Analysis of vibrational relaxation regions by means of the Rayleigh-line method

By N. H. JOHANNESEN

Department of the Mechanics of Fluids, The University of Manchester

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The physics of shock-waves with vibrational relaxation regions is recapitulated, and it is shown that exact methods of analysis can be developed from the classical Rayleigh-line equations by treating the real gas as an ideal gas with heat transfer. By using these methods to analyse experimental records of density distributions in relaxation regions, a large number of local values of the relaxation frequency, rather than a single over-all value, may be obtained from each shock-wave record.

1. Introduction

When a one-dimensional compression wave of finite amplitude travels into a gas at rest, the ultimate stable waveform, which propagates with constant velocity, is the result of a balance between two sets of influences. These are, as discussed in detail by Lighthill (1956), the convection which tends to steepen the waveform, and the various types of lag which resist this steepening.

We shall in this paper refer to the particular case of gases in which the lags in the various degrees of freedom of the molecule have markedly different effects. The translational and rotational degrees of freedom reach equilibrium in a very short time (after a few collisions) and the effects of their lag are confined to a narrow region at the front of the wave, the diffusion-resisted part of the wave. This is followed by a generally much wider region in which the vibrational degrees of freedom reach equilibrium. This region is called the relaxation region.

Waves in which both types of lag have an effect are called partly dispersed shock-waves. In some cases of very weak waves the relaxation alone gives sufficient resistance to the convective effects and the diffusion-resisted part of the wave is absent. Such waves are called fully dispersed.

In the present discussion we shall, in the case of partly dispersed waves, assume that the relaxation region is long compared with the diffusion-resisted region, in fact so much so that the thickness of the latter can be put equal to zero in the calculations. It is assumed throughout that the temperature is low enough and the pressure high enough for dissociation effects to be negligible.

Although the development of the stable waveform is most conveniently discussed in terms of a wave travelling into a stationary gas (this is also the case met with in the shock tube), for calculation purposes it is more convenient to consider the flow in a co-ordinate system fixed in the wave. This corresponds to the case of a gas passing through a stationary wave. Both distances and times will be measured from the downstream end of the diffusion-resisted part of the wave. Because of the assumption about the relative thicknesses of the two regions of the shock-wave, this definition is sufficiently accurate in most cases. It does, however, need modification in the case of a fully dispersed shock-wave.

It will be noted that in the definition adopted here the shock-wave is the whole of the wave. In the literature the wave is often described as a shock-wave followed by a relaxation region, and the term shock-wave therefore used for that part of the wave which in this paper, following Lighthill, is called the diffusion-resisted part of the wave.

Looking now at the passage of a diatomic gas through a stationary partly dispersed shock-wave, the processes may be described physically as follows. The gas approaches the shock-wave with conditions (1) and is compressed very rapidly in the diffusion-resisted part of the wave, so rapidly that the vibrational degrees of freedom are inactive. This means that the conditions at (a), just behind this part of the wave, can be calculated from the shock-wave equations ignoring the vibrational degrees of freedom. After (a) energy is fed into the vibrational degrees of freedom at a rate which depends on the pressure and temperature and on the difference between the local value of the vibrational energy and its equilibrium value at the local temperature. Temperature in this context means translational temperature, and it is assumed that the approach to vibrational equilibrium is so slow that the translational and rotational energies are in local equilibrium throughout the relaxation region. The final state with all the degrees of freedom in energy equilibrium is reached at (2), which is theoretically at infinity downstream.

The main theme of this paper is a discussion of the structure of the relaxation region, a problem which has received considerable treatment in the literature, but nevertheless remains far from clarified.

The ultimate goal from a practical point of view is to be able to predict the structure of the relaxation region for any shock-wave with given initial conditions. It will be shown that it is possible to do this very rapidly provided the rate of approach to equilibrium is known throughout the relaxation region.

We shall, for the time being, assume that the rate of change of vibrational energy at any point in the relaxation region is proportional to the difference between its local equilibrium value, $\bar{\sigma}$ (which is a function of the local temperature T), and its actual value, σ, so that a relaxation equation may be written

$$\frac{d\sigma}{dt} = \omega[\bar{\sigma}(T) - \sigma(t)]. \tag{1}$$

Here t is the time and ω is assumed to be a function of pressure and temperature only. Although (1) is strictly speaking only valid for a system of harmonic oscillators with small deviations from equilibrium (Landau & Teller, 1936; Herzfeld, 1955), nearly all work on the structure of relaxation regions has been done using this equation. It certainly forms a reasonable basis for the discussion of diatomic gases in which there is only one mode of vibration, in particular as neither theoretical nor experimental evidence is yet available which can suggest the form of a more complicated equation including the effects of anharmonicity and large departures from equilibrium.

For polyatomic molecules the situation is more complicated. In the case of several completely independent modes of vibration excited in parallel, it would be reasonable to write an equation of the form (1) for each mode. In actual molecules the energy transfer is probably a combination of simple transfer in parallel and various types of transfer in series, and the form of the appropriate relaxation equation is not known. Some slight progress has been made theoretically, but it seems likely that further progress must depend, at least in part, on more detailed experimental results than those already available.

All theoretical predictions of ω show that for an ideal gas, in which the specific heats depend on temperature only, ω is directly proportional to the pressure and may be written

$$\omega = p\Omega(T). \tag{2}$$

The temperature dependence of Ω is far more complicated. Relations similar to the one given by Gunn (1946),

$$\Omega = AT^{-1}\exp(-BT^{-\frac{1}{3}})\{1-\exp(-\theta/T)\}, \tag{3}$$

have been used in the plotting of most experimental results. A and B are constants depending on the gas only and θ is the characteristic temperature of vibration. The important term in this expression is $\exp(-BT^{-\frac{1}{3}})$ which follows from the Landau & Teller (1936) theory for the excitation probability. The power of T in the factor preceding the exponential depends, among other things, on the assumptions made in integrating this probability over the velocity distribution of the molecules. The bracket is often replaced by unity.

Experimental results confirm the general dependence of Ω on T but are not yet sufficiently accurate for judging the merits of the various forms of the less important terms in the expression. Ω must therefore be determined experimentally, and the present investigation was in fact started because of the apparent confusion in the literature as to the correct way of determining Ω from experimental observations of relaxation regions. As ω depends on both pressure and temperature and these both vary through the relaxation region (the temperature in strong shock-waves varying by a very large amount) it was felt that the common practice of ascribing to any particular relaxation region *one* value of ω and taking this as the value corresponding to certain 'mean' values of p and T was likely to lead to errors (or uncertainties) in Ω larger than those inherent in the experimental techniques used.

In § 2 it is shown that the variables in the relaxation region can be simply related by means of universal functions using the Rayleigh-line approach, and this approach is shown to lead to a simple method of determining local values of Ω throughout the relaxation region.

Most writers have used $\tau = 1/\omega$ to characterize the rate of approach to equilibrium and called it a relaxation time. This notation derived from the fact that if in (1) both ω and $\bar{\sigma}$ are taken to have constant values the equation integrates to give $\sigma-\bar{\sigma}_1 = (\bar{\sigma}_2-\bar{\sigma}_1)[1-\exp(-\omega t)]$ and $1/\omega$ is a conventional relaxation time. However, for the general case, in which we are interested in local rates of approach rather than over-all times, we prefer to use ω and call it a relaxation frequency.

2. Exact solutions using the Rayleigh-line method

The equations governing the transition through the shock-wave are:

$$\text{Continuity:} \qquad \rho v = \rho_1 v_1. \tag{4}$$

$$\text{Momentum:} \quad p+\rho v^2 = p_1+\rho_1 v_1^2. \tag{5}$$

$$\text{Energy:} \quad h+\tfrac{1}{2}v^2 = h_1+\tfrac{1}{2}v_1^2. \tag{6}$$

$$\text{State:} \qquad p = \rho RT. \tag{7}$$

Here h is the enthalpy and R is the gas constant. These equations relate variables at any point in the shock-wave, except in the diffusion-resisted part. They do not, however, relate the conditions at a point to the position of the point. Hence to introduce the x-co-ordinate we must use the relaxation equation (1) which can with $dx/dt = v$, $T = T(x)$, and $t = t(x)$, be written

$$v\frac{d\sigma}{dx} = p\Omega(T)\,[\bar{\sigma}(x)-\sigma(x)]. \tag{8}$$

If we know all the variables at a series of points $x_1, \ldots, x_p$ in the relaxation region we can at once find the local value of Ω in, say, the region x_n to x_{n+1}:

$$\Omega\left(\frac{T_n+T_{n+1}}{2}\right) = 2\frac{(v_n+v_{n+1})(\sigma_{n+1}-\sigma_n)}{(p_n+p_{n+1})(x_{n+1}-x_n)}[\bar{\sigma}_n+\bar{\sigma}_{n+1}-(\sigma_n+\sigma_{n+1})]^{-1}, \tag{9}$$

and each relaxation region will give values of Ω over the whole temperature range from T_a to T_2.

Experimental results are usually obtained as interferometer photographs and only one variable, the density ρ, is initially known as a function of x. In principle, all other variables can, using equations (4) to (7), be expressed as functions of ρ and the conditions at (a), but the expressions are very lengthy and numerical calculations of Ω using (9) would be very tedious. This is probably the reason why previous writers have not used (9) to find the local values of Ω, but instead introduced certain approximations and found a single value of Ω for each relaxation region.

We shall now show that it is possible to rearrange the exact equations so that the relations between the variables can be expressed as universal functions which have already been tabulated. This reduces very considerably the time involved in finding values of Ω from a known density distribution and makes calculations practicable.

The energy equation may be written

$$c_{p\alpha}T+\tfrac{1}{2}v^2+\sigma = c_{p\alpha}T_1+\tfrac{1}{2}v_1^2+\bar{\sigma}_1, \tag{10}$$

where $c_{p\alpha}$ is the specific heat at constant pressure ignoring vibration. If we put

$$\sigma - \bar{\sigma}_1 = q, \tag{11}$$

this becomes

$$c_{p\alpha} T + \tfrac{1}{2} v^2 = c_{p\alpha} T_1 + \tfrac{1}{2} v_1^2 - q. \tag{12}$$

We note that the equations (4), (5), (6), (7) and (12) are the equations governing the steady constant-area flow of an ideal gas with constant specific heats with heating or (as in the present case) cooling. We may therefore treat the non-equilibrium flow of the real gas through the shock-wave as that of an ideal gas (which we shall call the α-gas) from which heat is being extracted at a rate equal to that at which the energy increases in the vibrational modes of the real gas.

The real gas and the α-gas have at each point the same values of p, ρ, T and v, as these depend only on the translational energy which is in equilibrium. Other variables, such as stagnation temperature and Mach number, are useful parameters in the calculations when referred to the α-gas, but have no obvious meaning in the real gas except at stations (1) and (2).

To find all the required relations for the variables in the relaxation region we need only consider the α-gas and note that the quantity q increases monotonically from zero at station (a) to $\bar{\sigma}_2 - \bar{\sigma}_1$ at station (2). For the α-gas we know all quantities at station (1), namely m_1, T_1, T_{01}, p_1, v_1 and ρ_1. These are the same as for the real gas except the Mach number m_1, which is related to the Mach number M_1 of the real gas by

$$m_1 = M_1 (\gamma_1/\gamma_\alpha)^{\frac{1}{2}}, \tag{13}$$

and the stagnation temperature, T_{01}, which is only of interest for the α-gas and is

$$T_{01} = T_1(1 + \tfrac{1}{2}(\gamma_\alpha - 1) m_1^2). \tag{14}$$

Conditions (a) immediately behind the diffusion-resisted part of the shock-wave are found as those behind a normal shock-wave in the α-gas (the α-shock) with initial conditions (1). T_0 does not change through the diffusion-resisted part of the wave.

In the region (a) to (2) the ratio of the values of a certain quantity at two points can be expressed as a function of the Mach numbers of the α-gas at the two stations. Choosing as a reference station that at which $m = 1$, and using suffix b to indicate values at the reference station, we have the well-known Rayleigh-line relations (e.g. see Shapiro 1953):

$$\frac{T}{T_b} = \frac{(\gamma_\alpha + 1)^2 m^2}{(1 + \gamma_\alpha m^2)^2}, \tag{15}$$

$$\frac{T_0}{T_{0b}} = \frac{2(\gamma_\alpha + 1) m^2 (1 + \frac{1}{2}[\gamma_\alpha - 1] m^2)}{(1 + \gamma_\alpha m^2)^2}, \tag{16}$$

$$\frac{v}{v_b} = \frac{\rho_b}{\rho} = \frac{(\gamma_\alpha + 1) m^2}{1 + \gamma_\alpha m^2}, \tag{17}$$

and

$$\frac{p}{p_b} = \frac{\gamma_\alpha + 1}{1 + \gamma_\alpha m^2}. \tag{18}$$

These relations have been tabulated for $\gamma_\alpha = 7/5$, the value for diatomic and linear molecules (Shapiro 1953; Zucrow 1958). Available tabulations may not be detailed enough, but the range of m required for practical calculations is quite small and if necessary more detailed tables can be prepared very quickly.

So far we have described how to find the conditions at (a) and how to relate the variables within the relaxation region. Before describing the actual calculations in the relaxation region we must discuss the general behaviour of the variables in this region.

First let us look at the possible values of m_a. The minimum possible value of M_1 is unity which gives $m_1 = (\gamma_1/\gamma_\alpha)^{\frac{1}{2}}$. As M_1 increases, m_1 reaches a maximum value of unity for $M_1 = (\gamma_\alpha/\gamma_1)^{\frac{1}{2}}$. In the range $1 \leqslant M_1 \leqslant (\gamma_\alpha/\gamma_1)^{\frac{1}{2}}$, the shock-wave is fully dispersed and $m_1 = m_a \leqslant 1$. When $M_1 > (\gamma_\alpha/\gamma_1)^{\frac{1}{2}}, m_1 > 1$ and a diffusion-resisted part (α-shock) is present, corresponding to a normal shock-wave in the α-gas changing m from a value $m_1 > 1$ to a value $m_a < 1$. We therefore conclude that for all waves $m_a \leqslant 1$.

Equation (10) may be written

$$q/c_{p\alpha} = T_{01} - T_0 = T_{0a} - T_0. \tag{19}$$

As q increases when x increases through the relaxation region, T_0 must decrease. Differentiating (16) we find that $dT_0/dm > 0$ for $m < 1$, so that m decreases through the relaxation region. Similarly we find, by differentiating (17) and (18), that p and ρ increase while v decreases.

The behaviour of T is more complicated. Here we find that for decreasing m, T increases in the interval $1 > m > 1/(\gamma_\alpha)^{\frac{1}{2}}$ and decreases for $m < 1/(\gamma_\alpha)^{\frac{1}{2}}$. If, therefore, $1 > m_a > 1/(\gamma_\alpha)^{\frac{1}{2}}$ the temperature increases at the beginning of the relaxation region. Whether T increases throughout the relaxation region or reaches a local maximum depends on the range of m covered in the relaxation region. This again depends on the function $\bar{\sigma} = \bar{\sigma}(T)$ for the particular gas and cannot be discussed simply in terms of the initial conditions.

The calculation of the relaxation region can now be carried out as follows.

(1) From Equations (15) to (18), or using tables, find the reference values (suffix b) using the known conditions at either station (1) or station (a).

(2) Choose a succession of decreasing values of m, starting with m_a. For each value of m read from the tables of the values of T, T_0, v, ρ and p. (By taking as values of m those appearing as arguments in the table, interpolation is avoided.)

(3) From T and tabulated values of $\bar{\sigma}(T)$ find $\bar{\sigma}$.

(4) From T_0 find q from (19) and hence σ from (11).

(5) Continue this process until at station (2) $\sigma_2 = \bar{\sigma}_2$. The exact conditions at (2) are found very easily by 'overshooting' slightly and interpolating once.

It is interesting to compare this method of finding the equilibrium conditions at (2) with the usual method due to Bethe & Teller (1941). In their method the temperature at (2) is chosen and conditions at (1) calculated. If the equilibrium conditions behind a shock-wave with known initial conditions are required it is therefore necessary to carry out the calculations for at least two values of T_2 before interpolating, whereas in the method suggested above, the final values follow from a single calculation starting with the known initial conditions.

Having determined the variables through the relaxation region it is now straightforward to apply the results to the two cases of interest.

If ρ is known as an experimentally determined function of x, we can find the values of x at the points used in the tabulation of the variables in the relaxation region, in other words find $x = x(m)$, and (9) at once gives the local values of Ω.

If Ω is known as a function of T we know all quantities in the relaxation region except x, and (8) can be rewritten as

$$dx = \frac{v\,d\sigma}{p\Omega(\bar{\sigma}-\sigma)}, \tag{20}$$

and integrated numerically to give the values of x.

A good deal of thought was given to the choice of the most convenient parameter to be used in the calculations, and it was found that using the Mach number, m, of the α-gas gave by far the quickest calculation procedure. With the variables tabulated as functions of m with sufficiently small steps in m, interpolation in the tables is only necessary at stations (a) and (2). If, for example, a series of values of ρ, or equidistant values of x, were chosen, interpolation would be necessary at all points in the relaxation region.

3. Discussion and conclusions

It has been shown that the use of the Rayleigh-line equations reduces the numerical work involved in the calculation of the structure of relaxation regions or the derivation of relaxation frequencies from experimentally determined density distributions to such an extent that exact calculations become just as easy as approximate ones.

The use of the Rayleigh-line equations has the major advantage that a whole series of values of the relaxation frequency, each corresponding to a definite pressure and temperature, can be determined from each relaxation region density distribution. This reduces the experimental work very considerably, and, what is perhaps more important, it offers a method for detailed study of the relaxation equation. If the simple equation (1) is valid it will be found that values of Ω (i.e. ω reduced to a pressure of one atmosphere) depend on T only and not on where in the relaxation region they have been found. If, however, Ω depends also on the departure from equilibrium, this should be easily detectable, and it might be possible to find the form of the dependence.

Similarly, in the case of gases for which the simple relaxation equation would not be expected to hold, detailed analysis of the relaxation region may help to determine the more complicated relaxation equation.

The method is at present being used in this department to evaluate experimental results on strong (large departures from equilibrium) shock-waves in nitrogen and on weaker waves in carbon dioxide which has several modes of vibration with different relaxation frequencies.

In the following paper Blythe (1961) uses the exact calculation method outlined in the present paper to assess the various approximate methods which have been proposed in the literature, and he also includes illustrative numerical examples.

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