Linear Theory for Chemically Reacting Flows

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The limitations imposed by the linearization of rate equations in chemically reacting flow problems using equilibrium reference states are discussed. A general linearized differential equation using nonequilibrium reference states is presented. An extended linear theory based on the general linearized equation is developed and shown to be effective for many type of reacting flows involving substantial variations of flow parameters brought about by finite rate chemistry.

I. Introduction

CHEMICALLY nonequilibrium flow problems are of current importance in a number of applications ranging from gas dynamic lasers to rocket propulsion and re-entry aerodynamics. Because of the coupling between the finite rate chemistry and the dynamics of the flow, reacting flows with chemical nonequilibrium are considerably more difficult to treat than are corresponding flows of chemically inert gases. At the present, the majority of solutions of reacting flow problems are numerical and, as such, rely upon the availability of high-speed computers. The large number of flow parameter generally involved in reacting flow problems, moreover, have required very large amounts of computational efforts, even by modern computational standards, for the numerical solution of reacting flow problems of importance in applications. For this reason, current literature emphasizes the need of analytical methods that would produce solutions contributing to a better understanding of the various features of reacting flows as well as alleviating the large computer time required by numerical methods.

In developing analytical approaches to the reacting flow problems, it must be realized that the general nonlinear differential equations governing the flow presents great mathematical difficulties so that some simplifications of these equations are necessary. Several authors[1-6] have formulated linearized differential equations for reacting flows and obtained analytical results for flows over bodies of various shapes. Ideally, linear solutions should provide acceptable quantitative as well as qualitative answers within limitations imposed by the linearization procedures. For problems involving the flow of perfect gas, the advantages and limitations of the linear theory are well known. For reacting flow problems, however, the linearization of the rate equations introduces additional complications, and the linearization procedure frequently must be compromised[3,5] to resolve the complications. Principally because of these complications, the limitations of the linear theories as applied to reacting flow problems have not been established, and it has not been obvious that the linear theory can be successfully applied to problems for which finite rate chemistry brings about substantial variations of the dynamic variables of the flow. The main purpose of this paper is twofold: 1) to discuss the limitations imposed by the linearization of the rate equations, and 2) to present an extended linear theory that is effective for reacting flow problems involving large flow-parameter variations.

In formulating linearized differential equations for flow problems, the usually used reference state is that of a uniform undisturbed flow. Linear theories for reacting flow employ the concept of a "chemical relaxation time" in the linearization of the reaction rate equation.‡ The linear solutions then proceed on the assumption that this relaxation time can be approximated by a suitable constant value throughout the reacting flowfield. In reality, however, the relaxation time, because of its strong temperature dependence, generally vary substantially in reacting flows, even though the variations of other flow parameter are small. Consequently, linear results based on the undisturbed flow condition can give acceptable quantitative results only if the departure from the undisturbed flow condition is extremely small.[5]

The preceding observation was substantiated by the linear solution developed by Clarke[3] for a supersonic flow of a dissociating gas over a convex corner. Clarke linearized the governing differential equations assuming small departures of the chemically relaxing flow downstream of the corner from the uniform equilibrium flow upstream of the corner. Instead of evaluating the relaxation time based on the upstream flow condition, however, Clarke introduced an average relaxation time based on the downstream conditions. Clarke noted that the linear theory contains "classical defects." That is, even for the case of a chemically inert gas, the linear theory overestimates the pressure drop at the corner. He reported, however, that using the average relaxation time, the theory gives a pressure variation along the downstream wall which is in reasonable agreement with the results of method of characteristics obtained by Cleaver[7] for the case of a 5° turning angle at the corner. Clarke and McChesney[8] further showed that even for this case of a relatively small turning angle, the assumption of a constant average value for the relaxation time is not especially good. For large turning angle cases, the linear results of Clarke[3] exhibited substantial disagreement with the method of characteristics results of Appleton.[9] Sundaram[5] argued that the agreement between Clarke's linear results and Cleaver's method of characteristics

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‡ In a complex gas mixture, several chemical reactions can occur simultaneously and a corresponding number of relaxation times enter the problem. This paper, as well as previous linear theories, considers the problem in which a single chemical process is of importance. The analysis presented here, however, can be readily extended to multiple processes.

results is due to a large nonlinear correction to the relaxation time. Sundaram suggested that, for the flow over a convex corner, the appropriate reference state to use is the state immediately following the frozen expansion at the corner and not the state of the upstream flow approaching the corner. Sundaram showed that the linear solution obtained using this downstream reference state is in good agreement with Cleaver's method of characteristics results for a turning angle of 5°.

Wu and Sigman[6] developed a modified linear solution for the problem of free expansion of an initially uniform supersonic reactive flow into a region of constant pressure. In the case of a perfect gas, the problem of free expansion is equivalent to that of a flow over a convex corner with a straight downstream wall. However, with a finite rate reaction involved in the reacting flow problem, the bounding streamline downstream of the expansion fan is not straight and the free expansion problem is no longer equivalent to the convex corner problem. The modified linear solution of Wu and Sigman uses the asymptotic equilibrium condition on the bounding streamline as the reference state and incorporates procedures to account for the classical defects of the linear theory. The results thus obtained exhibit good agreement with the method of characteristics results[10] for cases of low as well as moderately high upstream to downstream pressure ratios in which chemical processes causes only moderate changes in the flow parameters. For cases in which substantial variations of the flow parameter resulted from finite rate chemistry, however, considerable deviations from the results of method of characteristics prevailed.

The extended linear theory developed in the present work differs from previous linear theories in that it allows more than one reference states to be used for any given problem and that the reference states need not be equilibrium states. With the extended theory, the chemically reacting flow is considered in zones, each with its own reference state. A linear solution is derived for each zone, the extent of which is determined by requiring the departure of flow parameters from the reference values in each zone to be within prescribed limits. The extended linear solutions is then obtained by combining the solutions of the successive zones.

The extended linear theory has been applied to several supersonic reactive flow problems, including flows over solid convex corner and wedges, the expansion and compression of a flow with a free boundary, and chemically relaxing flow downstream of a strong normal shock. Numerical illustrations are provided for the normal shock and the free expansion problems. The specific reactive process treated is the dissociation-recombination reaction of an oxygen like gas, $A_2 \rightleftarrows 2A$. Lighthill's[11] model of an ideal dissociating gas and a rate equation of the form suggested by Freeman[12] are used. The effectiveness of the extended linear theory is demonstrated by the remarkable agreement between the present results and the more exact numerical solutions of the nonlinear differential equations. The agreement prevailed for all cases studied, including cases involving substantial changes of flow parameters both from an undisturbed flow and within chemically reacting regions. Thus the usefulness of the extended linear theory is not restricted to problems where chemical reactions brings about only small changes in the flow, or where the departure from a single reference state is small. Another noteworthy feature of the extended linear theory is that, while the previous method[6] that has been successfully applied to problems involving moderately larger changes in the various flow parameter requires a prior knowledge of an asymptotic equilibrium state of the flow, no such knowledge is required by the extended theory. Rather, the asymptotic state is determined from the linear solution. As a consequence, the extended theory is applicable to a more general class of problems than are previous linear theories.

II. Formulation of Linearized Equations

The over-all conservation equations for the adiabatic and inviscid flow of a gas are expressible in the form[13]

$$(D\rho/Dt)+\rho\nabla\cdot\mathbf{v}=0 \tag{1}$$

$$\rho(D\mathbf{v}/Dt)+\nabla p=0 \tag{2}$$

$$\rho(Dh/Dt)-(Dp/Dt)=0 \tag{3}$$

where ρ, $\mathbf{v}$, p, and h are the density, the velocity, the pressure, and the enthalpy of the gas, respectively.

For a gas with only one nonequilibrium process, the equation of state and the rate equation are expressible in the forms

$$h=h(\rho,p,q) \tag{4}$$

$$Dq/Dt=\omega(\rho,p,q) \tag{5}$$

where q is a nonequilibrium process variable.

The set of Eqs. (1–5), together with appropriate initial and boundary conditions, permit the numerical solution of reacting flow problems, provided that the forms of the functions h and ω are known. In the formulation of linearized equations, however, it has been customary to introduce an equilibrium process variable q^*. In a nonequilibrium flowfield, the state of the gas is specified by three independent state variables. However, q^* is an equilibrium variable and therefore a function of only two independent state variables. The local value of q^* in an nonequilibrium flowfield depends on the selection of the two local state variables in the definition of q^*. Moore and Gibson[2] used the local temperature and density in defining q^*; Vincenti[1] used density and pressure; and Clarke[3] pressure and entropy. The resulting linearized equations obtained by the different authors, however, are similar in form. If q^* is considered a function of local density and pressure, then

$$q^*=q^*(\rho,p) \tag{6}$$

The set of Eqs. (1–6) forms a convenient basis for the formulation of linearized differential equations using an equilibrium reference state. The usual procedure is to express each local flow variable, including the local equilibrium process variable q^*, as a sum of a reference quantity and a disturbance quantity, i.e.,

$$\rho=\rho_r+\rho',\ \text{etc}$$

where the subscript "r" denotes the reference quantity and the prime denotes the disturbance quantity. The governing equations are then expressed in terms of the reference and disturbance quantities, and are linearized by retaining only terms of the first order in the disturbance quantities and their derivative. The resulting linearized equations are subjected to the restriction that the disturbance quantities and their derivatives are small in comparison with the local values at the reference state. The linearized version of Eqs. (1–6) can be combined to give a single partial differential equation, which, for the case of steady flow, is of the form[13]

$$v_r\tau_r\frac{\partial}{\partial x}\left(\frac{v_r^2}{a_{f,r}^2}\frac{\partial^2 f}{\partial x^2}-\nabla^2 f\right)+\left(\frac{v_r^2}{a_{e,r}^2}\frac{\partial^2 f}{\partial x^2}-\nabla^2 f\right)=0 \tag{7}$$

where x is the coordinate in the direction of $\mathbf{v}_r$, τ is a relaxation time defined by

$$\tau=-\left(\frac{\partial h}{\partial\rho}\right)\Big/\left(\frac{\partial\omega}{\partial q}\right)\left[\left(\frac{\partial q^*}{\partial\rho}\right)\left(\frac{\partial h}{\partial q}\right)+\left(\frac{\partial h}{\partial\rho}\right)\right] \tag{8}$$

The quantities a_f and a_e are, respectively, the frozen and equilibrium speeds of sound defined by

$$a_f^2=\left(\frac{\partial h}{\partial\rho}\right)\Big/\left(\frac{1}{\rho}-\frac{\partial h}{\partial p}\right) \tag{9}$$

and

$$a_e^2=\left(\frac{\partial h}{\partial\rho}+\frac{\partial h}{\partial q}\frac{\partial q^*}{\partial\rho}\right)\Big/\left(\frac{1}{\rho}-\frac{\partial h}{\partial p}-\frac{\partial h}{\partial q}\frac{\partial q^*}{\partial p}\right) \tag{10}$$

The quantity f can be any of the dependent variables, ρ, $\mathbf{v}$, p, h, q, or the disturbance potential ϕ such that $\mathbf{v}'=\nabla\phi$.

A generalized version of Eq. (7) which do not require the reference state to be an equilibrium state is obtainable by linearizing the set of Eqs. (1–5) without introducing Eq. (6). The linearized versions of Eqs. (1–5) are, for steady flow

$$\mathbf{v}_r\cdot\nabla\rho'+\rho_r\nabla\cdot\mathbf{v}'=0 \tag{11}$$

$$\rho_r(\mathbf{v}_r\cdot\nabla)\mathbf{v}'+\nabla p'=0 \tag{12}$$

$$\rho_r\nabla h'-\nabla p'=0 \tag{13}$$

$$h'=\left(\frac{\partial h}{\partial\rho}\right)_r\rho'+\left(\frac{\partial h}{\partial p}\right)_r p'+\left(\frac{\partial h}{\partial q}\right)_r q' \tag{14}$$

$$\mathbf{v}_r\cdot\nabla q'=\omega_r+\left(\frac{\partial\omega}{\partial\rho}\right)_r\rho'+\left(\frac{\partial\omega}{\partial p}\right)_r p'+\left(\frac{\partial\omega}{\partial q}\right)_r q' \tag{15}$$

where the subscript r refers to values of the various flow variables, not necessarily equilibrium values, at any specified point in the flowfield.

Equation (12) implies the existence of a disturbance potential ϕ such that

$$\mathbf{v}'=\nabla\phi \tag{16}$$

and

$$p'=-\rho_r\mathbf{v}_r\cdot\nabla\phi=-\rho_r\mathbf{v}_r\cdot\mathbf{v}' \tag{17}$$

Equations (11, 13, and 14) then require the following relations:

$$\mathbf{v}_r\cdot\nabla\rho'=-\rho_r\nabla\cdot\mathbf{v} \tag{18}$$

$$h'=-\mathbf{v}_r\cdot\mathbf{v}' \tag{19}$$

$$\mathbf{v}_r\cdot\nabla q'=\left\{\left[\rho_r\left(\frac{\partial h}{\partial p}\right)_r-1\right]\mathbf{v}_r\cdot\nabla(\mathbf{v}_r\cdot\mathbf{v}')+\rho_r\left(\frac{\partial h}{\partial\rho}\right)_r\nabla\cdot\mathbf{v}'\right\}\Big/\left(\frac{\partial h}{\partial q}\right)_r \tag{20}$$

Taking the gradient of each term in Eq. (15), dotting the resulting vectors with $\mathbf{v}_r$, and using Eqs. (17–20) give a second-order linear differential equation for the disturbance velocity vector

$$\tau_r^{+}\mathbf{v}_r\cdot\nabla\left[\frac{1}{a_{f,r}^{2}}\mathbf{v}_r\cdot\nabla(\mathbf{v}_r\cdot\mathbf{v}')-\nabla\cdot\mathbf{v}'\right]+\frac{1}{a_{\omega,r}^{2}}\mathbf{v}_r\cdot\nabla(\mathbf{v}_r\cdot\mathbf{v}')-\nabla\cdot\mathbf{v}'=0 \tag{21}$$

where

$$\tau^{+}=\left(\frac{\partial h}{\partial\rho}\right)\Big/\left(\frac{\partial\omega}{\partial\rho}\frac{\partial h}{\partial q}-\frac{\partial\omega}{\partial q}\frac{\partial h}{\partial\rho}\right) \tag{22}$$

and

$$a_\omega^{2}=\left(\frac{\partial\omega}{\partial q}\frac{\partial h}{\partial\rho}-\frac{\partial\omega}{\partial\rho}\frac{\partial h}{\partial q}\right)\Big/\left[\frac{\partial\omega}{\partial q}\left(\frac{1}{\rho}-\frac{\partial h}{\partial p}\right)+\frac{\partial\omega}{\partial p}\frac{\partial h}{\partial q}\right] \tag{23}$$

Since Eqs. (17–20), which relate the disturbance variables ρ', p', h', and q' to $\mathbf{v}'$, are linear, differential equations for each of the disturbance variables are easily obtainable by manipulating Eq. (21). Placing Eq. (16) into Eq. (21) gives a third-order differential equation for ϕ which is a generalized version of Eq. (7). It is not difficult to show that τ^{+} reduces to τ and a_ω to a_e with the restriction of an equilibrium referenced state.

The quantity a_ω, which has the dimension of velocity, may be referred to as the "constant rate speed of sound." For an adiabatic process, the first law of thermodynamics gives

$$dh-(1/\rho)\,dp=0 \tag{24}$$

Using Eq. (4) and considering the rate function ω to be dependent on the three prime variables ρ, p, and q, one obtains from Eq. (24)

$$dp=\left\{\left[\frac{\partial\omega}{\partial q}\frac{\partial h}{\partial\rho}-\frac{\partial\omega}{\partial\rho}\frac{\partial h}{\partial q}\right]\Big/\left[\frac{\partial\omega}{\partial q}\left(\frac{1}{\rho}-\frac{\partial h}{\partial p}\right)+\frac{\partial\omega}{\partial p}\frac{\partial h}{\partial q}\right]\right\}d\rho+\left\{\left[\frac{\partial h}{\partial q}\right]\Big/\left[\frac{\partial\omega}{\partial q}\left(\frac{1}{\rho}-\frac{\partial h}{\partial p}\right)+\frac{\partial\omega}{\partial p}\frac{\partial h}{\partial q}\right]\right\}d\omega \tag{25}$$

The coefficient of $d\rho$ in Eq. (25) is identical to the right side of Eq. (23). Therefore

$$a_\omega^{2}=\left(\frac{\partial p}{\partial\rho}\right)_{\omega\,=\,\text{const, adiabatic process}} \tag{26}$$

In other words, a_ω may be thought of as local speed of propagation of a small disturbance in an adiabatic medium with a constant rate function. It should be noted that the restriction of a constant rate function, which enters Eq. (26), is not equivalent to the requirement that the rate function is independent of ρ, p, or q individually. That is, the partial derivatives $\partial\omega/\partial\rho$, $\partial\omega/\partial p$, and $\partial\omega/\partial q$ need not vanish individually. Rather, the requirement is

$$d\omega=\frac{\partial\omega}{\partial\rho}d\rho+\frac{\partial\omega}{\partial p}dp+\frac{\partial\omega}{\partial q}dq=0 \tag{27}$$

In actual reacting flow problems Eq. (27) is, in general, not satisfied. The concept of constant rate speed of sound, though an artificial one, is nevertheless useful in the linear theory for reacting flow, as shall be shown. It should be noted that the equilibrium speed of sound, a_e, which appears in Eq. (7), can be defined only in an actual equilibrium state.[13] On the other hand, the constant rate speed of sound, a_ω, like the frozen speed a_f, can be evaluated for arbitrary values of ρ, p, and q, and is therefore defined whether or not the fluid is in an equilibrium state. It is further noted that the relaxation time τ^{+} which appears in Eq. (21) is also defined for any equilibrium or nonequilibrium state, while τ, which appears in Eq. (7) is unambiguously defined only for an equilibrium state. Equation (21) is therefore not restricted to an equilibrium reference state while Eq. (7) is.

Since the basic restriction of the linear solutions is that the deviations of the flow variables relative to their reference values are small, the choice of the reference state is of paramount importance in the linear solution. In most nonequilibrium flow problems of practical interest, the flow parameters vary substantially over the flowfield. If the reference state is restricted to an equilibrium state, then it can only correspond to an undisturbed state or a state asymptotically approached by the fluid. With neither choice, it is possible to have only small deviations of the flow parameters from their reference values over the entire flowfield. This consideration, together with the strong temperature dependence of the relaxation time which appears in the linearized equation, places a severe limitation on the range of applicability of previous linear solutions.

The fact that Eq. (21) does not require an equilibrium reference state effectively extends the range of applicability of the linear solutions by permitting the segmentation of the flowfield into zones, each with its own nonequilibrium reference state. The reference state for a given zone can be prescribed to be any known condition of the flow at a point within or on the boundary of that zone. If the extent of each zone is determined by requiring the departure of flow variables from their reference values to be within prescribed small limits, then the linearized equation provides an accurate description of the flow within each zone. If further the boundary conditions for each zone are suitable and adequately known, then a linear solution with good accuracy can be established for each zone. The solution for the entire flowfield is then obtained by combining the linear solutions for individual zones.

The approach that has been outlined is particularly suited for, although not limited to, problems where a marching procedure can be adopted so that the flow properties at a downstream boundary point of a preceding zone serve to establish reference values for the succeeding zone. It needs to be emphasized that the approach is based on linear solutions and should not be viewed as a numerical method. For many problems of practical interest, only a few zones may be needed to cover the flowfield of interest, and acceptable quantitative results can be obtained without the use of a high speed computer. It is noted in passing that the reference values for the flow parameters cannot be selected arbitrarily since the equation of state must be satisfied by the reference values. However, if the reference values are selected to correspond to the computed local values of the flow at any given point in the flowfield, the reference values do satisfy the equation of state within the context of the linear theory.

In the following section, the problem of flow relaxation behind a normal shock and of the supersonic free expansion are treated to illustrate the application of the extended linear theory. The specific reactive process considered is the dissociation-recombination reaction of a diatomic gas, $A_2 \rightleftarrows 2A$. Lighthill's model[11] of an ideal dissociation gas and a rate equation of the form suggested by Freeman[12] are used. That is, the process variable, q, is taken to be the degree of dissociation, α, defined as the mass fraction of the dissociated gas. The equations of state and the rate function are

$$h = R[(4+\alpha)T+\alpha\theta] \tag{28}$$

$$T = p/(1+\alpha)\rho R \tag{29}$$

$$\omega = cT^{\eta}\rho\left\{(1-\alpha)\exp\left(-\frac{\theta}{T}\right) - \frac{\rho\alpha^2}{\rho_d}\right\} \tag{30}$$

where η is a dimensionless constant, c is a constant whose dimension is such that the quantity $(cT^{\eta}\rho)$ has the dimension of $(\text{time})^{-1}$, R is the gas constant for the diatomic gas A_2, θ and ρ_d are constant whose dimensions are temperature and density, respectively.

Placing Eq. (29) into Eqs. (28) and (30) gives an equation of state and a rate equation of the forms (4) and (5). It can be shown that the quantities a_f, a_ω, and τ^+ are given by

$$a_f^2 = RT\left[\frac{(1+\alpha)(4+\alpha)}{3}\right] \tag{31}$$

$$a_\omega^2 = RTf/g \tag{32}$$

$$\tau^+ = \frac{(1+\alpha)(4+\alpha)}{cT^{\eta}\rho f} \tag{33}$$

where

$$f = \left\{(7+2\alpha+\alpha^2)+(1-\alpha^2)\left[\eta\left(1+\frac{\theta}{T}\right)+\left(\frac{\theta}{T}\right)\right]\right\}\exp\left(-\frac{\theta}{T}\right)+ \alpha\left\{2(4+2\alpha+\alpha^2)-\alpha(1+\alpha)\left[\eta-(2-\eta)\frac{\theta}{T}\right]\right\}\frac{\rho}{\rho_d} \tag{34}$$

$$g = \left\{3+(1-\alpha)\left[\eta\frac{\theta}{T}+\left(\frac{\theta}{T}\right)^2\right]\right\}\exp\left(-\frac{\theta}{T}\right)+\alpha\left(6-\alpha\eta\frac{\theta}{T}\right)\frac{\rho}{\rho_d} \tag{35}$$

The expression for a_f can be found in standard texts on reacting gas dynamics. The expressions for a_ω and τ^+ reduces, for the special case of $\eta = 0$, to expressions previously reported by Sundaram[5] who, in a study of the problem of relaxing flow over a solid convex corner, used the frozen flow condition at the corner after the expansion is completed as the reference condition to formulate a linearized equation.

III. Linear Solutions

There exists in the literature several linear solutions for reacting flows. In this section, the linear solutions for the one-dimensional relaxing flow behind a normal shock and for the free expansion of a supersonic reacting flow are discussed. The simplicity of the normal shock problem makes it an ideal vehicle for an investigation to establish the range of applicability of the extended linear theory. The supersonic free expansion problem constitutes an important aspect of studies such as rocket exhaust plume and reacting base flow. It offers an opportunity to demonstrate the effectiveness of the extended linear theory in treating relatively complex reacting flow problems which would otherwise require numerical integrations.

Normal Shock

The problem of steady, one-dimensional flow of a reacting flow through a normal shock has been studied by a number of authors. Freeman,[12] for example, presented nonlinear numerical results for an ideal dissociating gas with the equations of state and the rate function given by Eqs. (28–30). For the present problem, the flow is divisible into two distinguishable regions. The first region is a shock front in which translational, rotational, and vibrational energies are considered to adjust instantaneously (in the time scale pertinent to chemical reaction), resulting in abrupt changes in the flow variables, while the chemical composition is frozen and remains unchanged. Following the shock front is a region where chemical reactions bring about more gradual changes in the flow variables. In previous studies of the normal shock problem, the flow upstream of the shock front is considered to be uniform and in complete thermodynamic equilibrium. The second region is then referred to as the chemical relaxation zone. The condition of the flow at the beginning of the relaxation zone (i.e., immediately downstream of the shock front) is obtainable from the usual conservation equations for a normal shock with frozen chemical composition.§ Far downstream of the shock front, the state of the gas approaches asymptotically an equilibrium state, which is determinable from the shock relations for an equilibrium flow without considering nonequilibrium effects. In previous linear solutions[13] based on an equilibrium reference state, it has been pointed out that this downstream equilibrium state, rather than the upstream state, is the appropriate reference state for the relaxation zone. The linearized differential equation for the disturbance velocity is, according to Eq. (7)

$$\frac{d^2v'}{dx^2} + \frac{M_{e,b}^2-1}{\tau_b v_b(M_{f,b}^2-1)}\frac{dv'}{dx} = 0 \tag{36}$$

where b denotes the downstream equilibrium state, M_e is the equilibrium Mach number defined by $M_e = v/a_e$, M_f is frozen Mach number defined by $M_f = v/a_f$, and x is the distance from the shock front.

The solution of Eq. (36) is

$$v = v_b + c_1\exp\left[-\frac{(M_{e,b}^2-1)x}{\tau_b v_b(M_{f,b}^2-1)}\right]+c_2 \tag{37}$$

where c_1 and c_2 are constants of integration.

It is obvious that $c_2 = 0$ since $v = v_b$ at $x = \infty$. The constant c_1 cannot be evaluated using the asymptotic condition. It is possible, however, to determine c_1 using the condition of the flow at the beginning of the relaxation zone which are known from the frozen shock relations. In Ref. 13, it has been shown that within the context of the linear theory one has

$$\left(\frac{dv'}{dx}\right)_o = \left[\left(\frac{\partial\omega}{\partial\alpha}\right)_b\left(\frac{\partial h}{\partial\alpha}\right)_b(\alpha_o^* - \alpha_o)\right]\Big/\left[\rho_b\left(\frac{\partial h}{\partial\rho}\right)_b(M_{f,b}^2-1)\right] \tag{38}$$

where the subscript "o" refers to $x = 0$, i.e., the condition immediately after the shock front, $\alpha^* = \alpha^*(\rho, p)$.

Using Eq. (38) as a boundary condition, one obtains

$$v = v_b + \frac{v_b(\partial h/\partial\alpha)_b(\alpha_o^* - \alpha_o')}{\rho_b(M_{e,b}^2-1)[(\partial h/\partial\rho)_b+(\partial h/\partial\alpha)_b(\partial\alpha^*/\partial\rho)_b]}\times \exp\left[-\frac{(M_{e,b}^2-1)x}{\tau_b v_b(M_{f,b}^2-1)}\right] \tag{39}$$

Alternatively, if the velocity at $x = 0$, rather than its derivative, is used as a boundary condition, one has

$$v = v_b + (v_o - v_b)\exp\left[-\frac{(M_{e,b}^2-1)x}{\tau_v v_b(M_{f,b}^2-1)}\right] \tag{40}$$

Although Eq. (40) is equivalent to Eq. (39) within the context of the linear theory, they give different quantitative results for cases where the departure from the reference state, b, is not extremely small. In the following discussions, the results obtained using the initial derivative of a disturbance variable as a boundary condition is referred to as the linear solution. The results obtained using the initial value of a disturbance variable as a boundary condition is referred to as the modified linear solution.

If the reference state is not restricted to an equilibrium state, then from Eq. (21) one obtains a differential equation identical in form to Eq. (36) but with the reference state b replaced by r, the quantities $M_{e,b}$ and τ_b replaced by $M_{\omega,r}$ and τ_r^+, where $M_\omega = v/a_\omega$. The solution of this equation is

$$v' = c\left\{\exp\left[-\frac{(M_{\omega,r}^2-1)(x-x_r)}{\tau_r^+ v_r(M_{f,r}^2-1)}\right]-1\right\} \tag{41}$$

where x_r is the location where the reference quantities are evaluated and the condition $v_r' = 0$ has been utilized to determine one of the constants of integration.

§ It has been pointed out[13] that if the vibrational energy is in equilibrium at its fully excited value, then the gas behaves as a perfect gas across the shock front. It can be easily shown, in fact, that for the ideal dissociating gas with half-excited vibrational energy, the gas also behaves as a perfect gas with the gas constant and the ratio of specific heats taking on the values $(1+\alpha)R$ and $(4+\alpha)/3$, respectively. Perfect gas normal shock relations can therefore be used to establish the condition at the beginning of the relaxation zone.

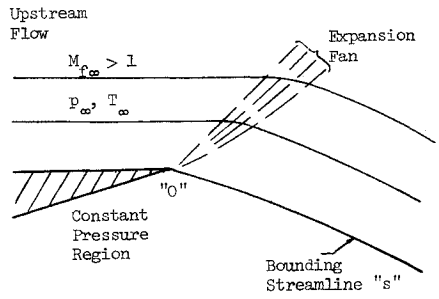

Fig. 1 Flow geometry for the supersonic free expansion problem.

With the aid of Eqs. (5) and (20), it can be shown that

$$\left(\frac{\partial v}{\partial x}\right)_r = -\left[\left(\frac{\partial h}{\partial \alpha}\right)_r \omega_r\right] \Big/ \left[\rho_r \left(\frac{\partial h}{\partial \rho}\right)_r (M_{f,r}{}^2 - 1)\right] \tag{42}$$

The constant c can be determined by differentiating Eq. (41) and comparing the resulting expression at $x = x_r$ with Eq. (42). The velocity is then given by

$$v = v_r + \frac{v_r \omega_r \tau_r{}^+ (\partial h/\partial \alpha)_r}{\rho_r (\partial h/\partial \rho)_r (M_{\omega,r}{}^2 - 1)} \left\{ \exp\left[-\frac{(M_{\omega,r}{}^2 - 1)(x - x_r)}{\tau_r{}^+ v_r (M_{f,r}{}^2 - 1)} \right] - 1 \right\} \tag{43}$$

In the following discussions, the results obtained using nonequilibrium reference states is referred to as the extended linear solution.

For one-dimensional flow problems, the local disturbance thermodynamic properties of the gas are linearly related to the local disturbance velocity by Eqs. (17–20). (Note that Eqs. (18) and (20) can be integrated directly.) Alternatively, the thermodynamic properties ρ, p, and h are related to the local velocity and the flow condition upstream of the shock through the nonlinear conservation equations. The local chemical process variable is therefore related to the local velocity and the upstream condition though the equation of state. In the present work, these nonlinear relations are used to calculate the local values of ρ, p, h, and q from the linear solution for v. Specifically, the following relations are used

$$\rho = \rho_\infty v_\infty / v \tag{44}$$

$$p = p_\infty + \rho_\infty v_\infty (v_\infty - v) \tag{45}$$

$$h = h_\infty + \tfrac{1}{2}(v_\infty - v)(v_\infty + v) \tag{46}$$

and

$$\alpha = \{ -(p - \rho h + \rho R\theta) + [(p - \rho h + \rho R\theta)^2 - 4\rho R\theta(4p - h\rho)]^{1/2} \} / (2\rho R\theta) \tag{47}$$

where the subscript "∞" denotes flow conditions upstream of the shock front.

Supersonic Free Expansion

A linear solution for the steady, two-dimensional supersonic free expansion of a reactive gas, initially uniform and in thermodynamic equilibrium over a sharp corner into a region of constant pressure was developed by Wu and Sigman[6] using an equilibrium state asymptotically approached by the gas far downstream of the corner as the reference state. Certain modifications were introduced in Ref. 6 to account for the classical defects of the linear theory. With these modifications, acceptable results were obtained for cases involving moderately high upstream to downstream pressure ratios. However, because of the restriction that the reference state must correspond to an equilibrium condition, the range of applicability of the modified linear theory is still rather limited. Furthermore, the computations of the asymptotic condition of the flow, needed in the modified linear solution, is not a simple procedure. To resolve these difficulties, a linear solution based on nonequilibrium reference state is presented here.

The flow geometry for the free expansion problem is sketched in Fig. 1. As in the case of a perfect gas, the flow passes through an expansion fan centered at the corner. However, with the relaxation time entering the problem through finite rate reaction, the Mach lines in the expansion fan are not straight. The bounding streamline, i.e., the streamline forming the constant pressure boundary of the flow downstream of the expansion fan, is also not straight. The velocity magnitude and the enthalpy have constant values along the bounding streamline by virtue of the momentum and the energy equations. The direction of the velocity vector, the density, and the chemical process variable, however, changes along the bounding streamline as a result of chemical reactions. Special emphasis is placed in the present work on the flow along the bounding streamline.

Using a reference state corresponding to a local flow condition on the bounding streamline, one obtains from Eqs. (14) and (15)

$$\frac{d\alpha_s'}{ds} + \frac{1}{\tau_r{}^+ v_s} \alpha_s' = \frac{\omega_r}{v_s} \tag{48}$$

where the subscript "s" denotes properties on the bounding streamline, v_s being a constant, and s is the streamline coordinate measured downstream of the corner.

The solution of Eq. (48) is

$$\alpha_s = \alpha_r - \tau_r{}^+ \omega_r \left[\exp\left(-\frac{s - s_r}{\tau_r{}^+ v_s} \right) - 1 \right] \tag{49}$$

From Eq. (14), noting that $h_s' = 0$ and $p_s' = 0$, one has

$$\rho_s = \rho_r - \frac{(\partial h/\partial \alpha)_r}{(\partial h/\partial \rho)_r} \alpha_s' \tag{50}$$

Thus ρ_s' depends linearly on α_s' and decays exponentially with $s/\tau_r{}^+ v_s$. Alternatively, one has from Eqs. (28) and (29)

$$\rho_s = \frac{(4 + \alpha_s) p_s}{(1 + \alpha_s)(h_s - R\theta\alpha_s)} \tag{51}$$

Equation (51) is used to calculate local values of ρ_s using the known values of α_s; p_s, and h_s being constants. Similarly, $\tau_s{}^+$ and ω_s are determinant once α_s is known.

The linear solution for the angle of deflection, i.e., the change of flow direction from that upstream of the corner, along the bounding streamline proceeds by the use of a Laplace transform method. The approach used follows very closely that of Ref. 6 in which the asymptotic equilibrium state on the bounding streamline was the reference state. The somewhat lengthy derivation is not included here. The result is

$$\theta_s = \theta_{fs} \exp\left(-\frac{B^2 + 1}{2\tau_r{}^+ v_s} x \right) I_o\left(\frac{B^2 - 1}{2\tau_r{}^+ v_s} x \right) + \theta_{es} \frac{B}{\tau_r{}^+ v_s} \int_o^x \exp\left[\left(-\frac{B^2 + 1}{2\tau_r{}^+ v_s} \eta \right) I_o\left(\frac{B^2 - 1}{2\tau_r{}^+ v_s} \eta \right) d\eta \right] \tag{52}$$

where

$$B^2 = \left(\frac{v_s{}^2}{a_{\omega,r}{}^2} - 1 \right) \Big/ \left(\frac{v_s{}^2}{a_{f,r}{}^2} - 1 \right) \tag{53}$$

and I_o is the modified Bessel function of the first kind and zeroth order. θ_{fs} is the change in flow direction that the flow undergoes upon passing through the Frozen Prandtl-Meyer expansion fan, θ_{es} is the change in flow direction that the flow would undergo upon passing through an equilibrium Prandtl-Meyer fan of the same strength.

At $s = 0$, the integral in Eq. (52) vanishes and one has $\theta_s = \theta_{fs}$. As $s \to \infty$, the integral approaches $(\tau_r{}^+ v_s)/B$, and one has $\theta_s = \theta_{es}$. Thus Eq. (52) gives the correct limiting values for θ_s. Equation (52) permits the evaluation of θ_s for all values of s. If the bounding streamline is divided into segments, then values of $\tau_r{}^+$ and B_r can be established for each segment based on appropriate local values of ρ_s and α_s (p_s being a constant). The use of Eq. (52), however, requires a prior knowledge of θ_{es}. Although θ_{es} can be evaluated from the equilibrium flow Prandtl-Meyer relations, it is desirable to develop an approach with which this asymptotic value of θ_s can be obtained directly from the extended linear theory. It is noted here that a linear solution for the complete flowfield, including that interior of the bounding streamline, is obtain-

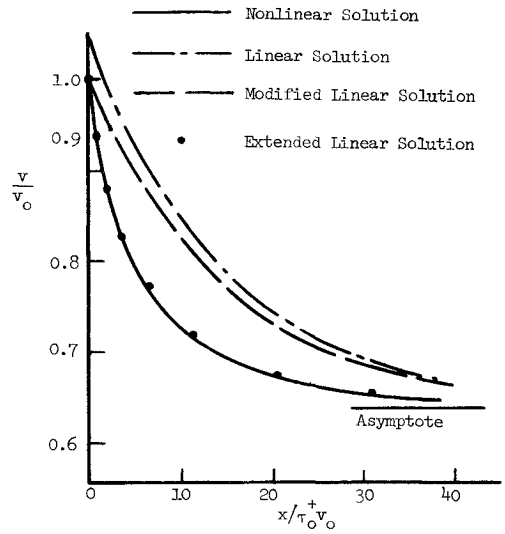

Fig. 2 Velocity behind normal shock.

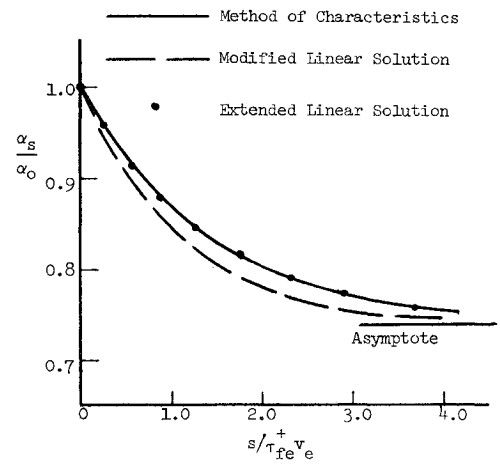

Fig. 4 Degree of dissociation along bounding streamline.

able.[14] This linear solution permits the use of a marching procedure for the evaluation of θ_s without requiring a knowledge of θ_{es}. Inasmuch as the modified linear theory[6] yielded excellent results for θ_s, the lengthy analysis for the linear solution for the complete flowfield is not included in the present paper.

IV. Results and Discussions

Some results of the extended linear theory are shown in Figs. 2–5 for an oxygen-like ideal dissociating gas with $\eta = -1.5$, $c = 1.188$ cm^3-°K$^{3/2}$/g-sec, $R = 2.598 \times 10^6$ erg/°K-g, $\theta = 59{,}500$°K, and $\rho_d = 150$ g/cm^3.

The normal shock results are presented in Figs. 2 and 3 for the case of a uniform equilibrium upstream flow with $M_{f\infty} = 2.00$, $p_\infty = 0.488$ atm, $T_\infty = 3500$°K. Figure 2 shows the extended linear result as well as three other solutions for the velocity profile in the relaxation zone. The nonlinear solution shown is a fourth-order Runge-Kutta solution of the nonlinear equations. The linear solution is obtained from Eq. (39). The modified linear solution is obtained from Eq. (40). The four solutions for the degree of dissociation in the relaxation zone are presented in Fig. 3. Figures 2 and 3 show that, for the given case with substantial variations of the flow parameter brought about by chemical reactions in the relaxation zone, the extended linear theory gives results in remarkable agreement with the more exact nonlinear solution. This remarkable agreement prevails for all the other flow properties and for the several other cases with different sets of flow conditions that have been studied. The linear solution and the modified linear solution, on the other hand, deviated substantially from the nonlinear solution for cases involving substantial variations of the flow parameters within the relaxation zone. It is concluded that the extended linear theory is an important improvement over previous linear theories and that for many problems with known or obtainable linear solutions, the availability of the extended linear theory makes it unnecessary to use numerical method requiring the availability of high-speed computers.

In obtaining the extended linear results for the normal shock problem, the relaxation zone is divided into segments each with its own nonequilibrium reference state. The reference values for each segment are chosen to correspond to local values of the flow at the terminal point of the preceding segment. The length of the segment is then determined by requiring the departure of the flow variables from their reference values to be within prescribed limits. For the normal shock problem, it is convenient to prescribe a criterion limiting the velocity variation within each segment. The excellent results shown in Figs. 2 and 3 were obtained using the criterion $|v'/v_r| \leqq 0.025$ in each segment. Using this procedure resulted in fourteen segments for the entire

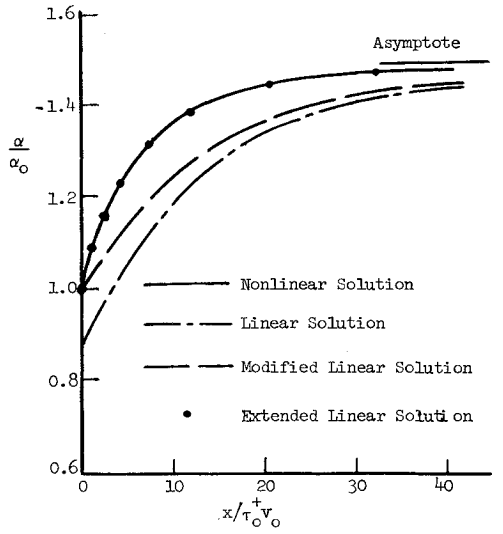

Fig. 3 Degree of dissociation behind normal shock.

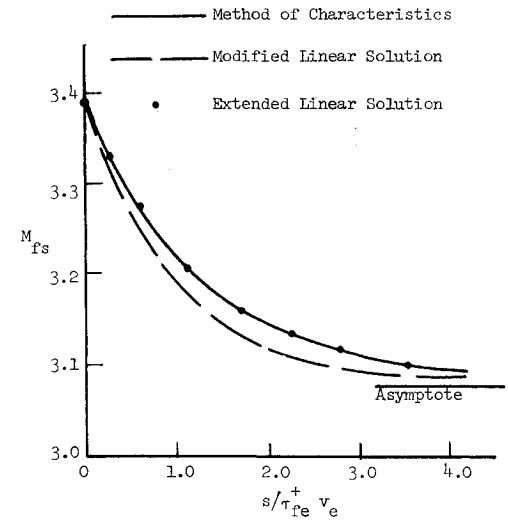

Fig. 5 Frozen Mach number along bounding streamline.

relaxation zone. These segments increased in length as the distance from the shock front is increased. Alternative procedures can be adopted to reduce the number of segments in the relaxation zone. For example, instead of the terminal point of the preceding segment, the point within the new segment where the velocity is 0.976 time the value at the preceding terminal point may be used as the reference point for the new segment. By placing the reference point within each segment in this manner, the velocity criterion $|v'/v_r| \leqq 0.025$ is satisfied and the number of segments in the relaxation zone is reduced by approximately a factor of two.

It needs to be emphasized that, since the extended linear theory permits the segmentation of the relaxation zone, there is no longer a restriction on the variation of the flow parameters over the relaxation zone as a whole. The only requirement is that the variations of flow properties and their derivatives be kept small over each segment. Thus for cases involving small variations of flow parameter over the entire relaxation zone, very few segments are needed. For cases involving larger variations, a larger number of segments are required.

Results for the supersonic free expansion problem are presented in Figs. 4 and 5 for the case of a uniform equilibrium upstream flow with $M_{f\infty} = 2.58$, $p_\infty = 4.746$ atm, and $T_\infty = 3720°$K, and a downstream boundary pressure of 1.414 atm. The extended linear result for the degree of dissociation along the bounding streamline is shown in Fig. 4. Also shown in Fig. 4 are results obtained using the numerical method of characteristics[10] which treats the nonlinear partial differential equations governing the flow, and the modified linear results[6] using the equilibrium asymptotic state as the reference state. In Fig. 5 are shown the results for the frozen Mach number along the bounding streamline. The figures show that, for this given case with a moderately high pressure ratio of 3.36 and a moderately large change of flow parameters brought about by chemical reactions (the degree of dissociation changes by more than 20% along the bounding streamline), the extended linear theory gives results in excellent agreement with the more exact results of the method of characteristics. This excellent result is not influenced by the magnitude of variation of flow parameters along the bounding streamline. In contrast, the modified linear theory gives results in excellent agreement with the method of characteristics only for cases involving small variations of flow parameters along the bounding streamline; this agreement deteriorates with increasing variations of the flow parameters so that, for the present case with a moderately large variation, a noticeable deviation from the method of characteristics result is evident.

The improvements made possible by the extended linear theory is attributable to its ability to analyze the flowfield in individual segments. The results shown in Figs. 4 and 5 are obtained by requiring the degree of dissociation within each segment to deviate from its reference value for that segment by less than 2.5%. By choosing the reference point for each segment to be the terminal point of the preceding segment, eleven segments are needed to cover the entire bounding streamline. By placing the reference point for a new segment in the interior of the segment in the manner suggested for the normal shock problem, the number of segments needed reduces to six.

Results based on the extended linear theory have been obtained for the angle of deflection for the case discussed. As previously pointed out, however, excellent results for the angle of deflection are obtainable using the modified linear theory. Therefore no striking improvement can result from the use of the extended theory. It is noted, however, that the success of the modified theory in predicting the angle of deflection for the present case is a direct consequence of the fact that the angle of deflection is only weakly dependent on the chemical process. For the present case, the angle of deflection changes by less than 2.5° along the bounding streamline. The use of a single reference state for the evaluation of the angle of deflection is therefore led to accurate results. This weak dependence on the chemical process, of course, cannot be expected to prevail for other flow variables or for other types of problems.

Based on the results of the present work, it is concluded that the use of the nonequilibrium reference states effectiveness extends the range of applicability of the linear theory. By considering a chemically reacting flow in successive zones, each with its own nonequilibrium reference state, the variation of the flow parameters over the entire flowfield need not be restricted to small values. The extended linear theory offers a viable alternative to the numerical methods presently required. The method is generally useful to problems for which a linear solution is either existing or obtainable.

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