Comparison of exact and approximate methods for analysing vibrational relaxation regions

By P. A. BLYTHE

Department of the Mechanics of Fluids, The University of Manchester

(Received 4 September 1960)

The validity of various solutions for the vibrational relaxation region in shock-waves, and of the assumptions on which they are based, has been assessed by comparison with an exact solution obtained by numerical integration of the relaxation equation, and also by use of the Rayleigh-line equations. Estimates of errors in the values of the relaxation frequency, determined by means of these solutions, are given.

1. Introduction

In the preceding paper (Johannesen 1961) a discussion of the basic physics of vibrational relaxation regions in shock-waves was given. The paper presented a method whereby the exact shock-wave equations (equations (4), (5) and (6) of Johannesen) could be solved for any given temperature dependence of the relaxation frequency ω, assuming the simple relaxation equation

$$\frac{d\sigma}{dt} = \omega(\overline{\sigma} - \sigma) \tag{1}$$

to hold. (The notation used in this paper is the same as that used by Johannesen, unless otherwise stated.)

Alternatively the method could be used to obtain, from experimental records, local values of ω, rather than over-all ones.

In this paper an exact numerical integration has been carried out for a strong shock-wave in nitrogen using Gunn's expression for ω,

$$\omega = ApT^{-1}\exp(-BT^{-\frac{1}{3}})\,[1 - \exp(-\theta/T)], \tag{2}$$

where A and B are constants.

This numerical solution is referred to as the exact solution and previously published solutions are compared with it. These previous solutions are all approximate in the sense that they either use simplified forms of the shock-wave equations or make certain other simplifying assumptions (e.g. ω constant).

For weak waves the previous solutions are compared with an analytical solution which is based on ω and c_{vib} constant. These are valid assumptions for such waves.

By regarding the exact numerical solution as a representation of an experimental record it is possible to assess the accuracy with which ω would be determined from such a record by means of the previous approximate solutions. (Note that these previous solutions obtain over-all values of ω, and not local values.)

The numerical integration was done for a shock-wave in nitrogen of Mach number $M_1 = 8{\cdot}0$, and with T_1, the temperature ahead of the shock-wave, equal to 300 °K. Values of $\bar{\sigma}$ were taken from N.B.S. Circular no. 564. The results were obtained in the form of the density ratio, etc., as functions of $\omega_m x/v_m$, where the suffix m denotes the value of the quantity at the point in the relaxation region corresponding to $T = \frac{1}{2}(T_a + T_2)$, so that only the value of the constant B, occurring in equation (2), was required. By fitting (2) to Blackman's experimental results it was found that $B = 223\ (°\mathrm{K})^{\frac{1}{3}}$.

It is unlikely that the use of a slightly different relationship between ω and T would alter the main conclusions reached in this paper.

Because of the labour involved, prior to Johannesen's paper, in obtaining solutions to the exact shock-wave equations for varying ω, previous workers made various assumptions in an attempt to simplify matters.

Many of these assumptions concerned the energy equation, and this fact affords a convenient means of classifying the solutions. Energy equations that have been used are: (*a*) exact, (*b*) constant-enthalpy, (*c*) Bethe–Teller ($d\bar{\sigma}/d\sigma$ = constant), and (*d*) constant-internal-energy. All these assumptions have the advantage that they eliminate the velocity from the energy equation. The validity of these assumptions is assessed by means of the Rayleigh-line equations and numerical checks.

The other main type of assumption is to consider ω and c_{vib} constant in the relaxation region. When the assumption of constant ω is made it is, of course, only possible to obtain an over-all value of ω from such a solution.

A full list of solutions discussed in this paper, together with the assumptions made in obtaining any particular one of them, is given in table 1. When a solution is mentioned in the text it will be followed by a Roman numeral corresponding to its position in this list.

Sections 2 to 6 deal with these solutions and assumptions. The conclusions reached in these sections are summarized in section 7. In section 8 previous methods of determining ω are discussed.

2. Exact-energy-equation solutions

The numerical solution already mentioned belongs to this class and, as stated, is called the exact solution.

If ω and c_{vib} are assumed constant in the relaxation region, then it is possible to integrate the relaxation equation analytically using the correct shock-wave equations. This can be done for both fully and partly dispersed shock-waves (ii and vi).

The assumption of constant ω is by no means valid for strong shock-waves in which departures from a mean value can be as high as 20 or 30 %. Even for fairly weak waves, if the temperature ahead of the shock is high, some account may have to be taken of the variation in ω.

The latter of the two assumptions, constant c_{vib}, predicts that the equilibrium vibrational energy will be a linear function of the temperature in the relaxation region, and for most shock-waves this is a reasonable assumption.

No.	Solution	Form of energy equation used	Assumptions concerning		Further assumptions
			ω	c_{vib}	
(i)	Exact	Exact	—	—	—
(ii)	Analytical solution for partly dispersed shock-waves (Blythe)	Exact	Constant	Constant	—
(iii)	Broer's analytical solution	Exact	Constant	Constant $= (c_{\mathrm{vib}})_1$	—
(iv)	Approximate form of analytical solution (ii)	Exact	Constant	Constant	Assume that the term $\log\{(v-v_2)/v_1\}$ dominates the relaxation
(v)	Lighthill solution for partly dispersed shock-waves	Exact	Constant $= \omega_2$	~ 0	Assume that the term $\log\{(v-v_2)/v_1\}$ dominates the relaxation
(vi)	Analytical solution for fully dispersed shock-waves (Blythe)	Exact	Constant	Constant	—
(vii)	Griffith–Kenney solution for fully dispersed shock-waves	Exact	Constant	Constant	Neglect variation of the v/v_1 term
(viii)	Lighthill solution for fully dispersed shock-waves	Exact	Constant	Constant	See Lighthill (1956); assumptions valid only for very weak waves
(ix)	Bethe–Teller and Gunn solutions for fully dispersed shock-waves	Exact	Constant	Constant	See Gunn (1946)
(x)	Constant enthalpy numerical solution	Constant-enthalpy	—	—	—
(xi)	Gunn	Constant-enthalpy	Constant	Constant	—
(xii)	Blackman	Constant-enthalpy	Constant	Constant	Constant pressure
(xiii)	Approximate form of Blackman's solution	Constant-enthalpy	Constant	Constant	Constant pressure, $x = \bar{v}t$, and $\rho_2/\{\rho_a+(\rho_2-\rho_a) \times \exp(-c_{pm}\omega_m x/c_{pa}\bar{v})\} \div$
(xiv)	Bethe–Teller numerical solution	Bethe–Teller	—	—	—
(xv)	Smiley–Winkler	Bethe–Teller	Exponential variation in v/ω; see equation (24)	—	—
(xvi)	Constant internal energy numerical solution (Herman & Rubin)	Constant-internal-energy	—	—	—
(xvii)	Constant $\bar{\sigma}$	—	—	—	Assume that $\bar{\sigma} = \bar{\sigma}_2$ in the relaxation region

TABLE 1

In order to integrate (1) analytically it is convenient to express the variables as functions of the velocity v. Equation (1) becomes

$$\frac{r\omega_m}{v_1}\frac{dx}{du} = \frac{u[b_1-(\gamma_\alpha+1)\,u]}{u^2-d_1u+d_2}, \tag{3}$$

where

$$\left.\begin{aligned} u &= v/v_1, \\ b_1 &= \gamma_\alpha + 1/m_1^2, \qquad b_2 = \tfrac{1}{2}(\gamma_\alpha - 1) + 1/m_1^2, \\ d_1 &= \frac{2\gamma_m b_1}{\gamma_\alpha(\gamma_m+1)}, \quad d_2 = \frac{v_1^2 b_2 + (\gamma_\alpha - 1)\,(\overline{\sigma}_1 + K)}{r v_1^2}, \\ \text{and} \qquad r &= \frac{(\gamma_\alpha - 1)\,(\gamma_m + 1)}{2(\gamma_m - 1)}. \end{aligned}\right\} \tag{4}$$

K is defined by $\overline{\sigma} = (c_{\text{vib}})_m T - K$. The constant value of ω was assumed to be ω_m.

Consider first of all partly dispersed shock-waves. The denominator on the right-hand side of equation (3) is proportional to $\overline{\sigma} - \sigma$. This is zero at the final equilibrium position and thus $v = v_2$ must be a root of the denominator. If the other root is λ then (3) is easily integrated to give

$$\frac{1}{\lambda - v_2/v_1}\left\{\left(\frac{v_2}{v_1}\right)^2\left(\frac{1}{m_2^2}-1\right)\log\left(\frac{v}{v_1}-\frac{v_2}{v_1}\right) - \lambda[b_1-(\gamma_\alpha+1)\,\lambda]\log\left(\lambda - \frac{v}{v_1}\right)\right\} + (\gamma_\alpha+1)\,v/v_1$$
$$= -\frac{r\omega_m x}{v_1} + \text{constant}. \tag{5}$$

A similar type of solution was obtained by Broer (1951), (iii), who assumed that $(c_{\text{vib}})_m = (c_{\text{vib}})_1$, an assumption that is valid only for weak waves.

A comparison between the above solution, (ii), (equation 5) and the exact solution (i) is shown in figure 1. As can be seen the solution appears to give a satisfactory mean prediction of the density as a function of x over the region in which the major portion of the density change occurs.

For strong shock-waves, the variations in the terms $\log(\lambda - v/v_1)$ and v/v_1 are small compared with the variation in $\log(v/v_1 - v_2/v_1)$. Thus one can approximate equation (5) to

$$\frac{v - v_2}{v_a - v_2} = \exp\left\{-\frac{r(\lambda - v_2/v_1)}{(v_2/v_1)\,(1/m_2^2 - 1)}\,\frac{\omega_m x}{v_2}\right\}. \tag{6}$$

This solution, (iv), is also plotted in figure 1. For weak waves the agreement between (6) and (5) becomes worse, as the term $\log(\lambda - v/v_1)$ becomes important.

Lighthill (1956) obtained a solution, (v), of the form

$$\frac{v - v_2}{v_a - v_2} = \exp\left(-\frac{\omega_2 x}{v_2}\right) \tag{7}$$

by assuming that on the right-hand side of equation (3) v could be replaced by v_2 except in the term $v - v_2$ in the denominator. Furthermore he assumed that the constant value of ω was ω_2, and that $\gamma_m \doteqdot \gamma_\alpha$.

This solution, (v), is thus valid only for waves in which $\gamma_m \doteqdot \gamma_\alpha$, and it is not valid for weak waves. Obviously it has only a limited range of application. Figure 1 shows this solution for a strong shock-wave in which γ_m is noticeably less than γ_α, and also ω_2 is considerably less than ω_m. It is immediately apparent that the errors which are introduced into the density curve by incorrect application of equation (7) are large.

In order to obtain the solution (vi) for fully dispersed shock-waves reconsider equation (3). The denominator on the right-hand side of this equation will now have roots $v = v_1$, and $v = v_2$, as there is now no diffusion-resisted part of the wave and (3) will be valid throughout the wave. Equation (3) can be integrated as before, and the result can be obtained from (5) by simply putting $\lambda = 1$. (In fact it can easily be shown that $\lambda = 1$ when $\gamma_m = \gamma_1$. Previously one distinguished between γ_m and γ_1 because of the presence of the diffusion-resisted part of the wave.)

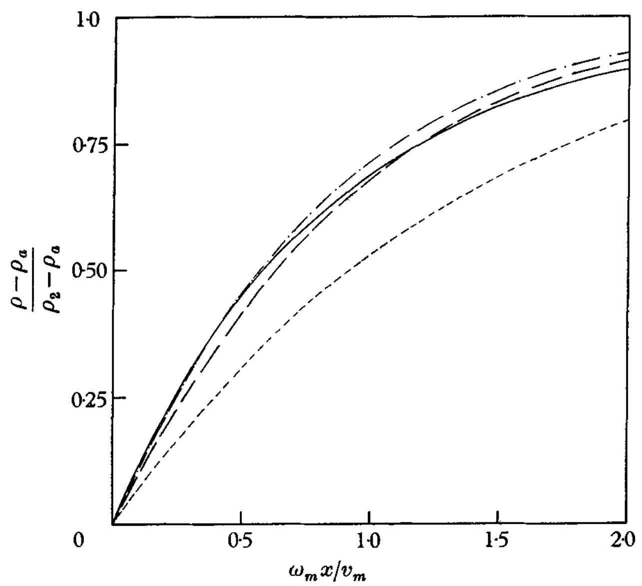

FIGURE 1. Comparison of solutions based on the exact energy equation. $M_1 = 8{\cdot}0$, $T = 300$ °K, in nitrogen. ———, Exact solution, (i); — —, analytical solution, (ii), (Blythe); — · —, approximate form of solution (ii); - - - -, Lighthill solution, (v).

Both the log terms are now equally important, though the term v/v_1 can be omitted without serious error (cf. Griffith & Kenny (1957), (vii)). Lighthill (1956), (viii), gives a full discussion of fully dispersed waves, but his analysis is only applicable to very weak weaves. Bethe & Teller (1941) and Gunn (1946), (ix), have also analysed fully dispersed waves but in terms of the temperature rather than the velocity. This solution, (ix), would be invalid if it were possible for the temperature to have a maximum in a fully dispersed shock-wave. This, however, is impossible for an ideal diatomic gas (neglecting anharmonicity) as the required condition is that $\gamma_1 < (13/11)$.

The preceding solution (ii) can be expressed in terms of the time t rather than the distance x. The expression corresponding to (5) is

$$\frac{1}{\lambda - v_2/v_1}\left\{\frac{v_2}{v_1}\left(\frac{1}{m_2^2}-1\right)\log\left(\frac{v}{v_1}-\frac{v_2}{v_1}\right)-[b_1-(\gamma_\alpha+1)\lambda]\log\left(\lambda-\frac{v}{v_1}\right)\right\}$$
$$= -r\omega_m t + \text{constant}. \qquad (8)$$

One can obtain a result similar to (6) from which a relaxation time τ_m for the velocity can be obtained. In fact

$$\tau_m = \frac{v_2/v_1\,(m_2^{-2}-1)}{r(\lambda - v_2/v_1)}\,\frac{1}{\omega_m}, \tag{9}$$

which has the limiting value

$$\tau_m \to 11/(14\omega_m) \tag{10}$$

as $m_1 \to \infty$, for a system of fully excited harmonic oscillators.

3. Constant-enthalpy solutions

The assumption of constant enthalpy in the relaxation region is one of the more common approximations made in the literature on this subject.

The energy equation (equation (6) of Johannesen's paper) is now replaced by

$$h = \text{constant},$$

or

$$c_{p\alpha}T + \sigma = \text{constant}. \tag{11}$$

As σ is calculated from this assumption, the condition that constant enthalpy be a good approximation is that

$$\left|\frac{\Delta h}{\Delta\sigma}\right| \ll 1. \tag{12}$$

From the Rayleigh-line equations it can be shown that

$$\frac{dh}{d\sigma} = \frac{(\gamma_\alpha - 1)\,m^2}{1-m^2}. \tag{13}$$

Obviously (12) is not satisfied for weak waves where m and m_1 are of order unity. However, as $m_1 \to \infty$, for a system of fully excited harmonic oscillators, equation (13) gives

$$\left(\frac{dh}{d\sigma}\right)_a \to \frac{1}{15};\quad \left(\frac{dh}{d\sigma}\right)_2 \to \frac{1}{22}.$$

(The effect of anharmonicity makes the second of these two limits smaller.)

This result, that the constant-enthalpy assumption is valid only for strong shock-waves, could have been anticipated from a knowledge of the temperature profile in weak shock-waves. For such shock-waves it is possible for the temperature to increase in the relaxation region, whereas the constant-enthalpy assumption predicts that the temperature must always decrease and hence leads to a totally incorrect qualitative picture. Further elaboration on this point is given later.

In order to check the conclusion concerning strong shock-waves numerical integration, (x), using the constant-enthalpy assumption, was performed for the case $M_1 = 8{\cdot}0$, $T_1 = 300\,^\circ\mathrm{K}$, in nitrogen. Before this can be done one has to decide what value the enthalpy should take. It was found that the '2' position value gave a better result than did the 'a' position value. The comparison with the exact solution, (i), is shown in figure 2, and, as can be seen, the assumption introduced little error in the density as a function of distance.

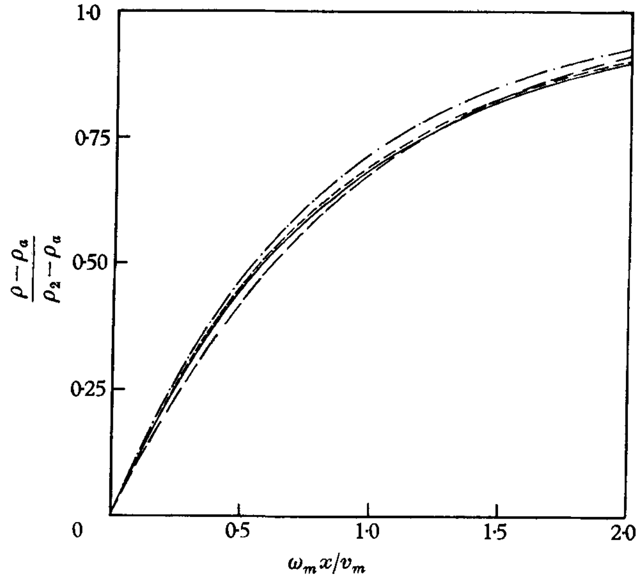

FIGURE 2. Comparison between the exact solution, (i), and the solutions based on the constant-enthalpy assumption. $M_1 = 8{\cdot}0$, $T_1 = 300$ °K, in nitrogen. ———, Exact solution, (i); – – –, constant enthalpy numerical solution, (x); — —, Blackman's solution, (xii); — · —, Blackman's approximate solution, (xiii).

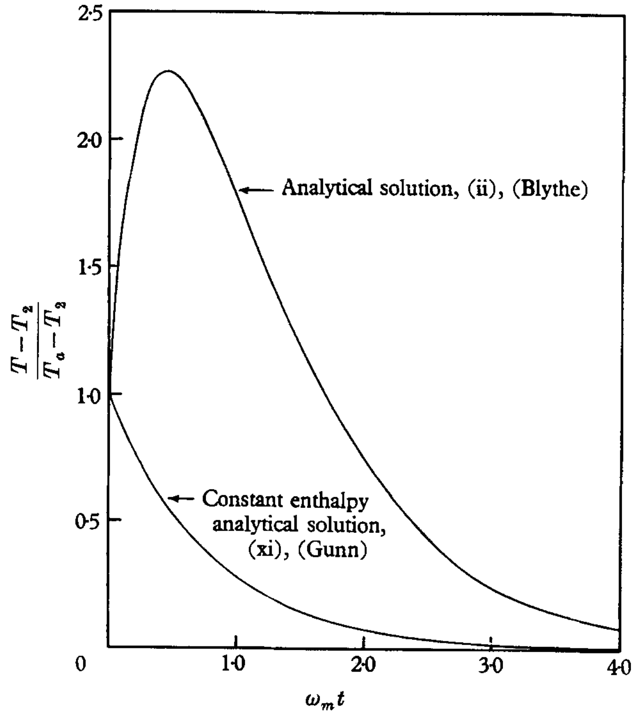

FIGURE 3. Comparison between solution (ii) which is based on the exact energy equation, and solution (xi), which is based on the constant-enthalpy assumption, for the temperature profile in the relaxation region in a weak shock-wave. $m_1 = 1{\cdot}15$, $T_1 = 3000$ °K, in nitrogen.

By the further assumption that ω and c_{vib} be constant an analytical solution for the temperature can be obtained using only the constant-enthalpy assumption and the relaxation equation. It is for this reason that the constant-enthalpy assumption has proved so useful in practice. (A similar remark could be made about the other energy equation assumptions.) This solution, (xi), was first obtained by Gunn (1946) and it can be written

$$\frac{T-T_2}{T_a-T_2}=\exp(-\omega_m t\, c_{pm}/c_{p\alpha}). \tag{14}$$

Equation (14) is, of course, invalid for weak waves. This is demonstrated quite strikingly in figure 3 where (14) is compared with the analytical solution (ii), which is based on the exact energy equation, for $m_1 = 1{\cdot}15$, $T_1 = 3000\,^\circ\text{K}$, in nitrogen. The temperature variation in this shock-wave is very small, even though $T_1 = 3000\,^\circ\text{K}$, and the assumptions of constant ω and constant c_{vib} are still valid. The discrepancy is thus due solely to the constant-enthalpy assumption. (Note that ω_m as previously defined would not, in general, be a sound estimate of the constant value of ω for shock-waves which have a maximum in the temperature profile in the vibrational relaxation region. For such shock-waves ω_m should be taken to mean the constant value, whatever that constant value is.)

Blackman (1956), (xii), further assumed constant pressure in the relaxation region from which

$$\frac{v-v_2}{v_a-v_2}=\exp(-\omega_m t\, c_{pm}/c_{p\alpha}),$$

or

$$\frac{\rho_2-\rho}{\rho_2-\rho_a}=\frac{(\rho_2/\rho_a)\exp(-\omega_m t\, c_{pm}/c_{p\alpha})}{1+(\rho_2/\rho_a-1)\exp(-\omega_m t\, c_{pm}/c_{p\alpha})}. \tag{15}$$

The constant-pressure assumption is reasonable except for weak waves. (The density always increases in the relaxation region, hence the constant-pressure assumption implies that the temperature must fall, a condition not valid in weak waves.)

Note that in this case the relaxation time for the velocity is given by

$$\tau_m = c_{p\alpha}/(c_{pm}\omega_m), \tag{16}$$

which has the limiting value of $7/(9\omega_m)$ for a system of fully excited harmonic oscillators. Comparison with the previously derived result (10) reveals that the limiting values are different by less than $(100\,\omega_m)^{-1}$.

In order to analyse his experimental results Blackman made the further assumption that the term $\rho_2/\rho_a - 1$ was small and hence that

$$(\rho_2/\rho_a)/\{1+(\rho_2/\rho_a-1)\exp(-\omega_m t\, c_{pm}/c_{p\alpha})\}$$

could be replaced by unity. Further he wrote $x = t/\bar{v}$ where $\bar{v}=\frac{1}{2}(v_a+v_2)$. Equation (15) then becomes

$$\frac{\rho_2-\rho}{\rho_2-\rho_a}=\exp\left(-\frac{c_{pm}}{c_{p\alpha}}\frac{\omega_m x}{\bar{v}}\right). \tag{17}$$

This exponential law (17), (xiii), has been deduced by means of a large number of assumptions and whether or not it is valid is very much open to question. It is certainly true that Blackman found experimentally that the density varied exponentially with distance in the relaxation region. However this simply requires that

$$\frac{\rho_2-\rho}{\rho_2-\rho_a} = \exp\left(-Cx\right)$$

where C is some constant, not necessarily equal to $\dfrac{c_{pm}}{c_{p\alpha}}\dfrac{\omega_m}{\bar{v}}$.

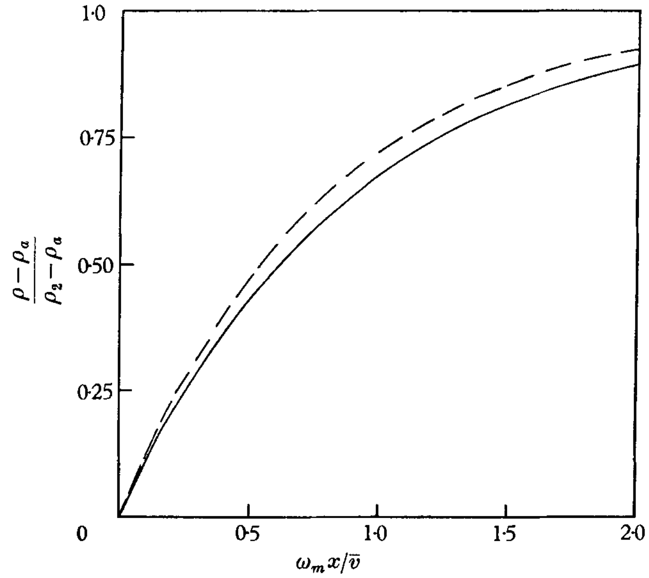

FIGURE 4. Comparison between the Blackman solution, (xiii), and solution (ii) for a weak wave. $m_1 = 1{\cdot}15$, $T_1 = 3000$ °K, in nitrogen. ———, Analytical solution, (ii), (Blythe); — —, Blackman's approximate analytical solution (xiii).

Figure 2 compares equation (17) with the exact solution (i) for a strong wave. As can be seen there is a marked discrepancy between the two solutions. Inclusion of the term neglected by Blackman (i.e. solution (xii), equation (15)) lessens this discrepancy (see figure 2).

For weak waves it is expected that equation (17) will be invalid because of the assumption of constant enthalpy. This prediction is confirmed in figure 4 where a comparison between equation (17) and solution (ii), which is based on the exact energy equation, for $m_1 = 1{\cdot}15$, $T_1 = 3000$ °K, is shown. (As previously pointed out the assumptions of constant ω and constant c_{vib} are perfectly valid in this wave.)

4. Solutions based on the Bethe–Teller assumption

Consider

$$\frac{d\bar{\sigma}}{d\sigma} = -\mu. \tag{18}$$

For $\mu = c_{\text{vib}}/c_{p\alpha}$ (18) is equivalent to the constant-enthalpy assumption. From the Rayleigh-line equations it can be shown that μ is strictly given by

$$\mu = \frac{c_{\text{vib}}}{c_{p\alpha}}\left[1-(\gamma_\alpha-1)\frac{m^2}{1-m^2}\right]. \tag{19}$$

Bethe & Teller (1941) assumed that μ was constant and calculated μ by matching the integrated form of (18) for constant μ, namely

$$\bar{\sigma}+\mu\sigma = \phi, \text{ a constant,} \tag{20}$$

to the boundary conditions at 'a' and '2'. Thus

$$\mu = \frac{\bar{\sigma}_a-\bar{\sigma}_2}{\bar{\sigma}_2-\bar{\sigma}_1}, \quad \phi = \bar{\sigma}_2\frac{(\bar{\sigma}_a-\bar{\sigma}_1)}{\bar{\sigma}_2-\bar{\sigma}_1}. \tag{21}$$

The condition that (20) be a valid method of calculating σ is that

$$\left|\frac{\Delta(\bar{\sigma}+\mu\sigma)}{\Delta\sigma}\right| \leqslant 1, \tag{22}$$

where μ is given by (21).

It can be shown that as $m_1 \to \infty$, for a system of fully excited harmonic oscillators,

$$\left(\left|\frac{d(\bar{\sigma}+\mu\sigma)}{d\sigma}\right|\right)_a \to \frac{1}{315}, \quad \left(\left|\frac{d(\bar{\sigma}+\mu\sigma)}{d\sigma}\right|\right)_2 \to \frac{2}{693},$$

so that the assumption is valid for strong shock-waves.

The analysis for weak waves is a little more difficult. For m^2 of order $1/\gamma_\alpha$ it can be shown from (19) that it is possible for μ to change sign in the relaxation region, although the form used, (21), predicts that μ will be positive or negative according as T_a is greater or less than T_2. Hence, for weak waves, an incorrect qualitative picture would arise, even though the criterion (22) might predict a good quantitative agreement. For even weaker waves, m of order unity, it is easily shown that (22) is not satisfied.

Hence as in the case of constant enthalpy, it would appear that this assumption is valid only for strong shock-waves.

A numerical integration, (xiv), was carried out using the Bethe–Teller assumption for a shock-wave of Mach number $M_1 = 8{\cdot}0$ in nitrogen at $T_1 = 300\,^\circ\mathrm{K}$. Excellent agreement was obtained with the exact solution (i) (see figure 5), thus verifying the above conclusion.

By assuming ω constant, one can easily derive similar results to those obtained by Gunn, (xi), and by Blackman, (xii, xiii), for the constant-enthalpy case. In fact all one has to do is to replace $c_{pm}/c_{p\alpha}$ by $1+\mu$ in the previous expressions. The conclusions concerning such solutions would be similar to those obtained before.

Smiley & Winkler (1954), (xv), attempted to improve this type of analytical solution by allowing for the variation in ω. From the relaxation equation (1) and equation (18) it can be shown that

$$\frac{\bar{\sigma}_2-\sigma}{\bar{\sigma}_2-\bar{\sigma}_1} = \exp\left[-\int_0^x (1+\mu)\frac{\omega}{v}\,dx\right]. \tag{23}$$

Smiley & Winkler then assumed that the variation of ω/v could be represented by

$$\frac{v}{\omega} = \left(\frac{v}{\omega}\right)_a + \left[\left(\frac{v}{\omega}\right)_2 - \left(\frac{v}{\omega}\right)_a\right]\left[1-\exp\left\{-\left(\frac{\omega}{v}\right)_a x\right\}\right]. \tag{24}$$

This assumption has no physical foundation and is purely a curve-fitting approximation. Nevertheless, as will be seen later, it turns out that this assumption leads to very satisfactory results.

Equations (23) and (24) are easily combined to give

$$\frac{\bar{\sigma}_2-\sigma}{\bar{\sigma}_2-\bar{\sigma}_1}=\left[\left(\frac{v}{\omega}\right)_2\left(\frac{\omega}{v}\right)_a\exp\left\{\left(\frac{\omega}{v}\right)_a x\right\}-\left\{\left(\frac{v}{\omega}\right)_2\left(\frac{\omega}{v}\right)_a-1\right\}\right]^{-s}, \tag{25}$$

where $s = (1+\mu)\,(v/\omega)_a\,(\omega/v)_2$.

The comparison between this solution, (xv), and the exact solution (i) for $M_1 = 8{\cdot}0$, $T_1 = 300\,°\mathrm{K}$, in nitrogen is shown in figure 5. The agreement is very good, confirming that (24) is a valid approximation. (It has already been established that the Bethe–Teller assumption is valid for strong shock-waves.)

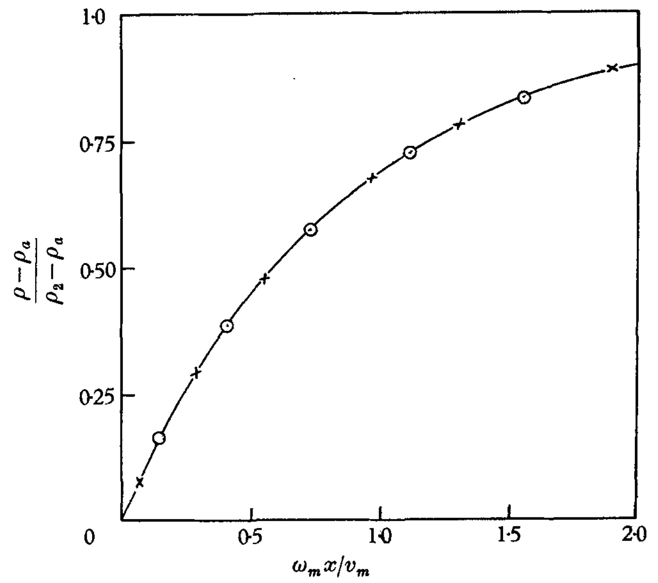

FIGURE 5. Comparison between the exact solution (i) and solutions based on Bethe–Teller assumption. $M_1 = 8{\cdot}0$, $T_1 = 300\,°\mathrm{K}$, in nitrogen. ———, Exact solution, (i); ⊙, Bethe–Teller numerical solution, (xiv); ×, Smiley–Winkler analytical solution, (xv).

5. Constant-internal-energy solution

Herman & Rubin (1959) made the assumption of constant internal energy in the relaxation region. It is very difficult to justify this assumption. Certainly the values of the internal energy at the two 'end' points differ far more than the values, for example, of the enthalpy.

The condition for this assumption to be valid is that

$$\left|\frac{\Delta e}{\Delta\sigma}\right| \ll 1, \tag{26}$$

where e is the internal energy.

It can be shown from the Rayleigh-line equations that

$$\frac{de}{d\sigma}=\frac{\gamma_a-1}{\gamma_a(1-m^2)}. \tag{27}$$

For weak waves, $m \doteqdot 1$ and the assumption is obviously erroneous. As $m_1 \to \infty$ it is found that for a system of fully excited harmonic oscillators

$$\left(\frac{de}{d\sigma}\right)_a \to \frac{1}{3},\quad \left(\frac{de}{d\sigma}\right)_2 \to \frac{7}{22}.$$

Thus it can hardly be said, for *any* Mach number, that the assumption is valid.

A numerical integration, (xvi), confirmed this prediction for a strong shock-wave (figure 6). (e_2 was used as the constant value; if e_a were used the disagreement would be slightly more marked.)

No analytical solutions using this assumption have been given, although one could easily be obtained in a way similar to that used to derive the constant-enthalpy solution (xi). It would, admittedly, be of little use.

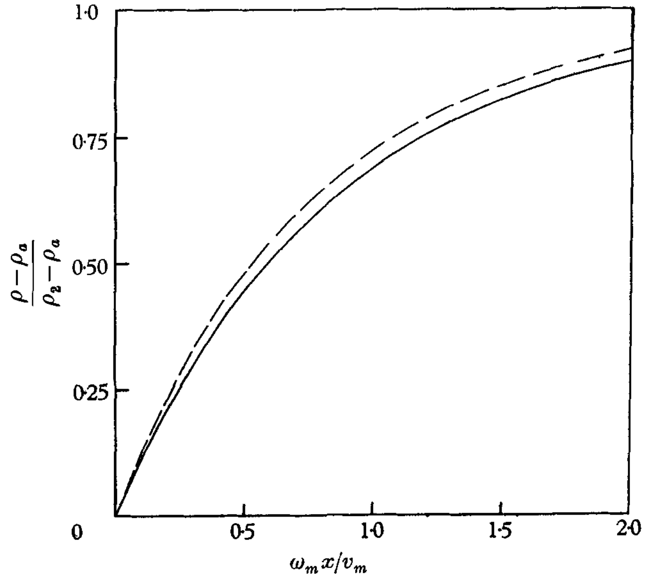

FIGURE 6. Comparison between the constant-internal-energy solution (xvi) and the exact solution (i). $M_1 = 8{\cdot}0$, $T_1 = 300$ °K, in nitrogen. ——— exact solution (i); — — constant-internal-energy numerical solution (xvi) (Herman & Rubin).

6. Constant-$\bar{\sigma}$ solution

If $\bar{\sigma}$ is assumed constant the relaxation equation can be integrated immediately for constant ω, (xvii). The constant value of $\bar{\sigma}$ must, of course, be $\bar{\sigma}_2$, and then

$$\frac{\bar{\sigma}_2-\sigma}{\bar{\sigma}_2-\bar{\sigma}_1} = \exp\left(-\omega_m t\right). \tag{28}$$

This was one of the earliest solutions obtained for vibrational relaxation regions.

It is expected that for strong shock-waves, in which both ω and $\bar{\sigma}$ vary by large amounts, this solution will give poor agreement with the exact solution (i). In fact from the Bethe–Teller assumption, which is valid for strong shock-waves, it can be shown that the relaxation equation will be of the form

$$\left.\begin{aligned} \frac{d\sigma}{dt} &= \omega'(\bar{\sigma}_2-\sigma), \\ \text{only if} \qquad \omega' &= (1+\mu)\,\omega. \end{aligned}\right\} \tag{29}$$

For strong shock-waves in a diatomic gas μ is roughly $\frac{2}{7}$.

For weak shock-waves in which the variation of temperature, and hence of ω and $\bar{\sigma}$, is small, agreement will be much better,

In order to obtain the density, temperature, etc., from such a solution one can either use the correct shock-wave equations or any of the previously discussed assumptions.

7. Conclusions from the preceding sections

Before proceeding to discuss the inverse problem, namely, for a given density distribution, what errors are introduced in ω, measured from such a distribution, by using the various solutions so far considered, the results obtained in the previous sections are summarized.

These conclusions are:

(1) The assumptions of constant ω and c_{vib} alone do not lead to any serious error in the density distribution.

(2) The constant-enthalpy assumption is valid for strong shock-waves only.

(3) The Blackman approximate solution, (xiii), for ρ, which is partly based on the constant-enthalpy assumption, gives only fair agreement even for strong shock-waves. However, inclusion of the term neglected by Blackman lessens this discrepancy for strong waves (solution (xii)).

(4) The Bethe–Teller assumption is valid for strong shock-waves and is superior to the constant-enthalpy assumption.

(5) The Smiley–Winkler solution, (xv), is excellent for strong shock-waves.

(6) The constant-internal-energy assumption is invalid for all shock-waves.

(7) The relaxation equation can be written in the form

$$\frac{d\sigma}{dt} = \omega(\bar{\sigma}_2 - \sigma)$$

for weak waves only. For strong shock-waves ω should be replaced by $(1+\mu)\,\omega$.

8. The determination of ω from experimental records

In sections 2 to 6 the merits of the various solutions for predicting the structure of the relaxation region for a given $\omega(p, T)$ have been discussed. The results obtained there can also be used to indicate probable errors in the value of ω which would be obtained if any of these solutions were used for the reverse process of determining ω from experimental results.

For this purpose regard the exact solution (i) (which gives, say, ρ as a function of $\omega_m x/v_m$) as representing the experimental data. Any other solution, say A, can be written in the form

$$f_A(\rho) = \omega_m x/v_m.$$

Obviously ω_m would be determined from such a solution by plotting $f_A(\rho)$ against x and fitting the best straight line. Thus by plotting f_A against f_{expt} an immediate check on the value of ω_m determined from A as compared with the true value is obtained.

Of the analytical solutions discussed only two have actually been used to determine ω from experimental results. These are the Blackman, (xiii), and Smiley–Winkler, (xv), solutions.

For the Blackman approximate solution, (xiii), $f_A \leqslant f_{\text{expt}}$ throughout the relaxation region for all shock-waves. Hence the Blackman value of ω_m will be an underestimate of the true value. In particular for $M_1 = 8{\cdot}0$, $T_1 = 300$ °K, in nitrogen it was found that the Blackman value would be roughly 10 % too low. (This is provided that the variation in ω/ω_m is correctly predicted by the expression (2), which appears to be a reasonable assumption from the available experimental data.)

For the weak wave $m_1 = 1{\cdot}15$, $T_1 = 3000$ °K, in nitrogen, the Blackman value would be approximately 12 % too low.

These estimates were obtained by plotting f_{Blackman} against f_{expt}. An attempt to draw the best straight line through these points creates the difficulty of how far into the relaxation region one should plot the points. Theoretically the relaxation region stretches from $x = 0$ to ∞ (for a partly dispersed shock-wave). In practice, however, measurements will probably be confined to a distance of, say, $2\omega_m/v_m$, and it was for this region that the best straight line was obtained.

If Blackman had not replaced the term

$$\frac{\rho_2/\rho_a}{1+(\rho_2/\rho_a-1)\exp\left(-\omega_m t c_{pm}/c_{pa}\right)}$$

by unity, i.e. if he had used his original solution, (xii), then the value of ω_m obtained would have been much improved for strong waves. In fact for $M_1 = 8{\cdot}0$, $T_1 = 300$° K, in nitrogen, the value would be only 1 % less than the true value.

It is perhaps worth mentioning that if one applies the same analysis to the analytical solution (ii), which is based on the exact energy equation, then it is found that the value of ω_m which would be obtained from this solution would differ by less than $\frac{1}{2}$ % from the true value for the strong shock-wave.

The second of the two solutions that have been used for evaluating ω is the one due to Smiley & Winkler, (xv). The agreement between this solution and the exact solution (i) was excellent for strong shock-waves. However, as (25) depends on both ω_a and ω_2 it is not possible to use this solution directly to obtain a value of ω from experimental records. To overcome this difficulty Smiley & Winkler assumed that

$$\left|\left(\frac{v}{\omega}\right)_2\left(\frac{\omega}{v}\right)_a - 1\right| \ll 1. \tag{30}$$

According to their results this assumption is permissible for carbon dioxide, the gas investigated by them, over the Mach-number range covered by them, $M_1 = 1{\cdot}5$ to 4. Equation (30) becomes invalid for stronger shock-waves in carbon dioxide. In general this will be true for most gases.

Also, it is doubtful whether it is permissible to use a relaxation equation of the form (1) for carbon dixoide, as presumably more than one relaxation frequency will exist (Greenspan & Blackman 1957). In the following discussion this last point will be ignored.

Smiley & Winkler measured the position at which

$$\frac{\rho_2-\rho}{\rho_2-\rho_a} = \frac{1}{e}.$$

Suppose this position was $x = S_l$, and that

$$\frac{\bar{\sigma}_2-\sigma}{\bar{\sigma}_2-\bar{\sigma}_1} = \exp(-l) \quad \text{at} \quad x = S_l. \tag{31}$$

Then from (25) and (31), using the approximation (30), it is found that

$$\left.\begin{aligned} \omega_a &\doteq \frac{v_a}{S_l}\left[\frac{l}{1+\mu}+k\left\{\left(\frac{v}{\omega}\right)_2\left(\frac{\omega}{v}\right)_a-1\right\}\right], \\ \text{where} \qquad k &= \frac{l}{1+\mu}-1+\exp\left(-\frac{l}{1+\mu}\right). \end{aligned}\right\} \tag{32}$$

From this equation, by first of all ignoring the small term $k\{(v/\omega)_2\,(\omega/v)_a-1\}$, a set of values of ω_a corresponding to p_a and T_a can be found. An empirical curve for ω as a function of T can then be established (assuming that ω is proportional to p). Secondly, by including the small term, obtained by means of the empirical curve, the final corrected value of ω can be found.

Smiley & Winkler assumed that $k = 1/e$, i.e. $l \sim 1+\mu$. Unfortunately over the range covered by them k varied from 0·28 to 0·18, while $1/e \doteq 0{\cdot}37$. This discrepancy leads to errors in ω of the order of 15 to 20 % for the stronger shock-waves (M_1 of order 4).

The main drawback of the methods of evaluating ω discussed in this section is that they determine only one over-all value of ω per relaxation region. The Blackman method in particular also leads to errors of the order of 10 % in this value. It is obvious that a method whereby local values can be accurately determined is needed.

Such a method was developed by Johannesen in the preceding paper. The amount of numerical work necessary was reduced to a minimum by the use of the Rayleigh-line equations.

The author would like to thank Dr N. H. Johannesen for his advice and criticism during the preparation of this paper, and also Mr H. K. Zienkiewicz for many helpful discussions. The author was in receipt of a grant from the Department of Scientific and Industrial Research during the course of this work.

REFERENCES

Bethe, H. A. & Teller, E. 1941 *Deviations from Thermal Equilibrium in Shock-Waves.* Cornell University.

Blackman, V. H. 1956 *J. Fluid Mech.* **1**, 61.

Broer, L. J. F. 1951 *Appl. Sci. Res.* A, **2**, 447.

Greenspan, W. D. & Blackman, V. H. 1957 *Bull. Amer. Phys. Soc.* **2**, 217.

Griffith, W. C. & Kenney, A. 1957 *J. Fluid Mech.* **3**, 286.

Gunn, J. C. 1946 *Aero Res. Coun., Rep. & Mem.* no. 2338.

Herman, R. & Rubin, R. J. 1959 *Phys. Fluids*, **2**, 547.

Herzfeld, K. F. 1955 Section H of *Thermodynamics and Physics of Matter* (Vol. 1 of *High Speed Aerodynamics and Jet Propulsion*). Princeton University Press.

Johannesen, N. H. 1961 *J. Fluid. Mech.* **10**, 25.

Lighthill, M. J. 1956 Article in *Surveys in Mechanics*, p. 250. Cambridge University Press.

Smiley, E. F. & Winkler, E. H. 1954 *J. Chem. Phys.* **22**, 1018.