. Boundary-Layer Characteristics

In addition to the profiles of the various quantities across the boundary layer, parameters that characterize the skin friction, heat transfer, and thickness of the boundary layer are desirable. The local skin friction is defined as

$$c_f(Re_{x_r})^{1/2} = \frac{(\rho\mu)_b}{(\rho\mu)_r} \left(\frac{2u_e x_r^{2j} (\rho\mu)_r}{\xi} \right)^{1/2} \left(\frac{\partial f'}{\partial \eta} \right)_b \quad (18)$$

The derivative in the foregoing expression is approximated as

$$\left(\frac{\partial f'}{\partial \eta} \right)_b = \left\{ \frac{f_2' + (\Delta\eta^2/2l)\beta(\bar{M}_e/\bar{M})\theta}{\Delta\eta[1 + (\Delta\eta/2l)(V - l')] } \right\}_b \quad (19)$$

where no slip at the wall has been assumed. At $x = 0$, the following term is of indeterminate form but has the values indicated:

$$[u_e x_r^{2j} (\rho\mu)_r / \xi]^{1/2} = (2j + 2)^{1/2} \text{ (stagnation point)} \quad (20a)$$

$$[u_e x_r^{2j} (\rho\mu)_r / \xi]^{1/2} = (2j + 1)^{1/2} \text{ (sharp body)} \quad (20b)$$

The heat-transfer parameter is defined in terms of the Nusselt number and Reynolds number as follows:

$$\frac{Nu}{(Re_{x_r})^{1/2}} = \frac{Pr_r}{Pr_b} \frac{(\rho\mu)_b}{(\rho\mu)_r} \frac{1}{2^{1/2}} \left(\frac{u_e x_r b^{2i} (\rho\mu)_r}{\xi} \right)^{1/2} \frac{\bar{c}_{pb} T_e}{(h_{es} - h_b)} \cdot \left\{ \frac{\partial \theta}{\partial \eta} + \frac{(h_A - h_M)}{\bar{c}_p T_e} \left(Le \frac{\partial c_A}{\partial \eta} + \frac{Le^T}{\theta} \frac{\partial \theta}{\partial \eta} \right) \right\} \quad (21)$$

where

$$\begin{aligned} Nu &= -q \bar{c}_{pr} x / [k_r (h_{es} - h_b)] \\ h_{es} &= c_{A_{es}} (h_A - h_M)_{es} + h_{M_{es}} + \frac{1}{2} u_{es}^2 \\ h_b &= c_{A_b} (h_A - h_M)_b + h_{M_b} \end{aligned}$$

The derivatives in the expression are approximated as

$$\left. \frac{\partial \theta}{\partial \eta} \right|_b = -\frac{1}{6\Delta\eta} [11\theta_{m,1} - 18\theta_{m,2} + 9\theta_{m,3} - 2\theta_{m,4}] \quad (22a)$$

$$\left. \frac{\partial c_A}{\partial \eta} \right|_b = -\frac{1}{6\Delta\eta} [11c_{Am,1} - 18c_{Am,2} + 9c_{Am,3} - 2c_{Am,4}] \quad (22b)$$

The thickness of the boundary layer is depicted by the displacement thickness and in terms of the transformed quantities is

$$\delta^* = \frac{(2\xi)^{1/2}}{\rho_e u_e r_b^j} \int_0^{\eta_e} \left[\left(\frac{1 + c_A}{1 + c_{A_e}} \right) \theta - f' \right] d\eta \quad (23)$$

At the stagnation point, the following term is indeterminate numerically but has the value shown:

$$\frac{(2\xi)^{1/2}}{\rho_e u_e r_b^j} = \left[-\frac{(\rho\mu)_r u_e}{(j+1)\rho_e p_e'} \right]^{1/2} \quad (24)$$

The evaluation of the displacement thickness is obtained with Simpson's method.

III. Numerical Calculations

A. Gas Model

The transport and thermodynamic properties and rate equation are taken to be the same as those employed by Chung and Anderson in order to make a comparison with their results in the first example. The binary mixture consists of oxygen atoms and molecules with the following thermodynamic properties:

$$\begin{aligned} \bar{c}_p &= c_{pA} = c_{pM} = 7010 \text{ (ft}^2/\text{sec}^2 \text{ } ^\circ\text{R)} \\ h_A &= c_{pA} T + 1.666 \times 10^8 \text{ (ft}^2/\text{sec}^2) \\ h_M &= c_{pM} T \end{aligned}$$

The transport properties are such that the following non-dimensional parameters are

$$l = 1 \quad Pr = 1 \text{ or } 0.7 \quad Le = 1 \text{ or } 1.4 \quad Le^T = 0$$

The rate equation for oxygen,

$$\begin{aligned} \frac{\dot{w}_A}{\rho} = & -\frac{(1 + c_A)^2 (2K_r) \rho^2}{2M_A^2} \left[\frac{c_A^2}{1 + c_A} - 529.054 \frac{K_p}{p} (1 - c_A) \right] \quad (25) \end{aligned}$$

where

$$2K_r = 1.70 \times 10^{22}/T^2 \quad K_p = e^{(15.8 - 108,000/T)}$$

was employed in the present examples. The foregoing properties are used in the following examples, except the second, where more accurate thermodynamic properties and rate equations are considered. One would expect that more accurate transport properties would have a large effect on the

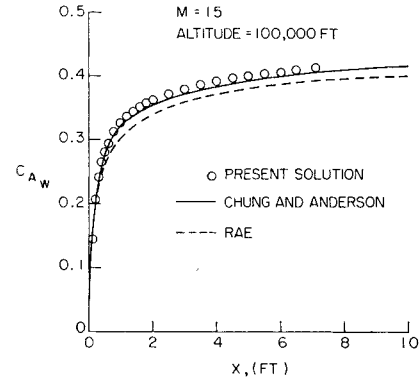


Fig. 1 Atom mass fraction at wall for an insulated and noncatalytic flat plate.

boundary-layer characteristics, but this has not been investigated.

B. Specific Examples

1. Insulated and noncatalytic flat plate

The boundary-layer flow on an insulated and noncatalytic flat plate is investigated and compared to result of Chung and Anderson,³ and Rae.⁵ For this comparison, the freestream conditions correspond to a Mach number of 15 and an altitude of 100,000 ft ($T_e = 392.4^\circ\text{R}$ and $p_e = 23.4265$ psf). The Prandtl and Lewis-Semenov numbers are taken as one in order to have all of the assumptions identical with the other two papers. At the outer edge of the boundary layer the oxygen is undissociated and the pressure is taken as a constant throughout the boundary layer.

The variation of the atom mass fraction at the wall is given in Fig. 1. Also shown in this figure are the results for the same problem as obtained by Chung and Anderson, and Rae. Since approximations are required in these two methods, the agreement with the present more exact solution is good.

2. Specified wall temperature and catalytic flat plate

The flow along a wall with zero pressure gradient, $T_w/T_e = 3$, and zero atom mass fraction at the wall has been investigated. In this example, $Pr = 0.7$ and $Le = 1.4$. With a freestream velocity of 15,734 fps (Mach number = 15) the boundary layer is essentially "frozen," since the temperature is not high enough for appreciable dissociation to occur. The skin friction and heat-transfer parameters are practically constant for the distance considered and are $c_f [Re_{x_r}]^{1/2} = 0.6645(0.6641)$ and $Nu/[Re_{x_r}]^{1/2} = 0.242(0.248)$. The values in parentheses are obtained from similar solutions for a perfect gas. The displacement thickness of the boundary layer is given in Fig. 2 and is approximately the same result as obtained from similar solution of a perfect gas. If the boundary-layer flow is assumed in local equilibrium, the displacement thickness is slightly less as shown. When the freestream velocity is increased to 25,000 fps, there is significant dissociation of oxygen downstream from the leading edge. Several temperature and atom mass fraction profiles are presented in Figs. 3 and 4. In addition to the nonsimilar nonequilibrium profiles (finite-difference solutions), similar profiles for the nonequilibrium flow are presented. These solutions predict a slightly lower temperature while the atom mass fraction is higher. The similar solutions are obtained by solving ordinary differential equations with two-point boundary conditions. These solutions become exceedingly difficult to obtain downstream from the leading edge as accurate initial guesses of the unknown boundary conditions at the wall are required for the usual integration procedures. The local equilibrium profiles, which are the same at all distances along the wall, are significantly different from the nonequilibrium

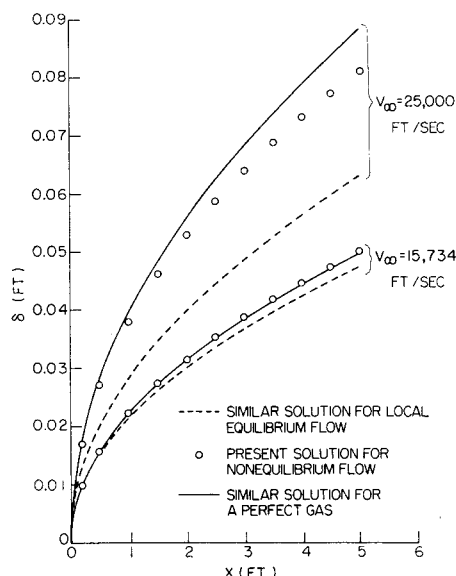


Fig. 2 Displacement thickness for flow along a catalytic flat plate with $T_w/T_e = 3$ (alt = 100,000 ft).

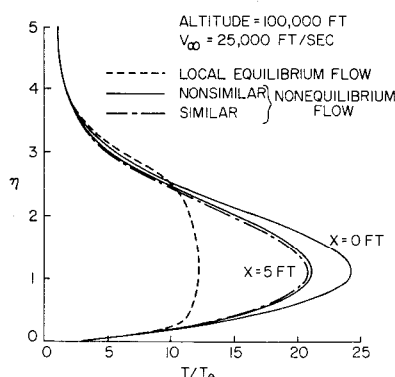


Fig. 3 Temperature profiles for a catalytic wall with $T_w/T_e = 3$ and $dp_e/dx = 0$.

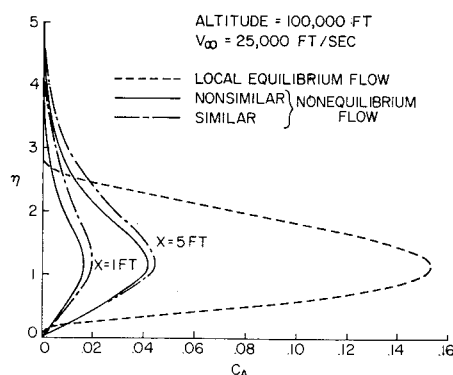


Fig. 4 Atom mass fraction profiles for a catalytic wall with $T_w/T_e = 3$ and $dp_e/dx = 0$.

profiles, as shown in Figs. 3 and 4. The velocity profiles for this example are the Blasius type and remain the same along the wall.

The effect on the boundary-layer properties of the rate constants and thermodynamic properties of the gas has been investigated. The production of atoms for a binary mixture is written as

$$\frac{\dot{w}_A}{\rho} = \bar{p} \frac{c_A}{M_A} \left\{ (1 - c_A) \left[\left(\frac{1 - c_A}{2c_A} \right) k_{f1} + k_{f2} \right] - \frac{2\bar{p}c_A^2}{M_A} \left[\left(\frac{1 - c_A}{2c_A} \right) k_{b1} + k_{b2} \right] \right\}$$

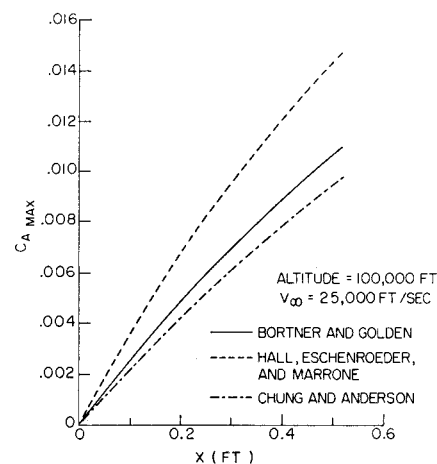


Fig. 5 Effect of rate constants on composition of the boundary layer on a catalytic wall with $T_w/T_e = 3$ and $dp_e/dx = 0$.

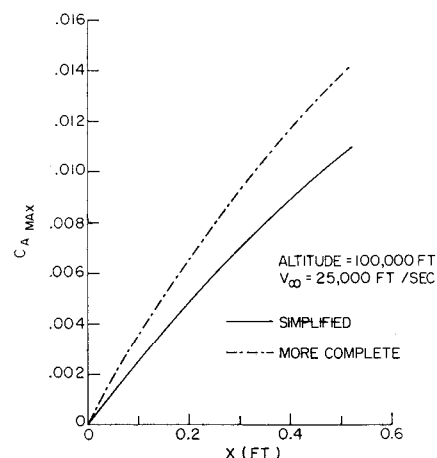


Fig. 6 Effect of thermodynamic properties on the composition of the boundary layer on a catalytic wall with $T_w/T_e = 3$ and $dp_e/dx = 0$.

where

$$k_{fr} = TK^{C2r} \exp(C0_r + C1_r/TK)$$

$$k_{br} = TK^{D2r} \exp(D0_r + D1_r/TK)$$

$$TK = T/1.8(^{\circ}K) \quad \bar{p} = 0.51536\rho(g/cm^3)$$

The constants used in the foregoing equation and the reference from which they were taken are given in Table 1. The last case gives the same equation as presented previously in (25). The result of using this set of constants is illustrated in Fig. 5 where the maximum atom mass fraction in the boundary layer is presented. There is a large influence on the composition of the boundary layer by the rate constants employed.

The specific heat and enthalpy has been determined from the following expressions which include translational, rotational, and vibrational energies:

$$c_{pA} = \frac{5}{2} \frac{R}{M_A}$$

$$c_{pM} = \frac{R}{M_M} \left[\frac{7}{2} + \left(\frac{\theta}{T} \right)^2 e^{\theta/T} (e^{\theta/T} - 1)^{-2} \right]$$

$$h_A = \frac{5}{2} \frac{R}{M_A} T + 1.666 \times 10^8$$

$$h_M = \frac{R}{M_M} T \left[\frac{7}{2} + \frac{\theta}{T} (e^{\theta/T} - 1)^{-1} \right]$$

where $\theta = 4014^{\circ}R$.

Table 1 Constants for k_{fr} and k_{br}

Ref.	Reaction	$C0_r$	$C1_r$	$C2_r$	$D0_r$	$D1_r$	$D2_r$
13	$r = 1(\text{O}_2 + \text{O}_2 \rightleftharpoons 2\text{O} + \text{O}_2)$	40.84869	-59,900	-0.5	37.62982	0	-0.5
	$r = 2(\text{O}_2 + \text{O} \rightleftharpoons 2\text{O} + \text{O})$	42.05085	-59,900	-0.5	38.81544	0	-0.5
12	$r = 1(\text{O}_2 + \text{O}_2 \rightleftharpoons 2\text{O} + \text{O}_2)$	49.63522	-59,380	-1.5	42.54523	0	-1.0
	$r = 2(\text{O}_2 + \text{O} \rightleftharpoons 2\text{O} + \text{O})$	42.18847	-59,380	-0.5	35.09847	0	0
3	$r = 1(\text{O}_2 + \text{O}_2 \rightleftharpoons 2\text{O} + \text{O}_2)$	62.03969	-60,000	-3.0	50.64682	0	-2.0
	$r = 2(\text{O}_2 + \text{O} \rightleftharpoons 2\text{O} + \text{O})$	62.03969	-60,000	-3.0	50.64682	0	-2.0

Table 2 Outer edge conditions for 10° cone

Altitude, ft	T_e , °R	p_e , psf	u_e , fps	T_w , °R
100,000	1989	630.2	20,600	3600
150,000	2065	72.82	20,600	2160
200,000	2016	11.46	20,590	1620

Table 3 Peak temperature and atom mass fraction for equilibrium

Altitude, ft	$(T_{\max}/T_e)_{\text{eq}}$	$(\bar{c}_{A_{\max}})_{\text{eq}}$
100,000	2.71	0.1094
150,000	2.34	0.1032
200,000	2.22	0.1051

With these more complete thermodynamic properties, the same problem has been solved, and the influence on the maximum atom mass fraction is shown in Fig. 6.

3. Cone with specified wall temperature and catalytic wall

The boundary-layer flow along a 10° cone (half-angle) with zero pressure gradient at three altitudes has been computed. The same gas model is employed as discussed earlier in Sec. A, and the Prandtl number is 0.7 whereas the Lewis-Somenov number is 1.4. The freestream velocity is taken as 21,000 fps for the three cases considered. Since the inviscid flow temperatures are relatively low, the flow at the surface of the cone or the edge of the boundary layer is determined from cone solutions for a perfect gas. The boundary conditions at the outer edge of the boundary layer and at the wall for the three cases are shown in Table 2. The oxygen at the edge of the boundary layer and at the wall is considered undissociated because of the low temperatures at these locations.

The temperature and atom mass fraction profiles along the cone are presented in Figs. 7 and 8. The velocity profiles remain the same along the cone and are the Blasius result. At 60 ft from the cone tip, the flow has not reached equilibrium. The local equilibrium profiles are shown in these figures and are the same at any distance along the body. The maximum temperature and atom mass fraction in the boundary layer are given in Figs. 9 and 10 for the three cases. The maximum temperature and atom mass fraction as obtained from local equilibrium solutions are given in Table 3. The flow at 200,000 ft is nearly frozen, whereas at 100,000 ft the flow has not reached equilibrium at the distances investigated.

The heat transfer by conduction is decreasing along the cone for the nonequilibrium boundary layer as can be seen from Fig. 7. The heat transfer by diffusion is increasing along the body which gives a total heat transfer approximately the same for the nonequilibrium and equilibrium boundary layer with a catalytic wall. The skin friction is not influenced by the nonequilibrium flow for this case with $l = 1$.

4. Hemisphere-cylinder

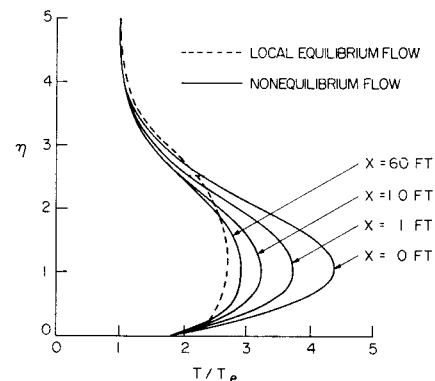
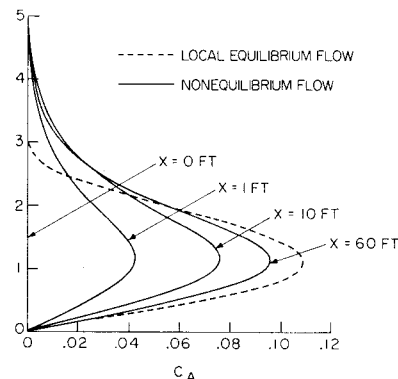
The nonequilibrium boundary layer has been computed on a hemisphere-cylinder with a 1-ft nose radius. The

body is considered at an altitude of 225,000 ft with a free-stream velocity of 20,000 fps. The flow is assumed to be in equilibrium at the stagnation point with the following properties:

$$\begin{aligned} u_{es} &= 0 & p_{es} &= 91.322 \text{ psf} \\ T_{es} &= 9880^\circ\text{R} & c_{A_{es}} &= 0.9993376 \end{aligned}$$

At this condition the boundary layer is sufficiently thin that the usual interaction with the inviscid flow can be neglected. However, the relaxation layer behind the shock wave is becoming large enough that the flow at the edge of the boundary layer could be slightly out of equilibrium.

The wall is catalytic with a temperature of 395.2°R ; hence, the mass fraction of atoms at the wall is taken at zero. To determine the flow at the edge of the boundary layer, the pressure distribution on the body is assumed as shown in Fig. 11. The equilibrium pressure distribution shown is a numerical result obtained for the inviscid flow field. The flow at the edge of the boundary layer was obtained as discussed in Sec. II-C with the assumed pressure. In starting the solution at the stagnation point, Eqs. (17a) and (17b) were employed with $p_\infty = 0.15719$ psf. In this example, the density-viscosity product at the reference condition is evaluated at the body and is $(\rho\mu)_r = (\rho\mu)_{b_0}(p_e/p_{e_0})$.

**Fig. 7** Temperature profiles for a 10° cone at 100,000 ft alt and $V_\infty = 21,000$ fps.**Fig. 8** Atom mass fraction profiles for a 10° cone at 100,000 ft alt and $V_\infty = 21,000$ fps.

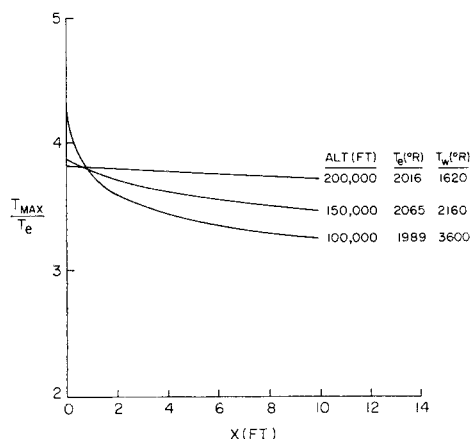


Fig. 9 Maximum temperature in boundary layer on a 10° cone ($V_\infty = 21,000$ fps).

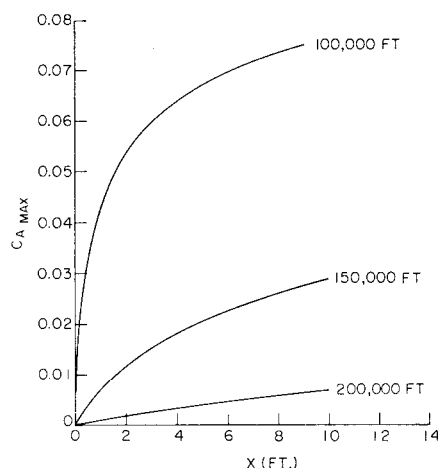


Fig. 10 Maximum mass fraction of atoms in boundary layer on 10° cone ($V_\infty = 21,000$ fps).

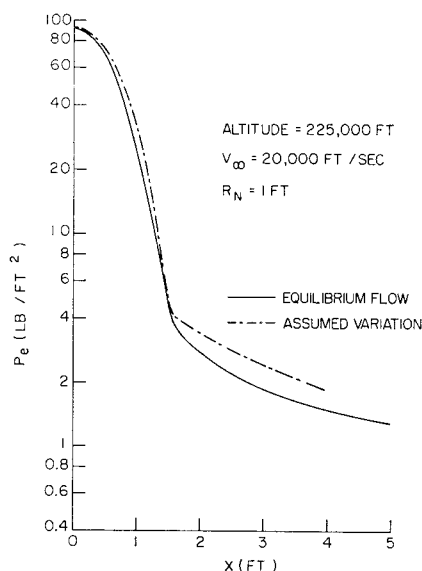


Fig. 11 Pressure distribution at the edge of the boundary layer.

The computed velocity and temperature at the edge of the boundary layer is given in Fig. 12. The flow is frozen since there is no change in the atom mass fraction in the distance investigated. For this case, the velocity and temperature on the cylinder at the outer edge of the boundary layer are appreciably smaller than that obtained when the flow is assumed in local equilibrium.

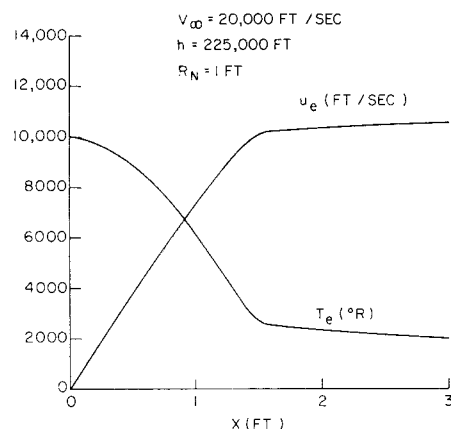


Fig. 12 Velocity and temperature at edge of boundary layer for a hemisphere cylinder.

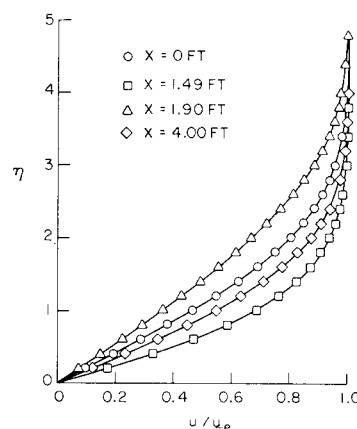


Fig. 13 Velocity profiles on the hemisphere cylinder.

The boundary layer has been computed from the stagnation point to 4 ft downstream. The extreme variation of the velocity profiles are presented in Fig. 13 whereas the temperature profiles are given in Fig. 14. The atom mass fraction profiles remain nearly the same for the distance computed. The heat transfer and skin friction resulting from these profiles are presented in Fig. 15. The variation of these parameters is similar to local equilibrium results except for the dip beyond the shoulder for the present case.

IV. Discussion

The complete partial differential equations of the laminar boundary layer for a chemical nonequilibrium binary gas have been solved with an implicit finite-difference scheme. As the equations are solved in a transformed plane where the boundary layer is of nearly uniform thickness, the solution can be started at the stagnation point or leading edge. The required initial profiles for starting the solution are similar solutions, which can be readily obtained if not already available. As the profiles do not change rapidly in the transformed plane, the solutions are obtained in a reasonable amount of computer time. With the implicit procedure employed, there have been no problems of stability or convergence of the solution.

With the finite-difference scheme, various boundary conditions have been employed for the nonequilibrium boundary-layer solutions, and results have been obtained on bodies with and without pressure gradients. Approximate solutions for a noncatalytic and insulated wall by Chung and Anderson, and Rae are in agreement with the present, more exact results. For flows with zero pressure gradient and a catalytic wall, the nonequilibrium effects are unimportant on the heat transfer and skin friction. However, the displacement thickness can be greatly changed when there is appreciable dissociation of the gas. The results for a cone at 21,000 fps show that the binary flow is nearly frozen at 200,000 ft alt whereas equi-

librium has not been obtained at 60 ft from the tip at 100,000 ft. The boundary-layer flow on the hemisphere cone at 225,000 ft alt and 20,000 fps is frozen. The examples show the importance of considering nonequilibrium flow as the composition and temperature in the boundary layer can be greatly different from local equilibrium or frozen solutions.

Nonequilibrium similar solution for a flat plate are reasonably close to the nonsimilar solution. However, the time and effort required presently to obtain the similar solutions limits the usefulness, since the nonsimilar results are more accurate and require less time.

Extension of the present procedure to a multicomponent fluid is being developed, and in this new program more complete transport properties will be employed.

Appendix: Numerical Solution of the Equations

There are many finite-difference schemes that can be employed to solve the boundary-layer equations. In this study an implicit procedure is used that is similar to the method developed in Ref. 11 but has been modified so that solutions downstream of stagnation point initial profiles can be obtained. The implicit procedures do not have the stability difficulties encountered with explicit schemes, and the truncation error can be of higher order than that of the explicit, or Duford-Frankel methods.

The flow field is divided into a grid or mesh of size $\Delta\eta$ and $\Delta\xi$ with $x = m \cdot \Delta\xi$ and $y = n \cdot \Delta\eta$. It is assumed that u , θ , and c_A are known at the grid points in the m th column and unknown in the $(m + 1)$ th column. In the implicit scheme

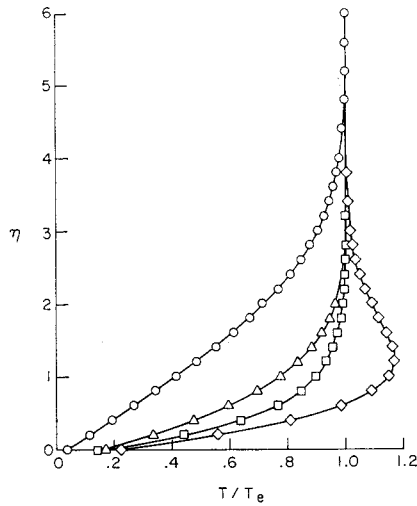


Fig. 14 Temperature profiles on the hemisphere cylinder.

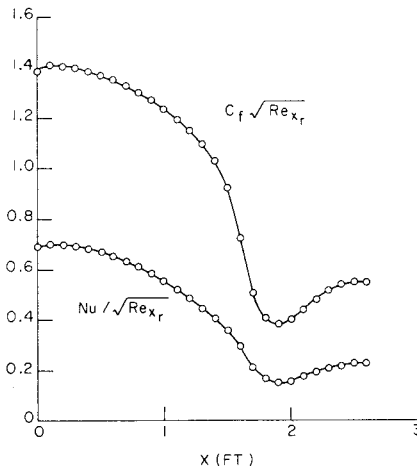


Fig. 15 Local skin friction and heat transfer for a hemisphere cylinder.

the various types of derivatives must be replaced by linear difference quotients, and the partial differential equations are evaluated at $(m + \frac{1}{2}, n)$. Let functions $H(\xi, \eta)$ and $T(\xi, \eta)$ represent the unknown quantities u , θ , or c_A in the boundary layer, so that the difference quotients at the point $(m + \frac{1}{2}, n)$ are written as

$$\partial H / \partial \xi = (H_{m+1,n} - H_{m,n}) / \Delta \xi \quad (A1a)$$

$$\partial H / \partial \eta = \frac{1}{2} H_{\eta} + (H_{m+1,n+1} - H_{m+1,n-1}) / (4\Delta \eta) \quad (A1b)$$

$$\partial^2 H / \partial \eta^2 = \frac{1}{2} H_{\eta\eta} +$$

$$(H_{m+1,n+1} - 2H_{m+1,n} + H_{m+1,n-1}) / (2\Delta \eta^2) \quad (A1c)$$

$$(\partial H / \partial \eta)^2 = H_{\eta}(H_{m+1,n+1} - H_{m+1,n-1}) / (2\Delta \eta) \quad (A1d)$$

$$(\partial H / \partial \eta)(\partial T / \partial \eta) = [H_{\eta}(T_{m+1,n+1} - T_{m+1,n-1}) + T_{\eta}(H_{m+1,n+1} - H_{m+1,n-1})] / (4\Delta \eta) \quad (A1e)$$

where

$$H_{\eta} = (H_{m,n+1} - H_{m,n-1}) / (2\Delta \eta)$$

$$H_{\eta\eta} = (H_{m,n+1} - 2H_{m,n} + H_{m,n-1}) / \Delta \eta^2$$

Product terms are written as

$$H^2 = H_{m,n} H_{m+1,n} \quad (A2a)$$

$$HT = \frac{1}{2} (H_{m,n} T_{m+1,n} + H_{m+1,n} T_{m,n}) \quad (A2b)$$

In all of the foregoing approximations (A1 and A2), terms of the order $\Delta \xi^2$ and $\Delta \eta^2$ have been neglected. To avoid nonlinear difference equations, terms of the following form are approximated as

$$T(\partial H / \partial \xi) = [T_{m,n} + \frac{1}{2} \Delta \xi (\partial T / \partial \xi)_{m,n} + \dots] [(H_{m+1,n} - H_{m,n}) / \Delta \xi + \dots] \approx T_{m,n} (H_{m+1,n} - H_{m,n}) / \Delta \xi \quad (A3)$$

where terms of the order $\Delta \xi$ have been neglected.

When the difference quotients and terms (A1-A3) are substituted in the boundary-layer equations (6), the resulting linear difference equations are written as

$$A_n w_{n+1} + B_n w_n + C_n w_{n-1} = D_n \quad (A4)$$

where

$$w_n = \begin{bmatrix} f'_{m+1,n} \\ \theta_{m+1,n} \\ c_{Am+1,n} \end{bmatrix}$$

The matrices A_n , B_n , C_n , and D_n are evaluated at m and the expressions for them are given in Ref. 14. Since the simultaneous linear algebraic equations resulting from all of the difference equations (A4) across the boundary layer are of a special form, an efficient algorithm is available (see Ref. 15) and is applied to these equations in Ref. 14. Thus, the values of w_n are readily computed across the boundary layer.

With $f'_{m,n}$ and $f'_{m+1,n}$ known, the transformed velocity V is determined from the continuity equation (6a). This equation is evaluated at the point $(n - \frac{1}{2})$ and $(m + \frac{1}{2})$, and the derivatives are written as

$$\partial f' / \partial \xi = (f'_{m+1,n} + f'_{m+1,n-1} - f'_{m,n} - f'_{m,n-1}) / \Delta \xi \quad (A5a)$$

$$\partial V / \partial \eta = (V_{m+1/2,n} - V_{m+1/2,n-1}) / \Delta \eta \quad (A5b)$$

and the quantity $f'_{m+1/2,n-1/2}$ becomes

$$f'_{m+1/2,n-1/2} = \frac{1}{4} (f'_{m+1,n} + f'_{m+1,n-1} + f'_{m,n} + f'_{m,n-1}) \quad (A5c)$$

In the foregoing approximations, quantities of the order of the step size squared are neglected. When these relations are substituted into the continuity equation (6a) the unknown transformed velocity becomes

$$V_{m+1/2,n} = V_{m+1/2,n-1} - \left(\frac{\xi}{L} + \frac{\Delta \eta}{4} \right) (f'_{m+1,n} + f'_{m+1,n-1} + \left(\frac{\xi}{L} - \frac{\Delta \eta}{4} \right) (f'_{m,n} + f'_{m,n-1})) \quad (A6)$$

If iteration is to be performed, the A , B , C , and D matrices are reevaluated with the better values of the quantities at $(m + \frac{1}{2}, n)$ now available. Then new values of w_n and $V_{m+1/2,n}$ can be obtained. Iteration may be performed at every step or not at all; in either case the foregoing procedure is applied at succeeding steps downstream until the boundary-layer flow along the body is determined.

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