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**NONEQUILIBRIUM CENTERED EXPANSION OF
A DISSOCIATED SUPERSONIC GAS FLOW**

OCTOBER 26, 1962

DOUGLAS REPORT SM-42492

**MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC.
SANTA MONICA CALIFORNIA**

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MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC
SANTA MONICA, CALIFORNIA

February 8 1963
A2-260-M/AT-AN-5

Subject: Transmittal of Douglas Aircraft Company, Inc., Research Reports SM-42492, SM-42603, and SM-42649

To: Headquarters
Armed Services Technical Information Agency
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Shanahan, R. J., and G. R. Inger. Nonequilibrium Centered Expansion of a Dissociated Supersonic Gas Flow. SM-42492, October 26, 1962.

Xerikos, J., and W. A. Anderson. A Critical Study of the Direct Blunt Body Integral Method. SM-42603, December 28, 1962.

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NONEQUILIBRIUM CENTERED EXPANSION OF A DISSOCIATED SUPERSONIC GAS FLOW

**OCTOBER 26, 1962
DOUGLAS REPORT SM-42492**

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Prepared Under the Sponsorship of
The Douglas Aircraft Company
Independent Research and Development
Program. Account No. 88010-376.

MISSILE SYSTEMS ENGINEERING

**MISSILE & SPACE SYSTEMS DIVISION
DOUGLAS AIRCRAFT COMPANY, INC.**

ABSTRACT

A ~~preliminary~~ *analysis* is presented
~~This report presents a~~ detailed analysis of the nearly-frozen, nonequilibrium supersonic expansion of a dissociated diatomic gas around a sharp, two-dimensional corner, assuming an incoming stream in dissociation equilibrium. The analysis is based on a small perturbation technique in which small local departures from frozen flow near the corner are treated. The analysis is necessarily restricted in lateral extent but covers the entire angular range of the flow field and, therefore, brings out the nonlinear aspects of the nonequilibrium behavior. An exact analysis is presented (in similitude form for a diatomic gas) in which numerical procedures are required to effect the solution. However, in the exact solution, the expression for the atomic species mass fraction has been placed in closed form and, in conjunction with appropriate approximations, is used to determine the thermochemical field in an additional solution (applicable to hypersonic flow) which is approximate but entirely in closed form. Some numerical results for the first-order nonequilibrium flow field are presented in which the main physical features of the nonequilibrium effects are shown, the influence of various thermochemical parameters are determined, and the accuracy of the approximate solutions is assessed.

TABLE OF CONTENTS

Section		Page
	Abstract	111
	Nomenclature	ix
1.	Introduction	1
2.	Governing Relations	2
2.1	Basic Equations	2
2.2	Reaction Rate	5
2.3	Speed of Sound	5
2.4	Boundary Conditions	6
2.5	Nondimensional Equations	7
3.	Nearly-Frozen Nonequilibrium Expansions	11
3.1	Perturbation Method	11
3.2	Frozen Expansion Solution	15
3.3	First-Order Solution	18
3.4	Approximate Solution for Hypersonic Flow	25
3.5	Numerical Results	26
4.	Concluding Remarks	29
	Appendix A	47
	Appendix B	49
	References	51

LIST OF FIGURES

Figure		Page
1	Flow Geometry and Coordinates	31
2A	Distribution of Dynamic and Thermodynamic Variables Within the Frozen Fan	32
2B	Distribution of Dynamic and Thermodynamic Variables Within the Frozen Fan	33
3A	Distribution of Thermodynamic Variables Within the Frozen Fan	34
3B	Distribution of Thermodynamic Variables Within the Frozen Fan	35
4A	Distribution of Thermodynamic Variables Within the Frozen Fan	36
4B	Distribution of Thermodynamic Variables Within the Frozen Fan	37
5A	Distribution of Thermodynamic Variables Within the Frozen Fan	38
5B	Distribution of Thermodynamic Variables Within the Frozen Fan	39
6A	Comparison of Exact and Approximate First- Order Solutions Within the Frozen Fan	40
6B	Comparison of Exact and Approximate First- Order Solutions Within the Frozen Fan	41
6C	Comparison of Exact and Approximate First- Order Solutions Within the Frozen Fan	42
7A	First-Order Nonequilibrium Field	43

LIST OF FIGURES

Figure		Page
7B	First-Order Nonequilibrium Field	44
7C	First-Order Nonequilibrium Field Polar Representation	45
7D	First-Order Nonequilibrium Field Polar Representation	46

NOMENCLATURE

Symbol

a	Speed of sound
A	Constant [see Eq. (2-13)]
B	Constant [see Eq. (2-13)]
C_p	Constant pressure specific heat
$\overline{C_p}$	Frozen constant pressure specific heat
g	Chemical potential (Gibbs function)
G	Function defined in Eq. (2-13)
g	$g/R_M T_\infty$
h	Specific enthalpy
h_D	Specific dissociation energy
$I_D(\gamma)$	Integral expression defined in Eq. (3-35)
$I_R(\gamma)$	Integral expression defined in Eq. (3-35)
k_R	Recombination rate constant
K_γ	$\overline{\delta_\infty}/\delta_\infty^\wedge$
K_M	C_{p_M}/R_M
K_p	Parameter defined in Eq. (2-21)
M	Mach number

NOMENCLATURE

Symbol

p	Pressure
P	p/p_{∞}
r	Radial coordinate
R	Gas constant
R_0	Universal gas constant
S	Specific entropy
s	S/R_M
T	Temperature
T_D	Characteristic dissociation temperature
U	Radial velocity
$\bar{U}$	$U/V_{R_{\infty}}$
V	Tangential velocity
$\bar{V}$	$V/V_{R_{\infty}}$
$V_{R_{\infty}}$	Incoming total velocity
α	Atomic mass fraction
γ	Actual specific heat ratio
$\bar{\gamma}$	Frozen specific heat ratio
$\hat{\gamma}$	Effective specific heat ratio
r'	Characteristic length [see Eq. (2-22)]
r	r'/r

NOMENCLATURE

Symbol

$\mathcal{J}$	Vorticity
$\overline{\mathcal{J}}$	$\mathcal{J}/V_{R_{\infty}}$
η	$[(\overline{\gamma}_{\infty}+1)/(\overline{\gamma}_{\infty}-1)]^{\frac{1}{2}}$
θ	Angular coordinate
μ	Mach angle
ν	Flow turning angle
ρ	Density
σ	ρ/ρ_{∞}
τ	T/T_{∞}
ψ	Reduced angular coordinate
ω	Recombination rate temperature exponent
w_A	Net rate of atomic species mass production

Subscripts

A	Refers to atomic species
F	Refers to frozen or zeroth order field
i	Index (generally refers to the i^{TH} chemical species)
M	Refers to molecular species
1	Refers to first order

Subscripts

I	Denotes conditions at initial frozen characteristic
II	Denotes conditions at final characteristic
∞	Refers to incoming stream

1. INTRODUCTION

The problem of the centered expansion of steady, supersonic, reacting gas flow around a sharp corner (Prandtl-Meyer flow) is of practical interest as a simple case of nonequilibrium flows that are encountered on bodies in high altitude, hypersonic flight (Refs. 1, 2). Moreover, the study of this problem constitutes a fundamental research tool with which to investigate the effects of homogeneous reactions on supersonic conical flow fields. Complete solutions for a dissociated gas mixture have been given in the case of an equilibrium expansion, where the dissociation and recombination rates are equal and much greater than the convection rate throughout the expansion fan (Refs. 3, 4, 5). The presence of a chemical reaction in local equilibrium does not change the basic self-similar nature of the solution that is observed in a perfect gas, since the flow remains isentropic and irrotational throughout with the characteristics emanating as straight lines from the corner. However, when the incoming flow velocity is sufficiently high and the density sufficiently low, the expansion can force the local reaction rates out of equilibrium. The finite dissociation-recombination rates introduce a nonisentropic, rotational effect into the problem, as well as a length scale proportional to radius that destroys the conicity of the flow. With increasing radius, there is a recombination-dominated (nonequilibrium) transition from completely frozen flow near the corner to an asymptotically-approached region of equilibrium flow far from the corner. When the incoming velocity is very high (and/or density very low), the entire expansion may become chemically frozen, in which case the flow again reverts to an isentropic, irrotational, self-similar behavior.

The theoretical description of a nonequilibrium centered expansion involves a set of coupled, nonlinear, partial differential equations. Therefore, in general, solutions must be obtained by a numerical technique based on

the method of characteristics for reacting gas flows (Refs. 5, 7, 8). However, valuable insight into the nonequilibrium effects can be gained by considering small departures from a self-similar solution by either (a) treating weak expansions, with small departures from conditions in the incoming gas stream, or (b) treating small local departures from the frozen flow near the corner. Method (a) features greater simplicity because the flow may be regarded as irrotational and the resulting linearized equations possess constant coefficients. This case has been treated by several investigators for both expansion and compression flows (Refs. 9, 10). The method is restricted to small turning angles but covers the entire lateral extent of the field. Method (b) is mathematically more complex since the coefficients in the linearized equations governing the nonequilibrium perturbations are complicated functions of the zeroth order self-similar solution. Moreover, the perturbations are not irrotational. Nevertheless, this approach is unrestricted as to flow turning angle and brings out the nonlinear aspects of the nonequilibrium behavior. This report presents a detailed analysis of a nearly-frozen, nonequilibrium supersonic expansion of a dissociated diatomic gas around a sharp, two-dimensional corner for the case of an equilibrium dissociated incoming stream. The present investigation constitutes a further extension of Napolitano's analysis (Ref. 8) in that the entire angular range of the flow field is treated, specific numerical results are given, and some approximate and exact closed form solutions are developed.

2. GOVERNING RELATIONS

2.1 Basic Equations

Consider the steady, adiabatic, supersonic expansion of a dissociated diatomic gas around a sharp two-dimensional corner, as shown in Fig. 1. Viscosity, heat conduction and diffusion effects are neglected, and the flow properties immediately ahead of the first expansion fan characteristic are assumed to be uniform. The governing equations for such a reacting gas flow are well-known (see, for example, Ref. 11). In the polar coordinate system of Fig. 1, they are expressed as follows.

Continuity

$$\frac{\partial(\rho U r)}{\partial r} + \frac{\partial(\rho V)}{\partial \theta} = 0 \quad (2-1)$$

Atom Mass Conservation

$$U \frac{\partial \alpha}{\partial r} + \frac{V}{r} \frac{\partial \alpha}{\partial \theta} = \frac{w_A}{\rho} \quad (2-2)$$

Radial Momentum

$$\rho \left(U \frac{\partial U}{\partial r} + \frac{V}{r} \frac{\partial U}{\partial \theta} - \frac{V^2}{r} \right) = - \frac{\partial p}{\partial r} \quad (2-3)$$

Tangential Momentum

$$\rho \left(U \frac{\partial V}{\partial r} + \frac{V}{r} \frac{\partial V}{\partial \theta} + \frac{UV}{r} \right) = - \frac{1}{r} \frac{\partial p}{\partial \theta} \quad (2-4)$$

Energy

$$h + \frac{U^2 + V^2}{2} = \text{CONST} = h_\infty + \frac{U_\infty^2 + V_\infty^2}{2} \quad (2-5)$$

Thermal Equation of State

$$p = \rho R_M (1 + \alpha) T \quad (2-6)$$

The specific enthalpy h is given as a function of α and T by the caloric equation of state:

$$h = \sum_i \alpha_i h_i = (1 - \alpha) \int_0^T c_{p_M} dT + \alpha \left(h_D + \int_0^T c_{p_A} dT \right), \quad (2-7)$$

where $C_{p_{A,M}}$ denotes the atomic or molecular specific heat and h_D is the dissociation energy of the gas. In the subsequent analysis, the rotational degrees of freedom of the molecule are assumed to be fully excited, and the effects of electronic excitation and vibrational nonequilibrium on the internal energy are neglected in comparison to the dissociation energy αh_D . Thus $C_{p_A} = 5R_M$ and C_{p_M} is a function of T ranging between $\frac{7}{2} R_M$ (no vibrational excitation) and $\frac{9}{2} R_M$ (completely excited vibration). To further simplify the analysis, C_{p_M} shall be regarded as a constant (i.e., vibration is "frozen" throughout the expansion). Hence Eq. (2-7) becomes

$$h = \bar{C}_p T + \alpha h_D, \quad (2-8)$$

where $\bar{C}_p = [K_M + (5 - K_M)\alpha]R_M$ is the frozen specific heat and $\frac{7}{2} \leq K_M \leq \frac{9}{2}$.

The entropy change along a streamline for reacting diatomic gas flow is (Refs. 6, 11):

$$T \left(U \frac{\partial S}{\partial T} + \frac{V}{T} \frac{\partial S}{\partial \theta} \right) = - (g_A - g_M) \frac{W_A}{p}, \quad (2-9)$$

where $g_{A,M} = h_{A,M} - T S_{A,M}$ denotes the "chemical potential" (or Gibbs function) for the atom or molecule (expressions for $S_{A,M}$, $g_A - g_M$ and S in terms of T , p and α are given in Appendix A). The following equivalent form of Eq. (2-9), namely Crocco's Theorem for a reacting gas, may also be obtained from (2-9) and the momentum equations:

$$T \frac{\partial S}{\partial T} + \frac{V}{T} f = - (g_A - g_M) \frac{\partial \alpha}{\partial T} \quad (2-10A)$$

$$T \frac{\partial S}{\partial \theta} - U f = - (g_A - g_M) \frac{\partial \alpha}{\partial \theta}, \quad (2-10B)$$

where $f \equiv \frac{\partial U}{\partial \phi} - \frac{\partial(VT)}{\partial T}$ is the vorticity in cylindrical coordinates. Both Eqs. (2-9) and (2-10) are very useful in obtaining a physical appreciation of the nonequilibrium dissociation effects on an inviscid flow.

2.2 Reaction Rate

The dissociation-recombination reaction for a diatomic gas is



where M , A denote a molecular or atomic particle and the third body X may be either of these two. For such a reaction, the net volumetric rate of atomic species mass production w_A can be written as

$$\frac{w_A}{\rho} = -2A_R \left(\frac{p}{R_0}\right)^2 T^{\omega-2} G(\alpha, p, T), \quad (2-12)$$

where

$$G(\alpha, p, T) \equiv \frac{\alpha^2}{1+\alpha} - (1-\alpha) \left(\frac{T}{273}\right)^A \frac{e^B}{Tp} e^{-T_0/T} \quad (2-13)$$

Here, A_R and ω represent the recombination rate constant and temperature exponent, respectively, A and B are constants (Appendix A), and $T_D = h_D / R_M$ is a characteristic dissociation temperature. The function $G(\alpha, p, T)$ has the important property of vanishing identically when thermochemical equilibrium prevails. Thus when reaction (2-11) is in local equilibrium in the flow, the equation $G = 0$ defines the corresponding solution to (2-2) for α .

2.3 Speed of Sound

The speed at which infinitesimally small disturbances propagate through a

dissociated diatomic gas can be written (Ref. 6) as

$$a = (\gamma \frac{p}{\rho})^{\frac{1}{2}} = \left\{ \left[\frac{\bar{\gamma} + j(\gamma - \bar{\gamma})}{1 - j \frac{p}{1 + \alpha} \left(\frac{\partial \alpha}{\partial p} \right)_T} \right] \frac{p}{\rho} \right\}^{\frac{1}{2}}, \quad (2-14)$$

where $j = 0$ when the gas is not in chemical equilibrium and $j = 1$ when the gas remains in equilibrium when subjected to an infinitesimal disturbance. Here, γ is the actual specific heat ratio of the dissociated gas, defined by

$$\gamma \equiv \frac{(\partial h / \partial T)_p}{(\partial h / \partial T)_p - \frac{1}{\rho} (\partial p / \partial T)_p}, \quad (2-15)$$

and $\bar{\gamma}$ is the frozen specific heat ratio

$$\bar{\gamma} = (\gamma)_{\alpha = \text{CONST}} = \frac{\bar{C}_p}{\bar{C}_p - (1 + \alpha) R_M} = \frac{K_M + (5 - K_M) \alpha}{K_M - 1 + (4 - K_M) \alpha} \quad (2-16)$$

According to (2-14), the velocity normal to a Mach wave equals the local "frozen" speed of sound (based on $\bar{\gamma}$) in any gas with a finite reaction rate. However, in a completely equilibrium-dissociated gas, the speed of sound based on $\hat{\gamma}$ ($\hat{\gamma} \leq \gamma \leq \bar{\gamma}$) must be used.

2.4 Boundary Conditions

If the incoming gas is uniformly dissociated, so that the initial expansion characteristic is straight, it must be either chemically frozen (after having previously undergone a highly nonequilibrium flow expansion) or in thermochemical equilibrium. In the former case, α_{∞} is an independent variable with $G(\alpha_{\infty}, p_{\infty}, T_{\infty}) \neq 0$, while in the latter case, α_{∞} is a function of p_{∞} and T_{∞} given by $G(\alpha_{\infty}, p_{\infty}, T_{\infty}) = 0$. Since any expansion of a chemically frozen stream must remain frozen, we shall consider only an equilibrium free stream. Consequently, the following conditions

define our problem as a supersonic expansion around a sharp corner (Fig. 1). At the initial expansion fan characteristic I,

$$\theta_I = \mu_I = \sin^{-1} \left(\frac{1}{M_\infty} \right) \quad (2-17)$$

$$\left. \begin{aligned} p &= p_\infty, \rho = \rho_\infty, T = T_\infty, \alpha = \alpha_\infty \\ U &= V_{R_\infty} \cos \theta_I, V = -V_{R_\infty} \sin \theta_I \end{aligned} \right\} \quad (2-18)$$

At $\theta = -\nu$, the tangential velocity component must vanish:

$$(V)_{\theta=-\nu} = 0 \quad (2-19)$$

The flow along the wall for a nonequilibrium expansion will be a function of τ since a relaxation toward equilibrium occurs with increasing stream-line distance.

2.5 Nondimensional Equations

It proves convenient to deal with the foregoing equations in an appropriately nondimensionalized form. Therefore, the following new independent variables are introduced:

$$\left. \begin{aligned} p &= p/p_\infty, \sigma = \rho/\rho_\infty, \tau = T/T_\infty \\ \bar{U} &= U/V_{R_\infty}, \bar{V} = V/V_{R_\infty}, \mathcal{S} = S/R_M, \mathcal{X} = g/R_M T_\infty \end{aligned} \right\} \quad (2-20)$$

Furthermore, we define the parameters

$$\tau_2 = T_2/T_\infty, K_p = \frac{e^{\frac{5}{2}(T_2/273)^A}}{4 p_{ATM}}, K_g = \bar{g}_\infty / \bar{g}_\infty^A \quad (2-21)$$

and a characteristic (flow length/recombination length) parameter

$$\Gamma = \frac{A_s (P_\infty / R_\infty)^2 T_\infty^{\omega-2}}{\sqrt{R_\infty}} \tau = \Gamma' \tau \quad (2-22)$$

Then Eqs. (2-1) - (2-6), using (2-8), (2-12) and (2-13), are transformed into the following set of six equations for the six unknowns α , P , σ , τ , $\bar{U}$ and $\bar{V}$:

$$\frac{\partial(\sigma \bar{U} \tau)}{\partial \tau} + \frac{\partial(\sigma \bar{V})}{\partial \theta} = 0 \quad (2-23)$$

$$\bar{U} \tau \frac{\partial \alpha}{\partial \tau} + \bar{V} \frac{\partial \alpha}{\partial \theta} = -2 \Gamma' \tau P^2 \tau^{\omega-2} \left[\frac{\alpha^2}{1+\alpha} - (1-\alpha) \frac{\tau^A K_p}{P} e^{-\frac{\tau}{T}} \right] \quad (2-24)$$

$$\sigma \left(\tau \bar{U} \frac{\partial \bar{U}}{\partial \tau} + \bar{V} \frac{\partial \bar{U}}{\partial \theta} - \bar{V}^2 \right) = - \frac{K_x \tau}{\bar{g}_\infty M_\infty^2} \frac{\partial P}{\partial \tau} \quad (2-25)$$

$$\sigma \left(\tau \bar{U} \frac{\partial \bar{V}}{\partial \tau} + \bar{V} \frac{\partial \bar{V}}{\partial \theta} + \bar{U} \bar{V} \right) = - \frac{K_x \tau}{\bar{g}_\infty M_\infty^2} \frac{\partial P}{\partial \theta} \quad (2-26)$$

$$\frac{\bar{g}_\infty M_\infty^2}{2 K_y} (\bar{U}^2 + \bar{V}^2 - 1) = \left[\frac{K_M + (5-K_M) \alpha_\infty}{1+\alpha_\infty} \right] (1-\tau) + \frac{\alpha_\infty - \alpha}{1+\alpha_\infty} [\tau_D + (5-K_M) \tau] \quad (2-27)$$

$$P = \left(\frac{1+\alpha}{1+\alpha_\infty} \right) \sigma \tau \quad (2-28)$$

The attending entropy relations become

$$\tau \bar{U} \frac{\partial \mathcal{S}}{\partial \tau} + \bar{V} \frac{\partial \mathcal{S}}{\partial \theta} = \left(\frac{A_s - A_M}{\tau} \right) \Gamma' \tau P^2 \tau^{\omega-2} G \quad (2-29)$$

or, in terms of Crocco's Theorem,

$$r \frac{\partial f}{\partial r} + \frac{\bar{r}_\infty M_\infty^2}{K_p} (1 + \alpha_\infty) \frac{\bar{V}}{\tau} \bar{f} = - \left(\frac{\bar{H}_A - \bar{H}_M}{\tau} \right) \frac{\partial \alpha}{\partial r} r \quad (2-30A)$$

$$\frac{\partial f}{\partial \theta} - \frac{\bar{r}_\infty M_\infty^2 (1 + \alpha_\infty)}{K_p} \frac{\bar{U}}{\tau} \bar{f} = - \left(\frac{\bar{H}_A - \bar{H}_M}{\tau} \right) \frac{\partial \alpha}{\partial \theta} \quad , \quad (2-30B)$$

where

$$\bar{f} = \frac{\partial(\bar{V}r)}{\partial r} - \frac{\partial(\bar{U})}{\partial \theta} = f / V_{R_\infty}$$

Note that, according to Appendix A, $\bar{H}_A - \bar{H}_M$ may be written in terms of the reaction function G as

$$\frac{\bar{H}_A - \bar{H}_M}{\tau} = \ln \left[\frac{P \tau^{-A} e^{\tau_0/\tau}}{(1-\alpha) K_p} G + 1 \right] \quad , \quad (2-31)$$

which properly vanishes at equilibrium ($G=0$). Finally, the boundary conditions transform to

$$\theta = \sin^{-1} \left(\frac{1}{M_\infty} \right) :$$

$$\left. \begin{aligned} P = \sigma = \tau = 1 \quad , \quad \alpha = \alpha_\infty \quad , \quad \frac{\alpha_\infty^2}{1 - \alpha_\infty^2} = K_p e^{-\tau_0} \\ \bar{U} = \frac{(M_\infty^2 - 1)^{\frac{1}{2}}}{M_\infty} \quad , \quad \bar{V} = - \frac{1}{M_\infty} \end{aligned} \right\} \quad (2-32)$$

$$\theta = -\mathcal{V} :$$

(2-33)

$$\bar{V} = 0$$

The foregoing equations are in a universal nondimensional form which is very convenient for parametric study of nonequilibrium expansions regardless of the method of solution. Furthermore, it is evident that $P, \tau, \alpha, \sigma, \bar{U}$ and $\bar{V}$ at a given M_∞ and $\mathcal{V}$ are the same at each point θ , r'/r for all combinations of incoming gas if the following parameters are held constant: K_M, ω, τ_D, K_P . That is, the following similitude law governs the flow:

$$P, \tau, \alpha, \sigma, \bar{U}, \bar{V} = f(M_\infty, \mathcal{V}; K_M, \omega, \tau_D, K_P; \theta, r'/r) \quad (2-34)$$

This similitude is in many respects analogous to that demonstrated in Ref. 12 for nonequilibrium, small disturbance hypersonic flows.

It is seen that the flow described by the foregoing equations cannot be conical in the presence of a finite dissociation-recombination rate, since the parameter Γ is a function of r . Furthermore, when $\Gamma \sim O[1]$ and $G \neq 0$, Eqs. (2-24), (2-29), and (2-30) show that the degree of dissociation, entropy and vorticity vary along streamlines as the flow expands around the corner. The effects of nonequilibrium chemical reaction involve a transition between frozen flow at the corner ($\Gamma = 0, G \neq 0, \alpha = \alpha_\infty$) and equilibrium flow far from the corner ($\Gamma \rightarrow \infty, G = 0, \alpha = \alpha(\theta) \leq \alpha_\infty$) across which the entropy increases and α decreases with r . The radial expanse of this transition region is governed by the magnitude of Γ' . When $\Gamma' \ll 1$, the radial scale vanishes from the problem and the entire expansion becomes a chemically frozen, conical flow. As Γ' is increased, the outer edge of the nonequilibrium zone moves inward. When $\Gamma' \gg 1$, the entire expansion (with the exception of a very small region near the corner) is in equilibrium and hence is again self-similar. In this case, of course, $\alpha(\theta)$ decreases through the expansion according to the relations $G = 0$ and

$$\frac{d\alpha}{d\theta} = \left(\frac{\partial \alpha}{\partial P} \right)_{EQ} \frac{dP}{d\theta} + \left(\frac{\partial \alpha}{\partial \tau} \right)_{EQ} \frac{d\tau}{d\theta} \quad (2-35)$$

The presence of chemical nonequilibrium also induces a curvature of the expansion fan characteristics. This curvature may be observed by noting that departures from frozen flow must introduce a reaction rate effect which is recombination-dominated and which therefore tends to reduce α , and increase τ and P .^{*} Thus for a given local turning angle, the Mach number increases with radius and the expansion fan characteristics curve upward and away from the frozen flow characteristics. At a sufficiently large distance from the corner, the characteristics become asymptotically parallel to (but not coincident with) the characteristics for a completely equilibrium expansion (Fig. 1). This lack of coincidence, which is a manifestation of the radial increase in entropy, vanishes when $\Gamma' \rightarrow \infty$.

3. NEARLY-FROZEN NONEQUILIBRIUM EXPANSIONS

3.1 Perturbation Method

We now consider small departures from a completely frozen expansion due to nonequilibrium dissociation effects. Since a nearly frozen flow is characterized by small values of $\Gamma = \Gamma' r$, we expand each of the dependent variables in a series of ascending powers of Γ :

$$\alpha(\theta, r) = \alpha_f(\theta) + \Gamma \alpha_1(\theta) + \Gamma^2 \alpha_2(\theta) + \dots$$

$$\tau(\theta, r) = \tau_f(\theta) + \Gamma \tau_1(\theta) + \Gamma^2 \tau_2(\theta) + \dots$$

^{*} When a dissociated gas is expanded, the nonequilibrium effects on resultant velocity and flow density are less significant than the corresponding effects on temperature and pressure.

etc., where subscript F denotes the local frozen expansion solution, subscript 1 denotes the local first order perturbations due to nonequilibrium effects, etc. Substituting into Eqs. (2-23) - (2-28), equating coefficients of like powers of Γ equal to zero and taking $K_y = 1$, we obtain a set of nonlinear ordinary differential equations for the zeroth order (frozen) flow field and a set of linear, nonhomogeneous, ordinary differential equations with variable coefficients for each of the first, second, etc., order perturbations. Confining our attention to first-order nonequilibrium effects, we have the following two sets of equations.

Zeroth Order (Frozen) Flow

$$\sigma_F \left(\bar{U}_F + \frac{d\bar{V}_F}{d\theta} \right) = -\bar{V}_F \frac{d\sigma_F}{d\theta} \quad (3-1)$$

$$\alpha_F(\theta) = \text{CONST} = \alpha_\infty \quad (3-2)$$

$$\left. \begin{aligned} \frac{d\bar{U}_F}{d\theta} - \bar{V}_F &= \bar{f}_F = 0 \\ \rho_F(\theta) &= \text{CONST} = \rho_\infty \end{aligned} \right\} \quad (3-3)$$

$$\sigma_F \bar{V}_F \left(\bar{U}_F + \frac{d\bar{V}_F}{d\theta} \right) = -\frac{1}{\gamma_\infty M_\infty^2} \frac{dP_F}{d\theta} \quad (3-4)$$

$$\frac{\gamma_\infty}{\gamma_\infty - 1} (1 - \tau_F) = \frac{\gamma_\infty M_\infty^2}{2} (\bar{U}_F^2 + \bar{V}_F^2 - 1) \quad (3-5)$$

$$P_F = \sigma_F \tau_F \quad (3-6)$$

First-Order Flow

$$2(\sigma_1 \bar{u}_F + \sigma_F \bar{u}_1) + \frac{d}{d\theta} (\sigma_F \bar{v}_1 + \sigma_1 \bar{v}_F) = 0 \quad (3-7)$$

$$\bar{u}_F \alpha_1 + \bar{v}_F \frac{d\alpha_1}{d\theta} = -2 P_F^2 \tau_F^{\omega-2} \underbrace{\left[\frac{\alpha_\infty^2}{1+\alpha_\infty} - (1-\alpha_\infty) \frac{K_P \tau_F^A}{P_F} e^{-\frac{\tau_F^A}{\tau_F}} \right]}_{G_F} \quad (3-8)$$

$$\sigma_F \left[\bar{u}_F \bar{u}_1 + \bar{v}_F \left(\frac{d\bar{u}}{d\theta} - \bar{v}_1 \right) \right] = - \frac{P_1}{\bar{\gamma}_\infty M_\infty^2} \quad (3-9)$$

$$\bar{v}_F \left(\frac{d\bar{v}_F}{d\theta} + \bar{u}_F \right) \sigma_1 + \sigma_F \left[\bar{v}_F \bar{u}_1 + 2 \bar{u}_F \bar{v}_1 + \frac{d}{d\theta} (\bar{v}_F \bar{v}_1) \right] = - \frac{1}{\bar{\gamma}_\infty M_\infty^2} \frac{dP_1}{d\theta} \quad (3-10)$$

$$\left(\frac{\bar{\gamma}_\infty}{\bar{\gamma}_\infty - 1} \right) \tau_1 + \left[\frac{\tau_D + (5-K_M) \tau_F}{1+\alpha_\infty} \right] \alpha_1 + \bar{\gamma}_\infty M_\infty^2 (\bar{u}_F \bar{u}_1 + \bar{v}_F \bar{v}_1) = 0 \quad (3-11)$$

$$\frac{P_1}{P_F} = \frac{P_1}{\sigma_F \tau_F} = \frac{\alpha_1}{1+\alpha_\infty} + \frac{\tau_1}{\tau_F} + \frac{\sigma_1}{\sigma_F} \quad (3-12)$$

The corresponding entropy and vorticity perturbation equations are

$$\bar{u}_F \delta_1 + \bar{v}_F \frac{d\delta_1}{d\theta} = \quad (3-13)$$

$$P_F^2 \tau_F^{\omega-2} \left[\frac{\alpha_\infty^2}{1+\alpha_\infty} - (1-\alpha_\infty) \frac{K_P \tau_F^A}{P_F} e^{-\frac{\tau_F^A}{\tau_F}} \right] \ln \left[\frac{P_F}{(1-\alpha_\infty) K_P \tau_F^A} e^{\frac{\tau_F^A}{\tau_F}} \right]$$

and

$$\mathcal{J}_1 = -\frac{\bar{\gamma}_\infty M_\infty^2 (1+\alpha_\infty)}{\tau_F} \bar{V}_F \bar{f}_1 = -\alpha_1 \ln \left[\frac{P_F e^{\frac{\tau_F^2}{2}} \alpha_\infty^2}{(1-\alpha_\infty^2) K_P \tau_F} \right] \quad (3-14A)$$

$$\frac{d\mathcal{J}_1}{d\theta} + \frac{\bar{\gamma}_\infty M_\infty^2 (1+\alpha_\infty)}{\tau_F} \bar{U}_F \bar{f}_1 = -\frac{d\alpha_1}{d\theta} \ln \left[\frac{P_F e^{\frac{\tau_F^2}{2}} \alpha_\infty^2}{(1-\alpha_\infty^2) K_P \tau_F} \right], \quad (3-14B)$$

where $\bar{f}_1 = \frac{d\bar{U}_1}{d\theta} - 2\bar{V}_1$

$$\begin{aligned} \mathcal{J}_1 = & \left[\frac{S_A^\circ - S_M^\circ}{R_M} - \ln p_\infty + (5-K_M) \ln \tau_F - \ln P_F + \ln \left(\frac{1-\alpha_\infty^2}{4\alpha_\infty^2} \right) \right] \alpha_1 \\ & + (1+\alpha_\infty) \left(\frac{\bar{\gamma}_\infty}{\bar{\gamma}_\infty - 1} \right) \frac{\tau_1}{\tau_F} - (1+\alpha_\infty) \frac{P_1}{P_F} \end{aligned} \quad (3-15)$$

The boundary conditions on the frozen and first-order solutions are

$$\theta = \sin^{-1} \left(\frac{1}{M_\infty} \right) : P_F = \tau_F = \sigma_F = 1, \bar{U}_F = \frac{(M_\infty^2 - 1)^{\frac{1}{2}}}{M_\infty}, \bar{V}_F = -\frac{1}{M_\infty} \quad (3-16)$$

$$P_1 = \tau_1 = \sigma_1 = \alpha_1 = \bar{U}_1 = \bar{V}_1 = 0 \quad (3-17)$$

$$\theta = -\pi : \bar{V}_F = \bar{V}_1 = 0 \quad (3-18)$$

3.2 Frozen Expansion Solution

Eqs. (3-1) - (3-6) describe the self-similar expansion of a thermally and calorically-perfect gas with a specific heat ratio $\bar{\gamma}_\infty(\alpha_\infty)$. Thus the effects of frozen dissociation on the expansion are bounded by the solutions for an undissociated perfect gas ($\bar{\gamma}_\infty = \gamma_M = 1.4$) and a pure monatomic gas ($\bar{\gamma}_\infty = \gamma_A = 1.667$) for a given M_∞ and $\mathcal{V}$. Since the details of the frozen flow field are needed to evaluate the coefficients and non-homogeneous terms in the first-order perturbation equations, a brief review of the zeroth-order solution will now be given.

The analysis is naturally divided into three distinct regions: A, B, and C (Fig. 1). In region A ahead of the first characteristic, the resultant velocity and thermodynamic properties are uniform while the tangential and radial velocity components are given by pure geometry. Thus, when $\theta \geq S_{IN}^{-1}(\frac{1}{M_\infty})$,

$$\begin{aligned} \sigma_F = \tau_F = P_F = V_{R_F} &= 1 \\ \bar{U}_F &= \cos \theta, \quad \bar{V}_F = -\sin \theta \end{aligned} \quad (3-19)$$

In region B within the expansion fan, the flow is determined by Eqs. (3-1) through (3-6) and (3-19). Combining (3-1), (3-3) and (3-6), we obtain

$$\bar{V}_F^2 = \frac{P_F}{M_\infty^2 \sigma_F} = \frac{\tau_F}{M_\infty^2} \quad (3-20)$$

which indicates that the tangential velocity component is equal to the local speed of sound in region B. Substituting the irrotationality condition (3-3) and (3-20) into the energy equation (3-5), the following first-order differential equation for $\bar{U}_F(\theta)$ is obtained:

$$1 + \frac{\eta^2 - 1}{M_\infty^2} = \bar{U}_F^2 + \eta^2 \left(\frac{d\bar{U}_F}{d\theta} \right)^2, \quad (3-21)$$

where

$$\eta^2 = \frac{\bar{\gamma}_\infty + 1}{\bar{\gamma}_\infty - 1} = 2 \left[\frac{KM + (5 - KM)\alpha_\infty}{1 + \alpha_\infty} \right] - 1$$

Taking into account the initial boundary condition on $\bar{U}_F$, Eq. (3-21) integrates to

$$\bar{U}_F = \left(\frac{\eta^2 - 1}{M_\infty^2} + 1 \right)^{\frac{1}{2}} \underbrace{\sin \left[\pm \frac{\theta - \theta_\infty}{\eta} + \sin^{-1} \left(\frac{M_\infty^2 - 1}{\eta^2 - 1 + M_\infty^2} \right)^{\frac{1}{2}} \right]}_{\psi}, \quad (3-22)$$

where the choice of sign in ψ is determined as shown below. Thus, using Eq. (3-3) and the boundary condition on $\bar{V}_F$, we obtain

$$\bar{V}_F = - \frac{1}{\eta} \left(\frac{\eta^2 - 1}{M_\infty^2} + 1 \right)^{\frac{1}{2}} \cos \psi \quad (3-23)$$

Denoting $\psi = \psi_\infty$ at $\theta = \theta_\infty = \sin^{-1} \left(\frac{1}{M_\infty} \right)$, such that

$$\psi_\infty = \sin^{-1} \left(\frac{M_\infty^2 - 1}{\eta^2 - 1 + M_\infty^2} \right)^{\frac{1}{2}} = \sin^{-1} \left(\frac{\eta}{\eta^2 - 1 + M_\infty^2} \right),$$

Eqs. (3-22) and (3-23) can be written as

$$\bar{U}_F = \frac{(M_\infty^2 - 1)^{\frac{1}{2}}}{M_\infty} \frac{\sin \psi}{\sin \psi_\infty} \quad (3-24)$$

$$\bar{V}_F = - \frac{1}{M_\infty} \frac{\cos \psi}{\cos \psi_\infty} \quad (3-25)$$

According to (3-20), the frozen temperature distribution in the expansion fan becomes

$$\tau_F = \frac{\cos^2 \psi}{\cos^2 \psi_x} \quad (3-26)$$

and, therefore, since the flow is isentropic,

$$P_F = (\tau_F)^{\gamma_\infty/(\gamma_\infty-1)} = \left(\frac{\cos \psi}{\cos \psi_x} \right)^{\gamma_x+1} \quad (3-27)$$

$$\sigma_F = (P_F)^{\frac{1}{\gamma_\infty}} = \left(\frac{\cos \psi}{\cos \psi_x} \right)^{\gamma_x+1} \quad (3-28)$$

The Mach number distribution in the fan now may be written as

$$\frac{M_\infty^2 (\bar{U}_F^2 + \bar{V}_F^2)}{\tau_F} \equiv M^2(\theta) = (M_\infty^2 - 1) \frac{\tan^2 \psi}{\tan^2 \psi_x} + 1 \quad (3-29)$$

The solution is completed by observing that the sign on $\theta - \theta_x$ in the foregoing definition of ψ must be such that $\tau_F, P_F, \sigma_F < 1$ (and $M^2 > M_\infty^2$) for $\theta < \theta_x$. Since $\psi_x < \frac{\pi}{2}$ for $M_\infty < \infty$, Eqs. (3-26) - (3-29) require $\psi > \psi_x$ ($\cos \psi < \cos \psi_x$) and hence a negative sign on $\theta - \theta_x$, i.e.,

$$\psi = \psi_x + \frac{\theta_x - \theta}{\gamma} = \sin^{-1} \left(\frac{M_\infty^2 - 1}{\gamma^2 - 1 + M_\infty^2} \right)^{\frac{1}{2}} + \frac{1}{\gamma} \left[\sin^{-1} \left(\frac{1}{M_\infty} \right) - \theta \right] \quad (3-30)$$

The solution in the third region, C, the uniform flow field downstream of the last frozen expansion fan characteristic which is parallel to the wall, again becomes quite simple. The thermodynamic properties and resultant

flow velocity are equal to their values at $\Theta = \Theta_{II}$, and the radial and tangential velocity components are given by

$$\left. \begin{aligned} \bar{U} &= (\bar{U}_F^2 + \bar{V}_F^2)^{\frac{1}{2}} \cos(\Theta + \nu) \\ \bar{V} &= -(\bar{U}_F^2 + \bar{V}_F^2)^{\frac{1}{2}} \sin(\Theta + \nu) \end{aligned} \right\} \quad (3-31)$$

Using (3-29), Θ_{II} is calculated as a function of M_∞ and ν by the relation

$$\tan(\Theta_{II} + \nu) = \pm \left(\frac{1}{\gamma} \right) \tan \left[\frac{\nu_{PM}(M_\infty, \gamma) + \frac{\pi}{2} - \Theta_{II}}{\gamma} \right], \quad (3-32)$$

where ν_{PM} is the Prandtl-Meyer turning angle function (Ref. 13) and where the choice of sign rests on obtaining the proper upward-running characteristic (discarding the downward-running member in this problem).

3.3 First-Order Solution

Eq. (3-8) is decoupled from the remaining first-order equations; a formal solution for $\alpha, (\Theta)$ can therefore be easily obtained. Switching to the independent variable ψ , inserting the proper frozen flow functions for the coefficients, and using the appropriate integrating factor (3-8) yields the following solution in region B:

$$\alpha, (\psi) = -2\gamma M_\infty \cos \psi_x (\cos \psi)^{\gamma^2} \int_{\psi_x}^{\psi} P_F^2 \tau_F^{\omega-2} (\cos \psi)^{-(\gamma^2+1)} G_F d\psi \quad (3-33)$$

with $\alpha, (\psi_x) = 0$. Using (2-13), (3-26) and (3-27), and noting that

$$K_p(1-\alpha_\infty) = e^{\tau_b} \frac{\alpha_\infty^2}{1+\alpha_\infty},$$

Eq. (3-33) can be written as

$$\alpha_1(\psi) = -\frac{\alpha_\infty^2}{1+\alpha_\infty} \eta M_\infty (\sec \psi_\infty)^{\eta^2+2\omega-4} (\cos \psi)^2 \left[I_R(\psi) - \frac{e^{\tau_b}}{(\sec \psi_\infty)^{\eta^2+1-2A}} I_D(\psi) \right] \quad (3-34)$$

where

$$I_R(\psi) = \int_{\psi_\infty}^{\psi} (\cos \psi)^{\eta^2+2\omega-3} d\psi \quad (3-35A)$$

$$I_D(\psi) = \int_{\psi_\infty}^{\psi} (\sec \psi)^{4-2\omega-2A} \exp(-\tau_b \cos^2 \psi_\infty \sec^2 \psi) d\psi \quad (3-35B)$$

represent contributions from the recombination and dissociation rates, respectively, the former being the predominant mechanism since α decreases with $\tau(\alpha, \leq 0)$. Eq. (3-35) correctly predicts that α_1 vanishes when the incoming stream is undissociated ($\alpha_\infty = 0$).

The foregoing quadratures must be carried out numerically for arbitrary values of η , ω and A . However, when $\eta^2+2\omega-3$ is an integer, (3-35A) may be evaluated in closed form directly from available integral tables (Ref. 14). Moreover, for $4-2\omega-2A$ equal to an even, positive integer, a closed form representation of (3-35B) in terms of the error function can be obtained (details are given in Appendix B).^{*} Fortunately,

^{*}The authors are indebted to Mr. T. Okamura of the Research Group, Missile Aero/Thermodynamics Section, for pointing out this representation.

the conditions for closed form integrability lie within the realm of practical interest, since ω is usually negative ($\omega \approx -1.5$) for diatomic gases. Therefore, a numerical evaluation of (3-35) for arbitrary values of η , ω and A can be avoided by a parametric study of the closed form solutions and subsequent interpolation.

In region C downstream of the last frozen expansion fan characteristic ($\theta \leq \theta_{II}$), the solution to (3-8) is straightforward. Here, the nonhomogeneous reaction rate term is constant and $\bar{U}_F$, $\bar{V}_F$ are given by (3-31). The resulting integration, subject to the initial condition $\alpha_1(\theta_{II}) = (\alpha_1)_{II}$, can be carried out in closed form and yields

$$\alpha_1 = (\alpha_1)_{II} \frac{S_{IN}(\theta + \gamma)}{S_{IN}(\theta_{II} + \gamma)} - \quad (3-36)$$

$$\underbrace{- \frac{2\alpha_{\infty}^2}{1+\alpha_{\infty}} \left[\frac{P_F^2 \tau_F^{\omega-2}}{(\bar{U}_F^2 + \bar{V}_F^2)^{\frac{1}{2}}} \right]_{II}}_{\alpha_1(\theta = -\gamma)} \left\{ 1 - \left[\frac{\tau_F^A e^{-\frac{\gamma}{\tau_F}(1-\tau_F)}}{P_F} \right]_{II} \right\} S_{IN}(\theta + \gamma) [COT(\theta + \gamma) - COT(\theta_{II} + \gamma)]$$

This solution describes a recombination-dominated relaxation downstream of the final frozen expansion fan characteristic in which the influence of the previous nonequilibrium flow history within region B continually diminishes as $\theta + \gamma$ decreases. At the wall, α_1 becomes completely independent of the flow in region B and may be calculated directly from the frozen solution.

The remaining first order perturbations may now be obtained by solving two additional differential equations. Napolitano, in his discussion of the problem, chose to evaluate the first-order entropy and radial velocity by quadratures and then determine the other flow field variables algebraically. This approach is suggested naturally when one observes that (3-13) is uncoupled from the remaining equations by the foregoing solution for α_1 . In practice, however, the advantage of this procedure is somewhat diminished

since the resulting integration must still be done numerically. Moreover, as shall be shown, it is more fruitful to proceed instead in terms of the vorticity field, particularly for the purpose of developing approximate, closed form solutions. Therefore, Eqs. (3-13) and (3-14) will henceforth be discarded.

Convenient relations governing the first-order vorticity perturbation

$$\bar{f}_1 = \frac{d\bar{U}_1}{d\Theta} - 2\bar{V}_1$$

may be easily derived. First, we eliminate $dP_1/d\Theta$ between (3-8) and (3-10), using (3-7), to yield

$$\bar{V}_F \sigma_F \frac{d\bar{f}_1}{d\Theta} = -\frac{d\sigma_F}{d\Theta} \left[\bar{V}_F^2 \frac{\sigma_1}{\sigma_F} + \bar{U}_F \bar{U}_1 + \bar{V}_F \bar{V}_1 \right] \quad (3-37)$$

A second vorticity relation is also obtained by combining (3-9), (3-11) and (3-12):

$$\frac{\bar{U}_F M_\infty^2 \bar{V}_F \bar{f}_1}{\tau_F} = -\left[\frac{\sigma_1}{\sigma_F} + \frac{M_\infty^2}{\tau_F} (\bar{U}_F \bar{U}_1 + \bar{V}_F \bar{V}_1) \right] + \left\{ \frac{\tau_D + (5-K_M) \tau_F}{\tau_F [(5-K_M) \alpha_\infty + K_M]} - \frac{1}{1+\alpha_\infty} \right\} \alpha_1 \quad (3-38)$$

These two relations are equivalent to the two momentum equations (3-9) and (3-10). Now within the frozen fan region B, where $\bar{V}_F^2 M_\infty^2 = \tau_F$, (3-37) and (3-38) may be combined so as to eliminate the common factor containing σ_1 , $\bar{U}_1$ and $\bar{V}_1$; then using (3-1) and (3-3), one obtains a linear first-order differential equation for $\bar{f}_1$ that readily integrates to the solution:

$$\bar{f}_1 = -\frac{P_F}{\bar{U}_F \eta (1+\alpha_\infty)} \int_{\eta_I}^{\eta} \frac{\bar{U}_F}{P_F} \left[\frac{2\tau_D}{\tau_F} + 2(5-K_M) - (\eta^2 + 1) \right] \alpha_1(\eta) d\eta \quad (3-39)$$

with $\alpha_1(\psi)$ known and the boundary condition $\bar{f}_1(\psi_\infty) = 0$. In region C downstream of the last frozen fan characteristic, the solution for $\bar{f}_1$ becomes quite simple, since by Eq. (3-37)

$$\bar{f}_1 = \text{CONST} = \bar{f}_1(\theta_\infty) \quad (\theta \leq \theta_\infty) \quad (3-40)$$

when $\frac{d\sigma_F}{d\theta} = 0$. Thus the nonequilibrium effect within region B results in a flow which emerges with a fixed rate of rotation proportional to γ throughout region C.

With $\bar{f}_1$ known, the differential equation governing the radial velocity perturbation $\bar{U}_1$ may now be determined. The expression $\bar{f}_1 = \frac{d\bar{U}_1}{d\theta} - 2\bar{V}_1$ and Eq. (3-38) are differentiated to obtain relations for $\frac{d\bar{V}_1}{d\theta}$ and $\frac{d\sigma_1}{d\theta}$, respectively. These relations along with (3-38) and the definition of $\bar{f}_1$ are then substituted into the first-order continuity equation (3-7). After a lengthy algebraic manipulation, the following equation is obtained.

$$\begin{aligned} & \left(1 - \frac{M_\infty^2 \bar{V}_F^2}{\tau_F}\right) \frac{d^2 \bar{U}_1}{d\theta^2} - \left[2 \frac{M_\infty^2 \bar{V}_F \bar{U}_F}{\tau_F} - \frac{d\sigma_F/d\theta}{\sigma_F} - \frac{M_\infty^2 \bar{V}_F^2}{\tau_F} \left(\frac{d\sigma_F/d\theta}{\sigma_F} + \frac{d\tau_F/d\theta}{\tau_F}\right)\right] \frac{d\bar{U}_1}{d\theta} \\ & + 2 \left[2 + \frac{M_\infty^2 \bar{U}_F \bar{V}_F}{\tau_F} \frac{d\tau_F/d\theta}{\tau_F} - \frac{M_\infty^2 (\bar{U}_F^2 + \bar{V}_F^2)}{\tau_F}\right] \bar{U}_1 = \left[1 + (2\bar{\gamma}_\infty - 1) \frac{M_\infty^2 \bar{V}_F^2}{\tau_F}\right] \frac{d\bar{f}_1}{d\theta} \end{aligned} \quad (3-41)$$

$$+ \left[\frac{d\sigma_F/d\theta}{\sigma_F} - (2\bar{\gamma}_\infty - 1) \frac{M_\infty^2 \bar{V}_F^2}{\tau_F} \left(\frac{d\sigma_F/d\theta}{\sigma_F} + \frac{d\tau_F/d\theta}{\tau_F}\right)\right] \bar{f}_1$$

$$- 2(\alpha_1 \bar{U}_F + \bar{V}_F \frac{d\alpha_1}{d\theta}) \left\{ \frac{\tau_F + (5 - K_M) \tau_F}{\tau_F [(5 - K_M) \alpha_\infty + K_M]} - \frac{1}{1 + \alpha_\infty} \right\} + \frac{2 \bar{V}_F \tau_F (d\tau_F/d\theta) \alpha_1}{[(5 - K_M) \alpha_\infty + K_M] \tau_F^2}$$

This second-order, linear differential equation for $\bar{U}_1$ was not given by Napolitano since his analysis was confined to region B within the frozen expansion fan. In this region, where $M_\infty^2 \bar{V}_F^2 = \tau_F$, the coefficient of $d^2 \bar{U}_1 / d\Theta^2$ is zero and Eq. (3-41) reduces to a first-order equation for $\bar{U}_1$ (which indeed it must, since only one boundary condition, $\bar{U}_1(\Theta_x) = 0$, is available). By taking advantage of the frozen flow relations, Eq. (3-41) may be further simplified to

$$\frac{d\bar{U}_1}{d\Theta} - \frac{\bar{V}_F}{2\bar{U}_F} \left[1 - \left(\frac{2+\gamma^2}{\gamma^2} \right) \frac{\bar{U}_F^2}{\bar{V}_F^2} \right] \bar{U}_1 = F(\gamma), \quad (3-42)$$

where

$$F(\gamma) \equiv \frac{\bar{P}}{2} - \left(\frac{\bar{V}_F}{1+\alpha_\infty} \right) \left[\frac{\tau_D}{\tau_F} + (5-K_M) - \frac{\gamma^2+1}{2} \right] \left[\frac{\alpha_1}{\gamma^2} + \frac{P_F^2 \tau_F^{\omega-2} \bar{G}_F}{(\gamma^2+1) \bar{U}_F} \right] \quad (3-43)$$

Subject to the boundary condition $\bar{U}_1(\Theta_x) = 0$, the solution to Eq. (3-41) may therefore be written as the following integral expression of known functions:

$$\bar{U}_1 = \frac{\gamma}{2} (\bar{U}_F \bar{V}_F \bar{P}_F)^{\frac{1}{2}} \int_{\Theta_x}^{\Theta} \frac{F(\gamma) d\gamma}{\bar{U}_F (\bar{U}_F \bar{V}_F \bar{P}_F)^{\frac{1}{2}}} \quad \Theta \geq \Theta_{II} \quad (3-44)$$

This equation is equivalent to the solution given by Napolitano. In contrast, the solution for $\bar{U}_1$ in region C is much more difficult, since the second-order term does not drop out ($1 \leq M_\infty^2 \bar{V}_F^2 / \tau_F \leq 0$ for $\Theta_{II} \leq \Theta \leq -\infty$). In this case, we have a two-point boundary value problem involving the initial value of $\bar{U}_1(\Theta_x)$ given by Eq. (3-44) and the condition

$$\frac{d\bar{U}_1}{d\Theta} (\Theta = -\infty) = \bar{f}_1 = \bar{f}_1(\Theta_{\infty}) \quad (3-45)$$

since $\bar{V}_1 = 0$ at the wall. With σ_F , τ_F and $\bar{f}_1$ constant for $\Theta < \Theta_{\infty}$, (3-41) may be reduced to

$$\begin{aligned} & \left(1 - \frac{M_{\infty}^2 \bar{V}_F^2}{\tau_F}\right) \frac{d^2 \bar{U}_1}{d\Theta^2} - \left(\frac{2M_{\infty}^2 \bar{U}_F \bar{V}_F}{\tau_F}\right) \frac{d\bar{U}_1}{d\Theta} + \left[4 - \frac{2M_{\infty}^2}{\tau_F} (\bar{U}_F^2 + \bar{V}_F^2)\right] \bar{U}_1 \\ & = 4 \left[\frac{\tau_D + (5-K_M) \tau_F}{\tau_F [(5-K_M) \alpha_{\infty} + K_M]} - \frac{1}{1+\alpha_{\infty}} \right] P_F^2 \tau_F^{\omega-2} G_F \quad \Theta < \Theta_{\infty}, \end{aligned} \quad (3-46)$$

where the right hand side is a constant. Unfortunately, a transformation of Eq. (3-46) to either normal or self-adjoint form does not yield a differential equation that can be solved in terms of quadratures. Therefore, to obtain the flow field downstream of the frozen fan region, (3-46) must be solved numerically.

With α_1 , $\bar{f}_1$ and $\bar{U}_1$ known, the remaining first-order variables $\bar{V}_1$, P_1 , σ_1 and τ_1 are determined algebraically from the relations

$$\bar{V}_1 = \frac{1}{2} \left(\frac{d\bar{U}_1}{d\Theta} - \bar{f}_1 \right) \quad (3-47)$$

$$P_1 = -\sigma_F \bar{V}_{\infty} M_{\infty}^2 (\bar{U}_F \bar{U}_1 + \bar{V}_F \bar{V}_1 + \bar{f}_1 \bar{V}_F) \quad (3-48)$$

$$\frac{\sigma_1}{\sigma_F} = \left[\frac{\tau_D + (5-K_M) \tau_F}{\tau_F [(5-K_M) \alpha_{\infty} + K_M]} - \frac{1}{1+\alpha_{\infty}} \right] \alpha_1 - \frac{M_{\infty}^2}{\tau_F} (\bar{V}_{\infty} \bar{V}_F \bar{f}_1 + \bar{U}_F \bar{U}_1 + \bar{V}_F \bar{V}_1) \quad (3-49)$$

$$\tau_1 = \tau_F \left(\frac{P_1}{P_F} - \frac{\sigma_1}{\sigma_F} - \frac{\alpha_1}{1+\alpha_{\infty}} \right), \quad (3-50)$$

all of which properly vanish at the initial expansion fan characteristic.

3.4 Approximate Solution for Hypersonic Flow

Before discussing numerical examples of the foregoing exact solutions, it is of interest to point out a simplified approximate solution for $M_\infty \gg 1$ which has been found to bring out many features of the first-order nonequilibrium flow field reasonably well.

Since the first-order atom concentration α_1 may be obtained analytically in closed form, it would be of interest to obtain approximate closed form analytical solutions for the remaining first-order thermodynamic variables in terms of α_1 . These solutions may be obtained for $M_\infty \gg 1$ by simplifying the analysis as follows. We may observe that the present problem is analogous in many respects to the nonequilibrium expansion of a dissociated gas in a hypersonic nozzle. Now in the latter case, it has been established that large departures from equilibrium have a relatively small effect on both the density and flow velocity in comparison to the corresponding effects on the local composition, temperature and pressure as long as the fraction of the total energy involved in dissociation is not large (≤ 25 percent) (Ref. 15). Therefore, in view of the aforementioned analogy, it may be argued that the nonequilibrium effects on density and the resultant velocity in the present problem may be neglected for the purpose of estimating P_1 and T_1 when the incoming stream is hypersonic and its dissociation energy is not too large a fraction of the total energy. Then on the basis of the assumptions

$$\sigma_1 \cong 0 \quad \bar{U}_1 \bar{U}_F + \bar{V}_1 \bar{V}_F \cong 0$$

we may dispense with two of the first order flow equations [conveniently, the differential equations (3-7) and (3-37)] and obtain the following purely algebraic solutions for T_1 , P_1 and $\bar{f}_1$:

$$T_1 \cong - \left[\frac{T_\infty + (5-K_M) T_F}{K_M + (5-K_M) \alpha_\infty} \right] \alpha_1 \quad (3-52)$$

$$P_i \cong -\sigma_F \left[\frac{\tau_D + (5-K_M)\tau_F}{K_M + (5-K_M)\alpha_\infty} - \frac{\tau_F}{1+\alpha_\infty} \right] \alpha_i \quad (3-53)$$

$$\bar{f}_i \cong - \frac{P_i}{\bar{v}_\infty M_\infty^2 \sigma_F \bar{V}_F} \quad (3-54)$$

These closed-form approximations are questionable in region C; for example, (3-54) does not correctly predict that $\bar{f}_i$ is a constant in this region and, in fact, yields $\bar{f}_i \rightarrow \infty$ at the wall ($\bar{V}_F = 0$). Nevertheless, as will be shown below, these formulae do bring out the essential features of hypersonic nonequilibrium flow within region B reasonably well.

3.5 Numerical Results

In this section, some numerical results for the first-order nonequilibrium flow field will be presented. We shall attempt to bring out the main physical features of the nonequilibrium effects, evaluate the influence of the various thermochemical parameters, and assess the accuracy of the approximate solution for hypersonic flow discussed in the foregoing section.

In Figs. 2a through 2f, angular distributions of the frozen and first-order variables in region B are presented for typical values of the physical parameters and three different Mach numbers. These curves pertain to all possible turning angles ν . The corresponding values of Θ_x for each ν and M_∞ [from Eq. (3-32)] are shown in the insert of Fig. 2a. It is observed that the sign of the atom concentration, temperature, pressure and vorticity perturbations is commensurate with a recombination-dominated behavior throughout region B ($\alpha_i < 0$, $\tau_i, P_i > 0$, $\bar{f}_i > 0$). The density perturbation is initially compressive ($\sigma_i > 0$) but subsequently becomes negative throughout much of the frozen fan region unless ν is quite small. In the examples shown, it is clear that the first-order flow field is highly nonlinear and rotational except in the case of very small total turning angles (the range of linearity decreasing rapidly with increasing

M_∞). Generally speaking, the perturbations increase very sharply at the beginning of the expansion and will in many cases attain a peak value in region B before the last frozen fan characteristic is reached. The initial rate of growth increases with M_∞ ; however, the maximum values are by comparison rather insensitive to M_∞ . Both σ_1 and P_1 increase more rapidly than α_1 and τ_1 , while $\bar{f}_1$ rises gradually and lags considerably behind the other perturbations. For $M_\infty \geq 5$, the radial velocity perturbation is extremely small throughout region B.

The influence of the three parameters τ_b , K_p and ω on the first-order distribution functions is shown in Figs. 3, 4 and 5, respectively. In Fig. 3, the nonequilibrium effects are seen to be quite sensitive to τ_b ; a 20 percent reduction in this parameter produces a ten-fold increase in the magnitude of the perturbations. Since the flow is recombination-dominated, the influence of τ_b is primarily the result of a change in the free stream dissociation level [see Eq. (3-34)]. An increase in K_p , as shown in Fig. 4, also increases the magnitude of the perturbations for the same reason. In Fig. 5, an increase in the recombination rate temperature exponent ω from -1.5 to zero is seen to produce roughly a 25 percent reduction in α_1 and τ_1 (with far less of a reduction in the remaining perturbations). This effect follows from the fact that the local recombination rate has been reduced. It is clear that any value of ω between -2 and -1 will yield essentially the same perturbation function solutions; hence, the major effect of changes in the value of ω lies in the small parameter Γ [Eq. (2-22)] and is proportional to $\tau_\infty^{\omega-2}$.

Shown in Fig. 6 are the distributions of τ_1 , P_1 and $\bar{f}_1$ based on the exact solution for $\alpha_1(\theta)$ and the approximations $\sigma_1 \approx \bar{u}, \bar{u}_F + \bar{v}, \bar{v}_F \approx 0$ [Eqs. (3-52) through (3-54)]. These simple closed-form approximations provide a satisfactory qualitative description of the flow in these examples, and are in good quantitative agreement with the exact solutions in the vicinity of $\theta = \theta_{xx}$ for all three Mach numbers shown. However, the initial rise and possible maxima in the perturbations are underestimated, so that (3-52) through (3-54) will be inaccurate throughout region

B for expansions with very small $\mathcal{V}$.* This result is to be expected, since it is seen from Fig. 2a that $\sigma_1 = 0$ is a poor approximation in the initial portion of region B.

Exact numerical solutions for the complete first-order nonequilibrium flow field in region C downstream of the last frozen expansion fan characteristic were not carried out.** However, an exact, closed form solution for α , has been given [Eq. (3-36)] and the corresponding value of $\mathcal{T}_1$ is known from the foregoing solutions in region B [Eq. (3-40)].

As an illustrative example of the complete first-order nonequilibrium flow field in region B, Figs. 7a through 7d present a composite solution for a typical case at $M_\infty = 10$ expanded through the maximum turning angle $\mathcal{V}_{MAX} = 19.2$ degrees with the following free stream conditions:

$$M_\infty = 10$$

$$V_{R_\infty} = 20,000 \frac{FT}{SEC}$$

$$T_\infty = 3,450^\circ K$$

$$P_\infty = 0.1 \text{ ATM} = 211.7 \frac{LB}{FT^2}$$

$$\mu_R = \frac{18.5 \times 10^{16}}{(4500^\circ K)^{1.5}} \cdot \frac{CM^6}{MOLE^2 \cdot SEC} \quad R_\infty = 6.140 \frac{FT \cdot LB}{MOLE \cdot ^\circ K}$$

$$P' = 0.142 \frac{1}{IN} \quad (Eq. 2-22)$$

The general effect of the nonequilibrium perturbation on the frozen thermochemical field can, of course, be anticipated from the foregoing analytical and numerical results (i.e., the marked change in τ , α and P and the

* In this case a linearized theory such as Ref. 10 can be used.

** These solutions are currently being programed; results will be reported in a future report.

less significant change in σ). However, the graphical presentation (Figs. 7a through 7d) of the composite flow field clearly shows to what degree the nonequilibrium effects may alter the basic field. In the initial portion of the fan, the nonequilibrium effects indicate a flow field recompression for $r > 1$ inch; this recompression is unrealistic and will not appear in the physical flow field. It follows that in the initial portion of the fan the radius of validity of the first-order solution is of order 1 or less and, in fact, at larger radii the indicated composite solution has been forced to relax through and away from the equilibrium solution. This excessive relaxation results in a completely unrealistic solution. As we proceed into the fan, however, the radius of validity of the solution is extended outward since the basic (frozen) flow field departs more and more from equilibrium. In the latter part of the fan (approaching the wall), the nonequilibrium effects become negligible since the flow field becomes frozen to all orders as it approaches its maximum expanded state. The behavior in the initial portion of the fan clearly emphasizes the important point that the application of any small perturbation technique such as is used in this analysis is not simply a matter of multiplication and addition. It is, rather, a careful process, foremost in which is the determination (or estimation) of regions of reasonable validity. These regions generally can be described only within the context of a specific problem and are dependent not only on the initial physical problem posed but also on the consistency or accuracy of the solution required.

4. CONCLUDING REMARKS

The problem of the centered expansion of steady, supersonic, chemically reacting diatomic gas flow around a sharp corner has been analyzed by treating small local departures from the frozen flow near the corner.

An exact solution utilizing a Lighthill-type gas model was presented in similitude form together with some numerical results for the first-order nonequilibrium flow field. This solution and the accompanying numerical results brought out the following features. The first-order species equation was placed in closed form and was shown to be independent of all but

the frozen solution in the expansion fan and at the downstream wall, acquiring a dependence on the previous first-order species solution in the region between the final frozen characteristic and the wall. The first-order variations of the thermo-chemical parameters show the flow field to be heavily recombination-dominated but not to the degree where the neglect of the dissociation effects will give an accurate assessment of the flow field. The first-order flow field is shown to be highly nonlinear and rotational except in the case of very small flow turning angles. The small range of linearity decreases rapidly with increasing free stream Mach number. In general, the nonequilibrium perturbations increase very sharply in the initial portion of the expansion and will in many cases obtain a peak value before the final frozen characteristic is reached. The initial rate of growth increases with increasing free stream Mach number, but the peak values are shown to be rather insensitive to the free stream Mach number.

Since it has been observed that for reacting expanding flow in a hypersonic nozzle large departures from equilibrium cause relatively small changes in density and flow velocity, an analogy was made with the present problem. An approximate solution was developed based on this analogy which allowed a completely closed form determination of the thermochemical field. These simple closed form approximations provide a good qualitative description of the flow field. When compared to the exact first-order solution, it is seen that the initial rise and the maximum values of the perturbations are underestimated. However, the exact and approximate solutions are in good quantitative agreement in the middle and latter portions of the fan.

FLOW GEOMETRY AND COORDINATES

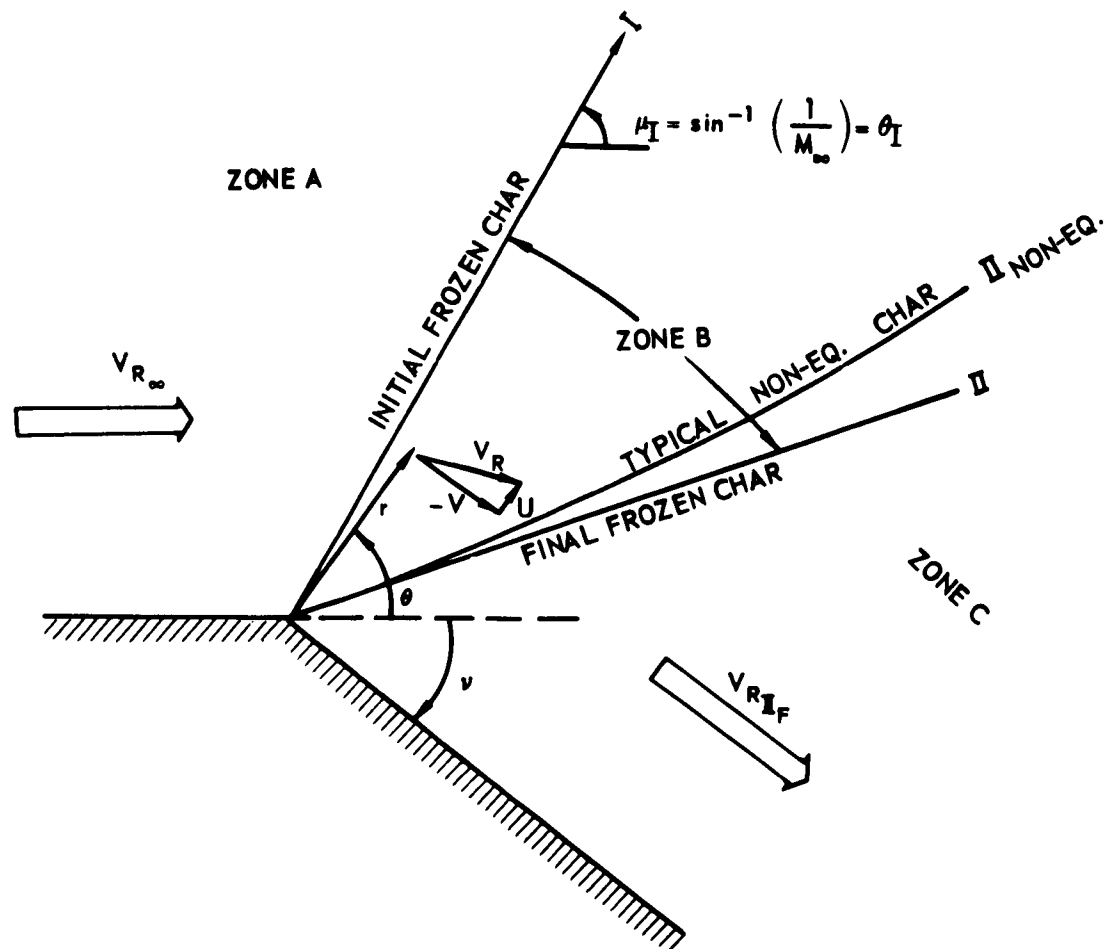


FIGURE 1

DISTRIBUTION OF DYNAMIC AND THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

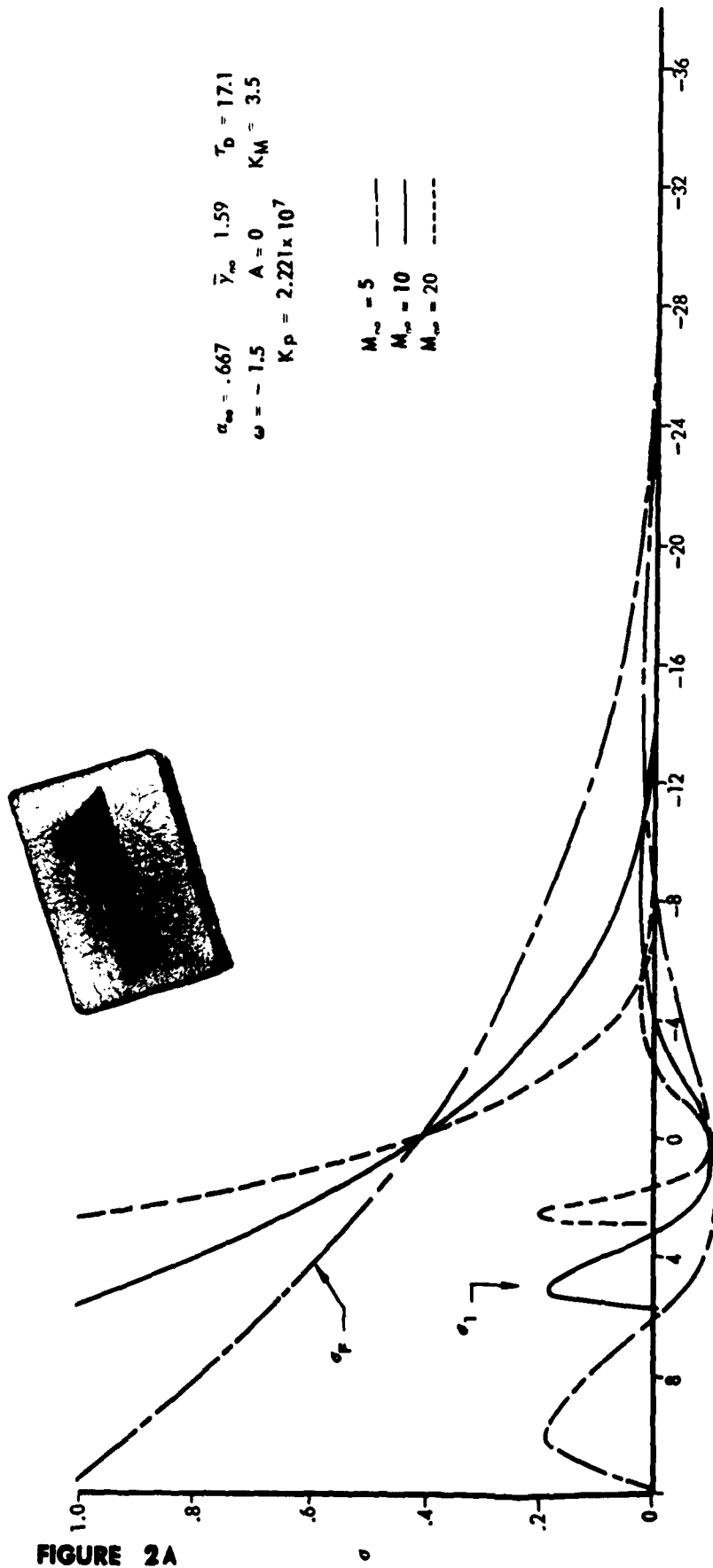
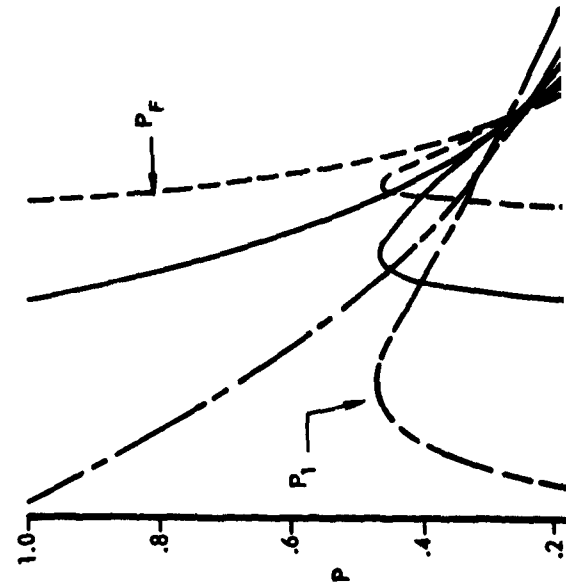
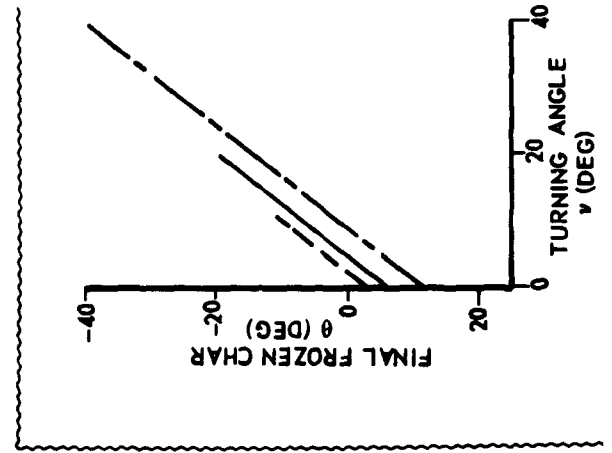
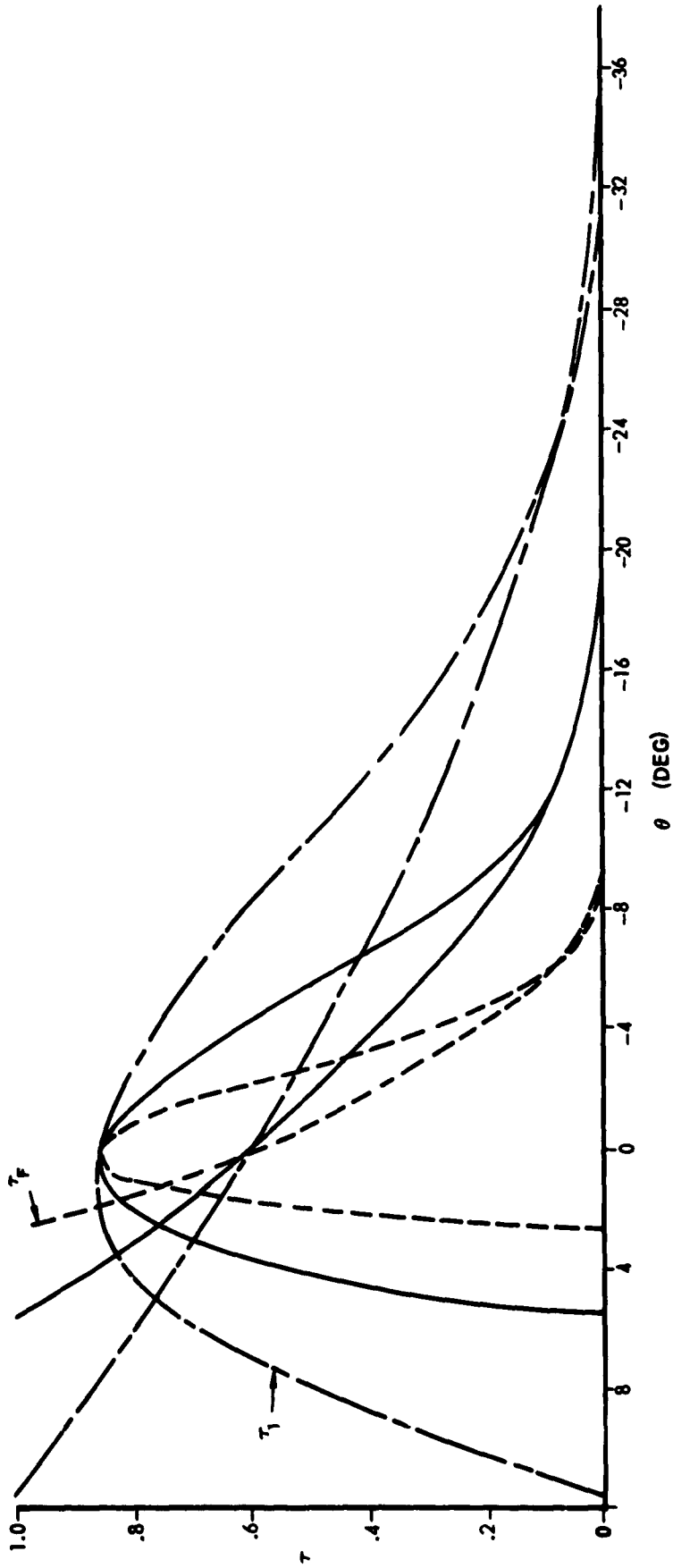
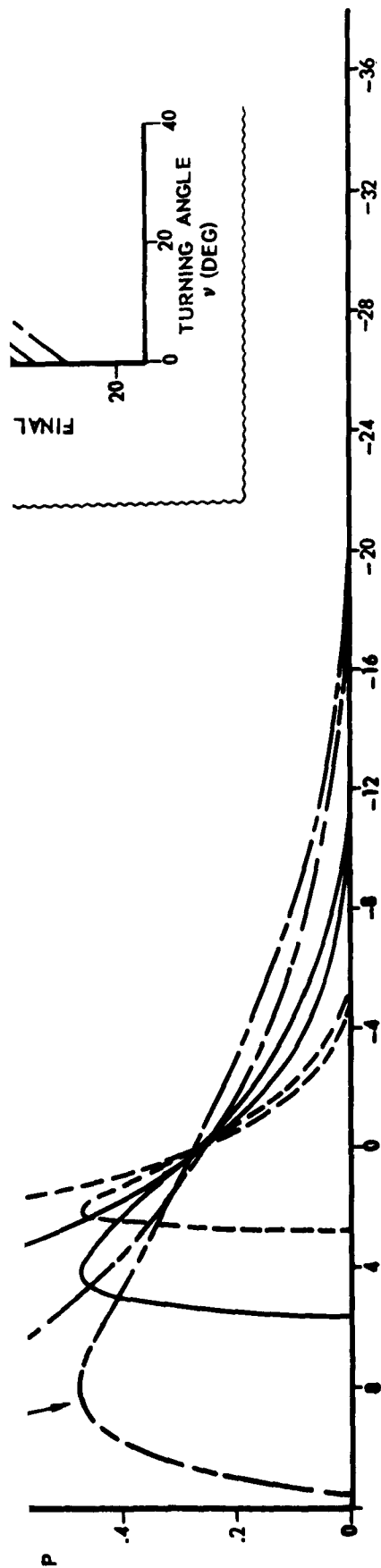


FIGURE 2A

$$\begin{aligned} \alpha_\infty &= .667 & \bar{\gamma}_\infty &= 1.59 & T_0 &= 17.1 \\ \omega &= -1.5 & A &= 0 & KM &= 3.5 \\ K_P &= 2.221 \times 10^7 \end{aligned}$$

$$\begin{aligned} M_\infty &= 5 & \text{---} \\ M_\infty &= 10 & \text{---} \\ M_\infty &= 20 & \text{---} \end{aligned}$$

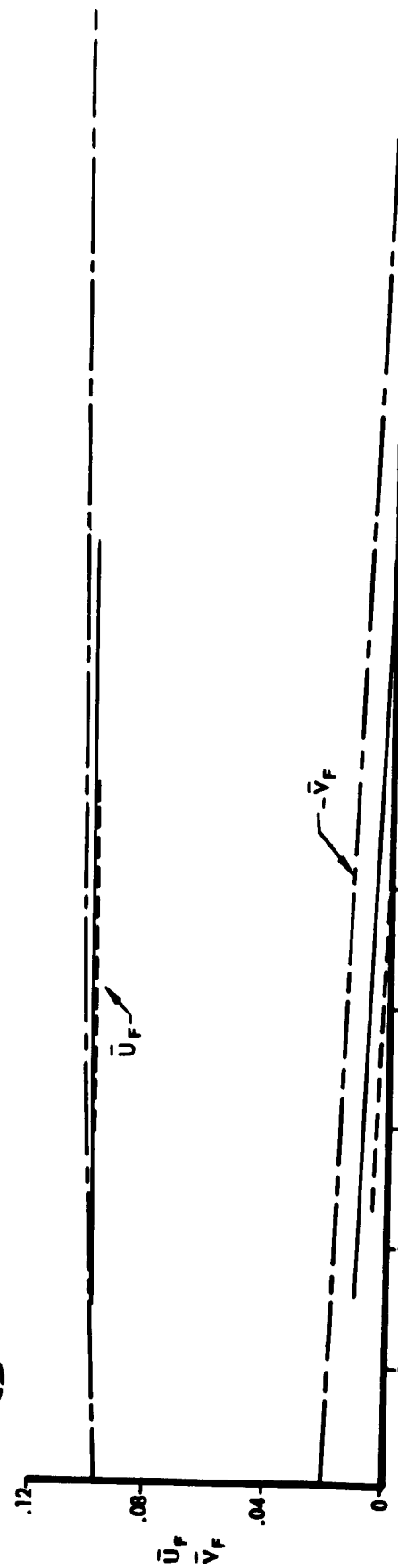
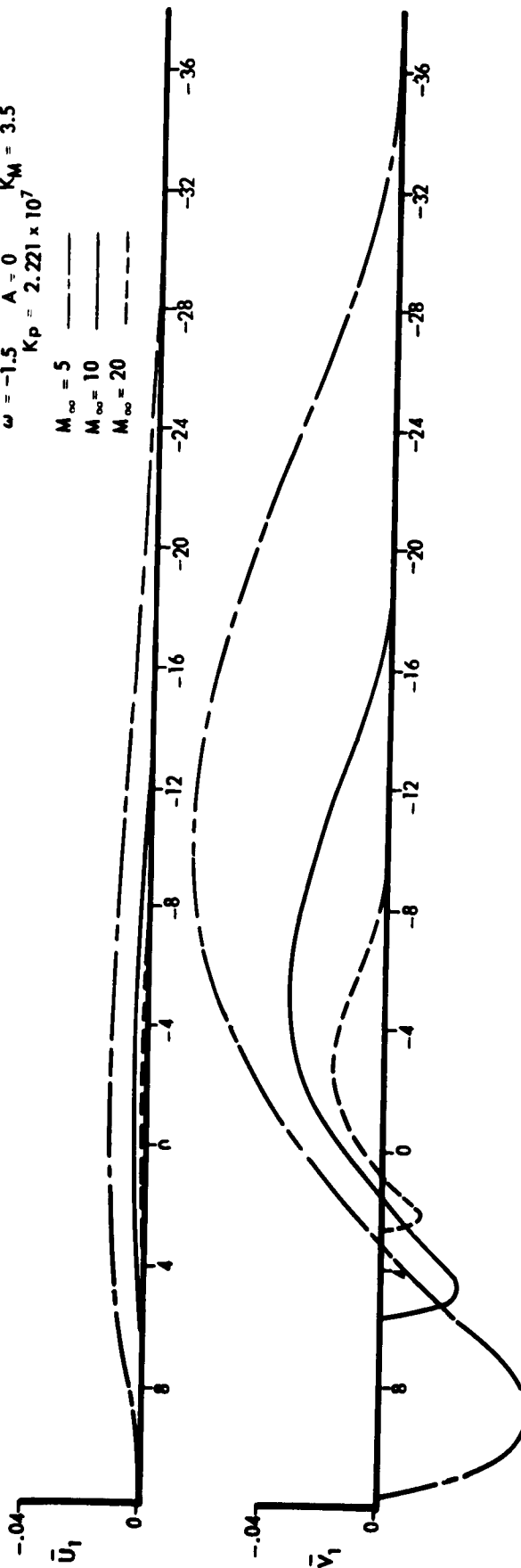




2

DISTRIBUTION OF DYNAMIC AND THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

$\alpha_\infty = .667$ $\bar{\gamma}_\infty = 1.59$ $\tau_D = 17.1$
 $\omega = -1.5$ $A = 0$ $K_M = 3.5$
 $K_P = 2.221 \times 10^7$
 $M_\infty = 5$ _____
 $M_\infty = 10$ _____
 $M_\infty = 20$ _____



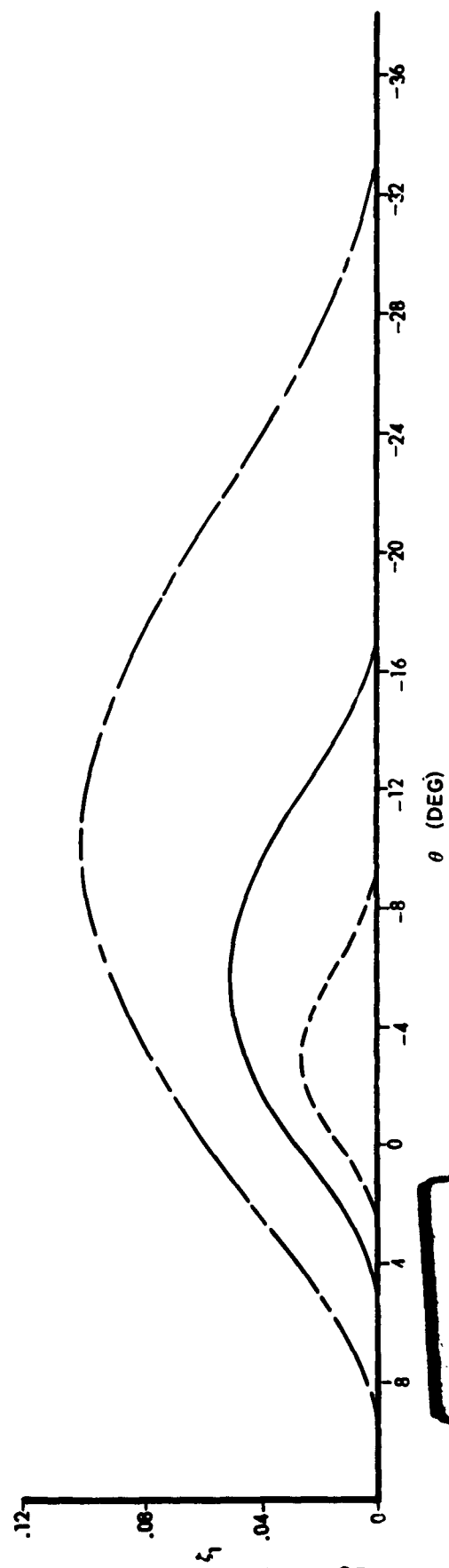
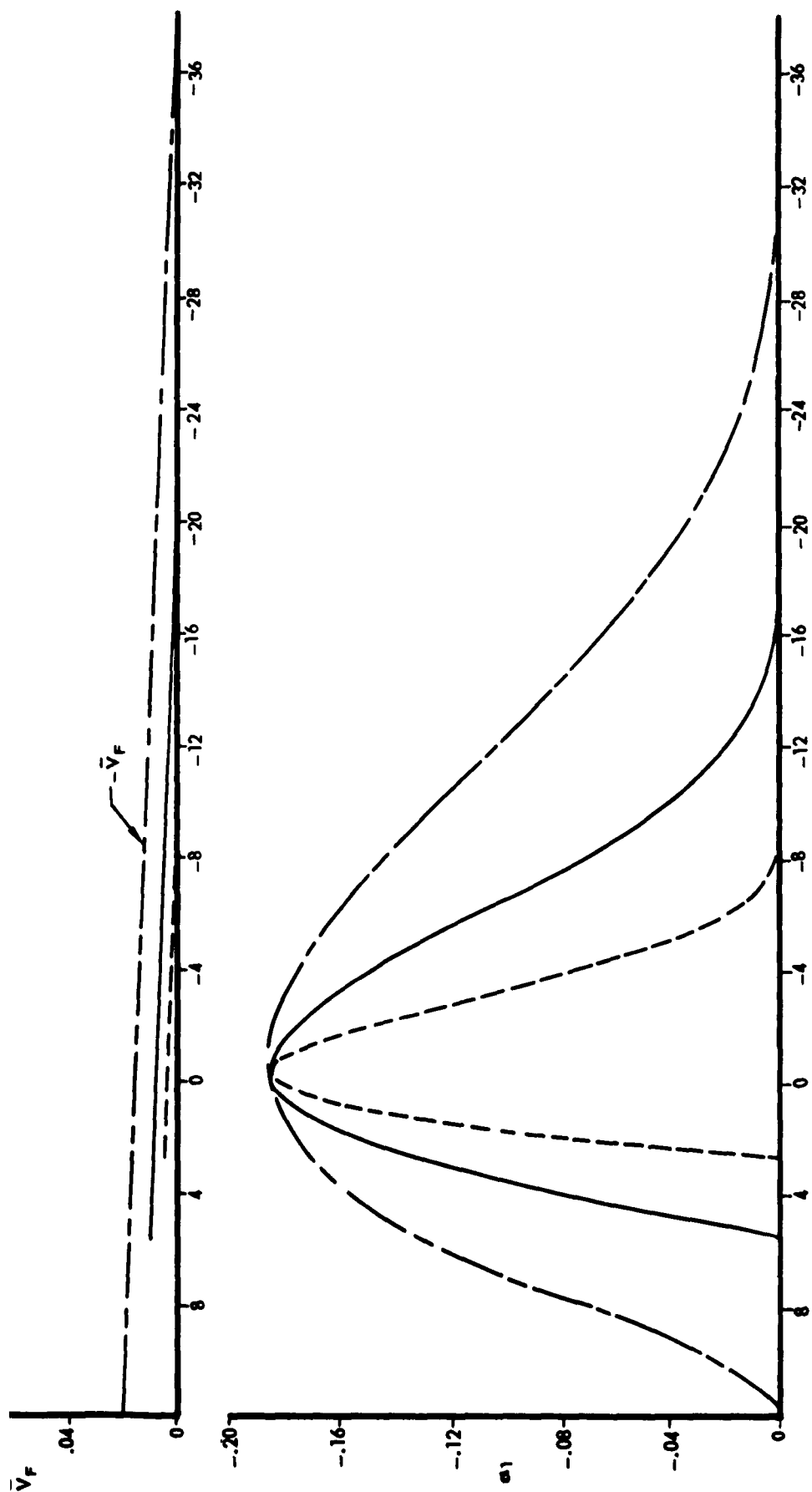


FIGURE 2B

2

DISTRIBUTION OF THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

$$M_\infty = 1.0 \quad K_p = 2.221 \times 10^7$$

$$\omega = -1.5 \quad A = 0 \quad K_M = 3.5$$

$$\tau_D = 17.1 \left\{ \begin{array}{l} \alpha_\infty = .667 \\ \bar{\gamma}_\infty = 1.59 \end{array} \right\} \text{ ————— }$$

$$\tau_D = 20.6 \left\{ \begin{array}{l} \alpha_\infty = .160 \\ \bar{\gamma}_\infty = 1.45 \end{array} \right\} \text{ - - - - - }$$

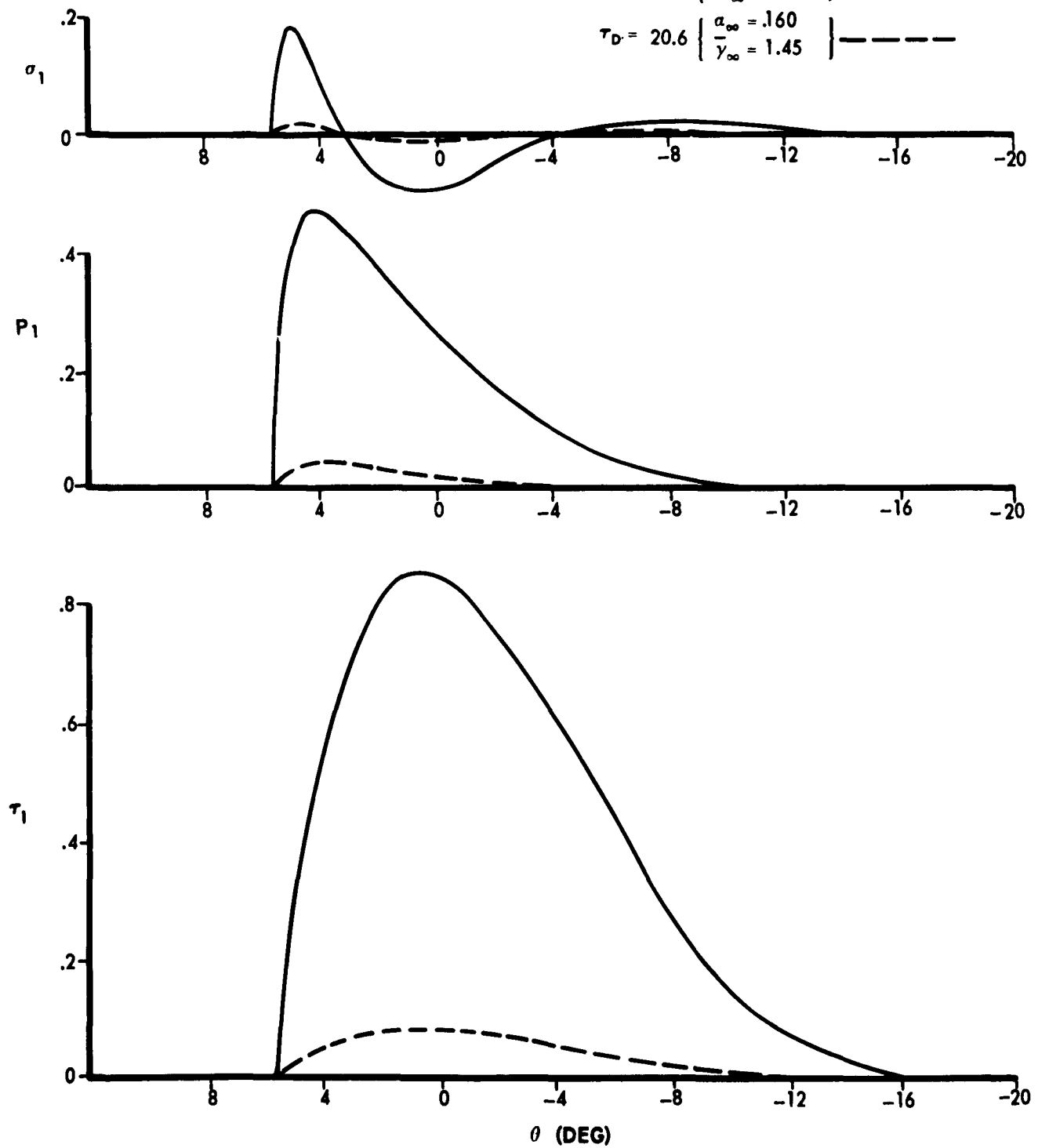


FIGURE 3A

DISTRIBUTION OF THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

$$M_\infty = 1.0 \quad K_p = 2.221 \times 10^7$$

$$\omega = -1.5 \quad A = 0 \quad K_M = 3.5$$

$$\tau_D = 17.1 \left\{ \begin{array}{l} \alpha_\infty = .667 \\ \bar{\gamma}_\infty = 1.59 \end{array} \right\} \text{ —————}$$

$$\tau_D = 20.6 \left\{ \begin{array}{l} \alpha_\infty = .160 \\ \bar{\gamma}_\infty = 1.45 \end{array} \right\} \text{ - - - - -}$$

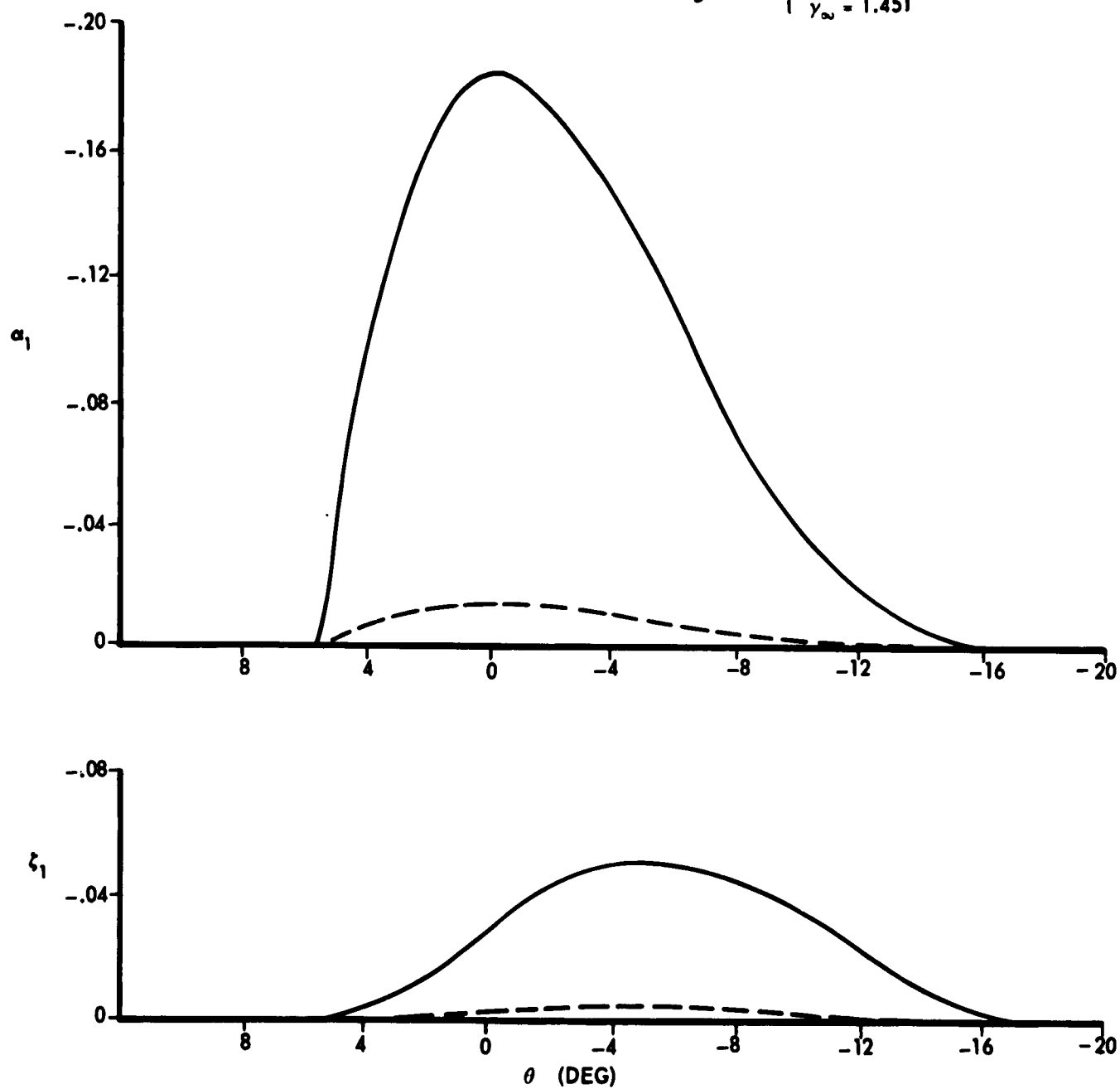


FIGURE 3B

DISTRIBUTION OF THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

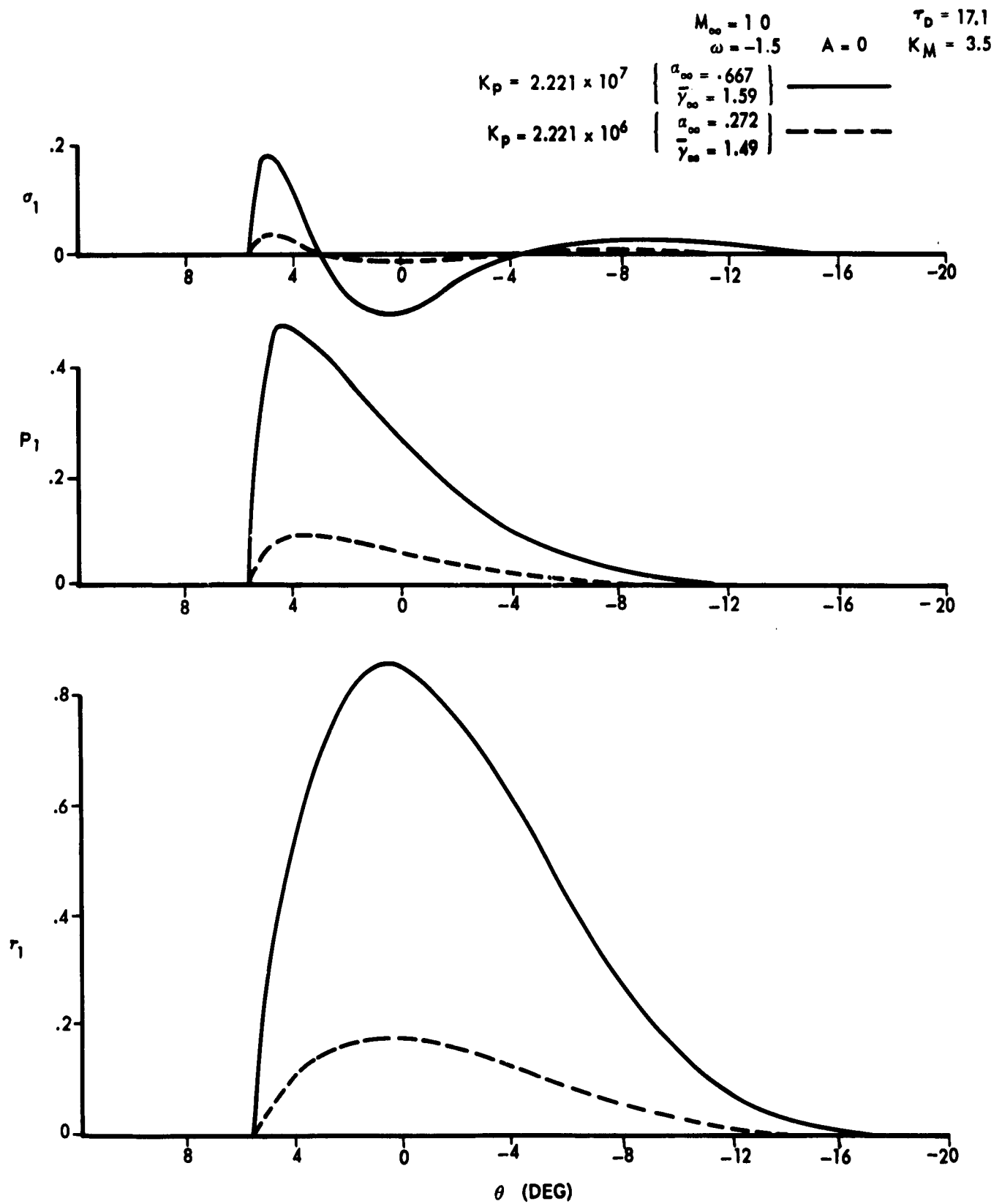


FIGURE 4A

DISTRIBUTION OF THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

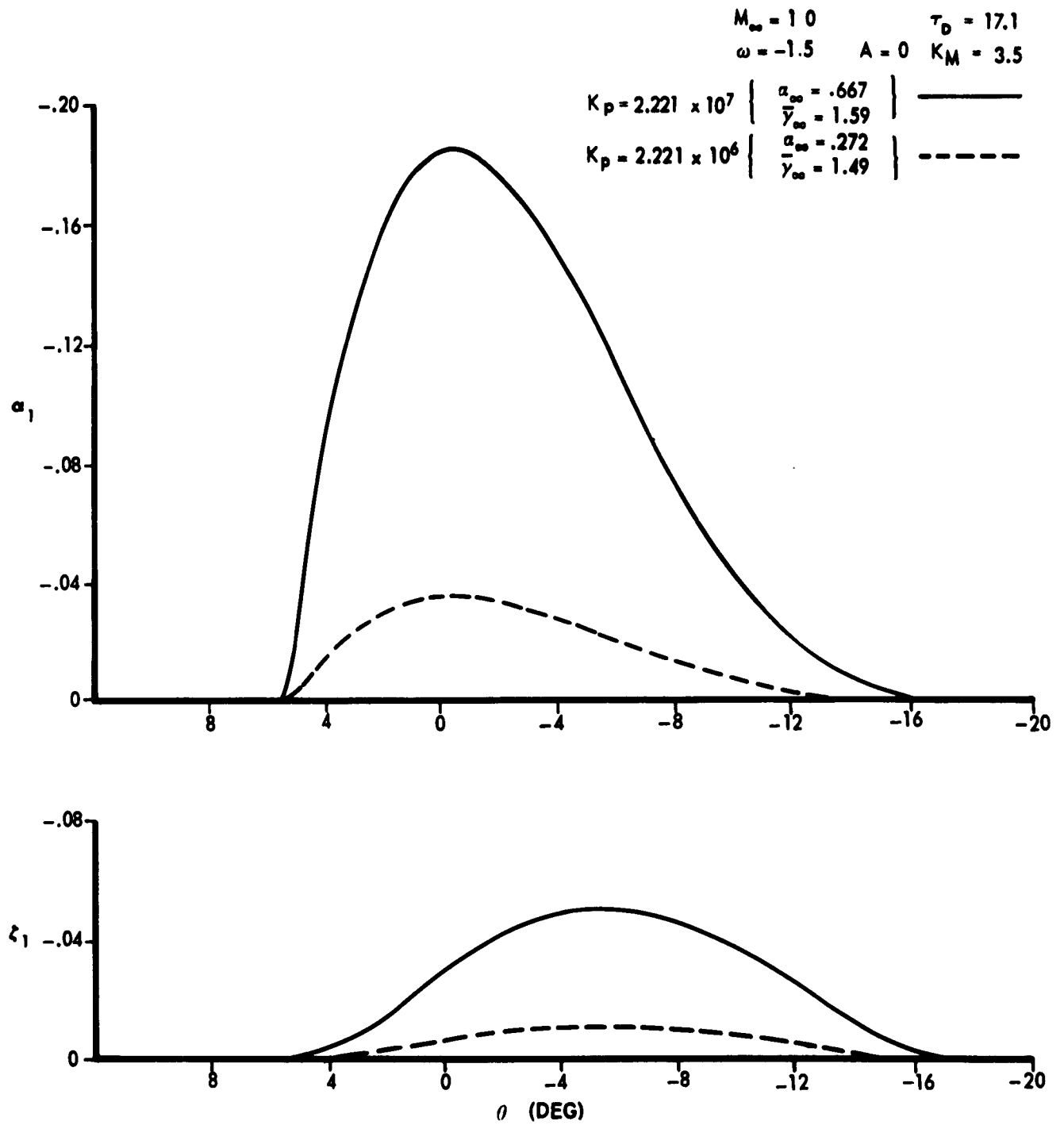


FIGURE 4B

DISTRIBUTION OF THERMODYNAMIC VARIABLES WITHIN THE FROZEN FAN

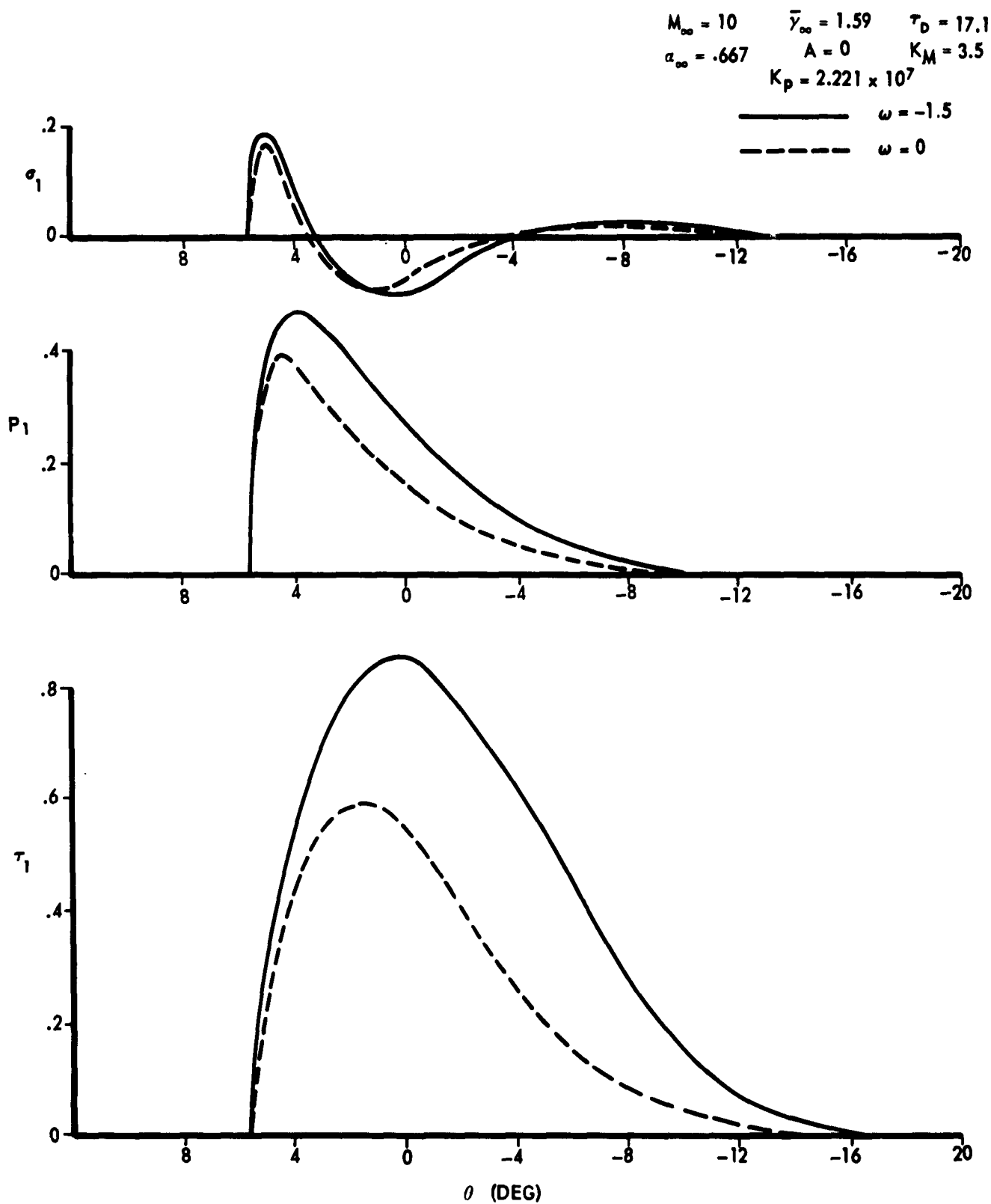


FIGURE 5A

DISTRIBUTION OF THERMODYNAMICS VARIABLES WITHIN THE FROZEN FAN

$$\begin{array}{lll}
 M_\infty = 10 & \bar{\gamma}_\infty = 1.59 & \tau_D = 17.1 \\
 \alpha_\infty = .667 & A = 0 & K_M = 3.5 \\
 & K_P = 2.221 \times 10^7 &
 \end{array}$$

$$\begin{array}{ll}
 \omega = -1.5 & \text{—————} \\
 \omega = 0 & \text{-----}
 \end{array}$$

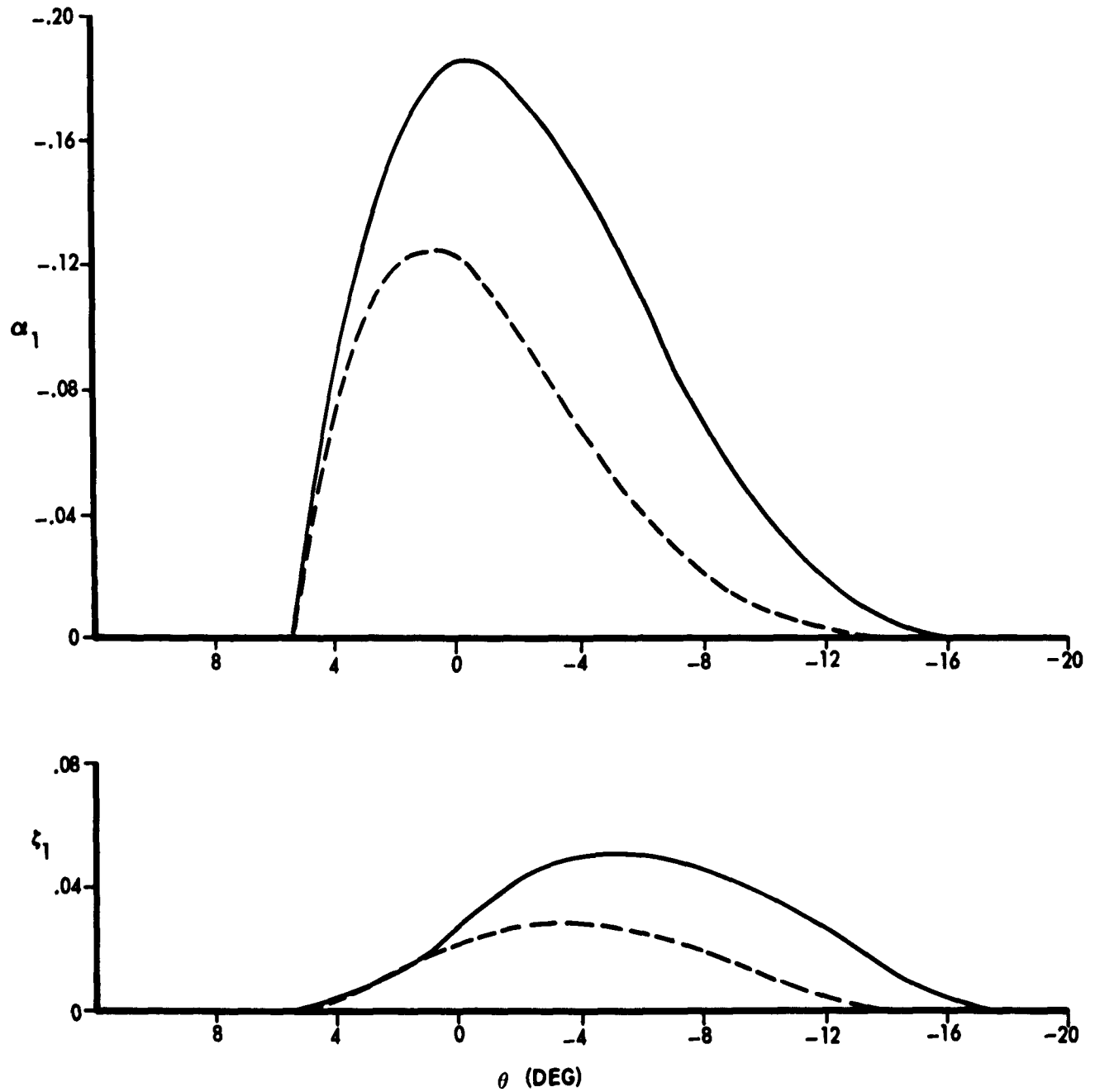


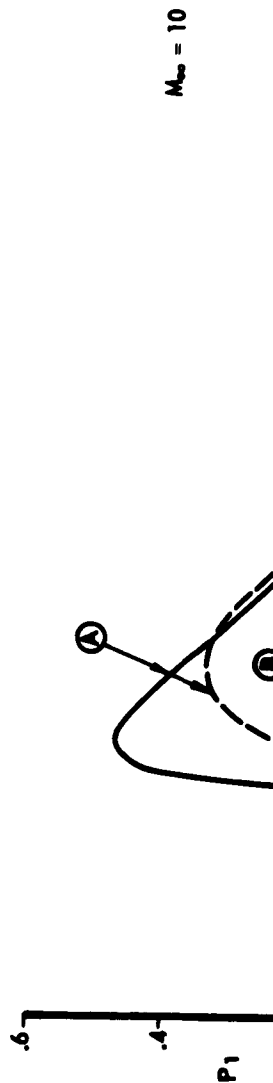
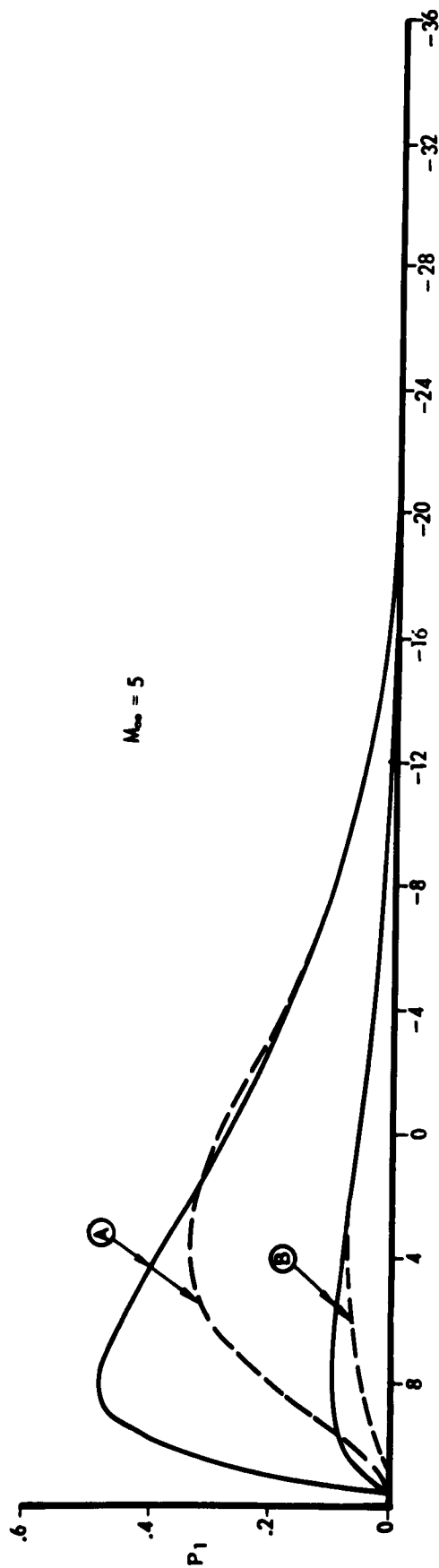
FIGURE 5B

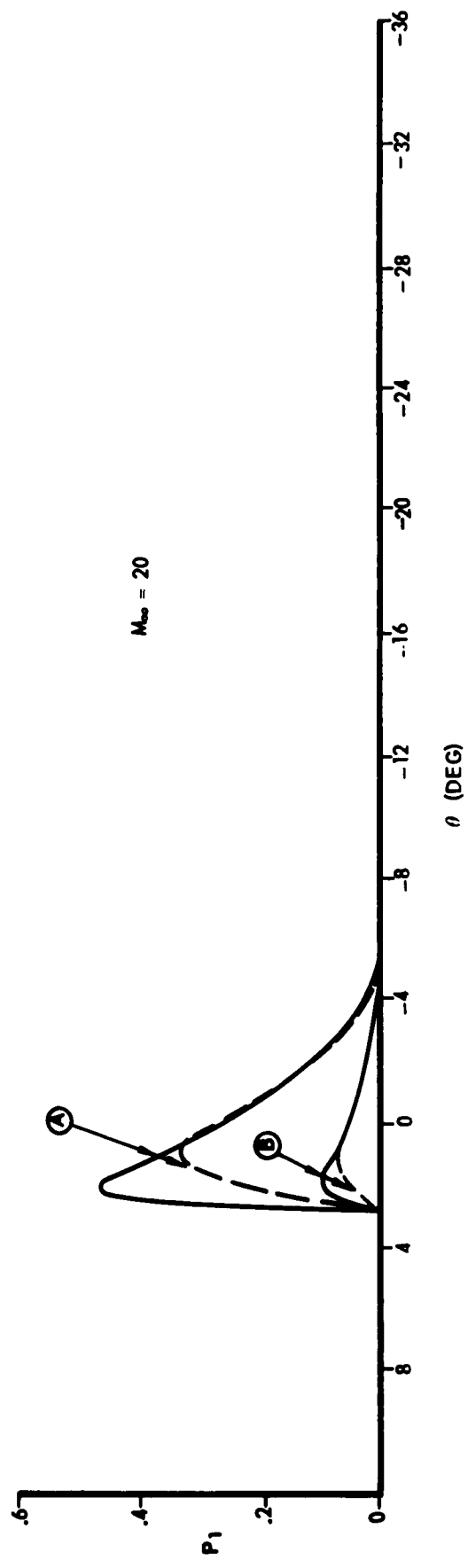
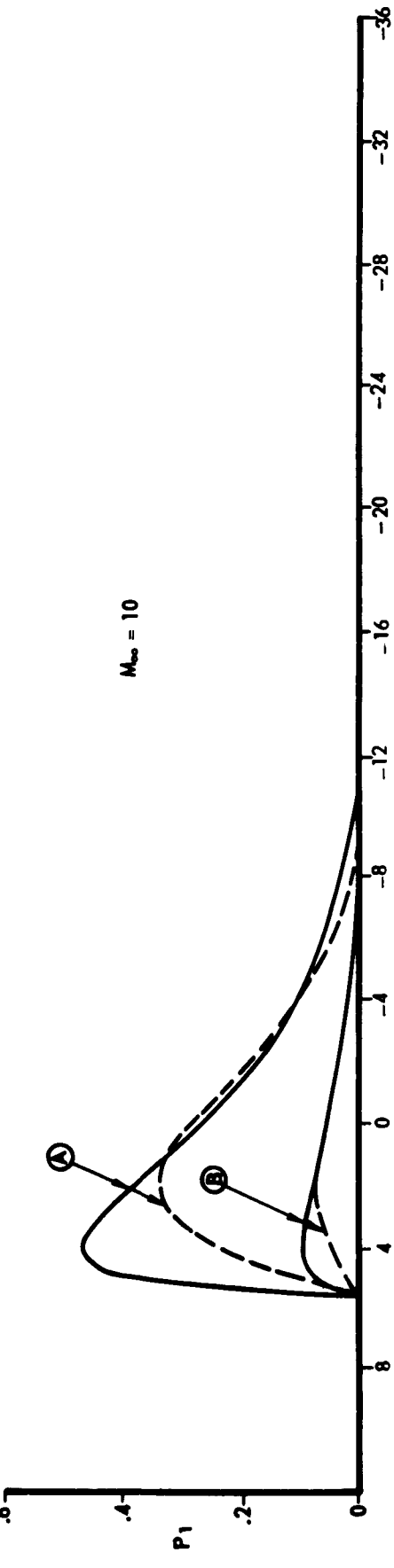
COMPARISON OF EXACT AND APPROXIMATE FIRST ORDER SOLUTIONS WITHIN THE FROZEN FAN

FIGURE 6 A



ALL CURVES	$\omega = -1.5$	$A = 0$
	$K_M = 3.5$	$\tau_D = 17.1$
	EXACT	---
	APPROX	---
CURVES (A)	$\alpha_{\infty} = .667$	$\bar{\gamma}_{\infty} = 1.59$
	$K_P = 2.221 \times 10^7$	
CURVES (B)	$\alpha_{\infty} = .272$	$\bar{\gamma}_{\infty} = 1.49$
	$K_P = 2.221 \times 10^6$	







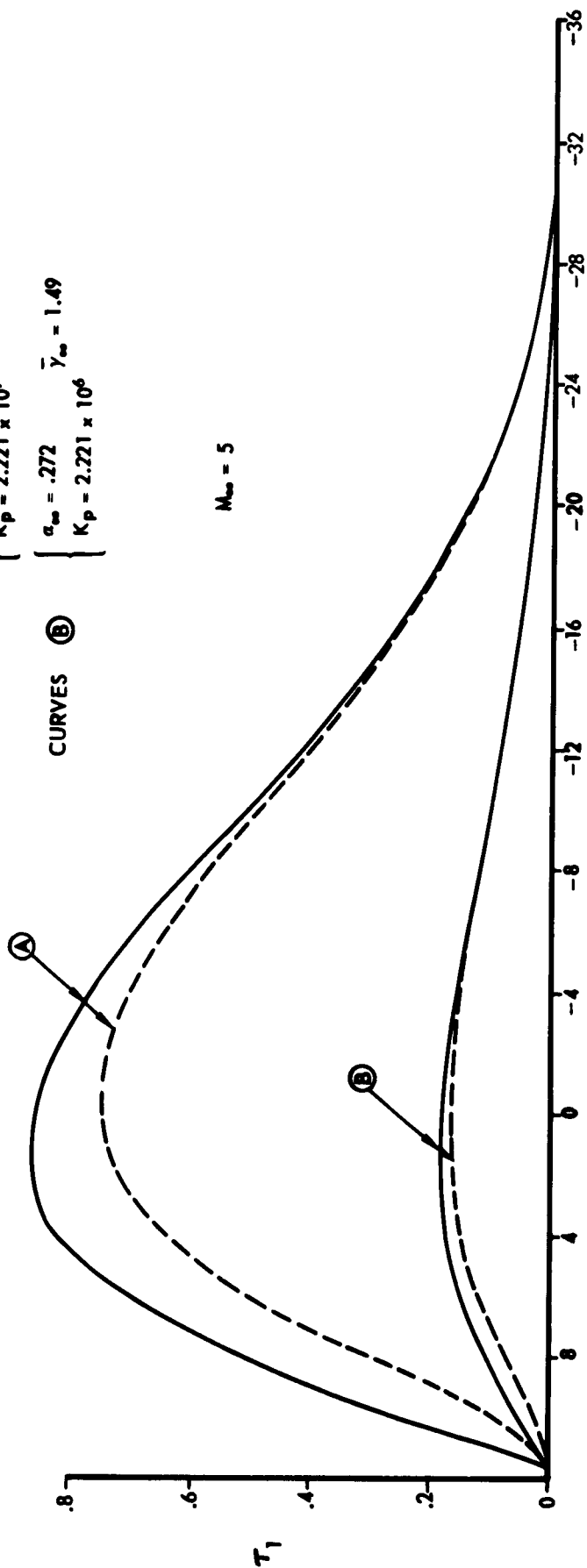
COMPARISON OF EXACT AND APPROXIMATE FIRST ORDER
SOLUTIONS WITHIN THE FROZEN FAN

ALL CURVES $\left\{ \begin{array}{l} \omega = -1.5 \quad A = 0 \\ K_M = 3.5 \quad \tau_D = 17.1 \\ \text{EXACT} \quad \text{---} \\ \text{APPROX} \quad \text{-----} \end{array} \right.$

CURVES (A) $\left\{ \begin{array}{l} \alpha_{\infty} = .667 \quad \bar{\gamma}_{\infty} = 1.59 \\ K_P = 2.221 \times 10^7 \end{array} \right.$

CURVES (B) $\left\{ \begin{array}{l} \alpha_{\infty} = .272 \quad \bar{\gamma}_{\infty} = 1.49 \\ K_P = 2.221 \times 10^6 \end{array} \right.$

$M_{\infty} = 5$



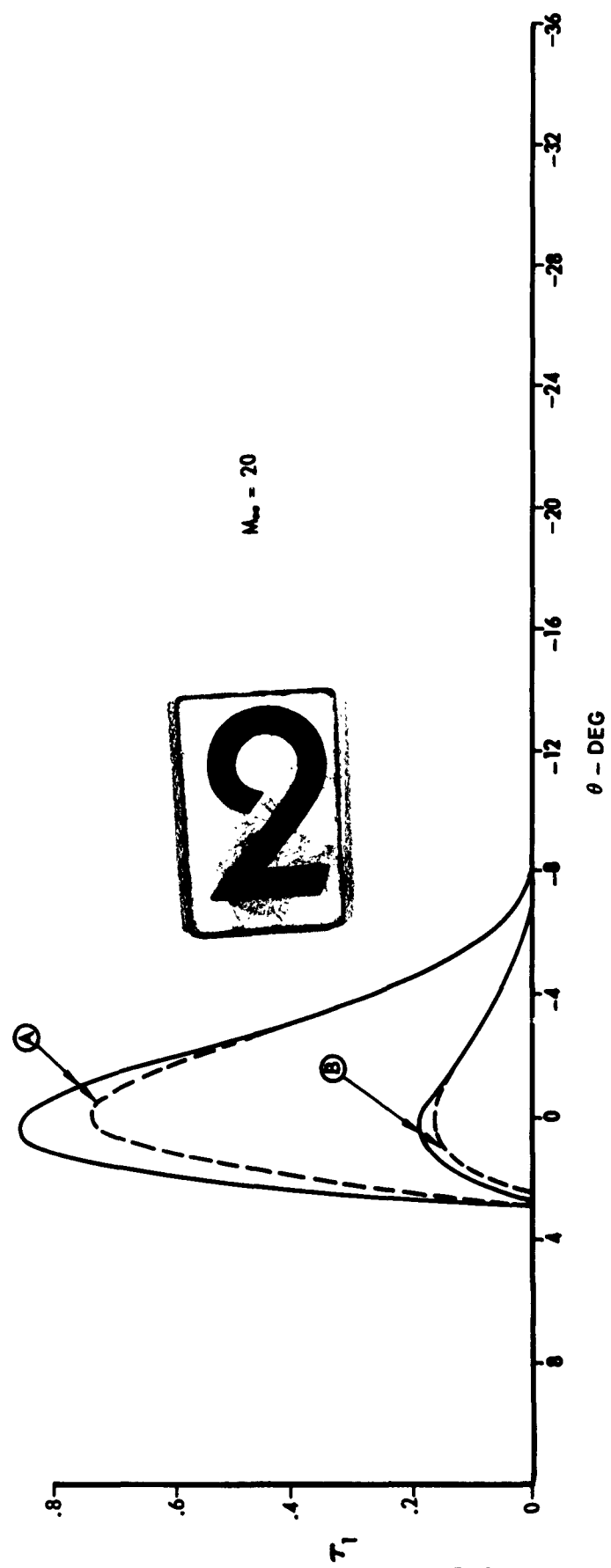
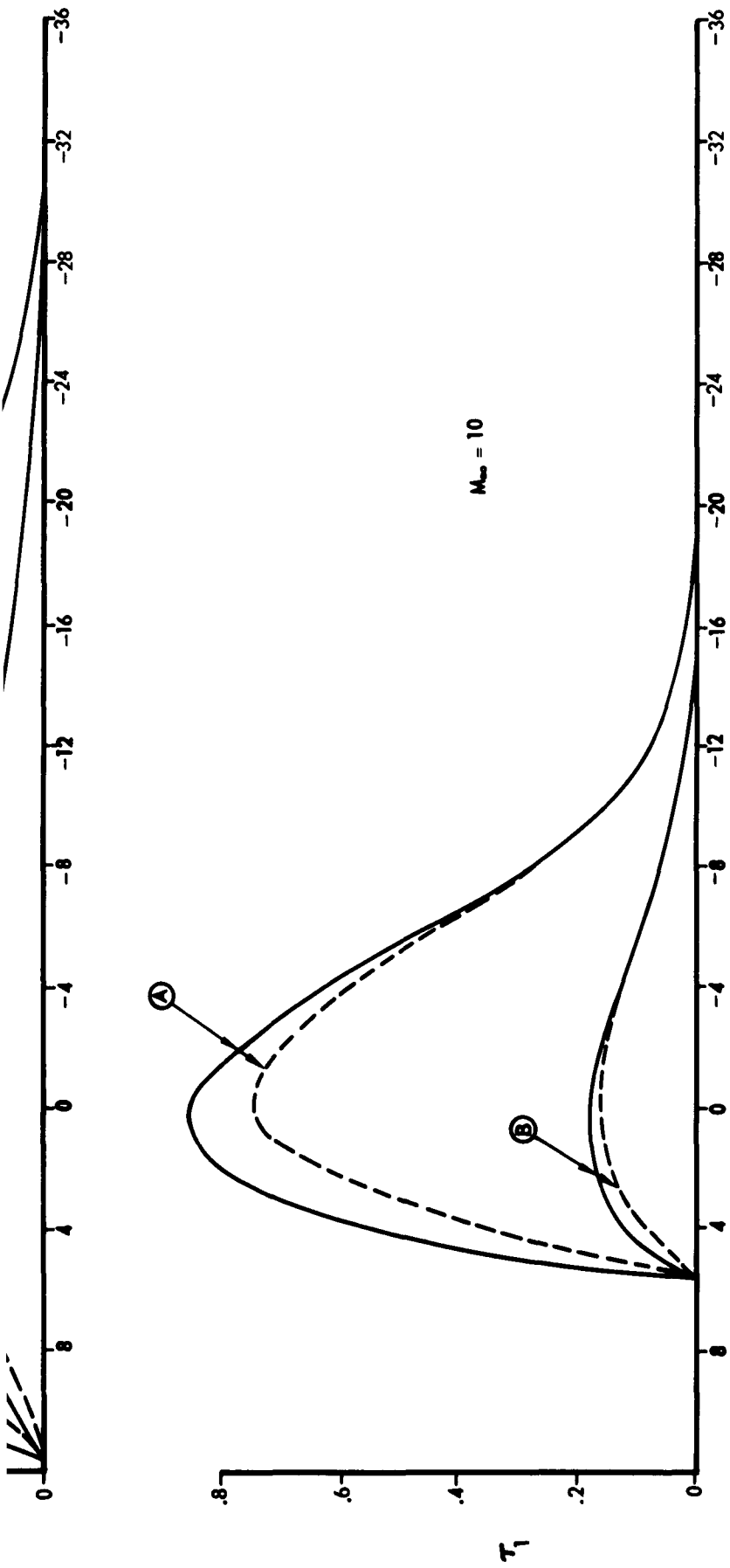


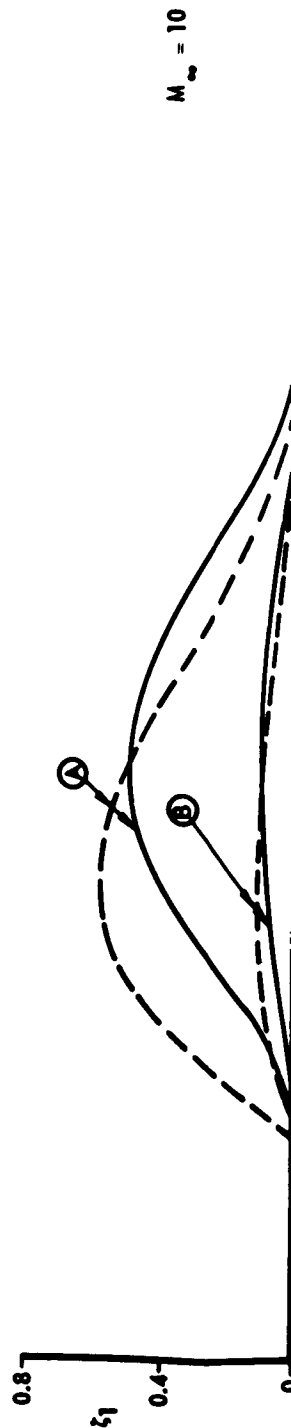
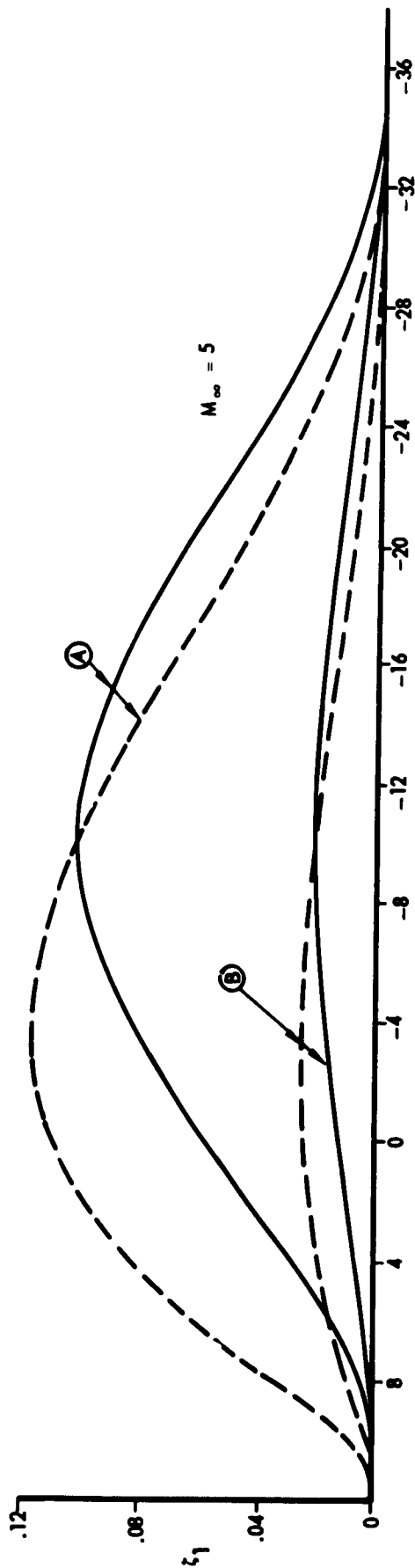
FIGURE 6 B

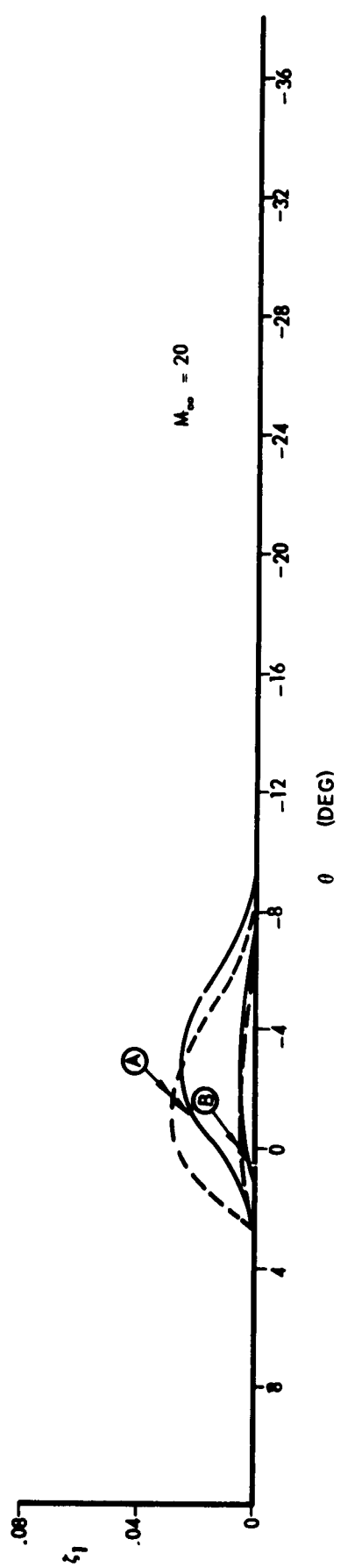
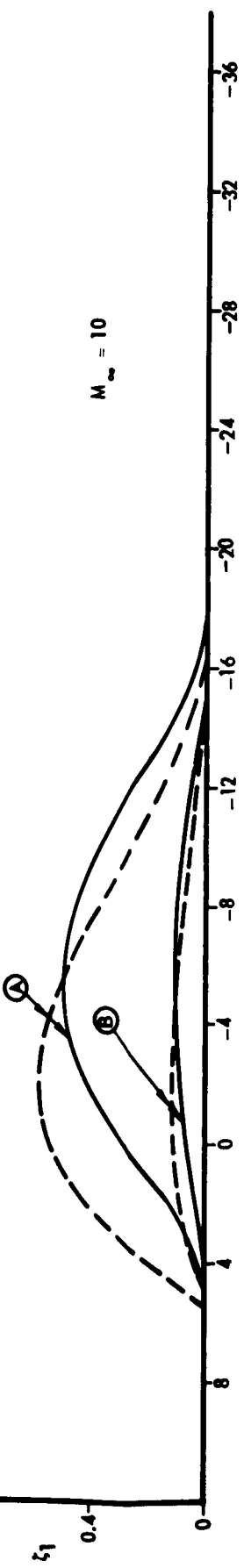
COMPARISON OF EXACT AND APPROXIMATE FIRST ORDER
SOLUTIONS WITHIN THE FROZEN FAN

FIGURE 6 C



ALL CURVES	$\omega = -1.5$	$A = 0$
	$K_M = 3.5$	$\tau_D = 17.1$
	EXACT	—
	APPROX	----
CURVES (A)	$\sigma_{\infty} = .667$	$\bar{\gamma}_{\infty} = 1.59$
	$K_P = 2.221 \times 10^7$	
CURVES (B)	$\sigma_{\infty} = .272$	$\bar{\gamma}_{\infty} = 1.49$
	$K_P = 2.221 \times 10^6$	





2

FIRST ORDER NONEQUILIBRIUM FIELD

$$\begin{aligned} \alpha_{\infty} &= .667 & \bar{\gamma}_{\infty} &= 1.59 & \tau_0 &= 17.1 \\ \omega &= -1.5 & A &= 0 & K_M &= 3.5 \\ M_{\infty} &= 1.0 & K_p &= 2.221 \times 10^7 & \Gamma' &= 0.142/\text{IN} \end{aligned}$$

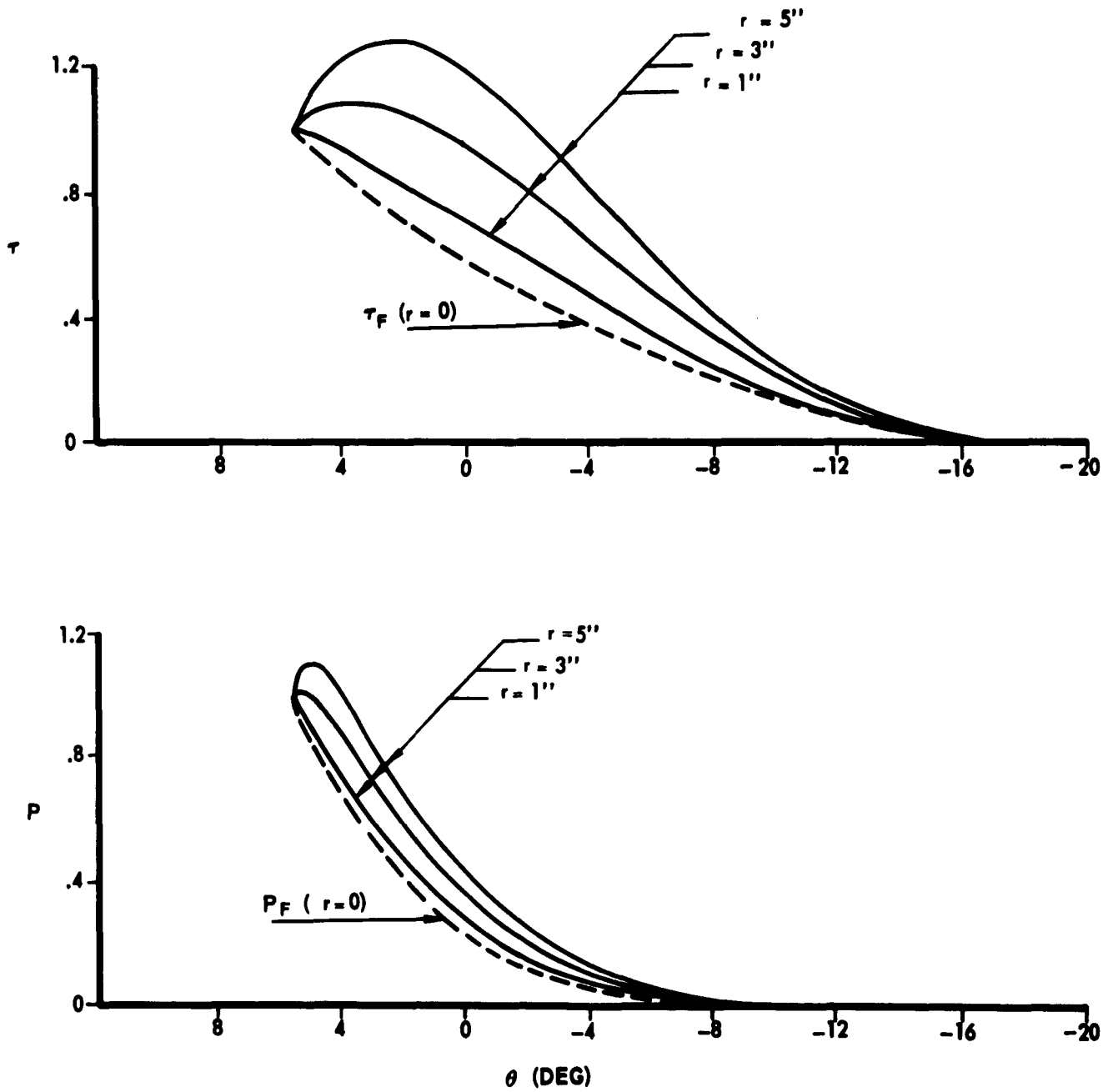


FIGURE 7A

FIRST ORDER NONEQUILIBRIUM FIELD

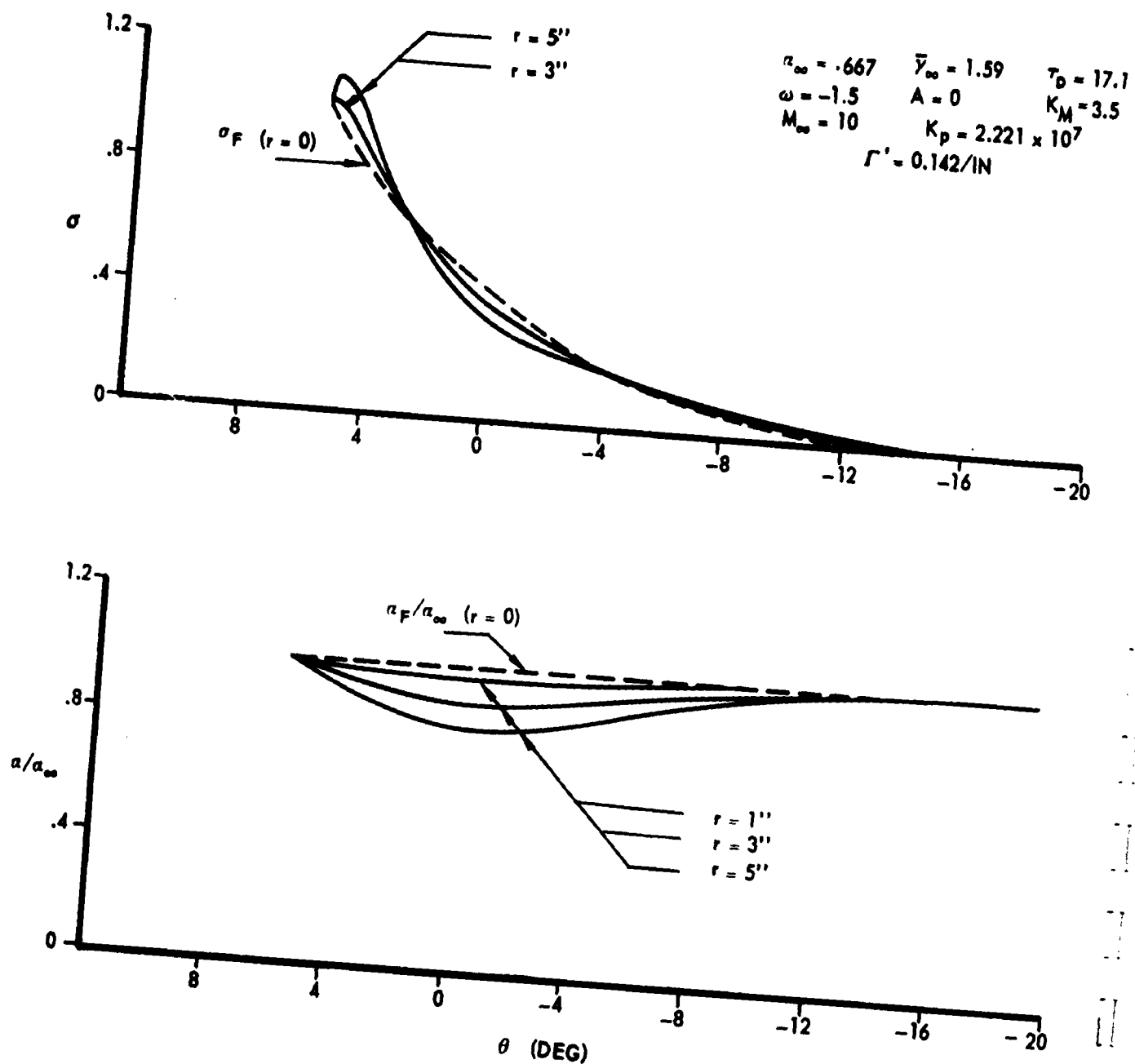


FIGURE 7B

FIRST ORDER NONEQUILIBRIUM FIELD POLAR REPRESENTATION

$$\begin{aligned} \alpha_{\infty} &= .667 & \bar{\gamma}_{\infty} &= 1.59 & \tau_D &= 17.1 \\ \omega &= -1.5 & A &= 0 & K_M &= 3.5 \\ M_{\infty} &= 10 & K_p &= 2.221 \times 10^7 \\ \Gamma' &= 0.142/\text{IN} \end{aligned}$$

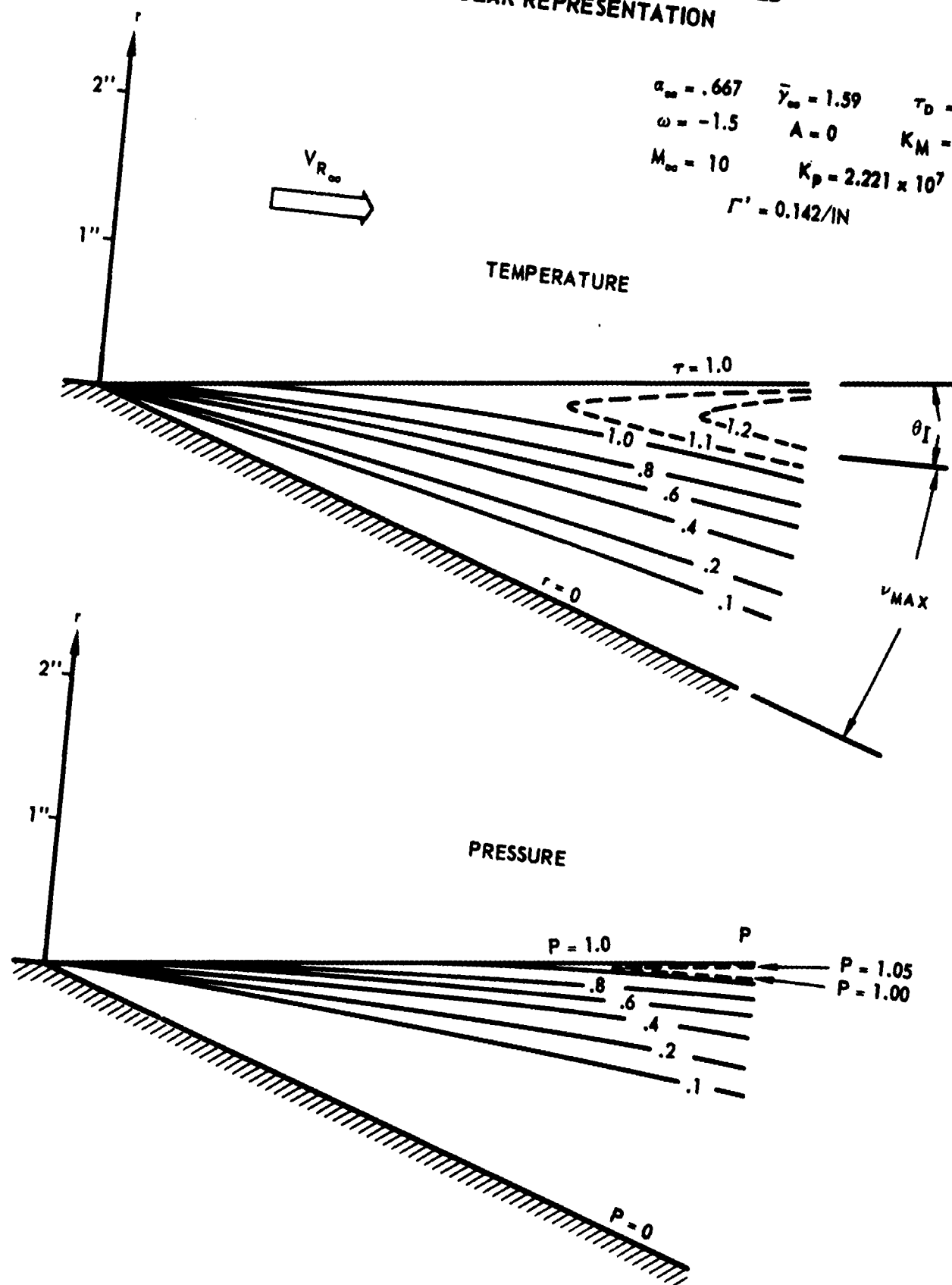


FIGURE 7C

FIRST ORDER NONEQUILIBRIUM FIELD POLAR REPRESENTATION

$$\begin{aligned} \alpha_{\infty} &= .667 & \bar{\gamma}_{\infty} &= 1.59 & K_M &= 3.5 \\ \omega &= -1.5 & A &= 0 & \tau_D &= 17.1 \\ M_{\infty} &= 1.0 & K_P &= 2.221 \times 10^7 \\ \Gamma' &= 0.142/\text{IN} \end{aligned}$$

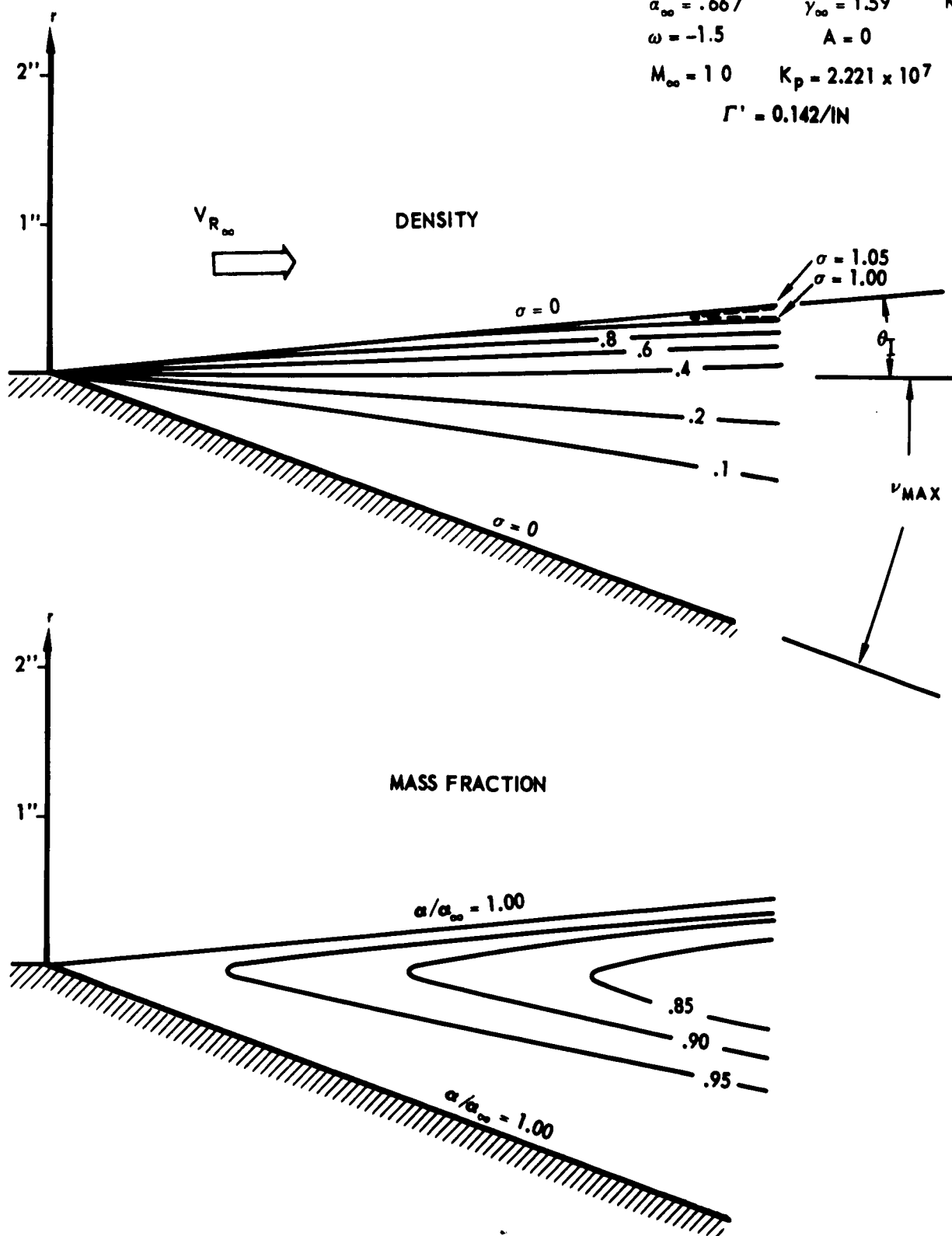


FIGURE 7D

APPENDIX A

ENTROPY AND FREE ENERGY OF A DISSOCIATED DIATOMIC GAS

The specific entropy of a thermally and calorically perfect gas species is

$$S_i = S_i^{(o)} + C_{P,i} \ln \frac{T}{T_o} - R_i \ln p_i, \quad (A-1)$$

where T_o is an arbitrary reference temperature, $S_i^{(o)}$ is the entropy at T_o and one atmosphere pressure, and p_i is the partial pressure in atmospheres. The corresponding specific entropy for a dissociated diatomic gas mixture is thus

$$S = \sum_i \alpha_i S_i = \frac{S_M^{(o)}}{R_M} + \frac{\alpha(S_A^{(o)} - S_M^{(o)})}{R_M} + \frac{\bar{C}_P}{R_M} \ln \frac{T}{T_o} - (1+\alpha) \ln p - \ln \left[\left(\frac{2\alpha}{1+\alpha} \right)^{2\alpha} \left(\frac{1-\alpha}{1+\alpha} \right)^{1-\alpha} \right] \quad (A-2)$$

where we have taken $T_o = T_{\infty}$ for the expansion problem. The free energy difference $g_A - g_M$ is obtained from Eqs. (2-8), (A-2) and the definition $g_i = h_i - T S_i$:

$$\frac{g_A - g_M}{R_M T} = \ln \left\{ p \left(\frac{\alpha^2}{1-\alpha^2} \right) e^{\frac{T_{\infty}}{T} (5-K_M)} \exp \left[(5-K_M) \left(\frac{S_A^{(o)}(273) - S_M^{(o)}(273)}{R_M} \right) \right] \right\}, \quad (A-3)$$

using $\frac{\bar{C}_P}{R_M} = K_M + (5-K_M)\alpha$ and $S_{A,M}^{(o)} = S_{A,M}^{(o)}(273) + C_{P,A,M} \ln \left(\frac{T_o}{273} \right)$.

Now for thermodynamic equilibrium, both the reaction rate function G in Eq. (2-13) and $g_A - g_M$ must vanish. Hence a comparison of Eqs. (2-13) and (A-3) at equilibrium shows that the constants A and B in Eq. (2-13) may, in fact, be identified with the vibrational specific heat parameter K_M and the standard component entropies as follows:

$$A = 5 - K_M \quad B = \frac{S_A^{(o)}(273) - S_M^{(o)}(273)}{R_M} - A \quad (A-4)$$

Therefore, with the aid of Eqs. (A-4) and (2-13), Eq. (A-3) may be re-written in terms of G :

$$\frac{q_A - q_M}{R_M T} = \ln \left[\frac{1 + P \frac{e^{T_D/T}}{(1-\alpha) e^{(T/273)^3}}}{G+1} \right] \quad (A-5)$$

APPENDIX B

EVALUATION OF FIRST-ORDER DISSOCIATION INTEGRAL

The dissociation integral [Eq. (3-35b)] may be rewritten in a more useful form by employing the trigonometric substitutions $\sec^2 \psi = 1 + \tan^2 \psi = d(\tan \psi)$. Then letting $N_D = 4 - 2\omega - 2A$, $\lambda_D = \tau_D \cos^2 \psi_\infty$ and $X = (\lambda_D)^{\frac{1}{2}} \tan \psi$, we obtain Eq. (3-35b) as follows:

$$I_D(N_D, \psi) = \frac{e^{-\lambda_D}}{(\lambda_D)^{\frac{1}{2}}} \int_{\sqrt{\lambda_D} \tan \psi_\infty}^{\sqrt{\lambda_D} \tan \psi} \left(1 + \frac{x^2}{\lambda_D}\right)^{\frac{N_D-2}{2}} e^{-x^2} dx \quad (B-1)$$

It is immediately seen that when $N_D = 2$, the integral (B-1) reduces to the error function; thus

$$I_D(2, \psi) = \frac{\sqrt{\pi}}{2\sqrt{\lambda_D}} e^{-\lambda_D} \left[\text{ERF}(\sqrt{\lambda_D} \tan \psi) - \text{ERF}(\sqrt{\lambda_D} \tan \psi_\infty) \right] \quad (B-2)$$

If N_D is a positive, even integer > 2 , Eq. (B-1) may also be expressed in closed form by taking advantage of Eq. (B-1) with $N_D = 2$ and the following derivatives thereof:

$$\begin{aligned} \frac{dI_D(2, \psi)}{dx} &= \Phi = \frac{\sqrt{\pi}}{2} \frac{e^{-\lambda_D}}{\sqrt{\lambda_D}} e^{-x^2} \\ \frac{d^2 I_D(2, \psi)}{dx^2} &= -2x\Phi \\ \frac{d^3 I_D(2, \psi)}{dx^3} &= (4x^2 - 2)\Phi \end{aligned} \quad (B-3)$$

$$\frac{d^M I_D(2, \psi)}{dx^M} = 2^{M-1} \left[(-x)^{M-1} - \frac{(M-1)(M-2)}{4} (-x)^{M-3} + \frac{(M-1)(M-2)(M-3)(M-4)}{32} (-x)^{M-5} - \dots \right] \Phi$$

Thus, for example, we have

$$I_D(4, \psi) = \frac{e^{-\lambda_D}}{\sqrt{\lambda_D}} \int_{\sqrt{\lambda_D} \tan \psi}^{\sqrt{\lambda_D} \tan \psi} e^{-x^2} dx + \frac{e^{-\lambda_D}}{2(\lambda_D)^{\frac{3}{2}}} \int_{\sqrt{\lambda_D} \tan \psi}^{\sqrt{\lambda_D} \tan \psi} \left(e^{-x^2} + \frac{e^{\lambda_D}}{2} \frac{d^3 I_{D,2}}{dx^3} \right) dx$$

(B-4)

$$= I_D(2, \psi) \left(\frac{2\lambda_D + 1}{2\lambda_D} \right) - \frac{e^{-\lambda_D}}{2(\lambda_D)^{\frac{3}{2}}} \left[x e^{-x^2} \right]_{\sqrt{\lambda_D} \tan \psi}^{\sqrt{\lambda_D} \tan \psi}$$

In this way, one may proceed to evaluate Eq. (B-1) for $N_D = 6, 8, \dots$, etc., using progressively higher derivatives from Eq. (B-3).

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