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Nearly equilibrium dissociating boundary-layer flows by the method of matched asymptotic expansions

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The approach to equilibrium in a non-equilibrium-dissociating boundary-layer flow along a catalytic or non-catalytic surface is treated from the standpoint of a singular perturbation problem, using the method of matched asymptotic expansions. Based on a linearized reaction rate model for a diatomic gas which facilitates closed-form analysis, a uniformly valid solution for the near equilibrium behaviour is obtained as the composite of appropriate outer and inner solutions. It is shown that, under near equilibrium conditions, the primary non-equilibrium effects are buried in a thin sublayer near the body surface that is described by the inner solution. Applications of the theory are made to the calculation of heat transfer and atom concentrations for blunt body stagnation point and high-speed flat-plate flows; the results are in qualitative agreement with the near equilibrium behaviour predicted by numerical solutions.

1. Introduction

During recent years, there has been a widespread interest in the theoretical prediction of non-equilibrium-dissociating boundary-layer properties. As a result, a variety of numerical methods with varying degrees of accuracy and complexity have been developed for this problem. Despite such advances, however, simplified analytical solutions continue to be of interest in understanding the underlying physical behaviour of reacting boundary-layer flows. One such method of solution is the perturbation approach, where the gas-phase reaction effects are treated as small departures from either a chemically frozen (non-reacting) or a completely equilibrium (infinitely fast-reacting) flow. The analysis of the former situation proceeds in a straightforward way by expanding the local dependent variables about the frozen solution in a series of ascending positive powers of an appropriate (convection time/reaction time) ratio, yielding perturbation solutions that are uniformly valid throughout the boundary layer. These nearly frozen solutions have been investigated by Rae (1963) for the case of flat-plate flow and by Inger (1964) for an entire family of non equilibrium boundary-layer flows including pressure-gradient effects. In contrast, the nearly equilibrium situation, which involves a singular perturbation problem, has received relatively little attention. A theory has been proposed by Lenard (1962, 1963) in which a perturbation procedure analogous to that employed in the nearly frozen case is used. However, as will be shown, this theory does not yield a uniformly valid solution across the boundary layer and indeed fails to recognize the singular-perturbation nature of the problem. To date, a satisfactory theory of the approach to equilibrium in a dissociating boundary layer has not been given.

In the present paper, such a theory is developed based on the method of matched asymptotic expansions as described by Van Dyke (1964). This method, which has been successfully applied to a wide variety of singular-perturbation problems in fluid mechanics, enables one to obtain a uniformly valid description of the near equilibrium behaviour throughout the boundary layer. Our development of the theory will proceed as follows. First, the general non-equilibrium boundary-layer equations for a dissociating diatomic gas are formulated under a set of simplifying approximations (including a linearized-reaction-rate model) which allow analysis in closed form. The near equilibrium situation is then examined and its singular-perturbation nature defined. An outer solution, which is invalid near the wall, is obtained, a portion of which is equivalent to the complete solution proposed by Lenard. A corresponding inner solution accounting for the effects of the wall is then constructed and matched to the outer solution. Finally, specific applications of the theory are presented for both stagnation-point and flat-plate boundary-layer flow.

2. Governing equations

We consider non-equilibrium boundary-layer flow of a dissociating diatomic gas along an impervious axisymmetric or two-dimensional body which is either adiabatic or has a uniform surface temperature. The inviscid flow at the edge of the boundary layer is taken to be in chemical equilibrium and any pressure gradient therein is neglected. These assumptions are exact for wedges and cones at supersonic speeds and also apply approximately to a highly cooled stagnation point on a hypersonic blunt body (Lees 1956). Furthermore, the customary simplifying assumptions are made that the Prandtl and Lewis numbers are equal to unity and that both the density–viscosity product $\rho\mu$ and the mixture specific heat c_p are constants. Finally, to facilitate a closed-form analysis of the near equilibrium perturbation behaviour, the gas phase dissociation–recombination chemistry will be idealized by the linearized model previously used by Broadwell (1958) and Chung (1960). According to this model, the gas is assumed to have an equilibrium atom concentration–temperature relationship of the form

$$\alpha_{EQ} = C_1 + C_2 T$$

and a net volumetric dissociation rate

$$\dot{W} = K_R \rho (C_1 + C_2 T - \alpha), \tag{1}$$

where the constants C_1, C_2 and K_R depend only on the pressure and type of gas involved. It is understood, of course, that this linearized model is probably not a satisfactory quantitative representation of the dissociating diatomic gas chemistry in actual boundary-layer flows.

It is emphasized that the foregoing approximations are adopted solely as a matter of convenience in simplifying the discussion and are not essential to the basic ideas presented herein. The present work is thus aimed at studying the essential features of the near equilibrium boundary layer by the method of matched asymptotic expansions rather than at constructing an analysis suitable for detailed calculations in practical applications.

Introduce now the well-known boundary-layer variables (Lees 1956)

$$\eta = \rho_e u_e r_B^j (2\xi)^{-\frac{1}{2}} \int_0^Y (\rho/\rho_e)\, dY, \tag{2a}$$

$$\xi = C \int_0^X \rho_e \mu_e u_e r_B^{2j}\, dX, \tag{2b}$$

$$u = u_e\, df/d\eta = u_e f', \tag{2c}$$

where $j = 0$ or 1 for two-dimensional or axi-symmetric flows, respectively, $C = \rho\mu/\rho_e\mu_e$ is the Chapman–Rubesin constant, and the subscript e denotes conditions at the outer edge of the boundary layer. Then the equations of momentum, energy, and atom mass-concentration conservation take the form

$$ff'' + f''' = 0, \tag{3}$$

$$f\frac{\partial \alpha}{\partial \eta} + \frac{\partial^2 \alpha}{\partial \eta^2} - 2\xi f' \frac{\partial \alpha}{\partial \xi} = \tilde{\Gamma}\xi^R(\alpha - C_1 - C_2 T), \tag{4}$$

$$f\frac{\partial H}{\partial \eta} + \frac{\partial^2 H}{\partial \eta^2} - 2\xi f' \frac{\partial H}{\partial \xi} = 0, \tag{5}$$

where the terms on the right side of (4) are defined below. The total enthalpy H is related to the atom mass fraction and to the static temperature T by

$$H = c_p T + \alpha h_D + \tfrac{1}{2}u_e^2 (f')^2, \tag{6}$$

h_D being the dissociation energy per unit atom mass.

The parameter $\tilde{\Gamma}$ in (4) is a characteristic ratio of convection time to gas phase reaction time (or Damkohler number) for the boundary layer, defined by the expression† $\xi^R \tilde{\Gamma} = 2\xi K_R (u_e\, d\xi/dX)^{-1}$. It therefore characterizes the gross magnitude of the chemical reaction effects between the two extremes of chemically frozen ($\tilde{\Gamma} \to 0$) and completely equilibrium ($\tilde{\Gamma} \to \infty$) flow, and is regarded as the fundamental parameter in the present problem. The coefficient ξ^R of $\tilde{\Gamma}$ in equation (4) represents the streamwise variation of the reaction effect along the body. It causes the non-equilibrium boundary layer to be non-similar except in the special case of a stagnation-point flow on a symmetric body where $R = 0$.

The boundary conditions are as follows. At the outer edge of the boundary layer $\quad f'(\infty) = 1, \quad \alpha(\xi, \infty) = \alpha_e = C_1 + C_2 T_e, \quad T(\xi, \infty) = T_e$

and $\quad H(\xi, \infty) = H_e = c_p T_e + \alpha_e h_D + \tfrac{1}{2}u_e^2.$

At the body surface

$$f(0) = f'(0) = 0, \tag{7a}$$

$$T(\xi, 0) = T_W = \text{const.} \quad \text{or} \quad \partial H(\xi, 0)/\partial \eta = 0, \tag{7b}$$

$$H(\xi, 0) = c_p T_W + h_D \alpha(\xi, 0). \tag{7c}$$

† For supersonic flows over wedges or cones of semi-angle θ_B,

$$\tilde{\Gamma} = 2K_R \{[(2j+1)\sin\theta_B]^{2j/2j+1} u_e^{2(j+1)/2j+1} (C\rho_e\mu_e)\, 1/(2j+1)\}^{-1} \quad \text{and} \quad R = (2j+1)^{-1},$$

whereas, at the stagnation point of a blunt body,

$$\tilde{\Gamma} = K_R (1+j)^{-1} (du_e/dX)^{-1} \text{ and } R = 0.$$

If for the sake of simplicity the wall is taken to be either perfectly catalytic or completely non-catalytic with respect to atom recombination on the surface, we also have either

$$\alpha(\xi, 0) = \alpha_{EQ,W} = C_1 + C_2 T_W \quad \text{(perfectly catalytic),} \tag{8a}$$

or

$$\partial\alpha(\xi, 0)/\partial\eta = 0 \quad \text{(completely non-catalytic).} \tag{8b}$$

The solution of (3) subject to the stated boundary conditions is recognized as the classical Blasius velocity profile in a flat-plate boundary layer. For later purposes, it is noted here that near the wall this solution takes the series form (Rosenhead 1963)

$$f(\eta) = \tfrac{1}{2}A\eta^2 - B\eta^5 + \ldots, \quad \text{where} \quad A = f''(0) \simeq 0{\cdot}470 \quad \text{and} \quad B = 0{\cdot}0018.$$

3. The equilibrium solution

Before treating the near-equilibrium perturbation problem, it is helpful to first examine briefly the limiting equilibrium solution defined by the foregoing equations.

Formally, the equilibrium solution is associated with the limit $\tilde{\Gamma} \to \infty$. In this limit, since the left side of (4) must be finite, we obtain $\alpha_{EQ} = C_1 + C_2 T_{EQ}$, which is simply the local equilibrium composition–temperature relationship. Moreover, since this limiting solution obtains independently of the term ξ^R in (4), the equilibrium boundary-layer properties are clearly self-similar, i.e. a function of η alone, under the present boundary conditions. The energy equation (5) thus reduces to an ordinary differential equation with the following Crocco integral solution for the equilibrium total-enthalpy profile:

$$H_{EQ}(\eta) = H_{EQ,W} + (H_e - H_{EQ,W}) f'(\eta), \tag{9}$$

with $H_{EQ,W} = C_p T_W + \alpha_{EQ,W} h_D$. The corresponding equilibrium temperature profile is then found from (6) and (9) to be

$$T_{EQ}(\eta) = T_W + (T_e - T_W) f' + \frac{u_e^2 f'(1-f')}{2(1+D)c_p}, \tag{10}$$

where the parameter $D \equiv h_D C_2/c_p = h_D(\alpha_e - \alpha_{EQ,W})/c_p(T_e - T_W)$ may be interpreted as an average ratio of the dissociation energy change to thermal energy change across the boundary layer. In the present approximation, the result obtained by setting $D = 0$ in (10) is formally identical to the temperature profile for chemically frozen flow. Thus it can be seen that the effect of equilibrium gas-phase reaction decreases the average boundary-layer temperature by allowing some of the thermal energy produced by viscous dissipation to be absorbed in dissociation of the molecules.

The foregoing equilibrium solution ignores the atom-concentration boundary conditions on the wall. In fact, it can be seen from (8) that this solution is compatible with the wall only in the extreme case of a perfectly catalytic surface. Thus in considering the approach to equilibrium in the presence of a finite or zero heterogeneous atom recombination rate, one would expect to find a thin non-equilibrium sublayer adjacent to the wall wherein the equilibrium solution is never attained. This situation was first observed by Hirschfelder (1957) in his analysis of chemical reactions in a simple heat conductivity cell, and was subsequently discussed qualitatively for boundary-layer flows by Cheng (1957). In the present work, the sublayer phenomenon emerges more or less automatically from the method of analysis in that it essentially determines the scale of the inner solution near the wall.

In preparation for the non-equilibrium analysis to follow, it is convenient to rewrite (4) and (5) with deviations from the local equilibrium solution as the dependent variables. To do this, we first note from (6) that the non-equilibrium boundary-layer temperature profile can be written as

$$T(\xi,\eta) = T_{EQ}(\eta)+c_p^{-1}[H(\xi,\eta)-H_{EQ}(\eta)]-\frac{h_D}{c_p}[\alpha(\xi,\eta)-\alpha_{EQ}(\eta)]. \tag{11}$$

Defining $\Gamma = (1+D)\tilde{\Gamma}$ and the new dependent variables $\tilde{\alpha} = \alpha(\xi,\eta)-\alpha_{EQ}(\eta)$, $G = h_D^{-1}[H(\xi,\eta)-H_{EQ}(\eta)]$, the (11) and the foregoing properties of the self-similar local equilibrium solution enable the specie conservation and energy equations (4) and (5), respectively, to be rewritten as follows:

$$f\frac{\partial\tilde{\alpha}}{\partial\eta}+\frac{\partial^2\tilde{\alpha}}{\partial\eta^2}-2\xi f'\frac{\partial\tilde{\alpha}}{\partial\xi} = \Gamma\xi^R\left(\tilde{\alpha}-\frac{DG}{1+D}\right)-(f\alpha'_{EQ}+\alpha''_{EQ}), \tag{12}$$

$$f\frac{\partial G}{\partial\eta}+\frac{\partial^2 G}{\partial\eta^2}-2\xi f'\frac{\partial G}{\partial\xi} = 0, \tag{13}$$

subject to the boundary conditions

$$\tilde{\alpha}(\xi,\infty) = G(\xi,0) = 0, \tag{14a}$$

$$\tilde{\alpha}(\xi,0) = G(\xi,0) = 0 \quad \text{catalytic wall,} \tag{14b}$$

$$\partial\tilde{\alpha}(\xi,0)/\partial\eta = -\alpha'_{EQ}(0), \quad G(\xi,0) = \alpha(\xi,0) \quad \text{non-catalytic wall.} \tag{14c}$$

Since (13) is a linear homogeneous differential equation, it is clear from boundary conditions (14*a*) and (14*b*) that the solution for $G(\xi,\eta)$ is trivial unless the atom concentration on the wall deviates from equilibrium. Thus, for a perfectly catalytic wall, we have

$$G(\xi,\eta) = 0, \tag{15}$$

which simply expresses the well-known fact that the total enthalpy distribution across a boundary layer on a catalytic surface is invariant to gas-phase reaction when the Lewis number is unity.

4. The approach to equilibrium: outer solution

Consider (12) in the case of nearly equilibrium flow where Γ is very large. Now as $\Gamma\to\infty$, it can be seen that the quantity $\tilde{\alpha}-D(1+D)^{-1}G$ tends to vanish like $(\Gamma\xi^R)^{-1}$. Thus it is reasonable as a first attempt to solve (12) in the near equilibrium limit to assume a series expansion for the aforementioned quantity in the form

$$\tilde{\alpha}-D(1+D)^{-1}G = \sum_{N=1}^{\infty}\tilde{\alpha}_{o,N}(\eta)\,(\Gamma\xi^R)^{-N}, \tag{16}$$

where in anticipation of the non-uniformly valid nature of the problem the subscript o has been used to denote the outer solution so as to distinguish it from the inner solution (subscript i) given below. Then substituting (16) into (12), making use of (13) and collecting terms in like powers of Γ, we obtain the following equations governing the perturbation functions $\tilde{\alpha}_{o,N}$:

$$\tilde{\alpha}_{o\,1}(\eta) = f\alpha'_{EQ} + \alpha''_{EQ} = \alpha''_{EQ}(0)\,[f''(\eta)/A]^2, \tag{17a}$$

$$\tilde{\alpha}_{o,2}(\eta) = f\tilde{\alpha}'_{o,1} + \tilde{\alpha}''_{o,1} + 2Rf'\tilde{\alpha}_{o,1}, \tag{17b}$$

$$\tilde{\alpha}_{o,N}(\eta) = f\tilde{\alpha}'_{o,N-1} + \tilde{\alpha}''_{o,N-1} + 2R(N-1)\tilde{\alpha}_{o,N-1}, \tag{17c}$$

where (11) has been used to simplify the right side of (17a) as indicated. Equations (17) define the Nth-order atom concentration perturbation as an algebraic function of derivatives of the $\tilde{\alpha}_{o,N-1}$. Since all derivatives of the unknowns must vanish exponentially at $\eta \rightarrow \infty$ in a boundary-layer flow, it is seen that all the $\tilde{\alpha}_{o,N}(\infty) = 0$ as required by the outer boundary conditions (14a). However, the inner boundary conditions (14b)–(14c) obviously cannot be satisfied by these algebraic solutions, as is readily verified. The series solution (16) therefore cannot be a correct description of the near equilibrium behaviour near the wall but rather is in the nature of an outer asymptotic solution for large Γ. The difficulty of course arises from the fact that, when the expansion (16) is substituted into the specie conservation equation (12), *all* derivatives of the unknown $\tilde{\alpha}_{o,N}$ (including the highest-order or diffusion term) are lost, resulting in a singular-perturbation problem.

The energy equation (13) governing the total enthalpy perturbation $G(\xi, \eta)$ is a linear homogeneous differential equation that does not contain Γ explicitly. Therefore, in view of the boundary conditions (14a) and (14c), the solution for G will be proportional to the atom concentration perturbation on the wall with an implicit dependence on Γ as determined by this perturbation. Consequently, the solution for G throughout the boundary layer on a non-catalytic wall is determined completely by the inner atom-concentration solution, as will be shown below.

It is pointed out that the series solution (16) with the term $D(1+D)^{-1}G$ dropped is essentially the form proposed by Lenard (1962, 1963) as a *complete* solution for near-equilibrium boundary-layer flows. It is clear from the foregoing discussion, however, that for a perfectly catalytic wall ($G = 0$) his solution is only an outer asymptotic representation valid sufficiently far from the wall. Furthermore, in the non-catalytic wall case, Lenard's approach fails to give even a complete outer solution, since it neglects the asymptotic influence of the non-equilibrium enthalpy perturbation near the wall contained in the term

$$D(1+D)^{-1}G(\xi, \eta).$$

5. Inner solution and matching

The fundamental property required of the inner solution is that it should take proper account of the diffusion term and its balance with the homogeneous chemical reaction rate near the wall. Now atom diffusion and reaction are of the same order (and the outer solution fails) within a sublayer adjacent to the wall whose thickness η^* is of the order of $\eta^* \sim \Gamma^{-\frac{1}{2}}$, so that the inner solution should therefore be constructed in a new normal co-ordinate whose scale has been contracted by this thickness. Accordingly, we define the new independent inner variable $Q = \Gamma^{\frac{1}{2}}\eta$, in terms of which (12) can be rewritten for large Γ, as

$$\left.\begin{aligned}\frac{\partial^2\tilde{\alpha}}{\partial Q^2}+\frac{AQ^2}{2\Gamma^{\frac{3}{2}}}\left(1-\frac{2BQ^3}{A\Gamma^{\frac{3}{2}}}+\ldots\right)\frac{\partial\tilde{\alpha}}{\partial Q}-\frac{2\xi AQ}{\Gamma^{\frac{3}{2}}}\left(1-\frac{5BQ^3}{A\Gamma^{\frac{3}{2}}}+\ldots\right)\frac{\partial\tilde{\alpha}}{\partial\xi}\\ = \xi^R\left[\tilde{\alpha}-\frac{DG(\xi,0)}{1+D}-\frac{DQ\Gamma^{-\frac{1}{2}}}{(1+D)}\frac{\partial G}{\partial\eta}(\xi,0)-\ldots\right]-\frac{\alpha''_{EQ}(0)}{\Gamma}-\ldots,\end{aligned}\right\} \tag{18}$$

subject to the wall boundary conditions $\alpha(\xi, 0) = 0$ or $\partial\alpha(\xi,0)/\partial Q = -\Gamma^{-\frac{1}{2}}\alpha'_{EQ}(0)$. It is observed in (18) that the diffusion and leading reaction-rate terms are independent of Γ and balance exactly as convection effects vanish on the wall. Thus we are assured of accounting correctly for the non-equilibrium behaviour near the wall and the surface boundary conditions.

We now have to solve (13) and (18) subject to the stated boundary conditions. As suggested by the form of the above non-catalytic wall boundary condition, preliminary study shows that the solutions take the form of the following series expansions:

$$\tilde{\alpha} = \sum_{N=1}^{\infty} \tilde{\alpha}_{i,N}(\xi, Q)\,\Gamma^{-\frac{1}{2}N}, \tag{19}$$

$$G = \sum_{N=1}^{\infty} \tilde{\alpha}_{i,N}(\xi, 0)\,g_N(\eta)\,\Gamma^{-\frac{1}{2}N}, \tag{20}$$

where we require $\tilde{\alpha}_{i,N}(\xi,0) = 0$ on a catalytic wall or $\partial\tilde{\alpha}_{i,N}(\xi,0)/\partial\eta = -\alpha'_{EQ}(0)$ for $N = 1$ and zero otherwise on a non-catalytic wall and $g_N(\infty) = 0$, $g_N(0) = 1$. Substitution of the series (19) and (20) into (18) then yields the following sequence of linear second-order differential equations governing the inner perturbation distribution functions $\tilde{\alpha}_{i,N}$,

$$\xi^{-R}\frac{\partial^2\tilde{\alpha}_{i,1}}{\partial Q^2}-\tilde{\alpha}_{i,1} = -D(1+D)^{-1}\tilde{\alpha}_{i,1}(\xi,0), \tag{21 a}$$

$$\xi^{-R}\frac{\partial^2\tilde{\alpha}_{i,2}}{\partial Q^2}-\tilde{\alpha}_{i,2} = -\frac{D}{1+D}\left[\tilde{\alpha}_{i,2}(\xi,0)+Q\tilde{\alpha}_{i,1}(\xi,0)g'_1(0)\right]-\alpha''_{EQ}(0), \tag{21 b}$$

$$\xi^{-R}\frac{\partial^2\tilde{\alpha}_{i,3}}{\partial Q^2}-\tilde{\alpha}_{i,3} = -\frac{D}{1+D}\left[\tilde{\alpha}_{i,3}(\xi,0)+Q\tilde{\alpha}_{i,2}(\xi,0)g'_2(0)\right]. \tag{21 c}$$

We note from these equations that the Nth-order atom concentration perturbation involves only the $(N-1)$th-order enthalpy perturbations. Similarly, substitution of (20) into (13) yields the following equation governing the $g_N(\eta)$:

$$fg'_N+g''_N+NRf'g_N = 0, \tag{22}$$

where in arriving at this equation we have anticipated the results (shown below) that $\alpha_{i,N}(\xi,0) \sim \xi^{-\frac{1}{2}NR}$.

The differential equation (22) and boundary conditions $g_N(\infty) = 0$, $g_N(0) = 1$ constitute a type of Sturm–Liouville eigenvalue problem which arises frequently in boundary-layer theory. In the special case of stagnation-point flow $R = 0$, a simple analytical solution is easily obtained by comparing (22) with (3):

$$g_N(\eta) = 1 - f'(\eta) \quad (R = 0). \tag{23}$$

For arbitrary non-zero value of R, solutions of this eigenvalue problem (which must necessarily be numerical) are apparently unknown at present. However, in the case of flat-plate or supersonic wedge flow ($R = 1$), Fox & Libby (1963) have made a detailed study of the solution for even values of N; a complete tabulation of the first ten eigenfunction solutions possessing the property of exponential decay at $\eta \to \infty$ is given in their paper. There appear to be no comparable results for odd values of N, except in the case $N = 1$, where (22) can be integrated directly to the analytical solution

$$g_1(\eta) = \exp - \int_0^\eta f(\eta')\, d\eta' = A^{-1} f''(\eta) \quad (R = 1). \tag{24}$$

We now proceed to the determination of the inner atom concentration perturbations, hereafter restricting attention to the first three terms by dropping quantities of order Γ^{-2} and smaller. The general solutions of equations (21 *a*)–(21 *c*) that satisfy the boundary conditions are readily found to be

$$[\tilde{\alpha}_{i,1}(\xi, Q)]_{\text{cat.}} = E_1 \sinh \xi^{\frac{1}{2}R} Q, \tag{25a}$$

$$[\tilde{\alpha}_{i,1}(\xi, Q)]_{\text{non-cat.}} = E_1 \cosh \xi^{\frac{1}{2}R} Q + \{D\tilde{\alpha}_{i,1}(\xi, 0)/(1+D)\} + \xi^{-\frac{1}{2}R} \alpha'_{EQ}(0) \exp(-\xi^{\frac{1}{2}R} Q), \tag{25b}$$

$$[\tilde{\alpha}_{i,1}(\xi, 0)]_{\text{non-cat.}} = (1+D) E_1 + (1+D)\, \alpha'_{EQ}(0)\, \xi^{-\frac{1}{2}R}, \tag{25c}$$

$$[\tilde{\alpha}_{i,2}(\xi, Q)]_{\text{cat.}} = E_2 \sinh \xi^{\frac{1}{2}R} Q + \xi^{-R} \alpha''_{EQ}(0)\, [1 - \exp(-\xi^{\frac{1}{2}R} Q)], \tag{26a}$$

$$\begin{aligned}[(\tilde{\alpha}_{i,2}(\xi, Q)]_{\text{non-cat.}} = {} & E_2 \cosh \xi^{\frac{1}{2}R} Q + \xi^{-R} \alpha''_{EQ}(0) + \frac{D}{1+D}\, \tilde{\alpha}_{i,2}(\xi, 0) \\ & + \frac{D}{1+D}\, \tilde{\alpha}_{i,1}(\xi, 0)\, g'_1(0)\, [Q + \xi^{-\frac{1}{2}R} \exp(-\xi^{\frac{1}{2}R} Q)],\end{aligned} \tag{26b}$$

$$\begin{aligned}[(\tilde{\alpha}_{i,2}(\xi, 0)]_{\text{non-cat.}} = {} & (1+D)\, [E_2 + E_1 D \xi^{-\frac{1}{2}R} g'_1(0)] \\ & + (1+D)\, \xi^{-R} [\alpha''_{EQ}(0) + D g'_1(0)\, \alpha'_{EQ}(0)],\end{aligned} \tag{26c}$$

$$[\tilde{\alpha}_{i,3}(\xi, Q)]_{\text{cat.}} = E_3 \sinh \xi^{\frac{1}{2}R} Q, \tag{27a}$$

$$\begin{aligned}[\alpha_{i,3}(\xi, Q]_{\text{non-cat.}} = {} & E_3 \cosh \xi^{\frac{1}{2}R} Q + \frac{D}{1+D} \tilde{\alpha}_{i,3}(\xi, 0) \\ & + \frac{D}{1+D} \tilde{\alpha}_{i,2}(\xi, 0)\, g'_2(0)\, [Q + \xi^{-\frac{1}{2}R} \exp(-\xi^{\frac{1}{2}R} Q)],\end{aligned} \tag{27b}$$

$$\begin{aligned}[\tilde{\alpha}_{i,3}(\xi, 0)]_{\text{non-cat.}} = {} & (1+D)\, [E_3 + D \xi^{-\frac{1}{2}R} E_2 g'_2(0) + D^2 \xi^{-R} E_1 g'_1(0)\, g'_2(0)] \\ & + (1+D)\, D \xi^{-\frac{3}{2}R} g'_2(0)\, [\alpha''_{EQ}(0) + D g'_1(0)\, \alpha'_{EQ}(0)],\end{aligned} \tag{27c}$$

where the $E_1, E_2, E_3, \ldots$ are arbitrary constants. Now application of the asymptotic matching principle described by Van Dyke (1964), and as described in the appendix, shows that the inner and outer expansions will indeed match (neglecting exponentially small terms) if $E_1 = E_2 = E_3 = 0$. Thus the final inner solutions for the atom concentration perturbations can be written:

$$[\tilde{\alpha}_{i,1}(\xi, Q)]_{\text{cat.}} = 0, \tag{28a}$$

$$[\tilde{\alpha}_{i,1}(\xi, Q)]_{\text{non-cat.}} = \alpha'_{EQ}(0)\,\xi^{-\frac{1}{2}R}[D + \exp(-\xi^{\frac{1}{2}R}Q)], \tag{28b}$$

$$[\tilde{\alpha}_{i,2}(\xi, Q)]_{\text{cat.}} = \alpha''_{EQ}(0)\,\xi^{-R}[1 - \exp(-\xi^{\frac{1}{2}R}Q)], \tag{29a}$$

$$\begin{aligned}[\tilde{\alpha}_{i,2}(\xi, Q)]_{\text{non-cat.}} = {} & (1 + D)\,\xi^{-R}\alpha''_{EQ}(0) \\ & + Dg'_1(0)\,\xi^{-R}\alpha'_{EQ}(0)\,[D + \xi^{\frac{1}{2}R}Q + \exp(-\xi^{\frac{1}{2}R}Q)],\end{aligned} \tag{29b}$$

$$[\tilde{\alpha}_{i,3}(\xi, Q)]_{\text{cat.}} = 0, \tag{30a}$$

$$\begin{aligned}[\tilde{\alpha}_{i,3}(\xi, Q)]_{\text{non-cat.}} = {} & D\xi^{-\frac{3}{2}R}g'_2(0)\,[\alpha''_{EQ}(0) + Dg'_1(0)\,\alpha'_{EQ}(0)] \\ & \times [D + \xi^{\frac{1}{2}R}Q + \exp(-\xi^{\frac{1}{2}R}Q)],\end{aligned} \tag{30b}$$

from which we verify that $[\tilde{\alpha}_{i,N}(\xi, 0)]_{\text{non-cat.}} \sim \xi^{-\frac{1}{2}NR}$.

Since the wall boundary condition is compatible with the assumption of gas-phase dissociation–recombination equilibrium for a perfectly catalytic surface, the vanishing first-order atom concentration perturbation predicted by equation (28*a*) would be expected. In contrast, there does exist an incompatibility for a non-catalytic surface, and hence a non-vanishing first-order effect is obtained as indicated by (28*b*). Observe that this atom concentration perturbation is proportional to the equilibrium atom concentration gradient (atom diffusion flux) at the wall, which is in accord with physical reasoning.

The second-order inner atom concentration perturbation (29*a*) for a catalytic wall is non-vanishing, being directly proportional to $\alpha''_{EQ}(0)$, the *volumetric* equilibrium diffusion source of atoms at the surface. The corresponding non-catalytic wall solution (29*b*) involves in addition a term proportional to both the equilibrium atom *flux* into the surface and the first-order heat-transfer perturbation. The third-order catalytic-wall solution, which in general would be proportional to $\alpha'''_{EQ}(0)$, vanishes because $\alpha'''_{EQ}(0) = 0$ in the present gas model [see (10)]. In the non-catalytic case, the perturbation is composed of a term proportional to this third derivative (here zero) plus a term proportional to the second-order heat-transfer perturbation $g'_2(0)$. Thus we see that each successive inner perturbation solution is associated with progressively higher-order equilibrium atom-concentration gradients at the wall, beginning in the first perturbation with $\alpha''_{EQ}(0)$ in the non-catalytic wall case and in the second perturbation with $\alpha''_{EQ}(0)$ for a perfectly catalytic surface. Correspondingly, each higher order introduces larger powers of $\xi^{-\frac{1}{2}R}$ and hence increasingly stronger non-similar effects of non-equilibrium reaction. The present solution therefore correctly predicts that the dissociating gas flow in either plate, wedge or cone boundary layers always approaches equilibrium sufficiently far downstream of the leading edge. Finally, it can be seen from the inner specie equation (18) and its associated series solution (19)–(20) that diffusion and chemical reaction mainly govern the near equilibrium inner solutions; the explicit influence of *convection* (the second and third terms in (18)) enters only to order Γ^{-2} and higher. This is to be expected, since diffusion and reaction are the dominating effects within the low-velocity non-equilibrium sublayer near the wall where the inner solution applies. The main influence of convection is contained in the outer solution.

A typical composite atom concentration solution for near equilibrium flow, which is uniformly valid across the boundary layer up to order $\Gamma^{-\frac{1}{2}}$, is illustrated in figure 1. The smooth fairing of the inner solution into the outer asymptotic solution at sufficiently large distance from the wall is apparent. Also, the non-equilibrium sublayer near the walls whose thickness decreases with increasing Γ is clearly seen in this figure.

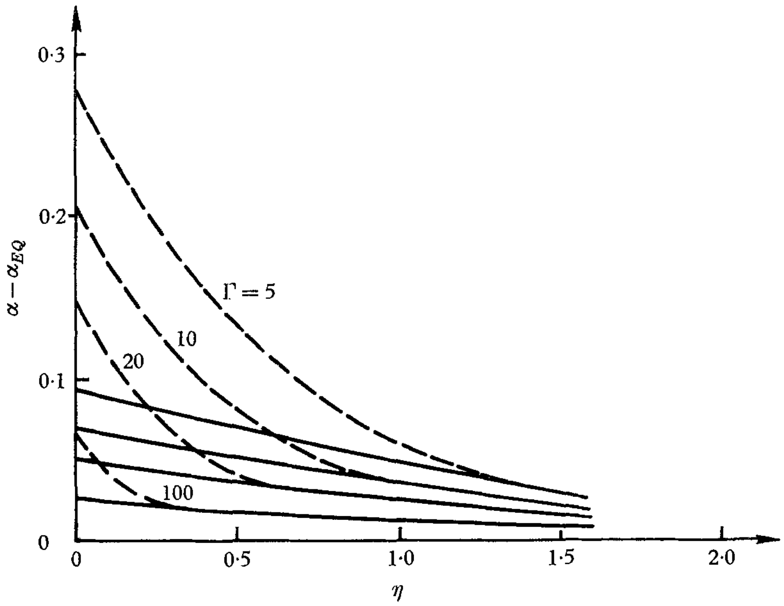

FIGURE 1. Typical composite perturbation solution. Stagnation point non-catalytic wall: $D = 0{\cdot}50$, $\alpha_e = 1{\cdot}0$, $\alpha_{EQ,W} \simeq 0$. ----, inner solution; ——, outer solution.

6. Some illustrative applications

The foregoing theory enables one to evaluate the near equilibrium behaviour of certain gross boundary-layer properties such as heat transfer that are important experimental observables. In the remainder of the paper some of these will be examined in two examples (blunt body stagnation and hypersonic flat plate flow), where numerical solutions of the non-equilibrium boundary-layer equations are available for comparison.

The heat transfer in the present theory for $L_e = 1$ is directly proportional to the total enthalpy gradient at the wall and is independent of the gas-phase reaction rate when the surface is perfectly catalytic. Consequently, a study of non-equilibrium reaction effects on heat transfer (and surface atom concentration) involves only the non-catalytic wall solutions. From equations (9), (20) and (28*b*)–(30*b*), we obtain for large Γ the following general relations governing the non-catalytic surface atom concentration and heat transfer, respectively:

$$\begin{aligned}\alpha(\xi,0) = {}& \alpha_{EQ}(0)+(1+D)\,(\Gamma\xi^R)^{-\frac{1}{2}}\alpha'_{EQ}(0)\\ &+(1+D)\,(\Gamma\xi^R)^{-1}[\alpha''_{EQ}(0)+Dg'_1(0)\,\alpha'_{EQ}(0)]\\ &+(1+D)\,D(\Gamma\xi^R)^{-\frac{3}{2}}g'_2(0)\,[\alpha''_{EQ}(0)+Dg'_1(0)\,\alpha'_{EQ}(0)]+\ldots,\end{aligned} \tag{31}$$

$$\begin{aligned}\frac{\partial H}{\partial\eta}(\xi,0) = {}& Ac_p(1+D)\left[T_e-T_W+\frac{u_e^2}{2(1+D)c_p}\right]+h_D(1+D)\,(\Gamma\xi^R)^{-\frac{1}{2}}g'_1(0)\,\alpha'_{EQ}(0)\\ &+h_D(1+D)\,(\Gamma\xi^R)^{-1}g'_2(0)\,[\alpha''_{EQ}(0)+Dg'_1(0)\,\alpha'_{EQ}(0)]\\ &+h_D(1+D)\,D(\Gamma\xi^R)^{-\frac{3}{2}}g'_2(0)\,g'_3(0)\,[\alpha''_{EQ}(0)+Dg'_1(0)\,\alpha'_{EQ}(0)]+\ldots,\end{aligned} \tag{32}$$

where $g'_1(0) = g'_2(0) = g'_3(0) = \ldots = -A$ for the stagnation point ($R = 0$) while $g'_1(0) = 0$ [equation (24)] and $g'_2(0) = -0{\cdot}950$ (Fox & Libby 1963) for the flat plate ($R = 1$).

Consider highly cooled blunt-body stagnation-point flow, where by virtue of the negligible viscous dissipation (10) yields $\alpha'_{EQ}(0) = A[\alpha_e-\alpha_{EQ}(0)]$ and $\alpha''_{EQ}(0) = 0$. Then (31) and (32) simplify to

$$\{\alpha(\xi,0)-\alpha_{EQ}(0)\}/\{\alpha_e-\alpha_{EQ}(0)\} = (1+D)\,[A\Gamma^{-\frac{1}{2}}-A^2D\Gamma^{-1}+A^3D^2\Gamma^{-\frac{3}{2}}-\ldots], \tag{33}$$

$$\partial H(\xi,0)/\partial\eta = Ac_p(1+D)\,(T_e-T_W)\,[1-DA\Gamma^{-\frac{1}{2}}+D^2A^2\Gamma^{-1}-D^3A^3\Gamma^{-\frac{3}{2}}+\ldots], \tag{34}$$

between which there exists the simple relation

$$\frac{H'_{EQ}(0)-\partial H(\xi,0)/\partial\eta}{D(1+D)^{-1}H'_{EQ}(0)} = \frac{\alpha(\xi,0)-\alpha_{EQ}(0)}{\alpha_e-\alpha_{EQ}(0)}. \tag{35}$$

According to (33) and (34) the first-order departure from equilibrium, which is proportional to $\Gamma^{-\frac{1}{2}}$, reduces the heat transfer by increasing the corresponding wall atom concentration and thereby reducing the driving enthalpy difference across the boundary layer. For large Γ, this result is in agreement with both Fay & Riddell's (1958) numerical solution and Inger's (1963) approximate analytical theory of the non-equilibrium stagnation-point boundary-layer problem. Moreover, by noting that the denominator of the left side of (35) is equal to the difference between the equilibrium and frozen heat transfer for the present gas model, this equation is also found to agree exactly with known results (Lees 1956; Inger 1963).

A second application of interest is the high-speed flat-plate boundary layer. In particular, we consider the special case of an adiabatic plate surface for which numerical solutions of the non-equilibrium boundary-layer equations are available. Here, we have

$$\alpha'_{EQ}(0) = 0, \quad T_{EQ}(0) = T_e+u_e^2/2c_p(1+D)$$

and

$$\alpha''_{EQ}(0) = -C_2A^2u_e^2/c_p(1+D),$$

so that setting $(\partial H/\partial\eta)_W = 0$ in (31) and (32) yields the following expressions for wall atom concentration and recovery temperature, respectively:

$$\alpha(\xi,0) = \alpha_{EQ}(0)-\frac{C_2A^2u_e^2}{c_p}[(\Gamma\xi)^{-1}-0{\cdot}95D(\Gamma\xi)^{-\frac{3}{2}}+\ldots], \tag{36}$$

$$T(\xi,0) = T_{EQ}(0)+\frac{0{\cdot}95ADu_e^2}{(1+D)c_p}[(\Gamma\xi)^{-1}+Dg'_3(0)\,(\Gamma\xi)^{-\frac{3}{2}}+\ldots]. \tag{37}$$

In contrast to the stagnation-point flow, departure from equilibrium within the highly dissipative boundary layer along an adiabatic flat plate decreases the non-catalytic wall atom concentration, the leading term in the near-equilibrium perturbation being proportional to $(\Gamma\xi)^{-1}$. Correspondingly, the local recovery temperature increases. This occurs because dissociation, acting as a heat sink, tends to reduce the recovery temperature (as is evident in the equilibrium limit); hence the decrease in dissociation level attending a departure from equilibrium causes an increase in $T(\xi, 0)$. These conclusions are in qualitative agreement for large Γ with the numerical results of Chung & Anderson (1960) and also with Broadwell's (1958) theory for non-equilibrium Couette flow.

7. Concluding remarks

This paper has shown that the method of matched asymptotic expansions can be used to solve the singular perturbation problem connected with the approach to equilibrium in a dissociating–recombining laminar-boundary-layer flow. Moreover, it has been demonstrated that, unlike the opposite extreme of nearly frozen flow, a straightforward parameter perturbation approach involving the characteristic gas-phase Damkohler number such as proposed by Lenard does not yield a uniformly valid solution across the boundary layer. Indeed, for a non-catalytic surface, most of the (small) departure from equilibrium is in fact buried in a thin non-equilibrium sublayer near the wall, where it is governed by an inner solution that depends only on the local equilibrium solution and derivatives thereof.

The qualitative predictions of the present theory concerning non-equilibrium effects on wall properties such as heat transfer are confirmed by the results of Broadwell (1958), Fay & Riddell (1958), Inger (1963) and Chung & Anderson (1960). Since the latter three investigations employed fairly realistic chemical reaction models of the gas, this agreement also verifies that the linearized reaction-rate model used here does account for the main physical features of the problem as assumed.

Stimulating discussions with Dr G. Emanuel are gratefully acknowledged.

Appendix. Matching of inner and outer solutions

Consider first the matching procedure for the perfectly catalytic wall case. From (15), (16) and (17) we have the outer solution for the atom concentration as

$$\tilde{\alpha}_0(\eta, \xi)_{\text{cat.}} = \{\alpha''_{EQ}(0)/\Gamma\xi^R\}\,[f''(0)/A]^2 + O(\Gamma^{-2}\xi^{-2R}) + \ldots,$$

which when rewritten in terms of the inner variable $Q = \Gamma^{\frac{1}{2}}\eta$ and expanded for large Γ [using the fact that $f'''(0) = 0$] becomes

$$\tilde{\alpha}_0(Q, \xi)_{\text{cat.}} = \alpha''_{EQ}(0)\,(\Gamma\xi^R)^{-1} + O(\Gamma^{-2}\xi^{-2R}) + \ldots. \qquad \text{(A 1)}$$

From (19), (25*a*), (26*a*) and (27*a*), the corresponding inner solution is

$$\begin{aligned}\tilde{\alpha}_i(Q,\xi)_{\text{cat.}} &= E_1\Gamma^{-\frac{1}{2}}\sinh\xi^{\frac{1}{2}R}Q + E_2\Gamma^{-1}\sinh\xi^{\frac{1}{2}R}Q \\ &\quad + \frac{\alpha''_{EQ}(0)}{\Gamma\xi^R}\,[1-\exp(-\xi^{\frac{1}{2}R}Q)] + E_3\Gamma^{-\frac{3}{2}}\sinh\xi^{\frac{1}{2}R}Q + O(\Gamma^{-2}) + \ldots\end{aligned}$$

which in terms of the outer variable η for large Γ becomes

$$\left.\begin{aligned}\tilde{\alpha}_i(\eta,\xi)_{\text{cat.}} &= \sinh(\eta\xi^{\frac{1}{2}R}\Gamma^{\frac{1}{2}})\sum_N E_N\Gamma^{-\frac{1}{2}N} \quad \text{if} \quad E_N \neq 0 \\ &= (\Gamma\xi^R)^{-1}\alpha''_{EQ}(0)\,[1-\exp(-\xi^{\frac{1}{2}R}\eta\Gamma^{\frac{1}{2}})] \quad \text{if} \quad E_N = 0.\end{aligned}\right\} \tag{A 2}$$

Neglecting exponentially small terms, expressions (A 1) and (A 2) will match as required if $E_1 = E_2 = E_3 = \ldots = 0$.

The non-catalytic wall case is treated in the same way. From (16), (17) and (20) [using the fact that $g''_N(0) = 0$ from (22)] the outer solution written in terms of the inner variable and expanded for large Γ is found to be

$$\begin{aligned}\tilde{\alpha}_0(Q,\xi)_{\text{non-cat.}} &= \frac{D\tilde{\alpha}_{i,1}(\xi,0)}{(1+D)\Gamma^{\frac{1}{2}}}\,[1+\eta g'_1(0)] + \frac{\alpha''_{EQ}(0)}{\Gamma\xi^R} \\ &\quad + \frac{D\tilde{\alpha}_{i,2}(\xi,0)}{(1+D)\Gamma}\,[1+\eta g'_2(0)] + \frac{D\tilde{\alpha}_{i,3}(\xi,0)}{(1+D)\Gamma^{\frac{3}{2}}} + O(\Gamma^{-2}) + \ldots.\end{aligned} \tag{A 3}$$

Equations (19), (25*b*), (26*b*) and (27*b*) yield the following expression for the corresponding inner solution in terms of the outer variable:

$$\left.\begin{aligned}\tilde{\alpha}_i(\eta,\xi)_{\text{non-cat.}} &= \cosh\eta\xi^{\frac{1}{2}R}\Gamma^{\frac{1}{2}}\sum_N E_N\Gamma^{-\frac{1}{2}N} \quad \text{if} \quad E_N \neq 0 \\ &= \frac{D\tilde{\alpha}_{i,1}(\xi,0)}{(1+D)\Gamma^{\frac{1}{2}}}\left[1+\eta g'_1(0) + \frac{g'_1(0)}{\xi^{\frac{1}{2}R}\Gamma^{\frac{1}{2}}}\exp(-\xi^{\frac{1}{2}R}\eta\Gamma^{\frac{1}{2}})\right] \\ &\quad + \frac{\alpha''_{EQ}(0)}{\Gamma\xi^R} + \frac{D\tilde{\alpha}_{i,2}(\xi,0)}{(1+D)\Gamma}\left[1+\eta g'_2(0) + \frac{g'_2(0)}{\xi^{\frac{1}{2}R}\Gamma^{\frac{1}{2}}}\exp(-\xi^{\frac{1}{2}R}\eta\Gamma^{\frac{1}{2}})\right] \\ &\quad + \frac{D\alpha_{i,3}(\xi,0)}{(1+D)\Gamma^{\frac{3}{2}}} + \frac{\alpha'_{EQ}(0)}{\xi^{\frac{1}{2}R}}\exp(-\xi^{\frac{1}{2}R}\eta\Gamma^{\frac{1}{2}}) \quad \text{if} \quad E_N = 0.\end{aligned}\right\} \tag{A 4}$$

Neglecting exponentially small terms, matching of (A 3) and (A 4) is obtained again by requiring $E_1 = E_2 = E_3 = \ldots = 0$.

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