

tion in electromagnetic theory, where one can "disguise" a retarded Lienard-Wiechert potential in such a manner that no one will recognize it by its odd terms; i.e., one can carry out a gauge transformation that gets rid of the odd terms. Nevertheless, this solution leads to a net loss of energy in the system.

The difference between electromagnetic and gravitational theory, however, is that the motion of the sources of the electromagnetic field is completely arbitrary. Therefore, there is no objection against introducing singular terms in the Lienard-Wiechert solution, so long as Maxwell's equations are satisfied. In the gravitational case, however, the motion of the sources is contained in the field equations—at least as long as one deals with a system which is only subject to its own

gravitational field. Thus, when talking about possible solutions of Einstein's field equations, one has to observe the prescriptions of the EIH method as well. The latter stands or falls with the assumption that no arbitrary singularities be introduced at higher stages of the method than the first one. Therefore, "disguised" retarded potentials have to be excluded.

Thus, it should be kept in mind that neither the question of the existence of gravitational waves as possible solutions of Einstein's field equations under the assumption of weird sources, nor the secular behavior of a double star, is discussed here. But we do state that there are no physically different solutions than the EIH one if a system of masses subject to their own gravitational field is considered.

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The Solution of the Boltzmann Equation for a Shock Wave

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It is pointed out that the distribution of molecular velocities in a strong shock wave in a gas is bimodal. Assuming the distribution function to consist of a sum of two Maxwellian terms with temperatures and mean velocities corresponding to the subsonic and supersonic streams, it is found that the space distribution, as determined by the solution of a transport equation, is appropriate to describe a shock wave. Comparison of the solutions of two different transport equations shows that the assumed distribution changes relatively slowly with time and so is an approximate stationary solution of the Boltzmann equation for strong shocks. The shock thickness found is considerably greater than that given by previous theories. The nominal thermal conduction coefficient is negative in the after part of the shock.

I. INTRODUCTION

THE calculation of the thickness of a shock wave in a gas, and of the distribution of density and velocity within it, is an interesting and challenging problem because of the failure of all standard methods of attack. In treatments of this problem by the equations of fluid mechanics, it was early recognized¹⁻³ that the effect of viscosity and of heat conduction must be taken into account. Solutions of the Navier-Stokes equation for a special case were obtained by Becker,⁴ who treated the coefficients of viscosity and of thermal conduction as constants. This solution was improved by Thomas,⁵ who allowed for the temperature variation of these quantities. The thickness calculated for strong shock waves by the Becker and Thomas theories are very different, and they show the importance of correct estimation of the dissipative effects in a shock wave. At the same time, the thickness obtained even by the Thomas theory is of the order of only a few mean free

paths. This throws doubt on the validity of the Navier-Stokes equations in a shock wave, for, according to the kinetic theory, these equations are only valid if the physical quantities defining the state of the gas change only by a small fractional amount in the distance of a mean free path.

In the kinetic theory of gases, the equations of fluid flow are obtained by solving the Boltzmann equation for the space and velocity distribution of the molecules by the Enskog-Chapman (E-C) method. This is a series solution for the distribution function, in which the expansion parameter is effectively $l/\Delta x$, where l is the mean free path and Δx the distance in which the distribution function changes by an appreciable fraction of itself.⁶ The first, or zero-order terms give the equations of flow of a frictionless fluid, the first-order terms give the Navier-Stokes equation, and the second-order terms the so-called Burnett equation.⁷ Thomas⁵ made some estimate of the effect of the Burnett terms, but since the value of $l/\Delta x$ for a shock wave indicated by

¹ W. V. M. Rankine, *Trans. Roy. Soc. (London)* **160**, 277 (1870).

² Lord Raleigh, *Proc. Roy. Soc. (London)* **A84**, 247 (1910).

³ G. I. Taylor, *Proc. Roy. Soc. (London)* **A84**, 371 (1910).

⁴ R. Becker, *Z. Physik* **8**, 321 (1923).

⁵ L. H. Thomas, *J. Chem. Phys.* **12**, 449 (1944).

⁶ For an exposition of this theory, see, for instance, Chapman and Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Teddington, England, 1939).

⁷ D. Burnett, *Proc. Math. Soc. (London)* **40**, 382 (1935).

the Thomas theory is not small, it is doubtful whether the whole E-C theory is applicable to a shock wave, as pointed out by Thomas and by Burnett himself. This question has apparently been settled by Wang-Chang,⁸ who made a thoroughgoing treatment of the shock-wave problem on the Enskog-Chapman theory, taking into account the effect of the third-order terms in the distribution function. She shows that the E-C theory yields expressions for the velocity distribution function in a shock wave and for its reciprocal thickness, which are series in powers of $M-1$, where M is the Mach number, and that these series converge so slowly that it is doubtful whether they have any validity unless N is only very slightly greater than 1, perhaps about 1.2. We must therefore conclude that the whole E-C theory is inapplicable to strong shocks.

In the E-C theory, the distribution function is represented as a "skewed" maxwellian one, the function having only one strong maximum. Now, in a strong shock wave, whose thickness is only a few mean free paths, we can expect that a considerable number of the maxwellian molecules of the bounding supersonic and subsonic streams penetrate into the center of the shock. This suggests that what characterizes the velocity distribution in a strong shock is the existence of two maxima of comparable magnitudes, i.e., that the distribution is bimodal in the sense of the theory of statistics. To represent such a distribution, a series of monocentric orthogonal functions such as is used in the E-C theory is inappropriate, since, for instance, the series of Sonine polynomials representing a bimodal sum of two maxwellian terms is only asymptotically convergent, as can easily be verified. To use orthogonal function theory, it would seem to be necessary to define and employ orthogonal functions of a two center variety, analogous to the molecular orbitals of quantum theory.

Instead of this, an approximate solution of the Boltzmann equation for a strong shock is here obtained by a method which can be regarded as the first step in an iterative scheme. For the initial solution, the distribution function is assumed to be the sum of two maxwellian terms with different temperatures and mean velocities but with unassigned space densities. The densities are obtained from the solution of a transport equation for u^n , where n is an integer and u is the component of molecular velocity in the stream direction. This choice is made for mathematical convenience. The calculations are carried out for $n=2$ and $n=3$. Comparison of the results gives some indication of the adequacy of the assumed distribution function. The agreement is not too close, the difference between shock-wave thickness calculated from the two cases amounting to 5 percent to 25 percent, depending on the Mach number. Nevertheless, the discrepancy for strong shocks is far less than that between the Becker and Thomas formulas. One

can expect, perhaps, that for M greater than about 2, the present solution gives a better picture of conditions in a shock wave than any of the hydrodynamical theories. On the other hand, while the solution makes the reciprocal of the shock thickness proportional to $M-1$ for $M-1$ small, as found by existing theories, the constant of proportionality is wrong. Thus, the present solution stands in need of correction for weak shocks.

The thicknesses found are considerably greater than those predicted by the Thomas theory. The thickness approaches a limit for infinite Mach number, but this limit is about twice as great as that given by the Thomas formula. It is interesting that previous treatments, as they improved their basic assumptions, have successively given increasing estimates for shock-wave thickness and so probably still err in defect. Probably the thickness given by the present treatment errs in excess and so provides an upper limit to the thickness; for the velocity distribution function used represents about the maximum in difference from "quasi-equilibrium" types of distribution, such as are assumed in the E-C theory underlying hydrodynamical treatments.

Since the space density, mean velocity, and all other macroscopic quantities are obtained directly from the distribution function, the solution involves only the Mach number and collision cross sections derivable from the intermolecular laws of force. It circumvents any use of fluid flow equations, or of the concepts of temperature, viscosity, and thermal conduction. It is evident *a priori* that these latter quantities here have only a nominal significance, for, because of the bimodal distribution, averages over the distribution lose their physical importance as defining the flow. For instance, very few molecules have the average velocity, few have a random component of velocity corresponding to the "temperature," and so on. Nevertheless, temperature, coefficient of heat conduction, etc. are still formally definable, and it is interesting to examine how they behave in the present model of a shock wave. It turns out that the heat flow vector is constant in direction throughout the shock, being always directed from the subsonic to the supersonic stream as expected. But for M greater than about 2, the "temperature" reaches a maximum within the shock, so that the gradient changes sign. Thus, the nominal thermal conduction coefficient is actually negative in the after part of the shock. Since the calculated thermal conduction coefficient is a second-order quantity sensitive to small errors in the assumed velocity distribution, too much significance cannot be given to the quantitative aspects of these results. Qualitatively, however, we can give them some significance, and they illustrate drastically the reason for failure of treatments of the shock-wave problem based on concepts of macroscopic fluid flow.

The calculations can be interpreted in a different way, as determining the time rate of change of an initially given distribution. From the time-dependent

⁸ C. S. Wang-Chang, *On the Theory of Thickness of Weak Shock Waves*, University of Michigan, Dept. of Engineering Report UMH-3-F (APL/JHU CM-503), August 19, 1948 (unpublished).

transport equations for w^2 and w^3 , one can calculate the life (i.e., the time for e -fold change) of the assumed velocity distribution considered as established initially. This life turns out to be of the order of ten to a hundred times the mean free time between molecular collisions, depending on the Mach number. Since, for an arbitrary initial distribution, the life, in general, would be of the order of the mean free time itself, the assumed distribution is something of an approximation to a steady-state solution.

It is to be noted that, for polyatomic gases, the treatment of the shock-wave problem by the ordinary Boltzmann equation, as here, is only an approximation due to relaxation effects. In a strong shock we must expect lack of equipartition of energy between translation and vibrational modes. An accurate treatment of this effect would require, at the same time, the consideration of the effect of the internal degrees of freedom in modifying the laws of collision. To the extent that laws of collisions between spheres are adequate, a treatment like the present one takes some account of relaxation effects by assuming the ratio of specific heats γ to have a value greater than the normal one. A comparison of the theory with experimental results would determine the effective γ and so permit an estimate of the importance of relaxation effects. The present theory is scarcely accurate enough to make such a comparison very significant, but it does give a dependence of shock-wave thickness on γ different from that given by the Thomas theory, and may be closer to the facts for strong shocks.

Finally, the concept of a double distribution, here used for a shock wave, may be appropriate in other cases, such as those of flame fronts, detonation fronts, and in the analysis of the interaction between a boundary layer and a shock front. Physically, the picture given is that of a mixture of two gases of different temperatures and mass motions. The Boltzmann equation describes the interaction between these two components and plays the role of an equation of chemical reaction. The reaction is a "bimolecular" one, corresponding to the fact that linearized solutions of the Boltzmann equation do not apply here and that its essentially quadratic character must be taken into account. In trying to set up such a theory, for instance for the two dimensional case applicable to analysis of boundary layer-shock-wave interaction, we would have eight variables to deal with for each of the two gas components; namely, the molecular density, temperature, and two space components of mass velocity. It would be natural to assume that in each volume element the directions of the mass velocities of the two gas components lay in the same line to a first approximation. As will be seen in the following, this provides two equations of a Rankins-Hugoniot character, relating the mass velocities and temperatures, and reducing the number of independent variables to six. The transport equation for mass, momentum, and energy would

provide four more equations, linear in the space densities, and there would be left two more relations to be obtained from the Boltzmann equation, quadratic in the space densities, which might be taken to be two more transport equations for judiciously selected quantities. Such an analysis naturally would be complicated, but it would be required if the transition from boundary layer to shock wave is only a few mean free paths in thickness, which may well be the case.

III. THE TRANSPORT EQUATION

If \mathbf{c} is the vector velocity of a molecule, u its x -component, t the time, and $f(x, \mathbf{c})$ the distribution function, the one-dimensional transport equation for an arbitrary $\Phi(\mathbf{c})$ is

$$\frac{\partial}{\partial t} \int \Phi f d\mathbf{c} + \frac{\partial}{\partial x} \int u \Phi f d\mathbf{c} = \int \int \int (\Phi' - \Phi) f f_1 g d\Omega d\mathbf{c}_1 d\mathbf{c}, \quad (1)$$

where g is the magnitude of the relative velocity \mathbf{g} of a colliding pair:

$$\mathbf{g} = \mathbf{c}_1 - \mathbf{c}. \quad (2)$$

Also, f_1 means $f(\mathbf{c}_1)$, and Φ' means $\Phi(\mathbf{c}')$, where \mathbf{c}' is the velocity of the first molecule after collision; $d\Omega$ is a differential cross section.⁹ We now assume f to be of the form

$$f = f_\alpha + f_\beta, \quad (3)$$

with

$$f_\alpha = n_\alpha(x) (m/2\pi k T_\alpha)^{3/2} \exp\{-(m/2k T_\alpha)(\mathbf{c} - i u_\alpha)^2\}, \quad (4)$$

and similarly for f_β with α replaced by β throughout. Here i is a unit vector in the x direction; m , the mass of a molecule; and k , Boltzmann's constant. The parameters $T_\alpha, c_\alpha, T_\beta, c_\beta$ are assumed independent of x and t . Substitution of Eqs. (3) and (4) in Eq. (1) gives an equation of the form

$$\frac{\partial}{\partial t} \int \Phi f d\mathbf{c} + \frac{\partial}{\partial x} \int u \Phi f_\alpha d\mathbf{c} + \frac{\partial}{\partial x} \int u \Phi f_\beta d\mathbf{c} = I_{\alpha\alpha} + I_{\alpha\beta} + I_{\beta\alpha} + I_{\beta\beta}, \quad (5)$$

where

$$I_{\alpha\beta} = \int \int \int (\Phi' - \Phi) f_\alpha f_\beta g d\Omega d\mathbf{c}_1 d\mathbf{c}. \quad (6)$$

If in Eq. (6) we interchange \mathbf{c}_1 and \mathbf{c} (which does not change the value of the integral), and also interchange α and β , throughout, the integral is restored to its original form, except that \mathbf{c}_1 and \mathbf{c} must be interchanged in $\Phi' - \Phi$. Thus we get $I_{\beta\alpha}$ by effecting the last change alone in the integral in Eq. (6). Also, since f_α and f_β are Maxwellian,

$$f'_\alpha f_{\alpha 1} = f_\alpha f_{\alpha 1}, \quad f'_\beta f_{\beta 1} = f_\beta f_{\beta 1},$$

⁹ The notation conforms generally to that of reference 6.

and from this, it follows¹⁰ that

$$I_{\alpha\alpha} = I_{\beta\beta} = 0. \tag{6a}$$

First take Φ in turn equal successively to the collisional invariants 1, u , and $c^2 + (2/m)E_i$, where E_i is the internal energy of a molecule. For these, the right-hand side of Eq. (5) vanishes; and for the steady state $\partial f/\partial t = 0$, we obtain the following equations expressing the conservation of matter, momentum, and energy:

$$\begin{aligned} n_\alpha u_\alpha + n_\beta u_\beta &= R, \\ n_\alpha(u_\alpha^2 + c_\alpha^2) + n_\beta(u_\beta^2 + c_\beta^2) &= P, \\ n_\alpha u_\alpha(u_\alpha + ac_\alpha^2) + n_\beta u_\beta(u_\beta^2 + ac_\beta^2) &= Q, \end{aligned} \tag{7}$$

in which R, P, Q are constants of the flow,

$$c_\alpha^2 = kT_\alpha/m, \quad c_\beta^2 = kT_\beta/m, \tag{8}$$

$$a = N_i + 5 = 2\gamma/(\gamma - 1), \tag{9}$$

where N_i is the number of internal degrees of freedom, and γ is the ratio of specific heats. The last of Eq. (7) assumes equipartition of energy between internal and translational degrees of freedom. In accordance with the introductory remarks, we can expect a for polyatomic gases to have an effective value less than the normal one because of relaxation effects.

In order that Eq. (7) be consistent when regarded as determining n_α, n_β , we must have

$$(u_\alpha^2 + c_\alpha^2)/u_\alpha = (u_\beta^2 + c_\beta^2)/u_\beta, \quad u_\alpha^2 + ac_\alpha^2 = u_\beta^2 + ac_\beta^2.$$

These equations, when solved for u_β and c_β , give

$$\begin{aligned} u_\beta &= [u_\alpha^2 + ac_\alpha^2]/[(a-1)u_\alpha], \\ c_\beta^2 &= [u_\alpha^2 + ac_\alpha^2]/[(a-1)^2u_\alpha^2 - (a-2)u_\alpha^2 - c_\alpha^2]. \end{aligned} \tag{10}$$

Equations (10), together with the first of Eqs. (7), are equivalent to the Rankine-Hugoniot equations giving the density, velocity, and temperature of the subsonic stream in terms of those of the supersonic stream.¹¹ Thus, only two parameters in Eq. (3) are independent.

To determine the space densities $n_\alpha(x), n_\beta(x)$, we need a choice which does not make the right-hand side of Eq. (5) vanish. The simplest choice is $\Phi = u^n$, for which the integrations can be carried out with relative ease. Let \mathbf{K} be the change in the velocity of the first molecule due to the collision, so that

$$\mathbf{K} = \mathbf{c}' - \mathbf{c} = \mathbf{c}_1 - \mathbf{c}_1'.$$

Let ψ be the angle between \mathbf{g} and \mathbf{K} , θ the angle between \mathbf{g} and \mathbf{i} (the x axis), ϵ the angle between the plane of \mathbf{g} and \mathbf{K} , and the plane of \mathbf{g} and \mathbf{i} . Then from the laws of collision,

$$\begin{aligned} u' - u &= K(\cos\theta \cos\psi + \sin\theta \sin\psi \cos\epsilon), \\ u_1 - u &= g \cos\theta, \quad K = g \cos\psi, \end{aligned} \tag{11}$$

¹⁰ See reference 6, pp. 66, 70.

¹¹ It is to be noted, however, that Eqs. (10) are more general than the Rankine-Hugoniot equations, since they must be satisfied at each point within a shock wave, in case $u_\alpha, u_\beta, c_\alpha, c_\beta$ are considered functions of position. Compare remarks in the introduction.

where u', u_1 are the x -components of $\mathbf{c}', \mathbf{c}_1$. Also if $\mathbf{g}' = \mathbf{c}_1' - \mathbf{c}'$ and χ is the angle between \mathbf{g} and \mathbf{g}' , χ is the angle of deflection in the center-of-gravity system and is related to ψ by

$$\psi = \frac{1}{2}(\pi - \chi). \tag{12}$$

Let b be the usual collision parameter, which for elastic spheres of diameter σ is given by

$$b = \sigma \sin\psi. \tag{13}$$

Then, for the $d\Omega$ in Eq. (1) we can write

$$d\Omega = b db d\epsilon. \tag{14}$$

III. THE CASE $\Phi = u^2$

Putting $\Phi = u^2$ in Eq. (6) and using Eqs. (11) and (14), we find

$$\begin{aligned} \int (u'^2 - u^2) d\Omega &= \int_0^\infty \int_0^{2\pi} (u'^2 - u^2) g b db d\epsilon db \\ &= 2\pi \int_0^\infty \{2u(u_1 - u) \cos^2\psi + (u_1 - u)^2 \cos^4\psi \\ &\quad + \frac{1}{2}[g^2 - (u_1 - u)^2] \cos^2\psi \sin^2\psi\} g b db. \end{aligned}$$

By the rule under Eq. (6), the corresponding expression in $I_{\alpha\beta} + I_{\beta\alpha}$ is obtained by interchanging u_1 and u in the above and adding the result to the original expression. Doing this, we get

$$\begin{aligned} 2\pi \int_0^\infty [g^2 - 3(u_1 - u)^2] \cos^2\psi \sin^2\psi g b db \\ = \frac{1}{2}\pi\psi_{11}^{(2)}(g)[g^2 - 3(u_1 - u)^2], \end{aligned} \tag{15}$$

where χ is given by 12 and

$$\phi_{11}^{(1)}(g) = \int_0^\infty (1 - \cos^2\chi) g b db \tag{16}$$

is the elementary cross section defined by Chapman and Cowling.¹² Substitution of Eqs. (4) and (15) in Eq. (6) gives

$$\begin{aligned} I_{\alpha\beta} + I_{\beta\alpha} &= n_\alpha n_\beta (m/2\pi k T_\alpha^{\frac{1}{2}} T_\beta^{\frac{1}{2}})^3 \\ &\times \int \int \exp\{- (m/2kT_\alpha)(\mathbf{c} - \mathbf{i}u_\alpha)^2 - (m/2kT_\beta)(\mathbf{c}_1 - \mathbf{i}u_\beta)^2\} \\ &\quad \times \frac{1}{2}\pi\phi_{11}^{(2)}(g)\{g^2 - 3(u_1 - u)^2\} d\mathbf{c}_1 d\mathbf{c}. \end{aligned}$$

Make the transformation

$$\mathbf{c} = \mathbf{i}u_\alpha + \mathbf{F} - \mathbf{G}T_\alpha/(T_\alpha + T_\beta)$$

and

$$\mathbf{c}_1 = \mathbf{i}u_\beta + \mathbf{F} + \mathbf{G}T_\beta/(T_\alpha + T_\beta)$$

and express the new coordinate vectors \mathbf{F}, \mathbf{G} in terms of spherical polar coordinates $F, \theta_F, \phi_F, G, \theta_G, \phi_G$, so that $d\mathbf{c}_1 d\mathbf{c} = F^2 \sin\theta_F d\theta_F d\phi_F dF \cdot G^2 \sin\theta_G d\theta_G d\phi_G dG$. The

¹² See reference 6, p. 157.

integrations with respect to $\theta_F, \phi_F, F, \phi_G$ can then be carried out, with the result

$$n_\alpha n_\beta [m/2k(T_\alpha + T_\beta)]^{3/2} \pi^{1/2} \int \int \exp\{-mG^2/2k(T_\alpha + T_\beta)\} \\ \times \phi_{11}^{(2)}(\{G^2 + 2G(u_\beta - u_\alpha) \cos\theta_G + (u_\beta - u_\alpha)^2\}^{1/2}) \\ \times \{G^2 - 2G(u_\alpha - u_\beta) \cos\theta_G + (u_\beta - u_\alpha)^2 \\ - 3(G \cos\theta_G + u_\beta - u_\alpha)^2\} \sin\theta_G d\theta_G G^2 dG.$$

Introduce the dimensionless quantities $G_0, u_{\alpha\beta}$ defined by

$$G = [(2k/m)(T_\alpha + T_\beta)]^{1/2} G_0, \quad (17)$$

$$u_\alpha - u_\beta = [(2k/m)(T_\alpha + T_\beta)]^{1/2} u_{\alpha\beta}. \quad (18)$$

Also put

$$r = G_0/u_{\alpha\beta} \quad (19)$$

and replace θ_G by a new variable of integration Z given by

$$r^2 - 2r \cos\theta_G + 1 = Z^2. \quad (20)$$

The limits of integration for Z are $|1+r|$ and $|1-r|$, corresponding to $\theta_G = +\pi$ and $\theta_G = 0$, the absolute values occurring because Z is proportional to the relative geometry g of a colliding pair, which is always taken to be a positive quantity. Substitution from Eqs. (17)–(20), in the integral yields an expression for $I_{\alpha\beta} + I_{\beta\alpha}$ of the form

$$I_{\alpha\beta} + I_{\beta\alpha} = n_\alpha n_\beta [(2k/m)(T_\alpha + T_\beta)]^{3/2} \pi^{1/2} \\ \times \int_0^\infty \exp(-G_0^2) H(G_0, u_{\alpha\beta}) G_0^2 dG_0, \quad (21)$$

where

$$H(G_0, u_{\alpha\beta}) = -[(2k/m)(T_\alpha + T_\beta)]^{-1/2} (u_{\alpha\beta}/4r) \\ \times \int_{|1-r|}^{|1+r|} \{3z^4 + 2(1-3r^2)z^2 + 3(1-r^2)^2\} \\ \times \phi_{11}^{(2)}\{u_{\alpha\beta}(2k/m)^{1/2}(T_\alpha + T_\beta)^{1/2}z\} \cdot z dz. \quad (22)$$

The integrations in Eq. (22) can be carried out for any of the laws of intermolecular force for which $\phi_{11}^{(2)}$ has been evaluated. For instance, for elastic spheres of diameter σ ,

$$\phi_{11}^{(2)}(g) = \frac{1}{3} g \sigma^2$$

(see reference 6, p. 197), and we find

$$H(G_0, u_{\alpha\beta}) = H_0(G_0, u_{\alpha\beta}),$$

with

$$H_0(G_0, u_{\alpha\beta}) = -(4/105)\sigma^2 u_{\alpha\beta}^3 (35 + 35r^2 - 7r^4 + r^6), \quad r < 1 \\ = -(4/105)\sigma^2 u_{\alpha\beta}^3 (8r^{-1} + 56r), \quad r > 1 \quad (23)$$

For Sutherland's model of elastic spheres with an attractive field of force, we have (see reference 6, p. 182)

$$\phi_{11}^{(2)}(g) = \frac{1}{3} g \sigma^2 + (\sigma^2/g)(kS/m),$$

where S is Sutherland's constant, which has the dimensions of a temperature. This gives

$$H = H_0 + H_s, \quad (24)$$

where H_0 is given by Eq. (23) and

$$H_s(G_0 u_{\alpha\beta}) = -\frac{2}{15} \frac{\sigma^2 u_{\alpha\beta}}{T_\alpha + T_\beta} (15 - 10r^2 + 3r^4), \quad r < 1 \\ = -\frac{16}{15} \frac{\sigma^2 u_{\alpha\beta}}{T_\alpha + T_\beta} \frac{1}{r}, \quad r > 1 \quad (25)$$

Substituting from Eqs. (24), (23), (25), (19) in Eq. (21) and carrying out the integration, we find, for Sutherland's model,

$$I_{\alpha\beta} + I_{\beta\alpha} = -\frac{1}{3} \pi^{1/2} \sigma^2 n_\alpha n_\beta \left[\frac{2k}{m} (T_\alpha + T_\beta) \right]^{3/2} \\ \times \left[A(u_{\alpha\beta}) + \frac{S}{T_\alpha + T_\beta} A_s(u_{\alpha\beta}) \right], \quad (26)$$

where

$$A(u) = \left(\frac{1}{u} + \frac{1}{u^3} - \frac{3}{4u^5} \right) \exp(-u^2) \\ + \left(2u + \frac{3}{u} - \frac{3}{2u^3} + \frac{3}{4u^5} \right) \operatorname{erf}u, \quad (27)$$

$$A_s(u) = \left(\frac{3}{2} - \frac{9}{4u^2} \right) \exp(-u^2) \\ + \left(3u^2 - 3 + \frac{9}{4u^2} \right) \frac{1}{u} \operatorname{erf}u, \quad (28)$$

with

$$\operatorname{erf}u = \int_0^u \exp(-s^2) ds.$$

In Eq. (5), we put $\partial f/\partial t = 0$, use Eq. (6a), substitute from Eq. (26) in the right-hand side, and evaluate the integrals on the left for f_α, f_β given by Eq. (4). Introducing the notation (8), the result is

$$u_\alpha(u_\alpha^2 + 3c_\alpha^2)(dn_\alpha/dx) + u_\beta(u_\beta^2 + 3c_\beta^2)(dn_\beta/dx) \\ + \frac{1}{3} \pi^{1/2} \sigma^2 (2c_\alpha^2 + 2c_\beta^2)^{3/2} n_\alpha n_\beta \\ \times [A(u_{\alpha\beta}) + S(T_\alpha + T_\beta)^{-1} A_s(u_{\alpha\beta})] = 0. \quad (29)$$

This is a differential equation determining the densities $n_\alpha(x), n_\beta(x)$ for the steady state. We assume the α stream to be the supersonic one and take the direction of flow to be positive. Then u_α, u_β , and $u_{\alpha\beta}$ are all positive. Let $n_0 = n_\alpha(-\infty)$ be the density of the supersonic stream a long way from the shock. The first of Eqs. (7) can then be written

$$n_\alpha u_\alpha + n_\beta u_\beta = n_0 u_\alpha. \quad (30)$$

If M is the Mach number of the supersonic stream, then

TABLE I. Values of B_0 , B_s , and B_1 as functions of the Mach number, for $\gamma=5/3$ and $7/5$.

M	$\gamma=5/3$			$\gamma=7/5$		
	B_0	B_s	B_1	B_0	B_s	B_1
1.0	0	0	0	0	0	0
1.1	0.1204	0.0171	0.0999	0.1122	0.0214	0.0923
1.2	0.2388	0.0568	0.2122	0.2108	0.0477	0.1872
1.3	0.3648	0.0793	0.3163	0.3169	0.0704	0.2835
1.4	0.4640	0.0943	0.4194	0.4196	0.0901	0.3805
1.6	0.6562	0.1202	0.6184	0.6106	0.1211	0.5688
1.8	0.8202	0.1350	0.8040	0.7825	0.1423	0.7575
2.0	0.9583	0.1417	0.9738	0.9346	0.1556	0.9318
2.5	1.2144	0.1381	1.3262	1.2385	0.1646	1.3092
3.0	1.3824	0.1226	1.5872	1.4561	0.1551	1.6028
5.0	1.6758	0.0652	2.1078	1.9586	0.0928	2.2264
10.0	1.8218	0.0195	2.4009	2.1227	0.0297	2.6016
∞	1.8740	0	2.5117	2.2147	0	2.7488

from Eqs. (8) and (9), the fact that u_α is the velocity of the supersonic stream, and the definition of the Mach number, we find that

$$M^2 = [(a-2)/a] \cdot (u_\alpha^2/c_\alpha^2). \tag{31}$$

Using Eqs. (30) and (10) to express n_β , u_β , and c_β in terms of n_α , u_α , and c_α , and using the results to eliminate the first three quantities from Eq. (29), we find that everything remaining can be expressed in terms of the Mach number as given by Eq. (31). Equation (29) is finally reduced to the form

$$dv_\alpha/dx + (B/l)v_\alpha(1-v_\alpha) = 0, \tag{32}$$

where

$$v_\alpha = n_\alpha/n_0, \text{ and } l = \frac{1}{2}\sqrt{2}\pi n_0\sigma^2, \tag{33}$$

so that l is the Maxwell mean free path in the supersonic stream.

$$B = \frac{2}{3(a-3)} \left(\frac{a-2}{\pi a} \right)^{\frac{1}{2}} \times \frac{[aM^4 + 2a(a-2)M^2 - a + 2]^{\frac{1}{2}}}{[M^2 - 1][M^2 + a - 1][aM^2 + a - 2]} \times \left\{ A(u_{\alpha\beta}) + \frac{S/T_\alpha}{1 + T_\beta/T_\alpha} A_s(u_{\alpha\beta}) \right\}, \tag{34}$$

$$u_{\alpha\beta} = [M^2 - 1]^{\frac{1}{2}} \left[\frac{1}{2}a(a-2) \right]^{\frac{1}{2}} \times [aM^4 + 2a(a-2)M^2 - a + 2]^{-\frac{1}{2}}, \tag{35}$$

and

$$T_\beta/T_\alpha = (M^2 + a - 2)(aM^2 - 1)/(a - 1)^2 M^2. \tag{36}$$

The solution of Eq. (32) is

$$v_\alpha = 1/(1 + e^{Bx/l}), \tag{37}$$

where the constant of integration is determined by choosing the origin $x=0$ as the point where $v_\alpha = \frac{1}{2}$. Solving Eq. (30) for n_β , substituting from Eq. (38), and

defining $v_\beta = n_\beta/n_0$, we find

$$v_\beta = (u_\alpha/u_\beta)(1 - v_\alpha) = (u_\alpha/u_\beta)/(1 + e^{-Bx/l}). \tag{38}$$

Here u_α/u_β can be expressed in terms of the Mach number and a . Equations (37) and (38) complete the solution of the problem. It is seen that v_α decreases from 1 at $x = -\infty$ to 0 at $x = +\infty$, while v_β increases from 0 to u_α/u_β . As we proceed from $x = -\infty$ to $x = +\infty$, one density grows at the expense of the other, and it is apparent that the solution is appropriate to represent a shock wave in which f_α is the velocity distribution in the supersonic stream and f_β that in the subsonic stream. The shock-wave thickness is determined by the quantity B defined by Eq. (34), in which the functions $A(u_{\alpha\beta})$, $A_s(u_{\alpha\beta})$ are defined by Eqs. (27) and (28), and $u_{\alpha\beta}$ is defined by Eq. (35), a by Eq. (9).

IV. THE CASE $\Phi = u^3$

The calculations for this case will only be summarized briefly. The integration over all types of collisions give for the contribution to

$$I_{\alpha\beta} + I_{\beta\alpha} \left[\int_0^\infty \int_0^\pi (u'^3 - u^3) g b d\epsilon db \right]_{\alpha\beta+\beta\alpha} = \frac{3}{4}\pi [u_1 + u] [g^2 - 3(u_1 - u)^2] \varphi_{11}^{(2)}(g).$$

From this point on, only the case of elastic spheres will be given. Carrying out the integrations by the same methods as before, we find

$$I_{\alpha\beta} + I_{\beta\alpha} = \frac{1}{2}\pi^{\frac{1}{2}}\sigma^2 n_\alpha n_\beta [(2k/m)(T_\alpha + T_\beta)]^2 \times \int_0^\infty \exp(-G_0^2) K(G_0, u_{\alpha\beta}) G_0^2 dG_0,$$

where

$$K(G_0, u) = -\frac{4}{35} \frac{aM^2 + a - 2}{(a-2)(M^2 - 1)} \{ 35u^4 + 35u^2G_0^2 - 7G_0^4 + G_0^6 u^{-2} + (2/3a)(105u^4G_0^2 + 21u^2G_0^4 + 3G_0^6 - G_0^8 u^{-2}) \}, \quad G_0 < u$$

$$= -\frac{4}{35} \frac{aM^2 + a - 2}{(a-2)(M^2 - 1)} \{ 8u^5G_0^{-1} + 56u^3G_0 - (8/3a)(-u^7G_0^{-1} + 12u^5G_0 + 21u^3G_0^3) \}, \quad G_0 > u.$$

Ultimately, an equation of the same form as Eq. (32) is obtained, with B replaced by B_1 given by

$$B_1 = \frac{4}{35\pi^{\frac{1}{2}}} \frac{a(a-2)(aM^2 + a - 2)}{M^2 + a - 2} (1C)[aM^4 + 2a(a-2)M^2 - a + 2] A_1(u_{\alpha\beta}), \tag{39}$$

$$C = a^2(a^2 - 4a + 1)M^4 + 2a(a-2)(2a^2 - 7a + 3)M^2 + (a-2)^2(a^2 - 6a + 3), \tag{40}$$

$$\begin{aligned}
 A_1(u) = & \frac{35}{2} u^2 \left[1 + \frac{3}{2u^2} - \frac{3}{4u^4} \right. \\
 & \left. - \frac{3}{a} \left(1 + \frac{1}{2u^2} + \frac{1}{4u^4} - \frac{3}{8u^6} \right) \right] \operatorname{erfu} \\
 & + u^3 \left[\frac{1}{2} + \frac{21}{2u^2} + \frac{105}{8u^4} - \frac{1}{a} \left(\frac{105}{4u^2} + \frac{315}{16u^6} \right) \right] \\
 & \times \exp(-u^2). \quad (40)
 \end{aligned}$$

V. RESULTS

The molecular density n at any point in space is given by $n = n_\alpha + n_\beta = (\nu_\alpha + \nu_\beta)n_0$. Substituting from Eqs. (37) and (38), and expressing u_α/u_β in terms of the Mach number by the use of Eqs. (31) and (10), we find

$$\frac{n}{n_0} = \frac{M^2 + a - 2 + M^2(a-1)e^{Bx/l}}{(M^2 + a - 2)(1 + e^{Bx/l})}. \quad (41)$$

The stream velocity \bar{u} is found by averaging u over the distribution, or more directly from the equation of continuity $n\bar{u} = n_0 u_\alpha$. Following the usual practice, we can define the density thickness of the shock wave as equal to $[n(+\infty) - n(-\infty)]/|dn/dx|_{\max}$, and the velocity thickness as $[\bar{u}(-\infty) - \bar{u}(+\infty)]/|d\bar{u}/dx|_{\max}$. Here $|dn/dx|_{\max}$ and $|d\bar{u}/dx|_{\max}$ are, respectively, the maximum absolute value of the density gradient and of the

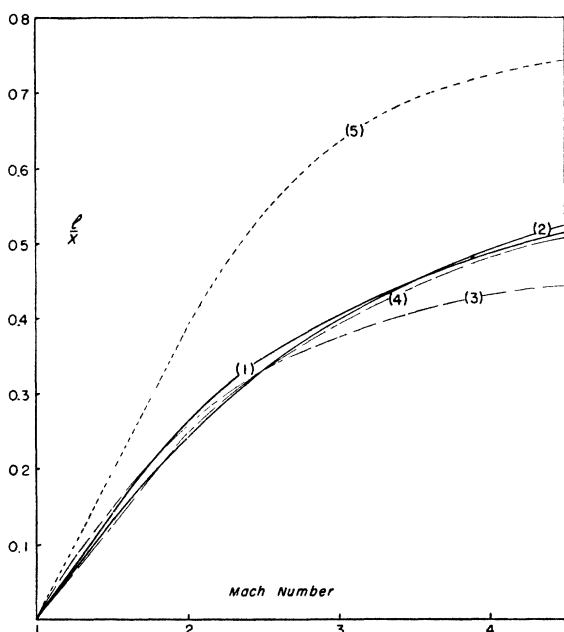


FIG. 1. Ratio of mean free path l to shock-wave thickness X as function of Mach number M . (1) Air at 300°K intake temperature, using u^2 transport equation with Sutherland model. (2) Air at 300°K using u^3 transport equation with elastic sphere model. (3) Helium at 300°K from u^2 equation with Sutherland model. (4) Helium at 300°K from u^3 equation with elastic sphere model. (5) Thomas curve for air.

TABLE II. Half-life of the distribution for various Mach numbers.

M	1.1	2	3	5	10	∞
Half-life	69	144	37	26	17	16

velocity gradient. It turns out that here the two thicknesses are the same and are given by

$$X = 4l/B. \quad (42)$$

The reciprocal thickness $1/X$ is therefore, proportional to the quantity B given by Eq. (34) or Eq. (39), according to whether u^2 or u^3 is used in the transport equation.

If we write Eq. (34) in the form

$$B = B_0 + B_s(S/T_\alpha), \quad (43)$$

B_0 determines the shock-wave thickness for the elastic sphere model and B_s the correction to this to account for the attractive forces of the Sutherland model. Table I gives B_0 , B_s , and B_1 as a function of the Mach number M , where B_1 is defined by Eq. (39), for $\gamma = 5/3$ and $\gamma = 7/5$. Figure 1 shows a plot of l/x for air and for helium, where x is the calculated shock-wave thickness and l the mean free path in the gas before the shock. The thicknesses calculated by using B of Eq. (34) and B_1 of Eq. (39) are both shown, and for comparison, the thickness given by the Thomas theory. For air, γ has been assumed to be 1.4, although a larger value should probably be used to allow for relaxation effects. It is seen that the thicknesses calculated from the u^2 and the u^3 transport equations are in good agreement for intermediate Mach numbers, but there is some discrepancy for the higher Mach numbers, particularly for monatomic gases.

In the time-dependent transport equation, (5), let us assume that f has the form (3) at $t=0$, where $n_\alpha(x)$, $n_\beta(x)$ are chosen to make $(\partial/\partial t)\int f\Phi d\mathbf{c} = 0$ for $\Phi = u^2$. Then $n_\alpha(x)$, $n_\beta(x)$ are given by Eqs. (37) and (38). Putting now $\Phi = u^3$, we get an equation for $\partial f/\partial t$ at time $t=0$, from which we can get an equation for say $\partial n_\alpha/n_\alpha \partial t$ at time $t=0$, measuring the fractional change with time of the supersonic component. It turns out that, if we express time in terms of the mean free time $t_{\alpha\beta}$ between collisions of α - and β -molecules, this quantity is independent of position and is given, for $\gamma = 7/5$, by

$$\begin{aligned}
 \left(\frac{\nu_\alpha}{t_{\alpha\beta}} \frac{\partial t}{\partial \nu_\alpha} \right)_{t=0} = & 2 \left(\frac{5}{2\pi} \right)^{\frac{1}{2}} \frac{M^2(5M^2+3)}{25M^4+90M^2+3} \\
 & \cdot \frac{4M^2}{M^2+3} \left(5 + \frac{30}{M^2} - \frac{3}{M^4} \right)^{\frac{1}{2}} D(u_{\alpha\beta}) \cdot \frac{1}{B_0 - B_1},
 \end{aligned}$$

where

$$D(u) = (u + 1/2u) \int_0^u \exp(-G^2) dG + \frac{1}{2} \exp(-u^2).$$

The half-life of the ν_α component, equal to $\ln 2$ times the above quantity, measures the half-life of the dis-

TABLE III. Distribution of nominal temperature T and nominal thermal conduction coefficient in the shock wave, for $\gamma=7/5$.

ν_α	T/T_β	$M=\sqrt{2}$ λ/λ_β	T/T_β	$M=2$ λ/λ_β	T/T_β	$M=\infty$ λ/λ_β
0	1.000	48.20	1.0000	-155	1.0000	-92.8
0.05	0.998	42.20	1.0002	-459	1.0058	-92.3
0.10	0.995	37.40	1.0002	+354	1.0112	-92.2
0.15	0.992	33.23	0.9997	115.5	1.0178	-92.5
0.20	0.988	29.57	0.9990	64.2	1.0240	-93.5
0.25	0.984	26.31	0.9974	42.2	1.0305	-95.3
0.30	0.979	23.48	0.9956	29.9	1.0380	-98.5
0.40	0.968	18.62	0.9876	16.94	1.0500	-113.5
0.50	0.953	14.76	0.9650	10.26	1.0612	-163.2
0.60	0.935	11.42	0.9526	8.31	1.0667	$\mp\infty$
0.70	0.910	9.08	0.9394	5.09	1.0560	74.1
0.75	0.897	7.99	0.9172	4.05	1.0370	46.6
0.80	0.880	6.99	0.8585	2.42	1.0000	20.6
0.85	0.862	6.11	0.8183	1.834	0.9305	11.28
0.90	0.842	5.31	0.7608	1.350	0.8000	5.80
0.95	0.818	4.06	0.6892	0.958	0.5465	2.53
1.00	0.792	3.89	0.5928	0.658	0	0.664

tribution in terms of $t_{\alpha\beta}$ and is shown in Table II for various Mach numbers. This indicates the degree to which the solution obtained from the transport equation for u^2 is a steady-state solution.

If \bar{u} is the mass velocity, T the temperature defined in terms of the translational energy of the molecules, and q the heat transport vector, the standard formulas of the kinetic theory give $n\bar{u} = n_\alpha u_\alpha + n_\beta u_\beta$, $3nkT/m = n_\alpha \langle (\mathbf{c} - \mathbf{i}\bar{u})^2 \rangle_{\alpha N} + n_\beta \langle (\mathbf{c} - \mathbf{i}\bar{u})^2 \rangle_{\beta N}$, and $q = n_\alpha \langle (u - \bar{u}) E_r \rangle_{\alpha N} + n_\beta \langle (u - \bar{u}) E_r \rangle_{\beta N}$, where $\langle \rangle_{\alpha N}$ indicates an average over the α distribution, $\langle \rangle_{\beta N}$ one over the β -distribution, and $E_r = (m/2)(\mathbf{c} - \mathbf{i}\bar{u})^2 + E_i$ is the sum of the kinetic energy relative to the mass motion and the internal energy for a molecule. Evaluating the averages we find

$$\begin{aligned} kT/m &= (1/n)(n_\alpha c_\alpha^2 - n_\beta c_\beta^2) + \frac{1}{3}(n_\alpha n_\beta/n^2)(u_\alpha - u_\beta)^2, \\ 2nq/m &= n_\alpha n_\beta [u_\alpha - u_\beta] \\ &\quad \times [a(c_\alpha^2 - c_\beta^2) + (u_\alpha - u_\beta)^2(n_\alpha - n_\beta)/n], \end{aligned}$$

where c_α , c_β are given by Eqs. (8). We can go on to define a thermal conduction coefficient λ by the usual formula $q = -\lambda \partial T / \partial x$. The resulting formulas for T and λ can be expressed in terms of the Mach number of the use of Eq. (31), and the values of n_α , n_β are given by Eqs. (37) and (38). In this way we get formulas showing the values of T and of λ as functions of position in the shock wave. The results are shown in Table III, where the ratios T/T_β , λ/λ_β are shown as functions of ν_α for $M=\sqrt{2}$, 2 and ∞ , and for $\gamma=7/5$. Here T_β is the temperature in the subsonic stream, λ_β the thermal conduction coefficient calculated for the conditions in the subsonic stream by the standard kinetic theory formulas for the elastic sphere model, and ν_α is given by Eq. (37). $\nu_\alpha=1$ corresponds to the supersonic edge of the shock wave, $\nu_\alpha=0$ to the subsonic edge.

As the table illustrates, for Mach numbers of 2 and greater, the temperature T reaches a maximum within the shock wave; and between this point of maximum T and the subsonic edge of the shock, λ is negative. This nominal λ is seen to differ by orders of magnitude from the ordinary kinetic theory value. Of course we cannot expect the present crude approximation to the distribution function to give correct results for λ , and, in any case, the simple formula $q = -\lambda \partial T / \partial x$ should be corrected, as for instance in the Burnett theory; but the anomalous values of λ give some indication of how far the flow in a shock wave differs from that described by equations of the Navier-Stokes type, if the distribution function here used is any approximation to the actual distribution.

In seeking to improve the present theory, it is natural to attempt an iterative solution of the Boltzmann equation itself, taking as initial solution the f given by Eqs. (3) and (4). The collision integral can be evaluated, at least in powers of $M-1$, and this has been done; but the results suffer from the defect that they do not vanish identically for $u=0$, as the Boltzmann equation requires. This makes carrying out of the next step difficult because of the occurrence of a $1/u$ singularity, although the integrals of the second step are finite in spite of this. But more appropriate would be the introduction, in the initial function, of "skew" terms of the type $f_\alpha^{(0)}[(\mathbf{c} - \mathbf{i}u_\alpha)^2 - 5kT_\alpha/m][u - u_\alpha]$, $f_\alpha^{(0)}[(u - u_\alpha)^2 - \frac{1}{3}(\mathbf{c} - \mathbf{i}u_\alpha)^2]$, where $f_\alpha^{(0)}$ is given by Eq. (4), and similar β terms. Such terms occur in the first-order solution of the E-C theory. The coefficients of the various terms could be adjusted in such a way as to give, in the limit $M \rightarrow 1$, the form of f required by the E-C theory and, at the same time, to give the vanishing of the collision integral for $u=0$.

Recent measurements of shock wave thickness by Cowan and Hornig¹³ and by Greene, Cowan, and Hornig¹⁴ using the optical reflectivity method, show thicknesses significantly greater than those predicted by the Thomas theory, in accordance with the results found here.

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¹³ G. R. Cowan and D. F. Hornig, J. Chem. Phys. **18**, 1008 (1950).

¹⁴ Greene, Cowan, and Hornig, J. Chem. Phys. **19**, 427 (1951).