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ON THE DISTRIBUTION OF ENTROPY  
WITHIN THE  
STRUCTURE OF A NORMAL SHOCK WAVE  
  
by  
Morris Morduchow and Paul A. Libby

AUGUST 1962



POLYTECHNIC INSTITUTE OF BROOKLYN

DEPARTMENT  
of  
AEROSPACE ENGINEERING  
and  
APPLIED MECHANICS

Pibal Report No. 759

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SUMMARY

A unified mathematical account is given of the available knowledge, together with additional new results of the entropy distribution through a normal shock wave. The most notable feature of this distribution is the fact that as long as heat conductivity is present the entropy will first increase within the shock until it reaches a maximum value at a certain point inside of the shock, and then diminishes to its final value behind the shock. A physical discussion of the results is given in addition to a review of the phenomena not usually included in the analysis of shock wave structure but which enter when the strength of the shock wave is sufficiently great so that the chemical reactions take place.

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A systematic review of classical shock wave structure according to the Navier-Stokes equations is included here together with a discussion of the physical validity of these equations. The structure of, and the entropy distribution within weak shock waves in general, and shock waves of arbitrary strength with Prandtl numbers of 0,  $3/4$  and  $\infty$  are analyzed in detail, together with qualitative results for shock waves in general. The case of a shock wave in a fluid with heat conduction but without viscosity, affords an example of a system within which a discontinuous change of state to a lower entropy occurs.

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## LIST OF SYMBOLS

$a$	speed of sound, $a^2 = \gamma p / \rho = \gamma R T$
$c_p, c_v$	specific heats at constant volume and at constant pressure, respectively
$C_1, C_2, C_3$	constants [Eqs. (10), (11) and (16), respectively]
$D$	constant defined by Eq. (29); also, diffusion coefficient
$E$	internal energy
$h$	enthalpy
$k$	coefficient of heat conductivity
$Le$	Lewis-Semenov number
$L(u, T), M(u, T)$	functions in Eqs. (14) and (13), respectively
$m$	constant, defined by Eq. (6)
$M_1$	Mach number ( $= u_1 / a_1$ ) in front of shock wave (at $x = -\infty$ )
$N$	number of species
$p$	pressure
$Pr$	Prandtl number ( $= \mu c_p / k$ )
$q$	heat flux
$R$	gas constant ( $= c_p - c_v$ )
$R_0$	universal gas constant
$S$	entropy (per unit mass)
$t$	shock wave thickness
$T$	absolute temperature
$u$	velocity of flow
$V_i$	diffusive velocity of species $i$
$\dot{w}_i$	mass volumetric rate of production of species $i$

## LIST OF SYMBOLS (Contd)

$W_i$	molecular weight of species $i$
$x$	distance <sup>⊕</sup> along flow
$Y_i$	mass fraction of species $i$
$\bar{Y}_j$	element mass fraction of element $j$
$\beta$	$= u_1 (1 + \gamma M_1^2) / (2\gamma M_1^2)$
$\gamma$	ratio of specific heats ( $= c_p / c_v$ )
$\kappa$	bulk viscosity coefficient
$\lambda$	compression viscosity
$\mu$	coefficient of viscosity
$\mu_{ij}$	number of atoms of element $j$ per molecule of species $i$
$\bar{E}$	$= \rho_1 a_1 x / \mu_1$
$\bar{E}$	independent variable defined by Eq (64)
$\rho$	mass density
$\tau$	(shear) stress component

### Subscripts

$0$	value at $x = 0$ (for case of weak shock waves only)
$1$	value in front of the shock wave ( $x = -\infty$ )
$2$	value behind the shock wave ( $x = +\infty$ )
$c$	value at point of discontinuity (for case of $\mu = 0$ only)
$i$	related to species $i$
a prime (')	denotes derivative with respect to $x$
a bar (-)	denotes normalization with respect to values at $x = -\infty$ ; e.g., $\bar{u} \equiv u/u_1$ , $\bar{T} \equiv T/T_1$

## I - INTRODUCTION

For roughly the past twenty years the distribution of the entropy through a normal shock wave has been of interest to a variety of investigators. The most noteworthy aspect of the entropy distribution is that although the velocity, specific volume, temperature and pressure of a gas all vary monotonically across the shock structure, the entropy, instead of also varying (in particular, increasing) monotonically throughout the shock, increases only at first, passes through a maximum within the shock, and then actually diminishes to its final value behind the shock. This phenomenon has proved of such interest that a perusal of the literature indicates that this fact appears to have been discovered independently at least four different times in the period from 1944 to 1961. In view of this situation and in view of the intrinsic interest in the entropy distribution, the purpose of this paper is to present a systematic investigation of the distribution of the entropy throughout the structure of a normal shock wave, including essentially all knowledge of this distribution that has been heretofore obtained, in addition to new results obtained here by the present authors. To make this account as self-contained as possible, a unified mathematical presentation is first given of shock wave structure, including the various known exact closed-form solutions for various special cases, namely extremely weak shocks in general and shock waves of arbitrary strength with Prandtl numbers of 0,  $3/4$ , and  $\infty$ . Because of the important role played by the heat conductivity in the entropy distribution, the case of zero Prandtl number is discussed here in somewhat greater detail than ordinarily found in the

literature. The entire analysis in this paper is based on the Navier-Stokes equations of flow; accordingly, a review is given here of the physical validity of these equations for the shock-structure problem. Finally, additional physical effects such as dissociation and ionization, which arise in strong shock waves, are briefly discussed.

Historically, it may be noted that Rayleigh<sup>1,2</sup> in 1910 obtained exact solutions for the shock structure for the special cases of a gas without heat conductivity, but with viscosity, and of a gas without viscosity, but with heat conductivity. At about the same time, Taylor<sup>3,4</sup> obtained a solution for the structure of weak shock waves, including both viscosity and heat conduction. In 1922, Becker<sup>5</sup> solved the shock-structure problem for a Prandtl number of  $3/4$ ; this is still the only case for which a simple, closed-form exact solution for a shock wave of arbitrary strength, including both viscosity and heat conduction, exists. This case has also been considered by Roy<sup>6,7</sup>, Thomas<sup>8</sup>, Morduchow and Libby<sup>9</sup>, and Puckett and Stewart<sup>10</sup>. Roy<sup>6</sup> and Thomas considered the case of viscosity coefficient  $\mu$  proportional to the square root of the absolute temperature  $T$ , while Morduchow and Libby considered the more general case of  $\mu \sim T^n$  ( $n \geq 0$ ). References 8 and 9, in particular, showed the important influence of variable viscosity and heat conductivity in thickening the shock wave. A mathematical analysis of shock-wave structure under more general conditions (e. g., general Prandtl number) was subsequently made by von Mises (reference 11) and, independently, by Gilbarg<sup>12</sup>.

Concerning the entropy distribution within the shock-wave

structure, it appears that it was first found in 1944 by Roy<sup>6</sup>, considering the case of a Prandtl number of  $3/4$ , that the entropy will not increase monotonically across a shock, but will pass through a maximum at a certain point within the shock wave. Morduchow and Libby<sup>9</sup> subsequently also discovered (independently of reference 6) the non-monotonic behavior of the entropy for this case, and showed specific curves for the entropy distribution. Zeldovich (quoted in reference 13) in 1946 found a similar behavior of the entropy for a sufficiently weak shock wave in a gas with thermal conductivity but without viscosity, and Landau and Lifshitz (quoted in reference 13; see also reference 14) in 1954 noticed a similar behavior for extremely weak shock waves in general.

The quite recent interest in the entropy distribution through a shock is evidenced in papers by Roy<sup>7</sup>, Ackeret<sup>15</sup>, Golitsyn and Staniukovich<sup>13</sup>, and Serrin and Whang<sup>16</sup>. Serrin and Whang (who appear to have been unaware of any previous findings on the entropy) prove that the entropy will vary non-monotonically across a shock wave under quite general conditions. It will be seen here that the most important condition is that the gas have a positive thermal conductivity coefficient.

The analysis pertains explicitly to normal shock waves. However, it is noted that by adding a constant velocity normal to the x axis, i. e., a  $v$  velocity such that  $v = \text{constant}$ , the structure of plane oblique shock waves is implicitly being considered.

The authors hereby express their thanks to Mr. Herbert Fox for his aid in the calculations and to Professor M. H. Bloom for his useful discussions.

## II - BASIC EQUATIONS OF FLOW

The classical equations of continuity, momentum and energy for the one-dimensional steady flow of a compressible, viscous, heat-

conducting fluid (references 2 and 17) are respectively:

$$(\rho u)' = 0 \quad (1)$$

$$\rho u u' + p' - (4/3)(\mu u')' = 0 \quad (2)$$

$$\rho u E' + p u' - (4/3)\mu u'^2 - (k T')' = 0 \quad (3)$$

It will be assumed throughout the analysis that the fluid is homogeneous, and a perfect gas, i. e., that it obeys the ideal gas law and has constant specific heats. Later in connection with the analysis of strong shock waves a more accurate way of describing equations will be presented; several of these assumptions will be removed. Thus, here the internal energy  $E$  is assumed to be given by

$$E = c_v T \quad (4)$$

while the equation of state is assumed as

$$p = \rho R T \quad (5)$$

From Eq. (1) it follows that

$$\rho u = m \quad (6)$$

where  $m$  is a constant. Eq. (6) shows that the specific volume  $v (=1/\rho)$  will vary exactly like the flow velocity  $u$ , since  $v = (1/m)u$ . The entropy  $S$  per unit mass, omitting an additive constant, may be written as

$$S = c_v \log T - R \log \rho \quad (7)$$

In view of Eq. (6), S can also be expressed here as

$$S = c_v \log T + R \log u \quad (8)$$

From Eq. (8), in conjunction with Eqs. (4) - (6), it follows readily that  $\rho u T S' = \rho u E' + p u'$ . Hence the energy equation (3) can also be written in the form

$$\rho u T S' = (kT')' + (4/3)\mu u'^2 \quad (9)$$

Using (6), Eq. (2) can be integrated once to yield:

$$p + \mu u - (4/3)\mu u' = C_1 \quad (10)$$

where  $C_1$  is a constant. Substituting for p according to Eq. (10) into Eq. (3), it is found that the latter can be integrated once to yield:

$$mE + C_1 u - (m/2)u^2 - kT' = C_2 \quad (11)$$

where  $C_2$  is a constant. Since

$$p = mRT/u \quad (12)$$

Eqs. (10) and (11) can be written in the form

$$\mu u' = M(u, T) \quad (13)$$

$$kT' = L(u, T) \quad (14)$$

where M and L are given functions of u and T, and do not contain  $\mu$  or k. First order equations of the form (13) and (14) which determine directly T vs. u, have been used to analyze qualitatively the nature of

the general shock wave solutions (references 11 and 12).

As an alternative to Eqs. (13) and (14) another useful equation can be obtained by writing  $T = (pu)/(mR)$  and using the expression for  $p$  in terms of  $u$  and  $u'$  according to Eq. (10). Substituting then for  $T$  into Eq. (11), the following differential equation for the velocity  $u$  vs.  $x$  is obtained

$$u' \left[ u \left( \frac{4\mu}{3(\gamma-1)} + \frac{2k}{R} \right) - \frac{C_1 k}{Rm} \right] - \frac{4k}{3Rm} \left[ u(\mu u')' + \frac{4}{3} \mu u'^2 \right] = C_2 - \frac{\gamma}{\gamma-1} C_1 u + \frac{m(\gamma+1)}{2(\gamma-1)} u^2 \quad (15)$$

Here the gas relations  $R = c_p - c_v$  and  $\gamma = c_p/c_v$  have been used.

Finally, another fruitful equation can be obtained by noting that according to Eq. (12)  $p' = (mRT'/u) - (pu'/u)$ , substituting for  $p'$  into Eq. (2) and solving for  $pu'$ . Then putting this expression for  $pu'$  into Eq. (3), an equation is obtained which can be integrated once (cf. reference 9) to yield

$$(u^2/2) + c_p T - [k/mc_p] \left[ (4/3) Pr uu' + c_p T' \right] = C_3 \quad (16)$$

where  $C_3$  is a constant and  $Pr$  is the Prandtl number defined by

$$Pr = \mu c_p / k \quad (17)$$

Eqs. (3), (9), and (16) constitute three alternative forms of the energy equations. Eqs. (3) and (9) show the role of heat conductivity and viscous

dissipation in the determination of an energy balance. The importance of Eq. (16) is due to the appearance there of the "total" (or "stagnation") enthalpy  $[(u^2/2) + c_p T]$ .

All of the preceding equations are valid for arbitrary and variable viscosity and heat conductivity coefficients  $\mu$  and  $k$ .

### III - SHOCK-WAVE STRUCTURE

A unified mathematical account of the solutions for shock-wave structure, based on the set of equations in II, will be given here.

#### Discontinuous Shock Wave: $\mu = 0, k = 0$

If viscosity and heat conduction are neglected, i. e.,  $\mu = 0$  and  $k = 0$ , then Eqs. (6), (10), (16) and (5) become the following algebraic equations:

$$\begin{aligned}\rho u &= m \\ p + \rho u^2 &= C_1 \\ (u^2/2) + c_p T &= C_3 \\ p &= \rho RT\end{aligned}\tag{18}$$

These equations indicate a solution of the form  $p = \text{const.}$ ,  $\rho = \text{const.}$ ,  $T = \text{const.}$ ,  $u = \text{const.}$  However, if one solves for these quantities in terms of the constants  $m$ ,  $C_1$  and  $C_3$ , it is found that two possible sets of values for these quantities exist. The physical interpretation is that at some (here, arbitrary) point  $x = \xi$  there can be a discontinuity surface across which each quantity jumps from one constant value to the other

constant value. This discontinuity is a "normal shock wave," and the solution of Eqs. (18) may be considered to be

$$\begin{aligned} u = u_1, \rho = \rho_1, p = p_1, T = T_1 \quad (x < \xi) \\ u = u_2, \rho = \rho_2, p = p_2, T = T_2 \quad (x > \xi) \end{aligned} \quad (19)$$

where  $u_1, u_2, \rho_1, \rho_2$ , etc. are constants (Fig. 1). The "strength" of the shock wave is measured by the magnitude of the jump, such as  $p_2/p_1$ . The relationship between conditions ("1") ahead of the shock and conditions ("2") behind it can be found by noting that Eqs. (18) represent conservation conditions across the shock, namely, conservation of flux of mass, momentum, and energy, respectively, and hence

$$\begin{aligned} \rho_1 u_1 &= \rho_2 u_2 \\ p_1 + \rho_1 u_1^2 &= p_2 + \rho_2 u_2^2 \\ (u_1^2/2) + c_p T_1 &= (u_2^2/2) + c_p T_2 \end{aligned} \quad (20)$$

Eqs. (20), in conjunction with the gas law, can be used to solve for the ratios  $u_2/u_1, \rho_2/\rho_1$ , etc. in terms of a single parameter denoting the shock strength. One convenient parameter is the Mach number  $M_1 \equiv u_1/a_1$  in front of the shock. The solution of Eqs. (20) (other than the "trivial" solution  $u_2/u_1 = 1, \rho_2/\rho_1 = 1$ , etc.) in terms of  $M_1$  (e. g., reference 14) is

$$\begin{aligned} \rho_2/\rho_1 = u_2/u_1 &= [(\gamma - 1)M_1^2 + 2]/[(\gamma + 1)M_1^2] \\ p_2/p_1 &= [2\gamma M_1^2/(\gamma + 1)] - [(\gamma - 1)/(\gamma + 1)] \\ T_2/T_1 &= [2\gamma M_1^2 - (\gamma - 1)][(\gamma - 1)M_1^2 + 2]/[(\gamma + 1)^2 M_1^2] \end{aligned} \quad (21)$$

Eqs. (21) constitute one form of the well-known "Rankine-Hugoniot relations" between quantities in front of, and behind, a normal shock wave.

If  $M_1 > 1$ , it is found from Eqs. (21) that  $p_2/p_1$ ,  $\rho_2/\rho_1$ ,  $T_2/T_1 > 1$ , while  $u_2/u_1 < 1$ ; i. e., there arises a compression wave. If  $M_1 < 1$ , the inequalities are reversed (rarefaction wave). As far as Eqs. (20) or (21) are concerned, both compression and rarefaction waves would appear equally possible. The entropy  $S$ , however, also jumps across the shock and it is found (e. g., reference 14) that  $S_2 > S_1$  for compression waves, but  $S_2 < S_1$  for rarefaction waves. Consequently, the second law of thermodynamics requiring  $S_2 > S_1$ , may be invoked here to show that only compression waves may exist physically, and that a normal shock can therefore occur only when the flow is supersonic ( $M_1 > 1$ ). The use of the second law of thermodynamics here is in contrast with the results when viscosity and heat conductivity are taken into account. In that case, as will be subsequently seen, a shock-structure solution is mathematically possible only for  $M_1 > 1$ , and thus the second law becomes automatically satisfied.

#### Solutions with Viscosity and Heat Conduction in General. Boundary Conditions.

When  $\mu = k = 0$ , it has been seen that the shock "structure" consists merely of a discontinuity surface of zero thickness. In the presence of viscosity and heat conduction, however, the structure may now be expected to consist of a continuous transition from state 1 to state 2, with most of the change occurring in a small, but non-zero width about  $x = \xi$ . In particular, referring to Fig. 1, it may be expected

that now the actual distribution of the velocity (say) versus the distance  $x$  should be a continuous curve which is asymptotic to the straight line  $u = u_1$  as  $x \rightarrow -\infty$  (corresponding to state 1) and asymptotic to the straight line  $u = u_2$  as  $x \rightarrow +\infty$  (corresponding to state 2). Consequently, the appropriate boundary conditions to be imposed in solving the differential equations for the shock structure are that the flows be uniform at  $x = \pm\infty$ , i. e., the  $x$ -derivative of each of the flow variables must approach zero as  $x \rightarrow \pm\infty$ . Moreover, the Rankine-Hugoniot relations will hold between the states at  $x = \pm\infty$ . These relations are independent of the viscosity and heat conductivity coefficients.<sup>2</sup> Mises and (independently) Gilbarg<sup>11, 12</sup> have shown mathematically that there exists one and only one solution, namely the shock-structure solution, of the differential equations in II satisfying these uniform conditions at  $x = \pm\infty$ , for real gases in general, with positive viscosity and heat conductivity coefficients.<sup>3</sup> Also, Gilbarg<sup>12</sup> has shown mathematically that as  $\mu$  and  $k$  both independently approach zero for a real fluid, the shock layer approaches the discontinuous type of solution (Fig. 1) for  $\mu = 0$ ,  $k = 0$ . Although the equations for the general case must be solved numerically or approximately, a number of

<sup>2</sup>The validity of these latter two statements can also be seen mathematically by evaluating  $m$ ,  $C_1$  and  $C_3$  in Eqs. (6), (10) and (16) from conditions at  $x = -\infty$ , where  $u = u_1$ ,  $p = p_1$ , etc., and  $u' = p' = T' = 0$ . Then, to find  $u_2$ ,  $\rho_2$ ,  $p_2$  and  $T_2$  at  $x = +\infty$ , one must again put  $u' = p' = T' = 0$  in these equations. This leads to Eqs. (20). Physically, it should be noted that at points where the flow tends to be uniform, the viscosity and heat-conduction terms tend to vanish.

<sup>3</sup>The analysis is based on equations of the type (13) and (14) whence  $dT/du = (u/k)L(u, T)/M(u, T)$ . This equation determines solutions for  $T$  vs.  $u$ , i. e., in the  $(u, T)$  plane. The points 1 and 2, corresponding to  $x = \pm\infty$ , and satisfying the Rankine-Hugoniot relations, are the singular points of this differential equation, i. e., the points in the  $(u, T)$  plane where both  $L(u, T) = 0$  and  $M(u, T) = 0$ . The shock-structure solution is the unique solution joining these two points in the  $(u, T)$  plane.

instructive exact solutions have been obtained for certain special cases, and these will now be given.<sup>4</sup>

Prandtl Number of 3/4

If Pr has a constant value of 3/4, then Eq. (16) becomes a first-order linear differential equation in the stagnation enthalpy  $[(u^2/2) + c_p T]$ . The solution of this equation for uniform conditions at  $x = +\infty$  (cf. reference 9) is

$$(u^2/2) + c_p T = C_4 \quad (22)$$

where  $C_4$  is a constant. Thus, the stagnation enthalpy, which must in all cases [see Eqs. (20)] remain the same behind the shock ( $x = +\infty$ ) as in front of the shock ( $x = -\infty$ ), will in this case, and only in this case, also remain constant throughout the shock structure. Substituting into Eq. (10) for  $p$  in terms of  $u$  according to Eqs. (12) and (22), and solving for  $\mu u'$ , one finds  $\mu u' = F(u)/u$ , where  $F(u)$  is a quadratic in  $u$ . Since  $u' = 0$  at  $u = u_1$  and at  $u = u_2$ , it follows that  $F(u) \sim (u - u_1)(u - u_2)$ . Thus, it is found that

$$u \frac{du}{dx} = \frac{3(\gamma+1)}{8\gamma} m \frac{(u-u_1)(u-u_2)}{u} \quad (23)$$

<sup>4</sup>It may be remarked here that if the conditions of uniformity at  $x = -\infty$  or  $x = +\infty$  are relaxed, then there exist mathematically a considerable variety of flows, none of which, however, can extend over the full domain  $-\infty \leq x \leq \infty$  (cf. especially references 9 and 18). The present authors showed the existence of these solutions in reference 9 but did not discuss their physical significance. Dr. Antonio Ferri in a private communication pointed out that the solutions correspond to a source or sink of energy at a finite  $x$ . This suggests that experiments exhibiting this behavior could be performed, for example, by inserting a heated grid normal to a rarefied gas flow. The grid must not restrict excessively the gas flow so as to invalidate one-dimensionality but must provide for the addition of energy to the gas by upstream conduction.

Eq. (23) holds for variable, as well as constant,  $\mu$ . By differentiating (implicitly) the right side of Eq. (23) with respect to  $x$ , and noting that  $d/dx = (d/du) \cdot u'$ , it is readily found that

$$(\mu u')'_{u = \sqrt{u_1 u_2}} = 0 \quad (24)$$

In the solutions to be obtained for  $Pr=3/4$ , the origin for  $x$  will be chosen at the point of inflection of the velocity-distance curve. For constant  $\mu$ , this means that  $u = \sqrt{u_1 u_2}$  at  $x=0$ . For constant  $\mu$ , the solution of Eq. (23) is then

$$x = \frac{8\gamma}{3(\gamma+1)} \frac{\mu}{m} \left[ \left( \frac{u_1}{u_1 - u_2} \right) \log \left( \frac{u_1 - u}{u_1 - \sqrt{u_1 u_2}} \right) - \left( \frac{u_2}{u_1 - u_2} \right) \log \left( \frac{u - u_2}{\sqrt{u_1 u_2} - u_2} \right) \right] \quad (25)$$

For  $\mu$  varying in a prescribed fashion (e. g., with temperature  $T$ , and hence with  $u$ ), Eq. (23) can be solved by numerical integration.

From Eq. (23) it follows that a continuous solution for  $u(x)$  satisfying the conditions  $u = u_1$  at  $x = -\infty$  and  $u = u_2$  at  $x = +\infty$  is possible only if the flow is supersonic in the region ("1") ahead of the shock. One way of seeing this is to note that if  $u$  were to vary continuously from a value  $u_1$  to a higher value  $u_2$ , there must be some region where it is increasing while taking on some values between  $u_1$  and  $u_2$ . However, this is impossible, since  $(u-u_1)(u-u_2) < 0$  whenever  $u$  is between  $u_1$  and  $u_2$ , and hence according to Eq. (23)  $u' < 0$  whenever  $u$  is between  $u_1$  and  $u_2$ . Consequently,  $u_2$  must be less than  $u_1$ , and this, according to the Rankine-Hugonot relations (21), implies  $M_1 > 1$  (cf. also reference 9). Thus, a continuous shock-structure solution is mathematically possible

only for a supersonic flow in front of the shock. This conclusion, which has been established here for a Prandtl number of  $3/4$ , has been shown mathematically to hold for all positive Prandtl numbers (reference 11).

Typical curves showing the distribution of velocity  $u/u_1$  (or specific volume) and of temperature  $T/T_1$  are shown in Fig. 2.

General Prandtl Number.  $Pr = \infty$ .

From Fig. 2 it is seen that although the entire transition from state 1 to state 2 occurs over an infinite domain  $-\infty \leq x \leq \infty$ , by far the largest portion of this transition occurs over a relatively small distance, called the shock-wave thickness<sup>5</sup>, around the "center" ( $x=0$ ) of the shock. Also, the velocity, temperature, pressure and density all vary monotonically throughout the shock, the velocity decreasing and the others increasing. These results are typical of the shock-structure solutions in general, e. g. . for general Prandtl number.<sup>6</sup> For weak shock waves, for example, it will be seen below that the form of the shock-structure solution remains the same for all  $Pr$ , the latter, for a given  $u$ , affecting only the thickness of the shock wave. Mises<sup>11</sup> and Gilbarg<sup>12</sup> have shown that for the shock-structure solution in general,  $M(u, T) < 0$  and  $L(u, T) > 0$  throughout the shock. Hence, from Eqs. (13) and (14) it follows that  $u$  will in general decrease, and  $T$  will in general increase monotonically across the shock. From Eq. (6) it then follows that  $\rho$  will

<sup>5</sup> Various specific definitions (cf. references 4, 9, 19-21) of this thickness  $t$  have been proposed and used. The most common is  $t = (u_1 - u_2) / |du/dx|_{\max}$

<sup>6</sup> The only exception is the case of  $u=0$ ,  $k \neq 0$  ( $Pr=0$ ) for a shock wave whose strength exceeds a certain amount. This case will be discussed subsequently.

increase monotonically, and hence, according to Eq. (5), the pressure will also increase monotonically across the shock. Thus (except for  $Pr=0$ ) the solution for  $Pr=3/4$  may be regarded as the prototype of the general shock solutions.<sup>7</sup> In fact, for Prandtl numbers above  $3/4$ , the shock-wave structure changes relatively little. This can be seen explicitly by obtaining the shock-structure solution for the extreme case of a viscous fluid without heat conduction, i. e.,  $k=0$ ,  $\mu \neq 0$ ,  $Pr=\infty$ .

First, it should be noted that since  $u' = u'' = 0$  where  $u = u_1$  and  $u = u_2$ , the right side of Eq. (15) can be written as

$$C_2 - \frac{\gamma}{\gamma-1} C_1 u + \frac{m(\gamma+1)}{2(\gamma-1)} u^2 = \frac{m(\gamma+1)}{2(\gamma-1)} (u-u_1)(u-u_2) \quad (26)$$

Consequently for  $k=0$  Eq. (15) reduces to

$$\mu \frac{du}{dx} = \frac{3(\gamma+1)}{8} m \frac{(u-u_1)(u-u_2)}{u} \quad (27)$$

Eq. (27) is the same as the corresponding equation [Eq. (23)] for  $Pr=3/4$ , except that the right side of (27) no longer contains a factor of  $\gamma$  in the denominator. This implies that if  $u = F(x)$  is the solution for the velocity vs.  $x$  for  $Pr=3/4$ , then the solution now for the velocity is  $u = F(\gamma x)$ . Thus, as  $Pr$  varies from  $3/4$  to  $\infty$ , the shock-wave thickness is diminished by a factor of  $1/\gamma$ . Shapiro and Kline<sup>22</sup> have investigated approximately the effect of Prandtl number, in general, on the thickness

<sup>7</sup> It may be remarked that for air over a wide range of temperatures up to  $8000^\circ\text{K}$ ,  $Pr$  is close to  $3/4$ , namely,  $Pr \approx 0.72$ .

of shock waves and have found that as the Prandtl number increases the thickness decreases, this effect being greatest at low Prandtl numbers.

#### Weak Shock Waves.

A weak shock wave means here one in which  $(u_1 - u_2)$  is sufficiently small so that only the lowest necessary powers (namely, second) in  $(u_1 - u_2)$  need be retained in solving the equations. Thus, the solution obtained here will be valid for Mach numbers  $M_1$  only slightly greater than one. This solution is the only one among the known exact<sup>8</sup> closed-form solutions in which the Prandtl number is arbitrary. Moreover, as will be indicated more fully in the next section, there appears little doubt about its actual physical validity.

To the degree of approximation for the weak shock waves, the variation of  $\mu$  and  $k$  (e. g. with  $T$ ) may be neglected. Since  $u$  varies between  $u_1$  and  $u_2$ , it is seen from Eq. (26) that the right side of Eq. (15) will be of order  $(u_1 - u_2)^2$ . Hence, in Eq. (15)  $u'$  will be of order  $(u_1 - u_2)^2$ . Therefore, the  $u'^2$  term may be neglected. Moreover,  $u'' = (du'/du)u'$ ,  $\therefore u''$  is of order  $u'^2/(u_1 - u_2)$  or of order  $(u_1 - u_2)^3$  and hence the  $u''$  term may also be neglected in Eq. (15). Finally, to second powers in  $(u_1 - u_2)$ ,  $u$  may be replaced by  $u_1$  in the first factor of  $u'$  in Eq. (15). Thus, Eq. (15) reduces to the form

$$u' = (1/D)(u - u_1)(u - u_2) \quad (28)$$

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<sup>8</sup>Of course, strictly speaking, the solution to be given here for weak shocks is not "exact," except for  $(u_1 - u_2) = 0$ . However, for  $(u_1 - u_2)$  sufficiently small it will be arbitrarily close to the exact solution.

where  $D$  is a positive constant, namely<sup>9</sup>

$$D = \frac{2(\gamma-1)}{\rho_1(\gamma+1)} \left[ \frac{4u}{3(\gamma-1)} + \frac{k}{R} \left(1 - \frac{1}{\gamma}\right) \right] \quad (29)$$

From Eq. (28) it follows that  $u'' = 0$  where  $u = (u_1 + u_2)/2$ . Choosing the origin for  $x$  where  $u'' = 0$ , the solution of Eq. (28) can be written as

$$u - u_0 = \left( \frac{u_2 - u_1}{2} \right) \tanh \left[ \left( \frac{u_1 - u_2}{2D} \right) x \right] \quad (30)$$

where  $u_0 \equiv (u)_{x=0} = (u_1 + u_2)/2$ . The temperature, pressure, and density behave quite similarly to the velocity, since by Taylor's series the temperature (for example) will be  $T - T_0 = K(u - u_0) + \dots$ , where  $K = (dT/du)_0$ , and  $K \neq 0$ .<sup>10</sup> Thus, to the degree of approximation here,  $T$  varies linearly with  $u$ . Substituting for  $(u - u_0)$  and evaluating  $T_0$  and  $T_1$  so that  $T = T_1$  at  $x = -\infty$  and  $T = T_2$  at  $x = +\infty$ , one finds

$$T - \frac{T_1 + T_2}{2} = \left( \frac{T_2 - T_1}{2} \right) \tanh \left[ \left( \frac{u_1 - u_2}{2D} \right) x \right] \quad (31)$$

with exactly similar results for the density and the pressure. For weak shock waves it is seen that the form of the shock structure remains the same for all  $u$  and  $k$ . The latter affect only the constant  $D$  and hence,

<sup>9</sup>In evaluating  $D$ , it has been noted, first, that  $C_p = p_1 + m u_1^2$  [cf. Eq. (10) or (18)]. Moreover, since  $\gamma p_1 / \rho_1 = a_1^2$ , and  $M_1$  must be close to 1 here, the quantity  $p_1 / (\rho_1 u_1^2) = 1 / (\gamma M_1^2)$  may be replaced in  $D$  by  $1/\gamma$ .

<sup>10</sup>For the entropy, however,  $s' = (ds/du)_0 = 0$  (cf. Section IV below).

only the thickness  $t$  (see footnote 5) which for the weak shock waves will be

$$t = 4D/(u_1 - u_2) \quad (32)$$

Eqs. (32) and (29) show that an increase in  $\mu$  or  $k$  (or both) will increase the shock thickness. Eq. (32) shows that for weak shock waves the thickness decreases rapidly as the shock strength increases.

#### Physical Validity of the Shock-Structure Solutions

According to the shock-structure solutions obtained here, the shock-wave thickness, except for very weak shock strengths, will be on the order of the mean free path of the gas molecules upstream of the wave. This can be seen from the fact that the natural unit  $\delta$  (say) for  $x$  here [cf. e.g., Eq. (25)] is  $\delta = \mu_1 / (\rho_1 u_1) = (\mu_1 / \rho_1 a_1) / M_1$ , with  $M_1 > 1$ . For a standard aeronautical atmosphere<sup>11</sup> at one atmosphere pressure,  $\delta = (1.69 \times 10^{-6} / M_1)$  inches. This distance is of the order of magnitude of the mean free path  $\ell$  of the gas molecules in the kinetic theory of gases. This can be seen not only numerically, but also from the relation (e.g., reference 23)  $\mu = \alpha \rho \bar{c} \ell$ , where  $\bar{c}$  = average random (thermal) speed of the molecules  $\approx a$ , and  $\alpha$  is a constant with a value of roughly  $1/2$ . Thus  $\delta \approx \ell / (2M_1)$ . Specific theoretical values of the shock-wave thickness can be found, for example, in references 9 and 22. Because of these very low thicknesses, Becker<sup>5</sup>, who assumed constant viscosity

<sup>11</sup>  
 $\rho_1 = 0.00238$  slugs/ft<sup>3</sup>,  $p_1 = 14.7$  lb/in<sup>2</sup>,  $T_1 = 59 + 460 = 519^\circ\text{R}$ ,  $a_1 = \sqrt{\gamma RT_1}$   
 $= \sqrt{1.4(1715)(519)} = 1118$  ft/sec.

and heat-conducting coefficients and found thicknesses even lower than a mean free path  $\ell_1$  ahead of the shock for moderate Mach numbers  $M_1$ , originally questioned the physical validity of the solutions on the ground that the equations used here are valid only when characteristic distances along the flow at least exceed a mean free path. Subsequently, Thomas<sup>8</sup> and Morduchow and Libby<sup>9</sup> showed that taking into account the actual increase of  $\mu$  and  $k$  with temperature leads to significantly higher thicknesses.

The question of the physical validity of the basic equations used here and their replacement by more appropriate equations when they are not valid, is doubtless the most difficult in the problem of shock-wave structure. (Indeed, if the basic equations were known to be physically completely valid, the problem of the classical shock-wave structure, i. e., without effects such as dissociation or ionization, could be considered as essentially solved.) The basic equations, namely, the Navier-Stokes equations, used here are the continuum equations of flow of a gas, i. e., they can be obtained by considering the gas as a continuous fluid, in which a small isolated element of volume is to be in equilibrium under the macroscopic forces, namely, pressure, shear and inertia forces acting on this element. Moreover, the energy equation is also governed by macroscopic quantities acting on a volume element, namely, the heat conducted across the element (bringing in the temperature) and the work done by the pressure and shear forces. The Navier-Stokes equations, in particular, also involve the assumption that the stress components are linearly related to the rate-of-strain components, and the assumption

that the hydrostatic pressure is the arithmetic mean of the three normal stresses, making the bulk (rate of dilation) viscosity coefficient zero (cf. reference 2). The continuum equations are generally considered to lead to satisfactory descriptions of the flow at least whenever significant changes of state occur over distances  $L$  considerably greater than the mean free paths of the gas molecules. Thus, one criterion is that the Knudsen number ( $L/\ell$ ) must be at least of a certain magnitude. A related criterion for the validity of the continuum equations has been the number of collisions experienced by a molecule during its transit across the shock; Puckett and Stewart<sup>10</sup> have concluded, on this basis, that in the shock wave there are sufficient collisions for the molecules to attain equilibrium for their translational and rotational degrees of freedom, and that hence the continuum equations should be approximately valid. Such criteria, which are relatively simple and easy to apply, may be useful in the absence of further theoretical and experimental information but must be regarded as still somewhat arbitrary. Also, such criteria usually depend strongly on the point in the flow at which the mean free path is calculated (e. g., references 10 and 19). The following appear at present to be the only true criteria for determining the validity of the continuum equations for the shock-wave structure:

(a) How do the continuum solutions compare with reliable experimental determinations of the shock structure?

(b) How do the continuum solutions compare with sufficiently accurate solutions of the Boltzmann equation for the shock-structure problem?

Both criteria (a) and (b) are at present difficult to apply, but some progress has been made along each of these directions. Experimentally, limited data has been obtained from different techniques by Hornig, Greene and Cowan (references 20, 24-26), Sherman and Talbot<sup>21, 27</sup>, and Ballard and Venable<sup>28</sup>. In discussing the experimental results, it will be most suitable to review first the theoretical investigations according to the kinetic theory of gases and the role of the Navier-Stokes equations in this theory.

Although the physical validity of even the Boltzmann equation has at times been questioned in connection with shock structure, it may be assumed at present that this equation is physically valid for this case and that it holds, in fact, whenever the state of a gas does not change appreciably over a distance comparable to the molecular diameter (e. g., references 29-31). In the Boltzmann integro-differential equation the unknown is a distribution function indicating the distribution of velocities among the gas molecules in space and time, due to molecular collisions and inter-molecular forces. In a steady equilibrium state, i. e., with comparatively small or negligible gradients, the distribution function is of the well-known Maxwellian type. From the point of view of kinetic theory, the Navier-Stokes equations can be regarded as follows. The Boltzmann equation can be multiplied by a function  $\alpha(\xi)$  of the velocity vector  $\xi$  and integrated over the velocities. These yield various "moment" equations. In particular, if  $\alpha(\xi)$  is taken as 1,  $\xi$ , and  $\xi^2$  respectively, and average (macroscopic) quantities such as mean flow velocity  $\bar{u}$  and density  $\rho$  are appropriately defined (e. g., reference 30,

31 and 19) then for one-dimensional steady flow, equations of the following form are obtained

$$(\rho u)' = 0$$

$$\rho u u' + (p + \tau)' = 0 \quad (33)$$

$$\rho u (E' + u u') + [u(p + \tau)]' + q' = 0$$

where  $p$  is the (hydrostatic) pressure,  $\tau$  the  $x$ -component of (shear) stress, and  $q$  the  $x$ -component of heat flow. It is easily verified that the set of equations (33) is exactly equivalent to the set of mass, momentum, and energy equations (1) - (3), if one sets

$$\tau = -(4/3) \mu u' , \quad q = -k T' \quad (34)$$

Thus, the Navier-Stokes equations can be regarded as arising from Boltzmann's equation, provided that the expressions (34) are assumed for the stress component and heat flow, i. e.,  $\tau$  (linearly) proportional to velocity gradient  $u'$ , and  $q$  proportional to temperature gradient  $T'$ . Indeed, in the Enskog-Chapman scheme of solving the Boltzmann equation, a series solution in powers of a small parameter  $\epsilon$  (the mean free path) is sought; the results give a sequence of approximations to  $\tau$  and  $q$ , and the first approximation for  $\tau$  and  $q$  is that given by Eqs. (34) (reference 32). Thus, the Navier-Stokes equations are a first approximation in this scheme. It should be noted that the convergence of this scheme in general has not been established, and in fact now appears

even doubtful.<sup>12</sup> Talbot and Sherman<sup>27</sup>, in fact, have obtained numerically a solution for the shock structure according to the next higher approximation in this scheme, namely, the Burnett equations and have found (for Mach numbers up to 2 roughly) that the solutions do not differ significantly from the Navier-Stokes solutions and do not agree any better with experimental data. Zoller<sup>34</sup> had previously solved equations similar to, but not identical with, the Burnett equations, but could not obtain results above  $M_1 = 2.36$ . These solutions do not agree as well with experimental data as the Navier-Stokes or Burnett solutions (reference 27). An iterative method of solution of the Boltzmann equation has been constructed by Ikenberry and Truesdell<sup>33</sup> in which, again, the first iterates yield the Navier-Stokes equations. Grad (references 30 and 19) has obtained solutions for the shock structure by means of a thirteen-moment approximation to the Boltzmann equation. The solution breaks down for a Mach number of 1.65 or higher. Wang Chang<sup>35</sup> has obtained a kinetic theory solution, by series, for a weak shock wave. The convergence, however, is slow and the solution breaks down for shock waves of moderate strength.<sup>16</sup> Mott-Smith<sup>36</sup> has obtained an approximate solution for strong shock waves by assuming the distribution function within the shock to be a (variable) linear combination of the Maxwellian distributions in front of and behind the shock. This solution

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<sup>12</sup>Ikenberry and Truesdell<sup>33</sup> have shown that in the special case of a simple shearing flow, the Navier-Stokes solution may be considered as an asymptotic solution and every "higher approximation" is worse than it.

<sup>13</sup> Grad<sup>19</sup> has indicated that the convergence of this solution may be improved by expanding in a different parameter.

has not agreed well with experiments for Mach numbers below 2<sup>21, 27</sup>; however, a recent modification by Muckenfuss<sup>37</sup> to take into account more realistic intermolecular forces has led to improved agreement with experiment. In particular, for  $M_1$  up to about 1.8 the agreement with experiment is approximately as good as the Navier-Stokes solution, but at  $M_1 = 2.4$  the agreement with experiment appears appreciably better for the kinetic-theory solution. A further modification of the Mott-Smith type of solution has been recently made by Glansdorff<sup>38</sup> and Ziering, Ek and Koch<sup>39</sup>. It should be noted that for very weak shocks, the Navier-Stokes, thirteen-moment, Wang Chang, Burnett, and Zoller solutions all tend to agree with one another. An attempt has recently been made (Haviland<sup>40</sup>) to solve the Boltzmann equation by a Monte Carlo method in which the motion of a statistically large number of molecules is studied individually. The procedure, which requires a large scale computer and which according to its author should only be applied as a last resort, gave results for shock-wave structure which seem to agree most nearly with the theoretical calculations according to reference 39.

In appraising the Navier-Stokes equations it should be noted that in contrast to solutions along strictly kinetic theory lines, the Navier-Stokes equations have considerable flexibility. For example, intermolecular forces can be easily taken into account by permitting  $\mu$  and  $k$  to vary in a prescribed manner. Moreover, the ratio of specific heats  $\gamma$  can be prescribed. Finally, it is even possible, in a comparatively simple manner, to take into account relaxation effects for a

diatomic gas. In applying the Navier-Stokes equations (1)-(3) for a diatomic gas, it was originally found (e.g., references 20, 22, 24) that even for fairly weak shock waves, the observed shock thicknesses exceeded the calculated ones, whereas the agreement was definitely better for monatomic gases. This appears to be due primarily to the rotational degree of freedom of a diatomic molecule and to the fact that the attainment of thermal equilibrium for the rotational degree of freedom tends to lag behind the equilibrium for the translational degree of freedom<sup>41</sup>. Gilbarg and Paolucci<sup>42</sup> have pointed out that a thicker shock wave results from the Navier-Stokes equations if the latter are modified, for a diatomic gas, by introducing a bulk viscosity  $\kappa$  defined by  $\kappa = (2/3)\mu + \lambda$ , where  $\lambda$  is the compression viscosity (cf. reference 2). Actually,  $\tau$  may be written as (cf. reference 2)

$$\tau = -(2\mu + \lambda)u' \quad (35a)$$

In Eqs. (1) - (3) and in Eqs. (34), Stokes' relation,  $2\mu + 3\lambda = 0$ , or  $\kappa = 0$ , has been used. If, for a diatomic gas, this relation is dropped, then more generally  $\lambda = \kappa - (2/3)\mu$ , and

$$\tau = -[(4/3)\mu + \kappa]u' \quad (35b)$$

For air, Gilbarg and Paolucci and also Sherman<sup>21</sup> assumed  $\kappa = (2/3)\mu$  (corresponding to  $\lambda = 0$ ). It can be seen from Eqs. (33), (34), and (35b) that the effect of thus introducing a bulk viscosity is simply to replace  $\mu$  by  $[\mu + (3/4)\kappa]$ , i. e., the effect is the same as an increase in the shear viscosity coefficient  $\mu$ . According, for example, to Wang, Chang and

Uhlenbeck<sup>43</sup>, if the relaxation times are sufficiently small, then  $(\kappa/\mu)$  can be related to the relaxation time. Sherman<sup>21</sup> has found that by this means the Navier-Stokes equations lead to good agreement with experimental observations for diatomic gases for Mach numbers up to 2.0.

A rather clear comparison of experimental data with results of various theories can be found in references 21 and 27 where, briefly, it is concluded that for Mach numbers up to about 2.0, the Navier-Stokes equations (modified by  $\kappa$  for diatomic gases) lead to satisfactory agreement with experimental observations, while none of the other theories leads to any better agreement in this Mach number range, with several of them (such as the thirteen-moment approximation) leading to poorer agreement. For higher Mach numbers, it would at present, perhaps, appear somewhat premature to draw any definite conclusions. The greatest immediate need in this area is additional reliable experimental data in the higher Mach number range and a reliable mathematical estimate of the magnitude of the error in the more promising approximate solutions (such as the types in references 36 and 39) of the Boltzmann equation for this range. Of course, still more accurate solutions of the Boltzmann equation would also be desirable.

#### Heat Conduction Without Viscosity ( $Pr = 0$ )

For the case of  $u = 0$  ( $k \neq 0$ ), Eqs. (10) and (12) yield the following parabolic relation between  $T$  and  $u$

$$T/T_1 = (u/u_1) [1 + \nu M_1^2 (1 - (u/u_1))] \quad (36)$$

Moreover, Eq. (15) in conjunction with Eq. (26) reduces to

$$u'(u - \beta) = [mR(\gamma + 1)/4k(\gamma - 1)](u - u_1)(u - u_2) \quad (37)$$

where

$$\beta = u_1(1 + \gamma M_1^2)/(2\gamma M_1^2)$$

From Eqs. (36) and (37)

$$kT' = (m(\gamma + 1)/[2(\gamma - 1)])(u_1 - u)(u - u_2) \quad (38)$$

Eq. (37) shows that as  $u$  varies continuously from  $u_1$  to  $u_2$ ,  $u'$  cannot vanish except at the ends (if  $u \neq \beta$  there). Eq. (38) then shows that  $T'$  will be zero only at the front and rear ends of the shock, but will not be zero anywhere inside. In particular,  $T' > 0$  everywhere within the shock, i. e.,  $T$  will increase monotonically. However, according to Eq. (36),  $dT/du = 0$  at  $u = \beta$ . Consequently if the shock is strong enough so that  $\beta > u_2$ , then  $dT/du$  would vanish for some value of  $u$  inside of the shock structure, indicating that  $T$  would have a maximum there (cf. Fig. 3), in contradiction to the previous conclusion. This means that a transition from state 1 to state 2 with  $u$  changing continuously across the entire shock, would be impossible in such a case. (This can also be seen by noting that according to Eq. (37),  $dx/du = 0$  at  $u = \beta$ ; if this occurred within the shock, then there would result two different values of  $u$  for the same value of  $x$ ). Thus, it is seen that a completely continuous shock structure, in all the variables, will occur if and only if the shock is sufficiently weak so that  $\beta \leq u_2$ . This condition (using

Eqs. (21)) can be written in any of the following alternative forms

$$\frac{u_2}{u_1} \geq \frac{1}{2} + \frac{1}{2\gamma M_1^2} ; M_1^2 \leq \frac{3\gamma-1}{\gamma(3-\gamma)} ; \frac{u_2}{u_1} > \frac{\gamma+1}{3\gamma-1} \quad (39)$$

If  $\gamma = 1.4$ , for example, condition (39) becomes  $M_1 \leq 1.196$ . A result of this type was originally found by Rayleigh<sup>1</sup> and it indicates an interesting difference between the action of viscosity and heat conduction. As already seen, viscosity alone, without heat conduction, is capable of supporting a steady continuous shock structure regardless of the shock strength (cf. Eq. (27)); on the other hand, heat conduction alone, without viscosity, can support a steady continuous shock structure only if the shock is not too strong.

When condition (39) is satisfied the solution of Eq. (37) for constant  $k$  is<sup>14</sup>

$$x = \frac{4k(\gamma-1)}{mR(\gamma+1)} \left[ \frac{u_1 - \beta}{u_1 - u_2} \log \left( \frac{2(u_1 - u)}{u_1 - u_2} \right) - \frac{(u_2 - \beta)}{u_1 - u_2} \log \left( \frac{2(u - u_2)}{u_1 - u_2} \right) \right] \quad (40)$$

In Eq. (40) the origin for  $x$  has been chosen so that  $u = (u_1 + u_2)/2$  there. It can be verified, by solving for  $u'$  in terms of  $u$  according to Eq. (37) and differentiating that the point where  $u'' = 0$  will be different from the point where  $u = (u_1 + u_2)/2$ . (In fact when  $M_1$  is slightly below

<sup>14</sup> It may be remarked that in all four cases treated here for which  $x$  vs.  $u$  has been explicitly found ( $Pr = 3/4$ ,  $0 < \infty$  with constant  $\mu$  and  $k$ ; weak shock waves) the solutions are of the form  $x = A \log(u_1 - u) - B \log(u - u_2) + C$ , where  $A$  and  $B$  are certain constants, and  $C$  is an arbitrary integration constant.

$(3\gamma - 1)/[\gamma(3 - \gamma)]$ , the inflection point on the velocity curve will be far downstream, near  $u = u_2$ ).

If  $u_2/u_1 < (\gamma + 1)/(3\gamma - 1)$ , it has already been seen that a continuous solution for the entire shock structure will not exist. To see the nature of the solution in this case, it is recalled that since  $\beta > u_2$  now, and  $dT/du = 0$  at  $u = \beta$ , the curve  $T$  vs.  $u$  will have a maximum between  $u = u_1$  and  $u = u_2$  (see Fig. 3). This means that in this case the temperature will reach its final value  $T = T_2$  at a value of  $u$ ,  $u = u_c$  (say), between  $u_1$  and  $u_2$ .<sup>15</sup> An isothermal discontinuity then occurs at this point, the temperature remaining at  $T = T_2$ , but the velocity (and also other variables) jumping discontinuously to its final value  $u_2$  (cf. reference 14). The actual  $T$  vs.  $u$  curve is thus the curve  $1c2$  in Fig. 3, consisting of the arc  $1c$  and the horizontal line segment  $c2$ . Gilbarg<sup>12</sup> has proven mathematically that as  $\mu$  approaches zero, the solution of Eqs. (13) and (14) approaches this type of discontinuous solution. The location of the point "c" in Fig. 3 can be found by setting  $T = T_2$  in Eq. (36) and solving for  $u$ . One root must be  $u = u_2$  and the other root will be  $u = u_c$ , where

$$u_c/u_1 = [2\gamma M_1^2 - (\gamma - 1)]/[\gamma(\gamma + 1)M_1^2] \quad (41)$$

The velocity  $u$  will decrease continuously with  $x$  from  $u_1$  at  $x = -\infty$  until it reaches the value  $u_c$ , at which point it then drops discontinuously to  $u_2$  and remains at that value. Curves showing  $T$  and  $u$  vs.  $x$  in both the

<sup>15</sup> This is not true of the density or pressure, which will vary monotonically with  $u$  (cf. Eqs. (6) and (10) with  $u = 0$ ).

continuous and discontinuous cases are given in Figs. 4 and 5.<sup>16</sup> The special case of  $M_1^2 = (3\gamma - 1)/[\gamma(3 - \gamma)]$  is also included there.

#### IV - DISTRIBUTION OF ENTROPY

It has already been seen that the velocity, specific volume, pressure and temperature all vary monotonically across the entire shock width, the first two decreasing and the latter two increasing throughout (with the indicated modifications for  $Pr = 0$ ). The entropy, however, although it will be greater at the end of the shock ( $x = +\infty$ ) than ahead of it ( $x = -\infty$ ), will be found not to increase throughout the shock structure, but to increase from  $x = -\infty$  until it reaches a maximum somewhere within the shock, and then to decrease until its final value at  $x = +\infty$ . This anomalous behavior of the entropy will now be examined in detail, based on the Navier-Stokes equations, first for general flows (i. e., general Prandtl number), and then for the specific flows in Section III for which exact closed-form solutions have been found. For convenience the results obtained here will be put in the form of numbered theorems and corollaries and these can then serve as a convenient summary of the results developed here.

##### General Flows (Pr general)

In the first place, it should be noted that the heat conduction of

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<sup>16</sup> Fig. 4 of reference 20 sketching  $u$  vs.  $x$  in such a case is not quite accurate, since it indicates that  $u$  will vary continuously until it has the value  $u_2$  (where  $T' = 0$ ), with infinite slope, and then drops abruptly to  $u_2$ . Actually,  $u_2$  varies continuously only until it has the value  $u_2^c$ , which will occur upstream of the point where  $T' = 0$  (cf. Fig. 4 here), and then drops to  $u_2$ . The left-handed derivative  $u'$  will be finite at  $u = u_2^c$  (cf. Fig. 5 here).

the gas plays a key role in the non-monotonic behavior of the entropy. This can be readily seen by noting that for a gas without heat conduction, i. e., for a gas with  $k = 0$ , the energy equation would imply  $S' > 0$  within the entire shock structure; hence in this case the entropy would indeed increase throughout the shock. Physically this is simply due to the fact that heat keeps being added to the gas due to the viscous dissipation, while there is no heat being conducted away. Thus,

Theorem 1. In the absence of heat conduction, but in the presence of viscosity, the entropy would increase monotonically throughout the entire shock structure.

In the presence of heat conduction ( $k > 0$ ), however, it is actually not difficult to see that, in general, the entropy can no longer vary monotonically. This follows by considering conditions close to both ends ( $x = \pm\infty$ ) of the shock wave. Because of the strongly uniform conditions near each end, the derivative  $u'$  will be very small in these vicinities, and consequently  $uu'^2$  will be much smaller than  $(kT')'$  there. Hence, according to Eq. (9),  $S'$  will have the same sign as  $(kT')'$ , or  $T''$  (since  $k'T'$  may also be neglected here and  $k > 0$ ) in these neighborhoods. Since  $T$  vs.  $x$  will in general follow an S curve (cf., e. g., Fig. 2),  $T'' > 0$  near  $x = -\infty$  and  $T'' < 0$  near  $x = +\infty$ . Consequently  $S$  must be increasing near the upstream end of the shock structure, but must be decreasing near the downstream end.

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<sup>17</sup>It is interesting to note that despite the apparent simplicity of this argument, the very first reaction of most investigators in this or related fields on learning of this fact has been that of surprise.

The above argument, which gives some insight into the cause (namely, the role of heat conduction) of the anomalous behavior of the entropy, can be made mathematically more formal by considering solutions in the  $(u, T)$  plane, as in reference 16. Multiplying Eq. (9) by  $dx$ ,  $mT dS = d(kT') + (4/3)\mu u' du$ . Hence, from Eqs. (13) and (14)

$$mT dS = dL + (4/3) M du \quad (42)$$

At the end points 1 and 2 of the shock wave,  $L = 0$  and  $M = 0$  (cf. footnote 3). Hence, at each end point  $mT dS = dL$ . However,  $L > 0$  everywhere within the shock structure (references 11 and 12).  $\therefore dL > 0$ , and hence  $dS > 0$  at the front end, but  $dL < 0$  and hence  $dS < 0$  at the rear end. Thus, Theorem 2 follows.

Theorem 2. In the presence of heat conduction, the entropy will not increase monotonically throughout the shock structure, but will increase near the upstream edge of the wave, and if it varies continuously, will decrease near the downstream edge.

Corollary. If  $k > 0$  and  $S'$  is everywhere continuous, then  $S' = 0$  at some point within the shock wave.

In connection with Theorem 2 and its Corollary, it should be recalled that  $S$  and  $S'$  will in fact vary continuously in all cases except that of a sufficiently strong shock wave without viscosity. It should, of course, be immediately noted here that Theorem 2 does not violate the second law of thermodynamics, since only the entire shock structure with its uniform conditions at  $x = \pm \infty$  constitutes a closed system, and hence it is only required that  $S_2 > S_1$ . Further remarks on the physics

of Theorem 2 will be made subsequently.

From Eq. (9) it is seen that  $S' = 0$  where  $(kT')' = -(4/3)\mu u'^2$ , or where  $kT'' = -(4/3)\mu u'^2 - k'T'$ . Hence, if  $k > 0$ ,  $\mu > 0$  and  $k' \geq 0$  throughout the shock (as is ordinarily the case), then  $S' = 0$  at a point within the shock where  $T'' < 0$ . Keeping in mind the general S-shaped nature of the temperature distribution (cf., e.g., Fig. 2),  $T'' < 0$  downstream of the point where  $T'' = 0$ . Thus, Theorem 3 follows.

Theorem 3. If both heat conduction and viscosity are present and the heat conductivity coefficient is either constant or increasing throughout the shock, then the entropy will have its maximum value at a point within the shock structure which is downstream of the point of inflection of the temperature-vs.-distance curve.

If Eq. (2) is multiplied by  $(dx/d\rho)$  and use made of Eq. (6), then it is found that  $(dp/d\rho) - u^2 - (4/3)(\mu u')'(dx/d\rho) = 0$ . This equation holds everywhere inside of the shock where  $d\rho/dx \neq 0$  and hence at a point inside of the shock where  $S' = 0$ . Since at such a point  $(dp/d\rho) = a^2$ , Theorem 4 follows.

Theorem 4. At any point inside of the shock wave where  $S' = 0$ ,  $u^2 = a^2 - (4/3)(dx/d\rho)(\mu u')'$ .

This theorem yields the following important corollary.

Corollary. If at a point inside of the shock wave where  $S' = 0$  it is true that  $(\mu u')' = 0$ , then in addition  $u = a$  there, i.e., the speed must be locally sonic there. Conversely, if at a point inside of the shock where

$S' = 0$  it is true that the velocity is locally sonic, then also  $(\mu u')' = 0$  there.<sup>13</sup>

It should be noted that in the cases of a constant non-zero viscosity coefficient  $\mu$ , the condition  $(\mu u')' = 0$  means an inflection point in the velocity-vs.-distance curve. Details of the entropy distribution for various special cases will now be analyzed.

#### Weak Shock Waves

For this case it will be recalled  $\mu$  and  $k$  may be considered constant, while  $u'$  is second-order small. Consequently the  $u'^2$  term may be neglected in Eq. (9). Moreover, since  $u''$  is third-order small, so is  $T''$  and hence one may replace  $T$  by  $T_1$  on the left side of Eq. (9), solve for  $S'$  and integrate to obtain  $S - S_1 = [k/(mT_1)]T'$ . From Eq. (31) it then follows that

$$S - S_1 = \frac{k}{4mDT_1} (T_2 - T_1)(u_1 - u_2) \operatorname{sech}^2 \left( \frac{u_1 - u_2}{2D} \right) x \quad (43)$$

A result analogous to Eq. (43) has been obtained by a somewhat different procedure by Landau and Lifshitz<sup>14</sup>. According to Eq. (43)  $S - S_1$  varies symmetrically about  $x = 0$  and has its maximum value there (see Fig. 6). The point  $x = 0$  is also where  $u$ ,  $p$ ,  $\rho$  and  $T$  each have a value equal to

<sup>13</sup>In this connection it must be remarked that Golitsyn and Staniukovich<sup>13</sup> have stated (for constant  $\mu$ ) that in general  $u'' = 0$  where  $S' = 0$ , and hence have concluded also that in general  $S' = 0$  where  $u = a$ . Although, as will be seen for constant  $\mu$ ,  $u'' = 0$  at  $S' = 0$  for weak shock waves and for any shock waves when  $Pr = 3/4$ , Golitsyn and Staniukovich do not give any proof nor any reference for the truth of this statement in general. (They do give a reference for the proof of this statement for weak shocks.) This statement of Golitsyn and Staniukovich must at present, therefore, remain open to question for the general case when  $\mu \neq 0$ . When  $\mu = 0$ , it will be seen that the statement that  $u'' = 0$  where  $S' = 0$  is false.

the arithmetic mean of their values in front of and behind the shock (cf. Eqs. (30) and (31)). Moreover, at this point, according to Eqs. (30) and (31),  $u''$ ,  $p''$ ,  $\rho''$ ,  $T''$  all vanish. Hence, from Theorem 4, the velocity is locally sonic there. These results can be summarized by the following theorem.

Theorem 5. For extremely weak shock waves (with  $k > 0$ ), the entropy has its maximum at a point about which it varies symmetrically. At this point, the velocity is locally sonic. Moreover, the velocity, density, pressure and temperature curves vs. distance all have their points of inflection there, while each of these variables has a value equal to the arithmetic mean of its values ahead of and behind the shock.

It will be seen that for the other cases to be analyzed here, some of these statements continue to hold, while others do not. It may be noted that setting  $x = +\infty$  in Eq. (43) it is found that  $S_2 = S_1$ . This is a reflection of the fact that for extremely weak shocks,  $S_2 - S_1$  is actually only third-order small (cf. reference 14 or 44); the maximum value of  $S - S_1$  within the shock ( $x=0$ ) is, however, one order of magnitude larger, namely, second-order small. This limiting case of weak shocks, therefore, reveals especially strongly the non-monotonic character of the entropy variation through the shock.

Prandtl number of  $3/4$

From Eq. (22), which holds for this case,  $T' = uu'/c_p$ . Substituting for  $T'$  into Eq. (9), and also substituting  $k=(4/3)uc_p$  there, it is found that

$$\rho TS' = -(4/3)(uu')' \quad (44)$$

Integrating Eq. (44) over the entire shock and noting that  $u' = 0$  at each end, one obtains

$$\int_1^2 \rho T dS = 0, \quad \text{or} \quad \int_1^2 p dS = 0 \quad (45)$$

Since  $p$  is everywhere positive, the integral in Eq. (45) can vanish only if  $S'$  is positive in some places and negative in others. Hence,  $S$  cannot increase monotonically across the entire shock. This result has, of course, already been proven for more general cases (general  $Pr \neq \infty$ ), but the proof given here is interesting because of the rather interesting result given by Eq. (45) and because this is the reasoning first used in 1944 by Roy<sup>6</sup>, who may have been the first to discover the non-monotonic behavior of the entropy.<sup>19</sup> Moreover, equations analogous to (44) and (45), but with heat conduction replacing the role of the viscous shear stresses here, will subsequently be found to hold for a fluid with heat conduction but without viscosity ( $Pr=0$ ).

From Eq. (44) it follows that  $S' = 0$  where  $(\mu u')' = 0$ . From Eq. (24) it is recalled that this is the point where  $u = \sqrt{u_1 u_2}$ . Moreover, since  $\mu u'$  denotes the shear stress, the point where  $S$  is a maximum is in this case also the point where the shear stress is a (negative) maximum. Finally, from Theorem 4, it also follows that  $u = a$  there. These results all hold for variable as well as constant  $\mu$  and can be summarized by the

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<sup>19</sup> In Roy's paper the factor " $\rho$ " was omitted in Eq. (44), and instead of Eq. (45) it was inferred there that  $\int_1^2 T dS = 0$ .

following theorem.

Theorem 6. For a constant Prandtl number of 3/4, but otherwise variable viscosity and heat conductivity coefficients, the entropy will have its maximum value within the shock wave at the point where the shear stress is a maximum. At this point the velocity is locally sonic and has a value equal to the geometric mean of the values of the velocity ahead of and behind the shock.

Corollary 1. If  $Pr=3/4$  and the viscosity (and therefore the heat conductivity) coefficient is constant, then the entropy has its maximum value at the inflection point of the velocity-vs.-distance curve.

If  $\mu$  is variable, the  $S=S_{\max}$  where  $u u' + \mu u'' = 0$ . Hence, since  $u' < 0$ , it follows that if  $\mu$  is an increasing function of  $T$  (as is ordinarily the case), so that  $\mu' > 0$ , then  $S_{\max}$  occurs where  $u'' > 0$ , and therefore downstream of the inflection point on the velocity-distance curve. Thus:

Corollary 2. If  $Pr=3/4$ , and  $\mu$  (and  $\therefore k$ ) varies so that it increases throughout the shock, then the entropy will have its maximum value at a point downstream of the inflection point on the velocity-vs.-distance curve.

In actual cases (cf. Fig. 7) the point of maximum  $S$  may still be close to the inflection point on the velocity-distance curve. Typical curves showing the entropy distribution are given in Fig. 7. Additional curves can be found in references 9, 7, and 15.

#### Viscosity Without Heat Conduction ( $Pr=\infty$ )

It has already been pointed out that this is the one case in which the entropy will increase monotonically throughout the shock. This is illustrated in Fig. 8. It may be added that here is a case in which the velocity and, therefore, also the density behave almost exactly as for

the case  $Pr=3/4$  (compare Eqs. (27) and (23)), while the entropy has a qualitatively different behavior.

#### Heat Conduction Without Viscosity ( $Pr=0$ )

The case of a completely continuous shock structure ( $M_1^2 < (3\gamma-1)/[\gamma(3-\gamma)]$ ) will be discussed first. Putting  $\mu=0$  into Eq. (9), it is seen that in this case

$$mTS' = (kT')' \quad (46)$$

From this it follows that

$$\int_1^2 TdS = 0 \quad (47)$$

Eqs. (46) and (47) are analogous to Eqs. (44) and (45) for  $Pr=3/4$ . Eq. (47) indicates that without viscosity, the net heat added to the fluid as it crosses the shock is zero, i. e., without viscous dissipation, there will be as much heat conducted away from the fluid as into it.

From Eq. (46) it follows that  $S'=0$  where  $(kT')'=0$ . Hence,  $S=S_{\max}$  at the point where the heat flow  $kT'$  is a maximum. Moreover, differentiating the right side of Eq. (38), it is readily seen that  $(kT')'=0$  where  $u=(u_1+u_2)/2$ . It has been previously noted that at this point,  $u'' \neq 0$  (except in the limit of weak shocks). Since the pressure  $p$  in this case varies linearly with  $u$  (Eq. (10) with  $u=0$ ), it follows also that  $p=(p_1+p_2)/2$  at this point. (This, however, will not be true of the density or temperature). Finally, since  $u=0$  here, Theorem 4 shows that  $u=a$  at this point. These results all hold for variable, as well as constant,  $k$  and can be summarized by the following theorem.

Theorem 7. If heat conduction only is present, without viscosity, and the shock wave is sufficiently weak so that  $M_1^2 < (3\gamma-1)/[\gamma(3-\gamma)]$ , then the entropy will vary continuously. It will reach its maximum value where the heat flow is a maximum. At this point, the velocity is locally sonic and both the velocity and the pressure are equal to the arithmetic mean of their values ahead of and behind the shock.

From the fact that  $S' = 0$  where  $(kT')' = 0$ , the corollary below follows.

Corollary 3. Under the same conditions as in Theorem 7, the point at which the entropy reaches its maximum will be at the point of inflection of the temperature-vs.-distance curve if the heat-conductivity coefficient  $k$  is a constant, and will be downstream of this inflection point if  $k$  increases through the shock.

This corollary may be compared with Theorem 3.

If  $M_1^2 > (3\gamma-1)/[\gamma(3-\gamma)]$ , it will be recalled that the shock structure is continuous until  $T = T_2$ , where  $u = u_c$ . At this point an isothermal discontinuity occurs. The entropy in such a case will vary continuously from point "1" to this point "c", and will then change abruptly (at point "c") from its value  $S_c$  there to its final value  $S_2$ . Two questions of particular interest here are: (a) How does  $S_c$  compare with  $S_2$ , i. e., when the entropy jumps from  $S_c$  to  $S_2$ , does it jump to a higher or to a lower value? (b) During the continuous variation of the entropy from  $S_1$  to  $S_c$ , before the jump, does the entropy increase monotonically to  $S_c$ , or does it at first increase to some value,  $S_{max}$ , where it has a local maximum with zero slope ( $S' = 0$ ) and then decrease to  $S_c$ ?

Question (a) is readily answered. Since  $T_c = T_2$  and  $u_c > u_2$ , it follows from Eq. (8) that  $S_c > S_2$ . Hence, in the isothermal discontinuity here, the entropy jumps to a lower value. This is thus a (comparatively rare) example of a physical system within which a discontinuity to a lower entropy occurs. In regard to question (b), S will pass through a maximum with zero slope before the discontinuity if  $(u_1 + u_2)/2 > u_c$ . Substituting for  $u_2$  and  $u_c$  in terms of  $M_1$  according to Eqs. (21) and (41), this condition becomes

$$M_1^2 < (2\gamma - 1) / [\gamma(2 - \gamma)] \quad (48)$$

For  $\gamma = 1.4$ , for example, this condition is  $M_1 < 1.460$ . These results for the discontinuous case can be summarized by the following theorem.

Theorem 8. If heat conduction only is present, without viscosity, and the shock is sufficiently strong so that  $M_1^2 > (3\gamma - 1) / [\gamma(3 - \gamma)]$ , then the entropy will vary continuously within the shock structure until the temperature first attains its final value  $T_2$ . At this point an isothermal discontinuity occurs to the final state behind the shock, with the entropy dropping abruptly from a higher value here to a lower value. If, in particular,  $(3\gamma - 1) / [\gamma(3 - \gamma)] < M_1^2 < (2\gamma - 1) / [\gamma(2 - \gamma)]$ , then the entropy will first increase continuously until it reaches a maximum value with zero slope (where  $u = (u_1 + u_2) / 2 = a$ ), decreases continuously until  $T = T_2$ , and then drops abruptly to its still lower final value  $S_2$ . Finally, if  $M_1^2 > (2\gamma - 1) / [\gamma(2 - \gamma)]$ , then the entropy will increase continuously until  $T = T_2$ , and then will drop abruptly to its final value.

Theorem 8 (as well as Theorem 7) holds for variable as well as

constant  $k$ . Fig. 9 shows various types of entropy distribution in the case of heat conduction without viscosity.

#### Physical Remarks

The mathematical results developed here on the entropy distribution warrant at least some physical comment. From a macroscopic, thermodynamic point of view, the physical explanation for the non-monotonic distribution of the entropy, as already indicated, is relatively simple and is based on the heat conductivity of the gas. The heat added per unit time to a unit volume of the gas at any point is  $(kT')'$ . Because of the nature of the temperature distribution (e. g. , Fig. 2) within the shock structure,  $(kT')'$  is positive in the front part of the shock structure, and negative in the rear part. Consequently, in the rear part the fluid loses heat through conduction and when the time rate of this loss exceeds the rate of gain of heat by viscous dissipation, the entropy (as defined here, viz.  $dS=dQ/T$ ) will diminish. This is, of course, the content of Theorems 1-3 and their proofs.

The foregoing simple explanation for the behavior of the entropy, however, does not leave one entirely satisfied physically, since it is based on considering entropy change to be simply proportional to heat added (albeit with a variable factor  $1/T$ ) and is not concerned with the special significance of entropy itself, namely, as a measure of the "disorder" of a system. (In statistical mechanics, a system is associated with large "disorder" or "randomness" if its microscopic properties, e. g. , the distribution of molecular velocities for a gas, may be arranged in very many ways, all consistent with the same macroscopic properties.

(e. g., the temperature and pressure for a gas) of the system (cf., e. g., reference 45)). The results developed here indicate then that, in the presence of heat conduction, the state of the gas throughout a shock wave varies in such a way that although the state of disorder is greater behind than in front of the shock (second law of thermodynamics), there is an even greater state of disorder at certain points within the shock structure.

The chief difficulty in giving a completely satisfactory statistical mechanical interpretation of the results for entropy obtained here is that in a shock structure, there are large deviations from statistical equilibrium, i. e., there are very large gradients of the macroscopic state of the gas within the shock.<sup>20</sup> In such a case the definition of entropy  $S$  as used here should be replaced by the more general function  $H/\rho$ , where  $H$  is Boltzmann's H-function in the kinetic theory of gases. For Maxwellian distributions of velocity,  $H/\rho$  is indeed simply proportional to the negative of  $S$ , but for appreciable deviations from equilibrium, no such simple relation between  $S$  and  $H/\rho$  exists. (See, e. g., reference 31 for further details and derivations). It may still be expected, however, that at least for shock waves not too strong, the entropy  $S$  should correspond fairly well to  $H/\rho$ . It is noteworthy that in all of the

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<sup>20</sup> Another meaning of large deviation from equilibrium is that the molecular distribution of velocities is far from Maxwellian (cf., e. g., reference 29). For the shock structure, the distribution of molecular velocities is Maxwellian in the uniform conditions ahead of and behind the shock, but will not be exactly Maxwellian within the shock, and may be expected to be furthest from Maxwellian around the "center" of the wave.

special cases analyzed here in which the entropy  $S$  was non-monotonic ( $k \neq 0$ ),  $S$  had its maximum value, i. e., the "disorder" was a maximum, where the gradients of certain physically significant quantities (such as the shear stress or the heat flux) were a maximum (and perhaps where the deviations from a Maxwellian distribution might be largest). It may also be significant that in every case analyzed here, the velocity at this point was locally sonic, i. e., this is the point where the flow changes from supersonic to subsonic. Further interpretations along these lines can be made only from reliably accurate solutions of the Boltzmann equation, and calculations of  $H$  therefrom. It is of special interest to note that Haviland<sup>40</sup> has actually obtained distributions of  $H/\rho$  through a shock structure for  $M_1 = 2.0$  and  $3.0$ , by a Monte Carlo procedure, and has found  $H/\rho$  to pass through a minimum (corresponding to a maximum of  $S$ ) inside of the shock structure.

#### V - STRUCTURE OF SHOCK WAVES INVOLVING CHEMICAL REACTIONS

In the previous sections there have been discussed the structure of shock waves in general and the entropy distribution therein in particular; the classical assumptions of a homogeneous gas with constant coefficients of specific heat were employed. It is the purpose of this section to review the analysis applicable to the structure of shock waves which involve chemical reactions in the downstream region.<sup>21</sup> Such

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<sup>21</sup> The analysis in this section is a review and generalization of the studies of Hirschfelder, Curtiss and coworkers (cf., e. g., reference 46) pertaining to detonation waves and of Gattazides and Bloom<sup>47</sup> pertaining to strong shock waves in diatomic gases. See also the recent excellent review of detonation waves by Oppenheim and Stern<sup>48</sup>.

reaction arises when a chemically reactive mixture of gases upstream of the shock are raised by the initial compression in the shock to a state in which significant chemical reaction takes place. The steady state conditions across the waves are altered by the chemical reaction.

This type of wave, when the mixture upstream is a mixture of fuel and oxidizer, is called a detonation wave; it has been the object of investigation for roughly 80 years. Particular attention has been devoted to detonation waves satisfying the Chapman-Jouguet condition, that infinitely far downstream the flow velocity is equal to the local sonic velocity. It has been long recognized that this condition is not unique but corresponds to the physical situation usually occurring in the laboratory or in nature, e. g., in the case of mine explosions. Recent experimental techniques employing special supersonic wind tunnels (cf., e. g., Nicholls<sup>49</sup>, Gross and Chinnitz<sup>50</sup>, and Rhodes et al<sup>51</sup> have afforded opportunities to study detonation waves not satisfying the C-J condition.

It is also possible to obtain chemical reactions behind shock waves in diatomic gases such as air. If the shock is sufficiently strong, i. e., involves temperatures and densities in its downstream region sufficiently high, dissociation of the gas molecules takes place and the gas composition involves both atoms and molecules. The dissociation energy of the molecule is absorbed by the gas mixture altering both velocity and temperature. This is a form of chemical reaction which has been under intense study because of its importance in hypersonic aerodynamics. However, the only study of the structure of such waves

known to the authors is that of Gaitatzes and Bloom<sup>47</sup>. In general the physical situation leading to the establishment of the shock does not result in satisfaction of the Chapman-Jouguet condition.

The structure of shock waves involving chemical reaction can in some cases be idealized so as to separate the effects of viscosity and heat conductivity from those of chemical reaction. This model, which is applicable if the chemical reactions are relatively slow, results in a shock wave consisting of two regions; in an initial region the structure would be described by the equations employed above, perhaps generalized for variable specific heat. In this first region the creation and destruction of chemical species would be zero so that the chemical composition would be identical with that far upstream of the wave. In the second region, reaction would take place; to some approximation it is possible to neglect therein molecular transport, i. e., to neglect viscosity, conductivity and diffusion since for extended reaction zones the gradients may be sufficiently small to be inessential. The state of the gas at the downstream edge of the first region is chemically a non-equilibrium one with the approach to equilibrium occurring in the second region. This behavior has recently found importance in ultra-velocity air flows, i. e., those with velocities of 35,000 ft/sec and higher. In this velocity range radiation from the gas provides an important, and as the velocity increases the dominant, mode for energy transfer to the body; since this radiative transfer is highly temperature dependent ( $q_r \propto T^5$ ), it is found that non-equilibrium behavior which occurs behind the shock and which in this case leads to static temperatures higher than

equilibrium, plays a dominant role in determining this transfer. Rose and Teare<sup>52</sup> provide a recent review of this phenomenon.

For the purpose of describing in general the structure of shock waves with chemical reaction, the basic equations will be presented below. These equations should be considered extensions of the Navier-Stokes equations used above. Their validity for either detonation waves or for strong shock waves is subject to at least the same doubt as discussed above but their application is justified by their simplicity, flexibility and in general by the ignorance associated with the details of chemical kinetic and of molecular transport effects. The equations presented below are at least consistent if inaccurate; there is no experimental evidence known to the authors concerning their validity. In connection with the validity of the Navier-Stokes equations and their extensions to detonation waves and strong shock waves, attention is called to the importance of the temperature dependence of the viscosity coefficient on the shock wave structure as predicted by these equations for the classical case of homogeneous gases with constant coefficients of specific heat and  $P_r = 3/4$ . In shock waves involving chemical reaction the temperatures are sufficiently high so that large changes in the transport properties of the gas occur and thus so that relative

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<sup>22</sup>

The discussion of the basic equations presented here is based on the standard treatments of chemically reacting gas flows, e.g., in references 53 and 54

thickening of the wave occurs.<sup>23</sup>

The equations of conservation of mass and momentum (Eqs. (1) and (2)) are unaltered if reactions take place and if it is understood that the viscosity coefficient is now dependent upon composition as well as temperature. However, the energy equation, which can be written in several ways, is considered in the form:

$$\rho u [(u^2/2) + h]' - (kT')' - (4/3)(\mu uu')' + \left( \sum_{i=1}^N \rho_i V_i h_i \right)' = 0 \quad (49)$$

where the enthalpy  $h$  is now the enthalpy per unit mass of mixture;

$h = \sum_{i=1}^N Y_i h_i$ ;  $\rho_i V_i$  is the mass flux of species  $i$  due to diffusion per unit

area per unit time;  $h_i$  is the enthalpy of species  $i$  per unit mass including the chemical enthalpy; and where  $N$  species are assumed present. Eq. (49) can be integrated once to yield after some rearrangement

$$\begin{aligned} & [(u^2/2) + h] - [k/(m c_p)] \left\{ [(u^2/2) + h]' - [1 - (4Pr/3)] uu' \right\} \\ & + \sum_{i=1}^N \left\{ (h_i/m Pr) \mu Y_i' [1 + (Pr \rho_i V_i / \mu Y_i')] \right\} = C_3 \end{aligned} \quad (50)$$

where  $c_p = \sum_{i=1}^N Y_i c_{p,i}$ ,  $c_{p,i} = dh_i/dT$ , and where the Prandtl number involves

the mixture quantities,  $\mu c_p/k$ . Eq. (50) indicates that if, as previously,  $Pr=3/4$  and if  $Pr \rho_i V_i / \mu Y_i' = -1$  for all  $i$ , the previous energy equation with the enthalpy properly interpreted applies to this more general case of reacting flows. Now the

<sup>23</sup> As an example of the temperature dependence of the transport properties of air it may be noted that because of the onset of partial ionization, the conductivity of air behaves roughly as  $k \sim T^2$  for  $T \leq 8000^\circ K$  and as  $k \sim T^3$  for  $T \geq 8000^\circ K$ . This results in a sharp decrease in  $Pr$  for  $T \geq 8000^\circ K$  and suggests that some of the effects related to  $Pr=0$  described above may arise.

diffusional mass fluxes in general arise from gradients of pressure, temperature and composition (cf. references 53 and 54). In aeronautical applications the diffusional fluxes due to composition gradients are generally assumed to be dominant; accordingly, if a single diffusion coefficient  $D$  can be assumed, then

$$\rho_1 V_1 = - \rho D Y_1' \quad (51)$$

If  $\rho D Pr/\mu \approx Le \approx 1$ , then the actual reduction of Eq. (50) is realized. The parameter  $\rho D/\mu$  is the reciprocal of the Schmidt number,  $Sc$ , while  $Pr/Sc$  is the Lewis-Semenov number. The approximations attendant upon  $Le \approx 1$  are widely used because of the resulting simplifications in the gas dynamics of reacting flows although it is recognized that the actual Lewis number in mixtures involving species of widely different molecular weights (e. g., mixtures of atomic and molecular hydrogen in air) may be greatly different from unity.<sup>24</sup>

In the more general case wherein realistic transport descriptions are considered, the Prandtl number can be taken to be dependent on composition and temperature and the diffusional mass fluxes to be dependent on gradients in the flow variables in a more accurate manner. In particular, the contribution to the diffusional mass fluxes by composition gradients are described in matrix form as

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<sup>24</sup> In boundary layer flows the values of  $Pr=Sc=Le=1$  lead to essential simplification in the energy equation.



degrees of freedom were excited only after many collisions. As a reasonable approximation for gas mixtures it is customary to assume thermodynamic equilibrium with respect to all degrees of freedom except the vibrational ones.<sup>25</sup> For these, rate laws yielding  $e'_{v,i}$  in terms of state variables are required. The inclusion of this latter sophistication is vitiated in chemically reacting flows; the effect of coupling between the chemical effectiveness of collisions and the degree of vibrational or rotational excitation is so complex, and available estimates of reaction rates in practically interesting gas mixtures so poor, that it is generally not consistent from an accuracy point of view to describe non-equilibrium behavior in internal degrees of freedom. In the further discussion it will be assumed that full thermodynamic equilibrium prevails. Thus the forward and reverse reaction rates will be related by the equilibrium constant in each reaction step.

The species conservation equations are

$$\rho u Y_i' = -(\rho_i V_i)' + \dot{w}_i \quad i = 1, 2, \dots, N-1 \quad (53)$$

where  $\dot{w}_i$  is the mass volumetric rate of production of species  $i$ , i. e., gms/cc sec. Note that only  $N-1$  such equations must be considered since

<sup>25</sup>Hansen et al.<sup>55</sup> have recently suggested that at high temperatures rotational relaxation may be significant. Talbot and Scala<sup>56</sup> at the same time studied theoretically shock structure in a diatomic gas with rotational relaxation; their main motivation appears to be the determination of a suitable model, i. e., bulk viscosity or relaxation, for lagging internal degrees of freedom.

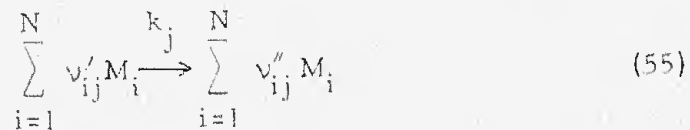
Eq. (1) assumes overall energy conservation. Eq. (53) indicates that the gradient of concentration of a given species at a generic point in the flow depends on diffusion and on chemical reaction. The creation term  $\dot{w}_i$  is determined by the mechanism of the chemical reactions involved; for a system involving L reaction steps

$$\dot{w}_i = W_i \sum_{j=1}^L (v''_{ij} - v'_{ij}) k_j \prod_{i=1}^N (Y_i/W_i)^{v'_{ij}} G_j^{n_j} \quad (54)$$

where  $v''_{ij}$  and  $v'_{ij}$  are the stoichiometric coefficients;  $k_j$  is the specific rate constant;  $G_j = 0$  is the equilibrium condition, i. e.,

$$G_j \equiv 1 - (\rho^m_j / K_{c,j}) \prod_{i=1}^N (Y_i/W_i)^{v''_{ij} - v'_{ij}}$$

$n_j = \sum_{i=1}^N v'_{ij}$ ;  $m_j = \sum_{i=1}^N v''_{ij} - v'_{ij}$ ;  $K_{c,j}$  is the equilibrium constant for reaction step j in terms of molal concentrations, and where the j<sup>th</sup> reaction step is symbolically given by



Eq. (53) can be integrated only formally because of the creation term, i. e.,

$$Y_i + (\rho_i V_i / m) = \int (\dot{w}_i / m) dx + \text{constant} \quad (56)$$

This equation indicates also the influence of diffusion mass flux and of

chemical reaction on the distribution of mass fractions.

The analysis of composition is simplified if the equations of element conservation are considered. Suppose in the general system involving  $N$  species there are  $M$  elements; the conservation of elements requires that throughout the flow

$$\sum_{i=1}^N \mu_{ij} \dot{w}_i / W_i = 0 \quad j = 1, 2, \dots, M \quad (57)$$

where  $\mu_{ij}$  is the number of atoms (or molecules) of element  $j$  in one molecule of species  $i$ . Eq. (57) suggests an element mass fraction  $\tilde{Y}_j$ , that is, the mass density of element  $j$  in all species per mass of mixture, given by

$$\tilde{Y}_j \equiv \sum_{i=1}^N \mu_{ij} W_j Y_i / W_i, \quad j = 1, 2, \dots, M \quad (58)$$

From Eq. (53) with Eqs. (57) and (58) considered, there is obtained

$$\rho u \tilde{Y}_j' = - \sum_{i=1}^N (\mu_{ij} W_j \rho_i V_i / W_i)' \quad (59)$$

or upon integration

$$m \tilde{Y}_j + \sum_{i=1}^N \mu_{ij} W_j \rho_i V_i / W_i = C_j \quad (60)$$

The set of equations providing the formal description of shock

structure in reacting gases is completed by an equation of state

$$p = \rho R_0 T \sum_{i=1}^N Y_i / W_i \quad (61)$$

where  $R_0$  is the universal gas constant; by equations yielding the coefficients of viscosity, specific heat and heat conductivity as functions of composition and state; and by descriptions of the functional dependence of the reaction rates and equilibrium constants on temperature.

The entropy distribution through the wave may be computed once the distributions of composition and the state variables are known: the entropy per unit mass of mixture is

$$S = -(R_0/W) \ln(pW) + \sum_{i=1}^N [Y_i S_i^{(0)} - (R_0 Y_i / W_i) \ln(Y_i / W_i)] \quad (62)$$

where  $S_i^{(0)}$  is the standard entropy of species  $i$  per unit mass of species  $i$  and where  $W$  is the mixture molecular weight,  $W^{-1} = \sum_{i=1}^N (Y_i / W_i)$ .

Consider now the application of these conservation equations at points of uniformity in the flow; i. e., at  $x = \pm \infty$ ; the mass and momentum conservation as before lead to

$$\rho_1 u_1 = m = \rho_2 u_2$$

$$m u_1 + p_1 = m u_2 + p_2$$

while Eqs. (50), (56) and (60) yield respectively

$$(u_1^2/2) + h_1 = (u_2^2/2) + h_2 \quad (63a)$$

$$Y_{i,1} = Y_{i,2} - \int_{-\infty}^{\infty} (w_i/m) dx, \quad i=1, 2, \dots, N \quad (63b)$$

$$\tilde{Y}_{j,1} = \tilde{Y}_{j,2}, \quad j = 1, 2, \dots, M \quad (63c)$$

since  $\rho_1 V_1$  vanishes for all  $i$  at  $x = \pm \infty$  (cf., e.g., equation (52)). If the initial and final states correspond to chemical as well as thermodynamic equilibrium, then the equations of mass, momentum, energy and element conservation (Eq. (63c)), i.e., those yielding simple algebraic relations relating the flow and state variables at 1 and 2, can be supplemented by an equation of state and by a sufficient number of the equilibrium conditions  $G_j=0$ ; e.g., for a chemical system with  $N$  species and  $M$  elements  $N-M$  equilibrium conditions must be specified. Thus, if all conditions corresponding to 1 are known, the aforementioned equations determine all conditions at 2; in the case of detonation waves satisfying the C-J condition, the velocity  $u_1$  is also unknown but the requirement that  $u_2$  equal the speed of sound at plus infinity completes the system of equations. Entropy considerations may have to be invoked in order to select the practical downstream conditions if multiple possibilities therefor arise.

In considering the shock wave structure it can thus be assumed that the end points, i.e., conditions at 1 and 2, are known. The range

<sup>28</sup> See reference 48 for a discussion of the appropriate speed of sound in view of the existence of the two limiting cases of "frozen" and "equilibrium" speeds of sound.

of independent variable can be changed from  $\pm\infty$  to, e. g., 0 to 1 and the numerical analysis can be simplified by introducing

$$\tilde{\xi} = (u_1 - u)/(u_1 - u_2) \quad (64)$$

Then the differential  $dx$  is eliminated from the energy, species and element conservation equations since  $' = d/dx = -u'(u_1 - u_2)^{-1} d/d\tilde{\xi}$  and since  $u'$  can be eliminated by the momentum equation integrated once. This transformation of the independent variable is singular at  $\tilde{\xi} = 0, 1$  so that the asymptotic behavior of the solutions for the dependent variables must be developed at these points. After the solutions in terms of  $\tilde{\xi}$  are obtained, the momentum equation can be integrated a second time by quadrature to obtain  $x = x(\tilde{\xi})$  subject to same condition fixing the origin of the  $x$  coordinate.

To give some indication of the effect of chemical reaction on the structure of a shock wave consider Fig. 10 which is taken with modification and extension from reference 47.<sup>27</sup> The conditions far upstream and downstream of the wave are shown. Characteristic of shock structure involving finite rate chemistry is the aforementioned overshoot of the temperature so that within the wave temperatures exceed  $T_2$ . The flow variables related by the momentum equation on the other hand, i. e., velocity and pressure behave much as in the classical shock wave. Shown in Fig. 10 is the distribution of the total mass fraction of dissociated species, in this

<sup>27</sup> In reference 47 Gaitatzes and Bloom considered a mixture of ideal dissociating gases behaving like oxygen and nitrogen, assumed  $Pr=3/4$  and  $Le=1$  for all species, neglected diffusion in the species conservation equation; and assumed thermodynamic equilibrium. Integration was started at conditions corresponding to  $-\infty$ , but at a finite value of  $x$ .

case 0 and N; clearly, an analysis based on the von Neumann-Doring-Zeldovitch model (cf. reference 48) of a detonation point, i. e., on a shock wave without chemical reaction followed in the downstream direction by a region of chemical reaction appears to be valid according to the assumptions of this analysis. More realistic descriptions of the transport phenomena may alter this conclusion.

The entropy distribution in the wave has been computed from Eq. (62) employing the temperature, pressure and composition profiles given by reference 47 and is shown in Fig. 10 in terms of  $(S-S_1)/R_0$ . It will be noted that the relatively simple entropy distributions arising in classical shock wave structure no longer arise; this is undoubtedly due to the interplay between heat conduction and chemical kinetics in this more general case. In the initial portion of the wave structure leading to a plateau in the entropy the effect of heat conduction predominates so that the simple behavior of the classical shock wave begins to appear. However, in the more downstream portions of the wave, chemical reaction, i. e., dissociation, takes place and leads to further increases in entropy. A slight maximum in the entropy occurs at  $\xi \approx 4$ , roughly, but no conclusion as to the significance or generality of this result can at present be drawn.<sup>28</sup>

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<sup>28</sup> After completion of this manuscript, a survey of the problems connected by shock structure by Talbot<sup>57</sup> appeared.

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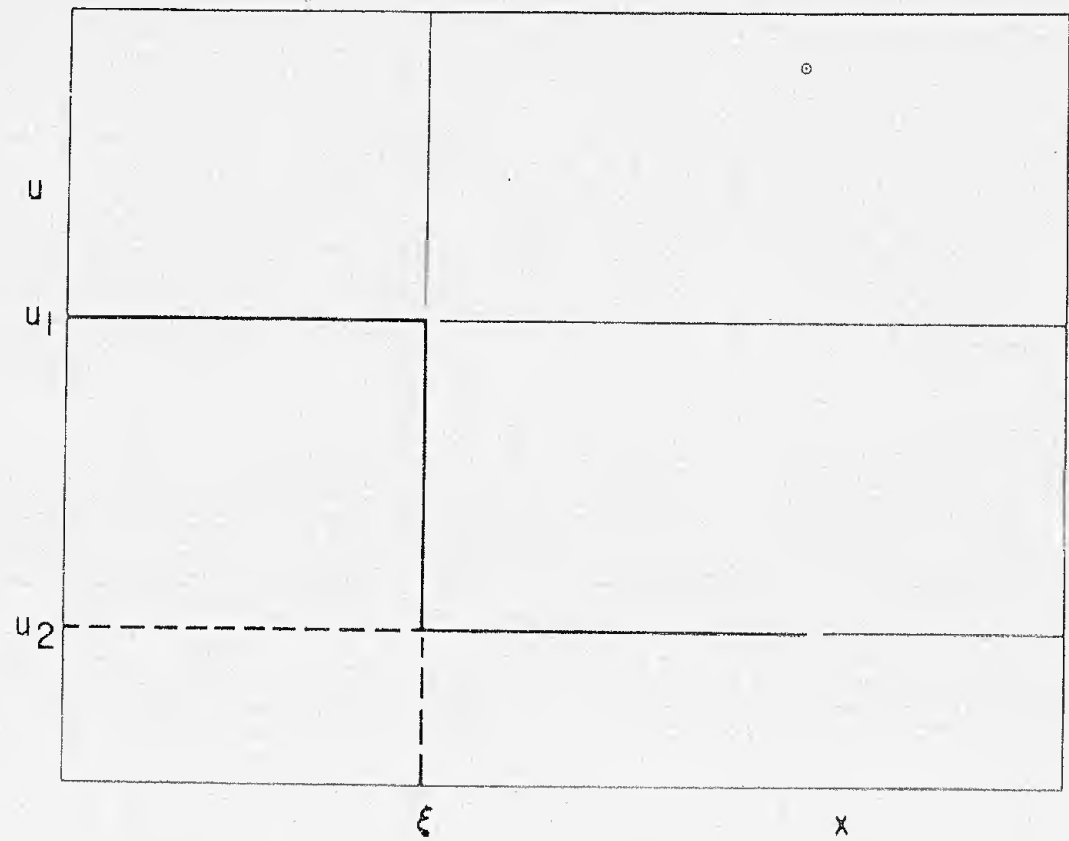


FIG. 1. VELOCITY DISTRIBUTION FOR A DISCONTINUOUS SHOCK WAVE:  $u = 0, k = 0$ .

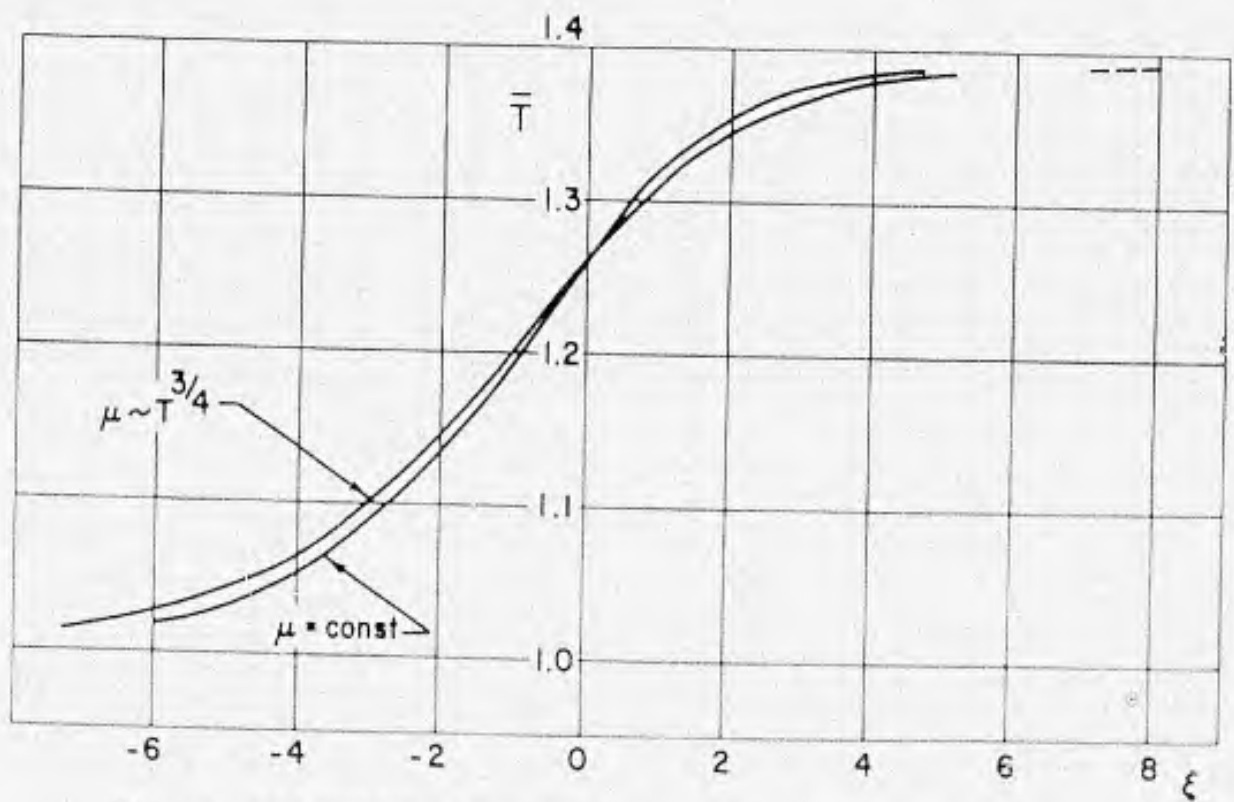
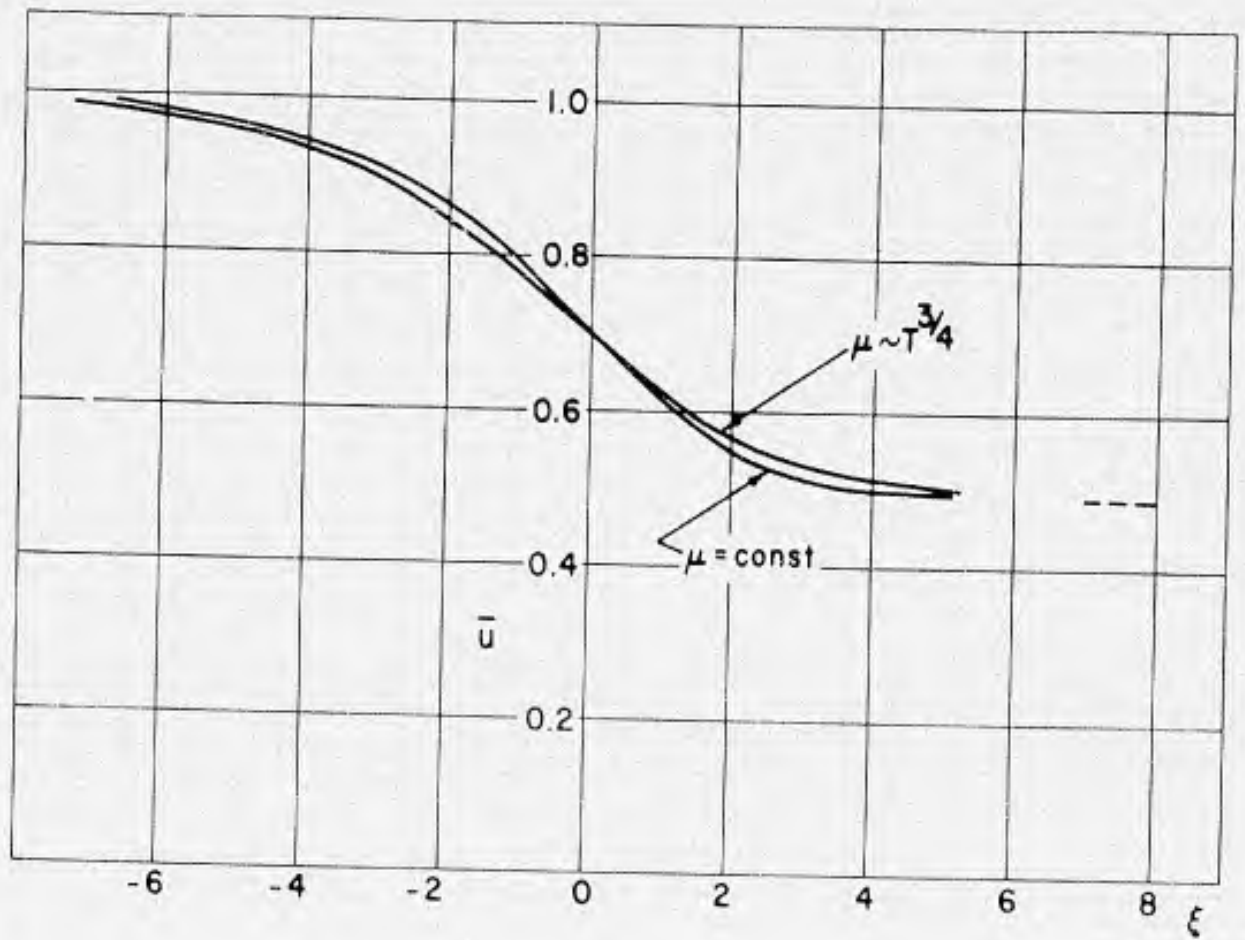


FIG. 2. VELOCITY AND TEMPERATURE DISTRIBUTIONS FOR  $Pr = 3/4$ ,  $M_\infty = 1.6$ ,  $\nu = 1.4$ .

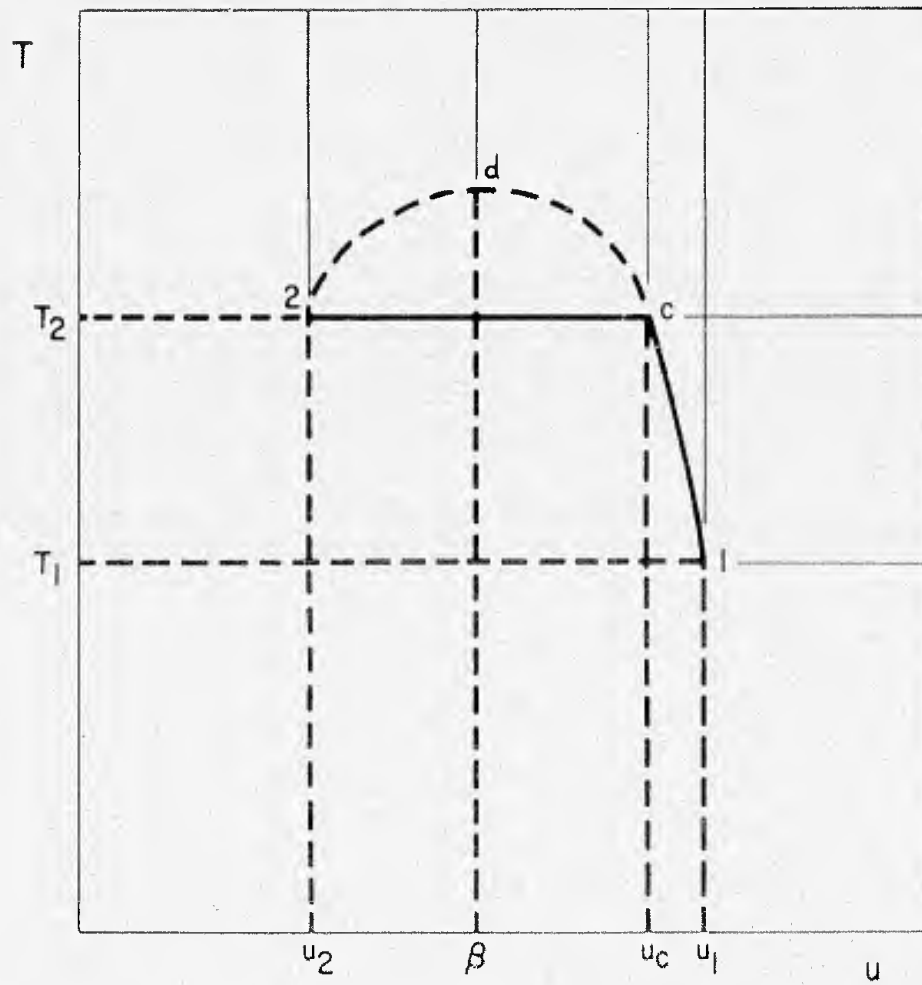


FIG. 3. TEMPERATURE VERSUS  $u$  FOR  $u = 0$ ,  
 $M_1^{\nu} > (3\nu - 1)/[\nu(3 - \nu)]$ .

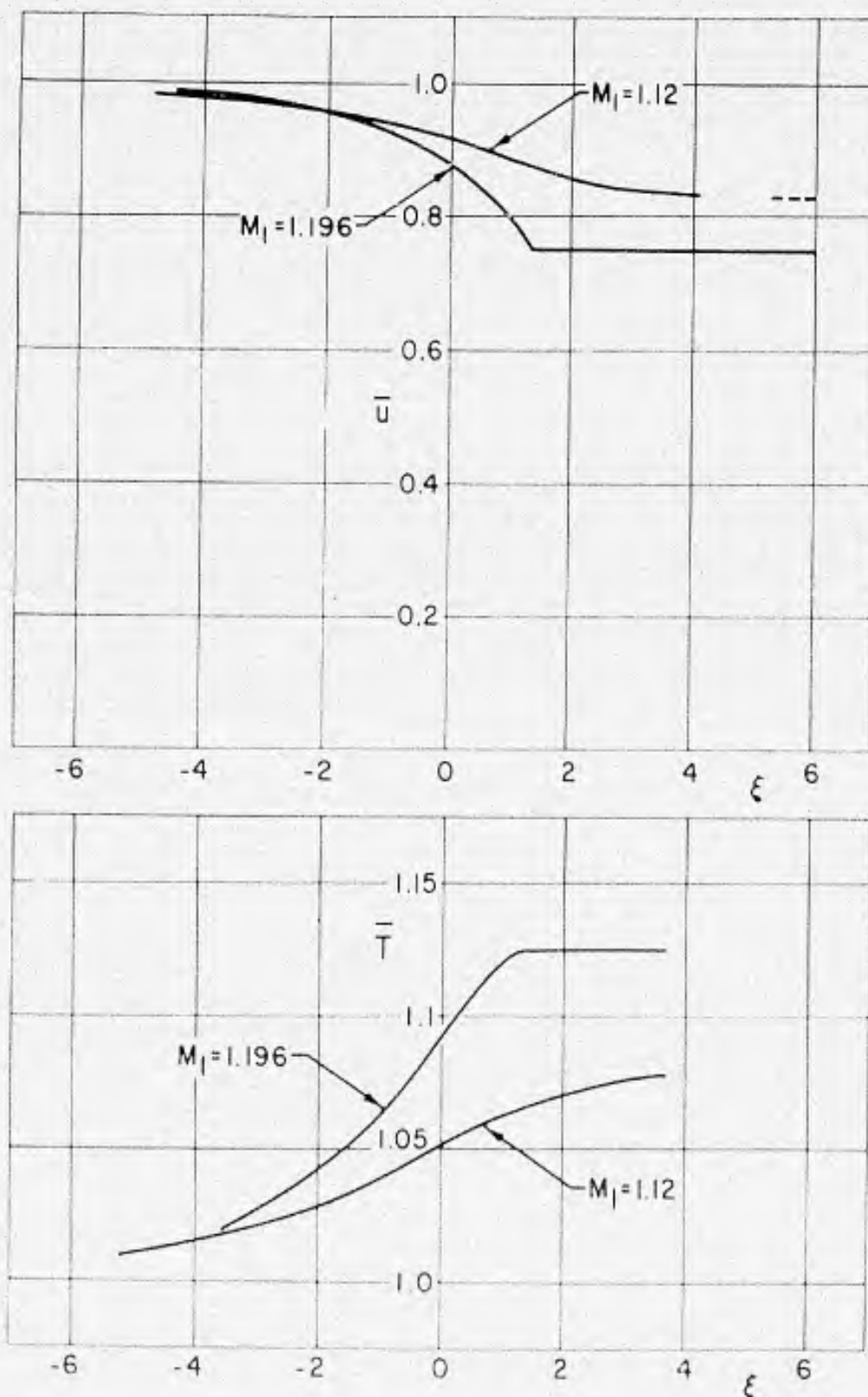


FIG. 4. VELOCITY AND TEMPERATURE DISTRIBUTIONS FOR  $\mu = 0$ ,  $k = \text{CONSTANT}$ ,  $\gamma = 1.4$ ; COMPLETELY CONTINUOUS CASE ( $M_1 \leq 1.196$ ).

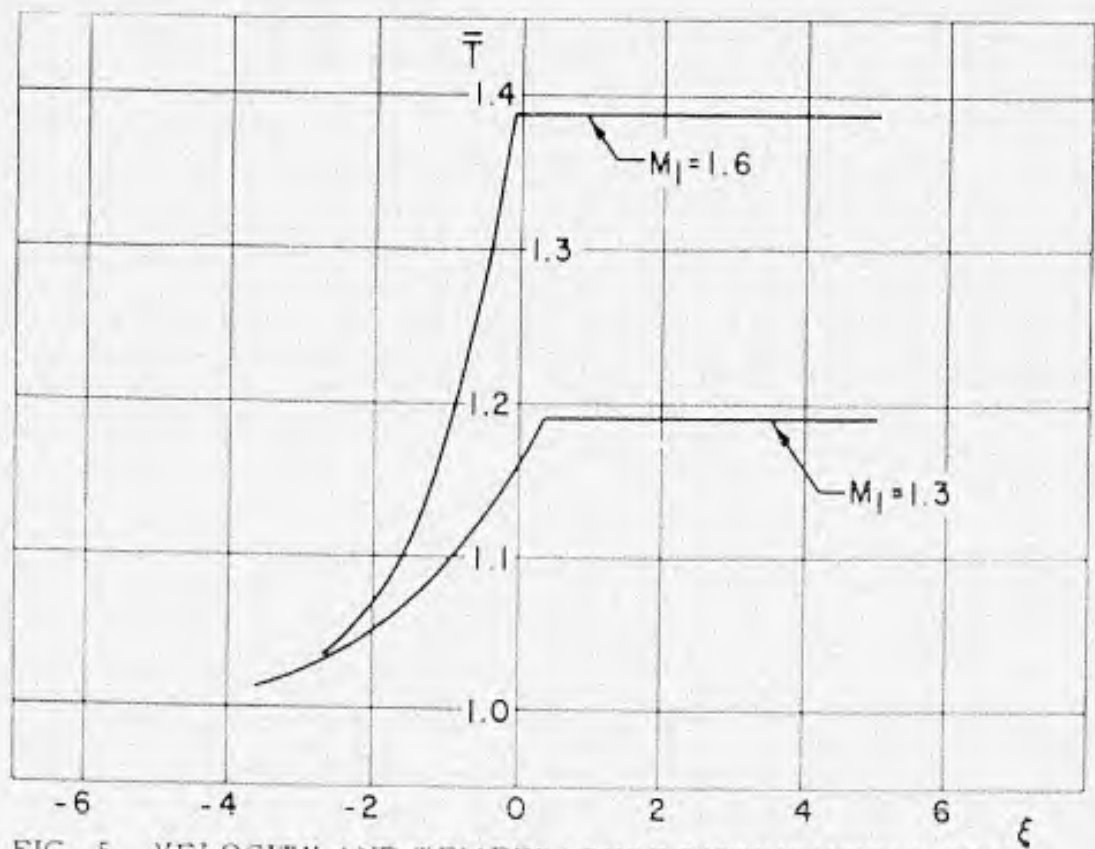
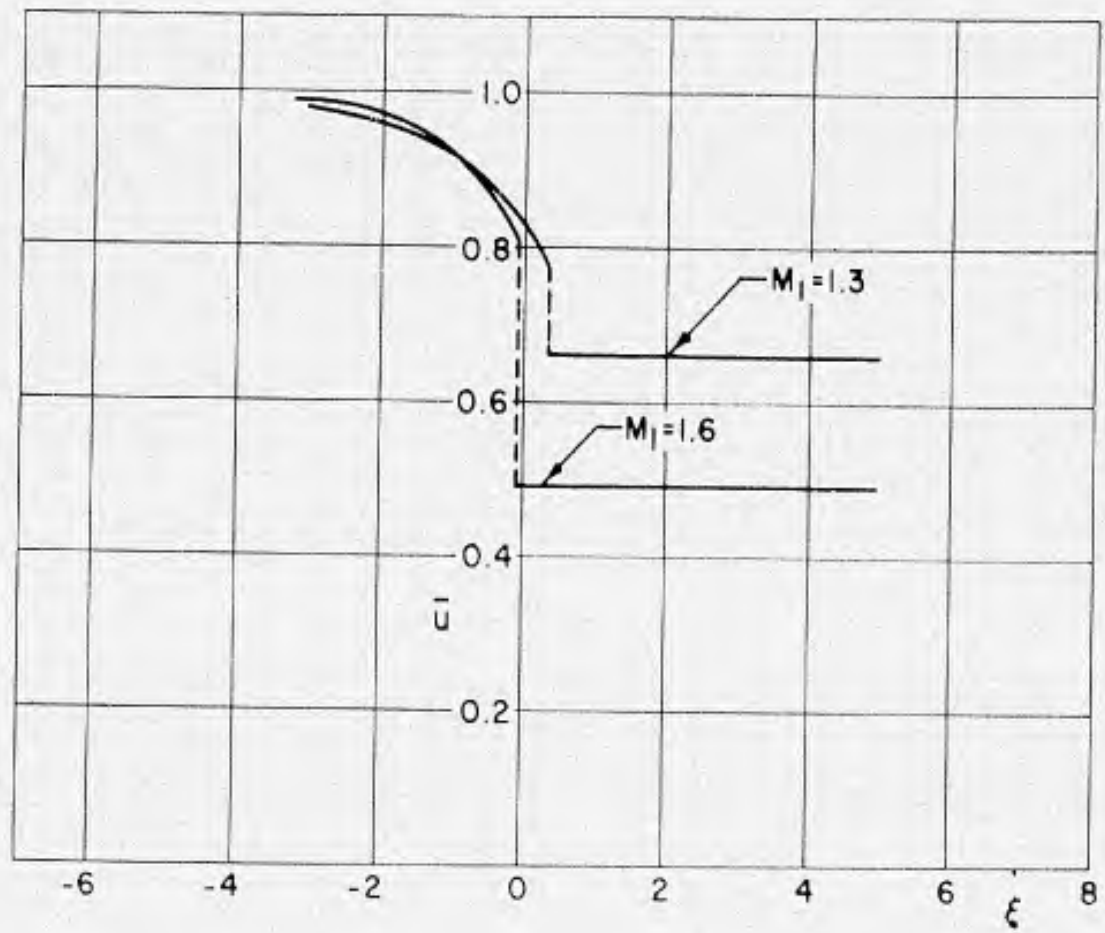


FIG. 5. VELOCITY AND TEMPERATURE DISTRIBUTIONS FOR  $\bar{u} = 0$ ,  $k = \text{CONSTANT}$ ,  $\gamma = 1.4$ ; DISCONTINUOUS CASE ( $M_1 > 1.196$ ).

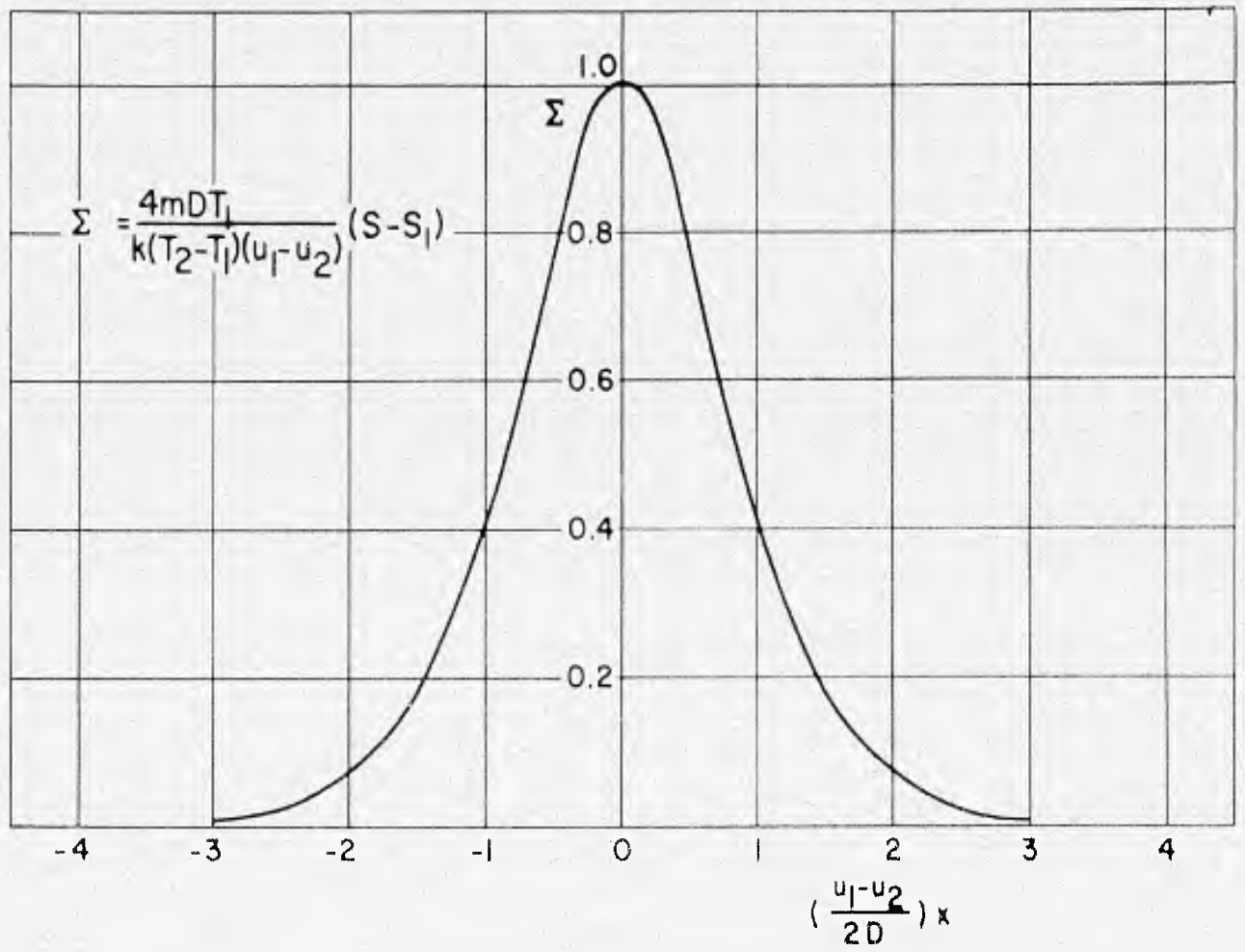


FIG. 6. ENTROPY DISTRIBUTION FOR EXTREMELY WEAK SHOCK WAVES.

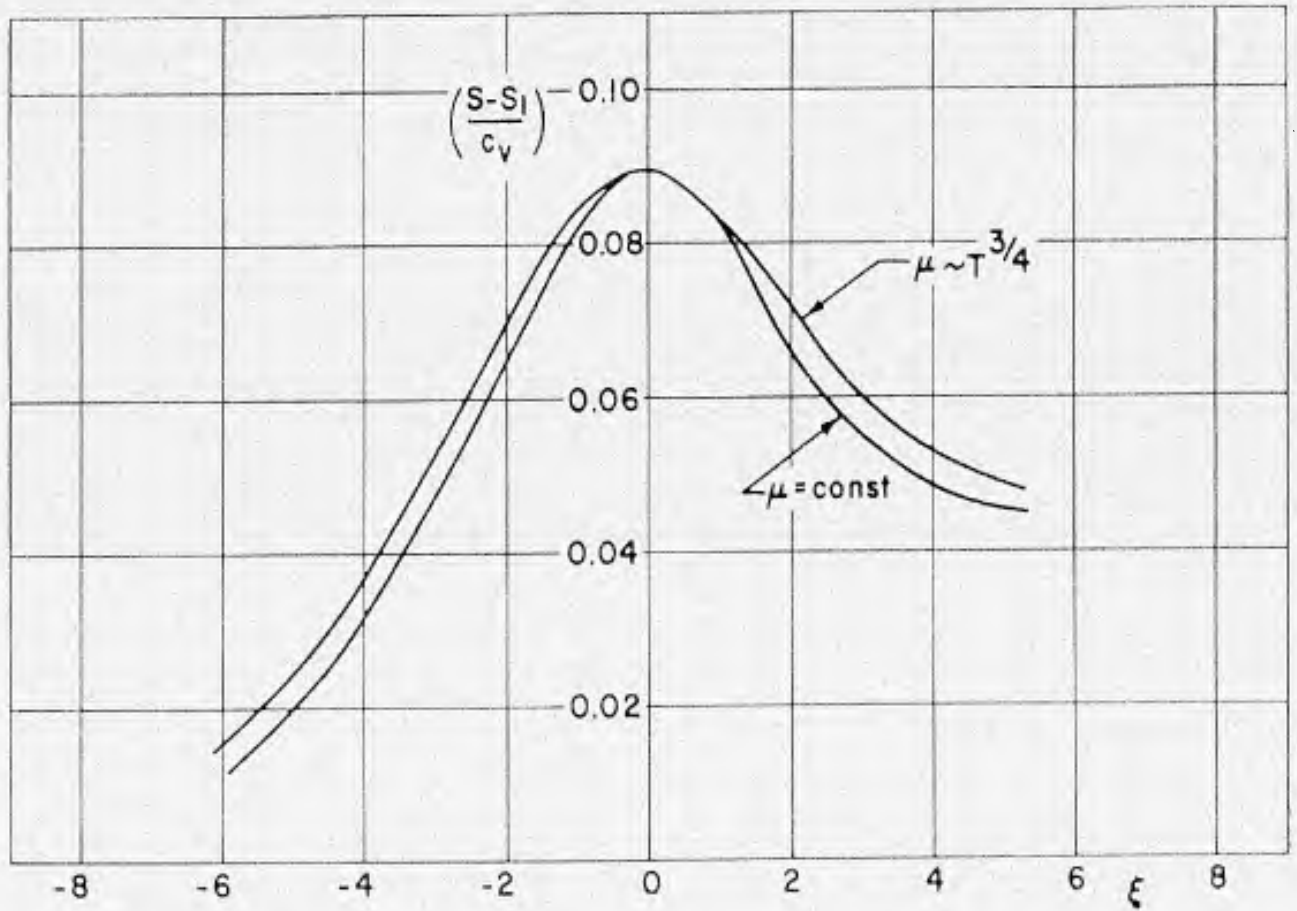


FIG. 7. ENTROPY DISTRIBUTION FOR  $Pr = 3/4$ ,  $M_1 = 1.6$ ,  $\nu = 1.4$ .

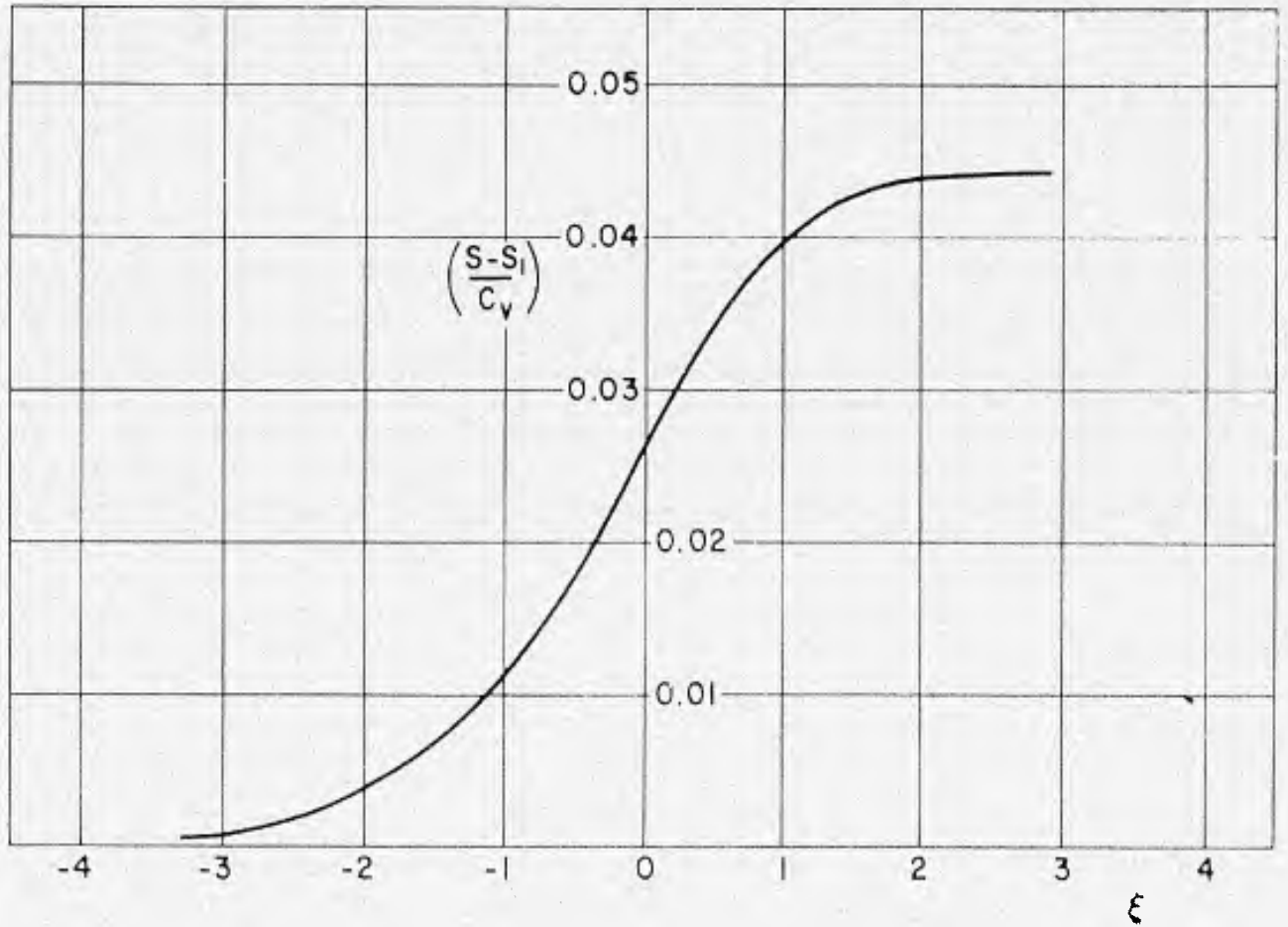


FIG. 8. ENTROPY DISTRIBUTION FOR  $\mu = \text{CONSTANT}$ ,  $k = 0$ ,  $M_1 = 1.6$ ,  $\nu = 1.4$ .

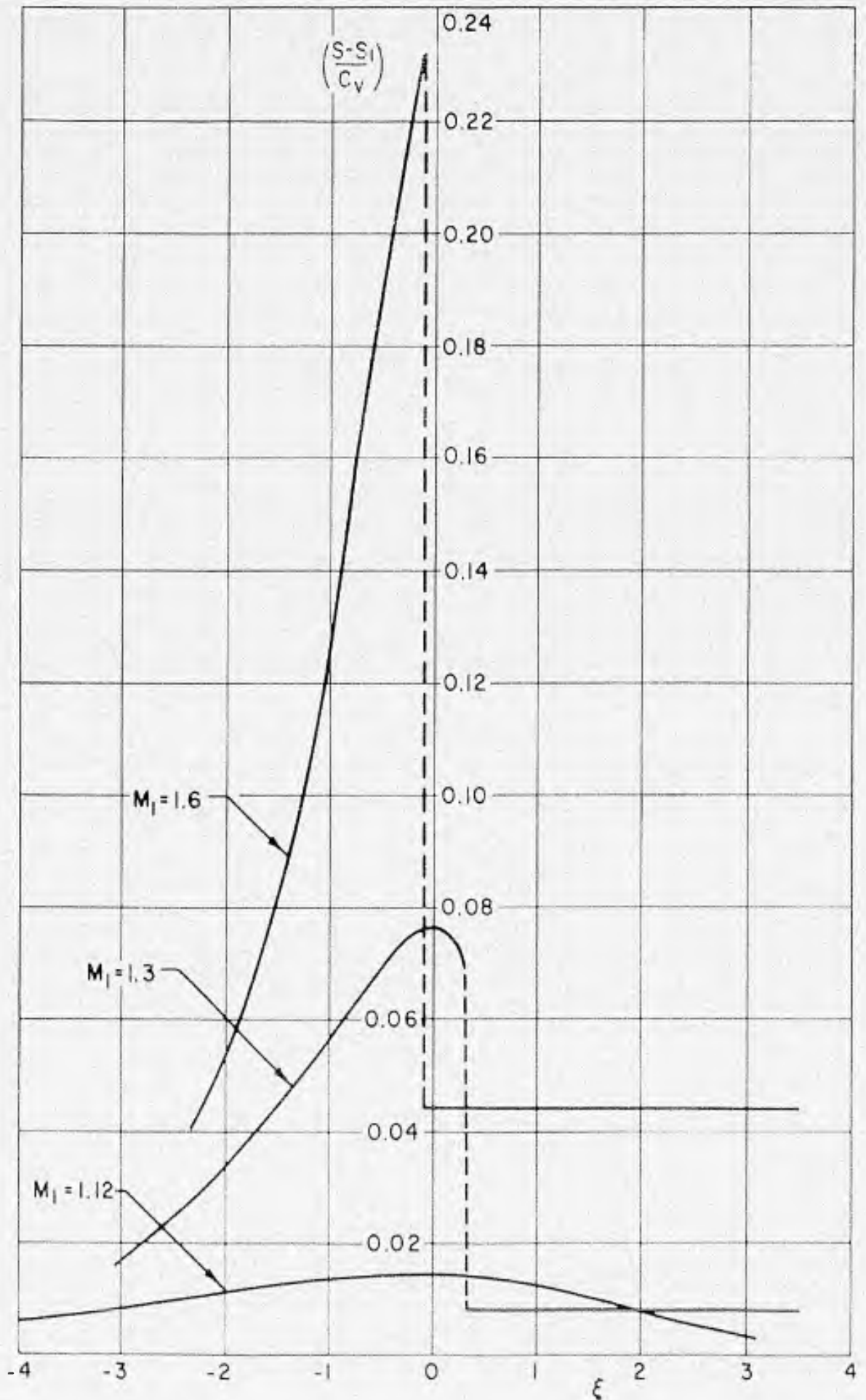


FIG. 9. ENTROPY DISTRIBUTION FOR  $u=0$ ,  $k = \text{CONSTANT}$ ,  $\gamma = 1.4$ .

## UPSTREAM CONDITIONS

$$T_\infty = 449^\circ\text{R}$$

$$\rho_\infty = 0.472 \text{ psf}$$

$$M_\infty = 24$$

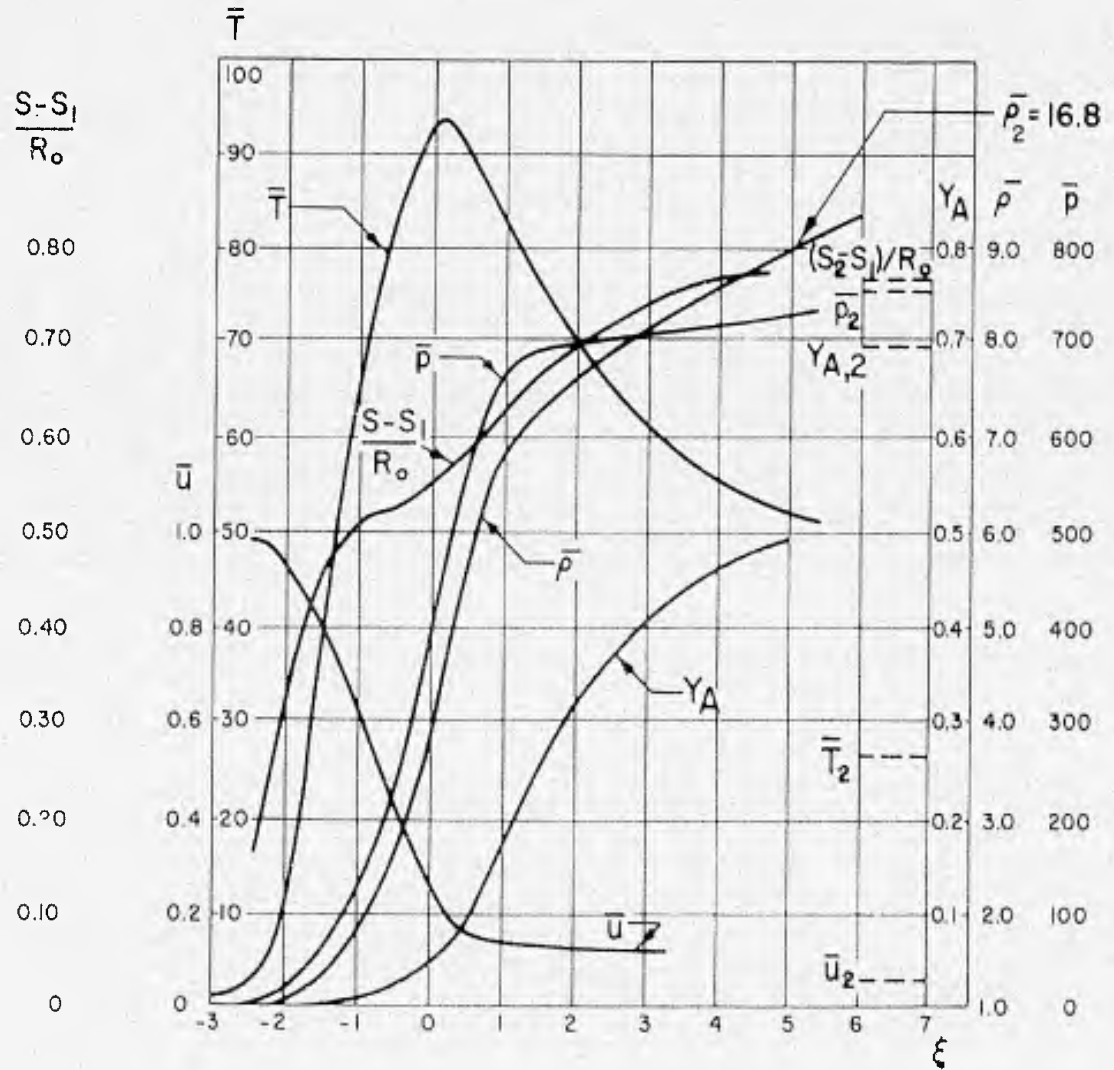


FIG. 10. TYPICAL VARIATION OF FLOW PROPERTIES ACROSS A NORMAL SHOCK WAVE IN THE PRESENCE OF RATE DISSOCIATION. (From Reference 47 with Modification and Addition)

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12. Summary: A unified mathematical account is given of the available knowledge, together with additional new results, of the entropy distribution through a normal shock wave. The most notable feature of this distribution is the fact that as long as heat conductivity is present the entropy will first increase within the shock until it reaches a maximum value at a certain point inside of the shock, and then diminishes to its final value behind the shock. A physical discussion of the results is given in addition to a review of the phenomena not usually included in the analysis of shock wave structure but which enter when the strength of the shock wave is sufficiently great so that the chemical reactions take place.

A systematic review of classical shock wave structure according to the Navier-Stokes equations is included here together with a discussion of the physical validity of these equations. The structure of, and the entropy distribution within weak shock waves in general, and shock waves of arbitrary strength with Prandtl numbers of 0,  $3/4$  and  $\infty$  are analyzed in detail, together with qualitative results for shock waves in general. The case of a shock wave in a fluid with heat conduction but without viscosity, affords an example of a system within which a discontinuous change of state to a lower entropy occurs.