TURBULENT BOUNDARY LAYER ON A CATALYTIC SURFACE IN A NONEQUILIBRIUM DISSOCIATING GAS

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The majority of the studies which consider the flow of a dissociating gas in a turbulent boundary layer are devoted to the investigation of either frozen or equilibrium flows on a flat plate.

The frozen turbulent boundary layer has been studied by Dorrance [1], Kutateladze and Leont'ev [2], and Lapin and Sergeev [3]. A study of the effect of catalytic recombination processes at the plate surface on the heat transfer in a frozen turbulent boundary layer was made by Lapin [4].

Kosterin and Koshmarov [5], Ginzburg [6], Dorrance [7], and Lapin [8] have studied the turbulent boundary layer on a plate in equilibrium dissociating gas.

The calculation of the heat transfer in a turbulent boundary layer on a catalytic plate surface with nonequilibrium dissociation was made by Kulgein [9]. In this study the nonequilibrium nature of the dissociation process was taken into account only in the laminar sublayer, while the flow in the turbulent core was considered frozen. The solution was found numerically using a computer by means of a laborious iteration process.

The present paper reports a method for calculating the turbulent boundary layer on a flat catalytic plate with arbitrary dissociation rate. The method, constructed using the assumptions customary for turbulent boundary layer theory, is a successive approximation method. Good convergence of the method is assured by the fact that the effect of the nonequilibrium nature of the dissociation process on the parameter distribution in the boundary layer and, consequently, on the friction and heat transfer may be allowed for merely by finding corrections, usually relatively small, to the distribution of these parameters in the equilibrium or frozen flows. The basis of the study is the two-layer scheme of the turbulent boundary layer. The Prandtl and Schmidt numbers and also their turbulent analogs are taken equal to unity. As the model of the dissociating gas we use the Lighthill model of the ideal dissociating gas [10], extended by Freeman [11] to nonequilibrium flows.

1. Properties of dissociating gas.
Chemical kinetics leads to the following expression for the mass formation rate w_1 of the atomic component with dissociation of a diatomic molecule:

$$w_1 = \rho^2 [k_r (1+z) \rho_d m_1^{-2}] \times$$

$$\times [(1-z) \exp(-T_d/T) - (\rho/\rho_d) z^2]. \qquad (1.1)$$

Here ρ and T are, respectively, density and absolute temperature of the gas, z is the mass concentration of atoms in the mixture, m_1 is atomic weight, ρ_d and T_d are, respectively, the characteristic density and characteristic temperature of the gas [10], and k_r is the recombination rate constant. The subscripts 1 and 2 denote respectively quantities relating to the atomic and molecular components of the mixture.

In the general case the characteristic density is a variable quantity which depends on the temperature; however, for gases such as nitrogen and oxygen this variation is slight over a wide temperature range (1000–7000° K). This circumstance permitted Lighthill [10] to "linearize" the properties of the dissociating gas by making the assumption that ρ_d is constant or, what

amounts to the same thing, that the molecules are constantly excited with respect to the vibrational degrees of freedom to half their classical vibrational energy. This assumption leads to the number of degrees of freedom of the molecules (six) being twice the number of degrees of freedom of the atoms (three), as a result of which the heat contents at constant volume of the molecules and atoms per unit mass are the same ($c_{V1} = c_{V2}$), and the ratio of the specific heats for such a gas prior to dissociation is equal to 1.33 rather than 1.4 as for real gases.

The equation of state of the ideally dissociating gas has the form

$$p = \rho RT (1+z) \qquad (R = R_0/m_2). \qquad (1.2)$$

Here p is the gas pressure, R is the gas constant per unit mass of the molecules, R_0 is the universal gas constant, and m_2 is the molecular weight.

The magnitude H of the total enthalpy of the ideally dissociating gas is

$$H = RT(4+z) + Dz + \tfrac{1}{2} u^2 \qquad (D = RT_d). \qquad (1.3)$$

Here u is the velocity component in the boundary layer along the plate, and D is the dissociation energy per unit molecule mass.

2. Basic equations and boundary conditions.
With the assumption that the Prandtl and Schmidt numbers and their turbulent analogs are equal to unity, the differential equations for the momentum, energy, and diffusion of the atomic component of the averaged stationary motion of the reacting mixture in the turbulent boundary layer on the plate have the form

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y} \left[(\mu + \varepsilon) \frac{\partial u}{\partial y} \right], \qquad (2.1)$$

$$\rho u \frac{\partial H}{\partial x} + \rho v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y} \left[(\mu + \varepsilon) \frac{\partial H}{\partial y} \right], \qquad (2.2)$$

$$\rho u \frac{\partial z}{\partial x} + \rho v \frac{\partial z}{\partial y} = \frac{\partial}{\partial y} \left[(\mu + \varepsilon) \frac{\partial z}{\partial y} \right] + w_1. \qquad (2.3)$$

Here x, y and u, v are the coordinates and velocities along the plate and along the normal to the plate, respectively, and μ, ε are the dynamic and turbulent viscosity coefficients. We write the boundary conditions in the form

$$u = v = 0, \quad H = H_w,$$

$$\rho_w D_{12} (\partial z / \partial y)_w = k_w (z_w \rho_w)^n \quad \text{for} \quad y = 0;$$

$$u \to U_\infty, \quad H \to H_\infty, \quad z \to z_\infty \quad \text{as} \quad y \to \infty. \qquad (2.4)$$

Here k_W is the constant catalytic reaction rate, n is the reaction order, and D_{12} is the binary diffusion coefficient.

The condition for the concentration at the wall takes into account the effect of the wall catalytic properties on the atom recombination process; $(\partial z/\partial y)_W = 0$ for $k_W = 0$, which corresponds to a chemically isolated (absolutely noncatalytic) surface; $z_W \to 0$ as $k_W \to \infty$, which corresponds to an absolutely catalytic wall.

We shall assume that the gas flow outside the boundary layer is in a state of equilibrium dissociation.

3. Connection between the velocity, total enthalpy, and concentration profiles. From (2.1) and (2.2) and the boundary conditions (2.4) it follows that the velocity and total enthalpy profiles in the boundary layer are similar:

$$\frac{u}{U_\infty} = \frac{H - H_w}{H_\infty - H_w}. \qquad (3.1)$$

Substituting into (3.1) in place of the total enthalpy H its expression from (1.3), we obtain after simple transformations the connection of the temperature profile with the velocity and concentration profile:

$$T/T_d = [\bar{H}_w + (\bar{H}_\infty - \bar{H}_w)\bar{u} - \gamma\bar{u}^2 - z]/(4+z), \quad (3.2)$$
$$\bar{u} = u/U_\infty, \qquad \gamma = U_\infty^2/2D,$$
$$\bar{H}_w = H_w/D = z_w + (4 + z_w)(T_w/T_d),$$
$$\bar{H}_\infty = H_\infty/D = z_\infty + (4 + z_\infty)(T_\infty/T_d). \qquad (3.3)$$

Now we turn to the diffusion equation (2.3). Converting in this equation from the variables x, y to the Crocco variables x, u [12], we shall have

$$\rho u \frac{\partial z}{\partial x} = \frac{\tau^2}{\mu + \varepsilon}\frac{\partial^2 z}{\partial u^2} + w_1 \qquad (\tau = (\mu + \varepsilon)(\partial u/\partial y)). \quad (3.4)$$

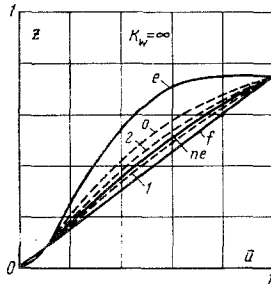Here τ is the friction stress in the boundary layer.

Fig. 1

For further simplification we shall consider the motion to be "quasi-stationary," i.e., such that the concentration profiles at each section depend only on the velocity ($\partial z/\partial x = 0$); in this case we obtain

$$\frac{d^2 z}{du^2} = -\frac{\mu + \varepsilon}{\tau^2} w_1 . \qquad (3.5)$$

We integrate (3.5) twice, determining the constants of integration from the wall conditions; then we have

$$z = z_w + \left(\frac{dz}{du}\right)_w u - \int_0^u du \int_0^u \frac{\mu + \varepsilon}{\tau^2} w_1 \, du. \qquad (3.6)$$

Taking account of the assumption made concerning the Schmidt number ($S = \mu_W/\rho_W D_{12} = 1$) and considering

only a first-order reaction (n = 1) at the catalytic wall, which is valid for wall temperatures which are not too
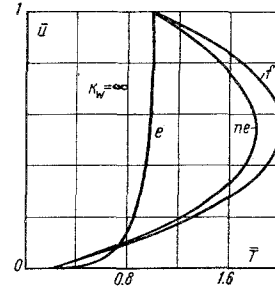

Fig. 2

high, we write the boundary condition for the concentration at the wall (2.4) in the form

$$\tau_w(dz/du)_w = k_w z_w \rho_w. \qquad (3.7)$$

Using the condition at the outer edge ($z = z_\infty$ for $u = U_\infty$) and (3.7), we find the relation for determining the atom concentration at the wall in the presence of catalytic absorption processes:

$$z_w = \left[z_\infty + \int_0^{U_\infty} du \int_0^u \frac{\mu + \varepsilon}{\tau^2} w_1 du\right]\left[1 + \frac{k_w \rho_w U_\infty}{\tau_w}\right]^{-1}. \quad (3.8)$$

It is more convenient for what follows to write (3.6) in the following form, which is easily obtained if we use the conditions at the outer edge of the boundary layer:

$$z = z_w + [z_\infty - z_w + J(1)]\bar{u} - J(\bar{u}), \qquad (3.9)$$

where

$$J(\bar{u}) = U_\infty^2 \int_0^{\bar{u}} d\bar{u} \int_0^u \frac{\mu + \varepsilon}{\tau^2} w_1 d\bar{u}. \qquad (3.10)$$

Thus, allowing for the effect of the nonequilibrium nature of the dissociation processes on the concentration distribution in the boundary layer amounts to calculating the quantity $J(\bar{u})$. In the particular case of frozen flow in the boundary layer ($w_1 = 0$) $J(\bar{u}) = 0$ and the atom concentration distribution is given by the expression

$$z = z_w + (z_\infty - z_w)\bar{u} . \qquad (3.11)$$

Turning to the determination of the quantity $J(\bar{u})$, we write it in the form

$$J(\bar{u}) = U_\infty^2 \int_0^{\bar{u}} d\bar{u} \int_0^{\bar{u}} \frac{w_1 d\bar{u}}{\tau(\partial u/\partial y)} . \qquad (3.12)$$

We introduce the universal coordinates

$$\varphi = u/v_*, \quad \eta = yv_*/\nu_w, \quad v_* = \sqrt{\tau_w/\rho_w}, \quad \nu_w = \mu_w/\rho_w . \quad (3.13)$$

We obtain

$$J(\bar{u}) = \xi^2 \nu_w \int_0^{\bar{u}} d\bar{u} \int_0^{\bar{u}} (w_1/\tau)\eta d\bar{u} \left(\xi = \frac{U_\infty}{v_*}, \eta^. = \frac{\partial\eta}{\partial\varphi}\right). \quad (3.14)$$

We must determine the dependence $\eta^. = \eta^.(\bar{u})$ in the viscous sublayer and in the turbulent core within the

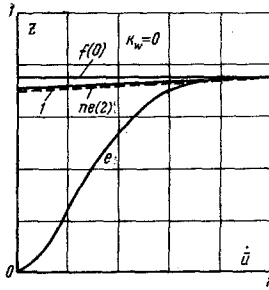framework of the two-layer scheme of the turbulent boundary layer which we have adopted in the present study.

Fig. 3

Making the simplifying assumption that the friction stress across the boundary layer is constant,

$$\tau = \text{const} = \tau_w \qquad (3.15)$$

and assuming at the same time that in the viscous sublayer the governing temperature will be the wall temperature, we can show [13] that in the sublayer the velocity profile has the form $\varphi = \eta$ and, consequently,

$$\eta = 1 \qquad \text{for } 0 \leqslant \bar{u} \leqslant \bar{u}_l \qquad (3.16)$$

For these same assumptions we can find [13] that the dimensionless velocity at the boundary of the viscous sublayer and the turbulent core is

$$U = \alpha/\zeta \qquad (\alpha = 11.5). \qquad (3.17)$$

Here α is an empirical turbulence constant.

Using the Karman formula for the turbulent friction stress

$$\tau = \rho \varkappa^2 (\partial u / \partial y)^4 / (\partial^2 u / \partial y^2)^2 \qquad (3.18)$$

and the assumption (3.15), we can show [13] that in the turbulent core

$$\eta = \frac{1}{f} \exp \left[\varkappa \zeta \int_{\bar{U}}^{\bar{u}} (\rho/\rho_w)^{1/2} d\bar{u} \right]$$

$$\left(U \leqslant \bar{u} \leqslant 1, \quad f = \frac{1}{\varkappa \alpha} \right). \qquad (3.19)$$

Here $\varkappa = 0.4$ is a second turbulence constant.

Returning to (3.14), we substitute therein (1.1) for the dissociation rate w_1, and then after simple transformations we obtain

$$J(\bar{u}) = C_r \frac{\zeta^4}{\text{Re}_w} \frac{\rho_w}{\rho_d} \int_0^{\bar{u}} d\bar{u} \int_0^{\bar{u}} \left(\frac{\rho}{\rho_w} \right)^3 (1 + z) \times$$

$$\times \left(\frac{\rho_d}{\rho} (1 - z) \exp \frac{-T_d}{T} - z^2 \right) \eta \cdot d\bar{u}$$

$$\left(C_r = \frac{x/U_\infty}{m_1^2/k_r \rho_d \rho_w}, \qquad \text{Re}_w = \frac{U_\infty \rho_w x}{\mu_w} \right). \qquad (3.20)$$

The quantity x/U_∞ is approximately equal to the time in which a particle travels the distance x from the leading edge of the plate. The quantity $m_1^2/k_r \rho_d \rho_w$

is proportional to the atom lifetime. Therefore, the coefficient C_r, representing the ratio of these two characteristic times, may be termed the recombination parameter. If this coefficient is large, the flow will be frozen.

In certain cases, for calculating the quantity $J(\bar{u})$ it is more convenient to use the expression for the dissociation rate w_1 written in terms of the equilibrium atom concentrations [14]:

$$w_1 = \frac{1}{2} k_r \rho^3 m_1^{-2} (1 + z) \frac{z_e^2 - z^2}{1 - z_e^2}, \qquad (3.21)$$

where z_e is the equilibrium atom concentration, determined by the equality

$$\frac{z_e^2}{1 - z_e} = \frac{\rho_d}{\rho} \exp \left(-\frac{T_d}{T} \right). \qquad (3.22)$$

In this case the quantity $J(\bar{u})$ may be calculated from the formula

$$J(\bar{u}) = \frac{1}{2} C_r \frac{\zeta^4}{\text{Re}_w} \frac{\rho_w}{\rho_d} \times$$

$$\times \int_0^{\bar{u}} d\bar{u} \int_0^{\bar{u}} \left(\frac{\rho}{\rho_w} \right)^3 (1 + z) \frac{z_e^2 - z^2}{1 - z_e^2} \eta \, d\bar{u}. \qquad (3.23)$$

4. Friction calculation. We may use the method presented in [8] for calculating the friction. Using this method, the friction coefficient c_f is expressed by the equality

$$\frac{c_f}{c_{f_0}} = \left(\frac{FK}{2N} \right)^2 \quad \left(F = 0.242 c_{f_0}^{-1/2}, \ K = \int_0^1 \left(\frac{\rho}{\rho_\infty} \right)^{1/2} d\bar{u} \right). \quad (4.1)$$

Here c_{f_0} is the local friction coefficient on a plate in an incompressible isothermal fluid flow. This coefficient may be calculated either from the familiar Karman formula

$$0.242 / \sqrt{c_{f_0}} = 0.41 + \lg (\text{Re}_\infty c_{f_0}), \qquad (4.2)$$

or from the simpler power formula

$$c_{f_\bullet} = 0.0263 \, \text{Re}_\infty^{-1/7} \qquad (\text{Re}_\infty = U_\infty \rho_\infty x / \mu_\infty). \quad (4.3)$$

The quantity N is determined from the solution of the equation

$$N + \lg N = \lg (\tfrac{1}{2} FK) + \tfrac{1}{2} (F + G) \quad \left(G = \lg \frac{\mu_\infty}{\mu_w} \right). \quad (4.4)$$

In place of (4.4) we may use the following approximate expression for N:

$$N = 0.25 + 1.64 [\lg (\tfrac{1}{2} FK) + \tfrac{1}{2} (F + G)]. \quad (4.5)$$

5. Computational sequence and example. The computational sequence using the method described, which is essentially a method of successive approximations, amounts to the following.

We first calculate the parameters z(u), T(u), $\rho(u)$, c_f, ζ of the boundary layer for the frozen [4] and equilibrium [8] flows.

As the zero approximation we may take either the parameters of the frozen flow denoted by the subscript f) or the parameters obtained as the arithmetic

mean of the parameters of the frozen and equilibrium flows, i.e., $a^{(0)} = 1/2(a_f + a_e)$ (the latter is usually preferable).

From (3.9), (3.10), and (3.20) [or (3.23)] we determine the concentration as a function of velocity $z^{(1)}(\bar{u})$ in the first approximation. Then, from (3.2) we find the temperature distribution $\bar{T}^{(1)}(\bar{u})$ in the boundary layer, and then from the known $z^{(1)}$ and $\bar{T}^{(1)}$ and the formula

$$\frac{\rho}{\rho_\infty} = \frac{T_\infty}{T} \frac{1 + z_\infty}{1 + z}$$

we calculate the density distribution $\bar{\rho}^{(1)}(\bar{u})$.

From the known density distribution we determine the friction coefficient $c_f^{(1)}$ (§4), the parameter $\zeta^{(1)}$ (3.14), and the parameter $\eta^{(1)}$ (3.19), etc.

We note that the convergence may be accelerated considerably if we take as the second approximation the half-sum of the zero and first approximations, i.e., $a^{(2)} = 1/2(a^{(0)} + a^{(1)})$.

The third approximation calculated on the basis of the resultant $a^{(2)}$ is quite satisfactory, and there is no need for further approximations in practice.

To illustrate the suggested method we made a calculation of the turbulent boundary layer on a slender wedge with half-angle 30° in a flow with velocity $U_\infty =$ $= 7$ km/sec at an altitude corresponding to a pressure of $2.85 \cdot 10^{-4}$ atm and temperature $T_\infty = 220°$ K. The wall temperature was taken as $T_w = 720°$ K.

In accordance with the Lighthill data [10], we took: $\rho_d = 130$ g/cm^3, $T_d = 59\ 000°$ K, $D = 3660$ cal/g.

For the recombination rate constant we took $k_r =$ $= 8.4 \cdot 10^{14}$cm^6/mol$^2 \cdot$sec, which corresponds to the value of this constant determined experimentally by Matthews [15] for $T = 3500°$ K, i.e., the variation of k_r with temperature was not considered.

The results of the calculation of the concentration and temperature profiles in the boundary layer on an absolutely catalytic plate ($k_w \to \infty$) are shown, respectively, in Figs. 1 and 2.

Figure 3 shows the concentration profile on a chemically isolated plate ($k_w = 0$). In making the calculation for this case the zero approximation was taken to be the concentration distribution in the frozen flow $z^{(0)} =$ $= z_f$. We see from Fig. 3 that allowing for the nonequilibrium nature of the dissociation led in this case to a comparatively slight variation of the concentration profile in comparison with z_f.

We note that in all the figures the letters e, f, and ne denote curves relating respectively to equilibrium, frozen, and nonequilibrium flows. The numerals on the figures denote the approximation number.

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