Characteristics of the equations of motion of a reacting gas

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SUMMARY

The equations of motion for a chemically reacting gas in the absence of viscosity and heat conduction are set up. It is shown that the characteristic speed defined by this set of equations is the high-frequency limit of the phase velocity of sound waves as long as the reaction rate is finite. At infinite reaction rate (chemical equilibrium) the characteristics suddenly change to the low-frequency sound speed. The nature of this transition is discussed in connection with a recent paper of Resler (1957).

1. INTRODUCTION

From the point of view of chemical thermodynamics there are no essential difficulties in writing down the equations governing the motion of a gas which is not in chemical equilibrium. This is done, for example, in the theory of irreversible thermodynamics and in papers on laminar flame speed. In these cases the main accent is on the chemistry.

If one is interested mainly in the dynamics of the gas flow some changes in the choice of variables prove to be advantageous. A special case, flow of an ideal gas with lagging vibrational or rotational heat capacity, has been discussed from this gasdynamical point of view in an earlier paper (Broer 1950). One of the results of this work was that the characteristics of this type of flow are determined by the high-frequency limit of the speed of sound.

Apparently this fact has been sometimes thought to be slightly puzzling. In a recent paper Resler (1957) has given another treatment from which it would appear that this property does not hold. As in the author's opinion this treatment is not entirely satisfactory, it is proposed to return to this question, generalizing some of the work of our first paper. We shall pay especial attention to the relations with sound dispersion and characteristic theories, and since we are solely concerned with the interaction of reaction and flow, we shall neglect the effects of viscosity, heat conduction, and diffusion. Moreover, for the sake of simplicity, a gas in which only one reaction occurs will be considered.

2. EQUATIONS OF MOTION

Under our assumptions the general equations of gasdynamics take the following familiar forms. The continuity equation is

$$\frac{D\rho}{Dt}+\rho\operatorname{div}\mathbf{v}=0, \tag{1}$$

the Eulerian equation of motion is

$$\frac{D\mathbf{v}}{Dt}+\frac{1}{\rho}\operatorname{grad}p=0, \tag{2}$$

and the energy equation is

$$\frac{D}{Dt}(\tfrac{1}{2}v^2+U)+\frac{1}{\rho}\operatorname{div}(p\mathbf{v})=0, \tag{3}$$

where U is the energy of the gas per unit mass and the other symbols have their usual meanings. Introducing the enthalpy per unit mass $H=U+p/\rho$ and using (1) and (2) we derive two equations equivalent to (3)

$$\frac{D}{Dt}(\tfrac{1}{2}v^2+H)-\frac{1}{\rho}\frac{\partial p}{\partial t}=0 \tag{4}$$

and

$$\frac{DH}{Dt}=\frac{1}{\rho}\frac{Dp}{Dt}. \tag{5}$$

In steady flow equation (4) yields the equivalent of Bernoulli's law $\frac{1}{2}v^2+H=$ const. on a streamline, but (5) is the most convenient form for most of our work.

In the gasdynamical treatment it is advisable to consider H as a function of p and ρ. Moreover, H will depend on a parameter q which determines the chemical composition of the gas. The energy equation (5) then can be written

$$H_\rho\frac{D\rho}{Dt}+\left(H_p-\frac{1}{\rho}\right)\frac{Dp}{Dt}+H_q\frac{Dq}{Dt}=0. \tag{6}$$

If there were several reactions we would have to consider a set of parameters, but we confine ourselves here to the case of one reaction. In order to have a complete set of equations, however, we still need an equation for the rate of change of q. It will be assumed that for each value of p and ρ, there exists one equilibrium value of q, which is denoted by $\bar{q}(p,\rho)$. The tendency of the reaction will then be to make q tend towards the momentary value of $\bar{q}$. We now suppose that q can be chosen in such a way that

$$\frac{Dq}{Dt}=-\alpha(q-\bar{q}) \tag{7}$$

is a good approximation to the rate equation. The reaction rate α (a positive quantity) depends on the state of the gas and is therefore a function of p, ρ and, possibly, q.

Once the functions $H(p,\rho,q)$, $\bar{q}(p,\rho)$ and $\alpha(p,\rho,q)$ are determined, the set of equations (1), (2), (6) and (7) is sufficient to describe the flow.

3. DISPERSION OF SOUND

As in the theory of sound propagation, we put $\mathbf{u} = \epsilon\mathbf{u}_1$, $p = p_0 + \epsilon p_1$ etc., substitute in the equations of motion and retain only terms of the first order in ϵ. In order to obtain plane progressive waves we take all first-order quantities proportional to $\exp i(\omega t - kx)$. The resulting set of homogeneous equations for the amplitudes can be solved only when its determinant vanishes. This condition then yields the required relation between ω and k.

Remembering that $q_0 = \bar{q}(p_0, \rho_0)$ since the undisturbed gas is in equilibrium, the indicated programme can be carried through by means of simple and straightforward calculations. The resulting expression for the square of the phase-velocity of sound is

$$\frac{\omega^2}{k^2} = \frac{-H_\rho(i\omega+\alpha) - \alpha H_q \bar{q}_\rho}{(H_p - 1/\rho)(i\omega+\alpha) + \alpha H_q \bar{q}_p}. \tag{8}$$

In this dispersion equation the suffix zero in the coefficients has been dropped. We can rearrange the equation by introducing limiting speeds for high and low frequencies

$$c^2 = \frac{-H_\rho}{H_p - 1/\rho} \quad \text{and} \quad \bar{c}^2 = \frac{-(H_\rho + H_q \bar{q}_\rho)}{(H_p + H_q \bar{q}_p) - 1/\rho}. \tag{9}$$

From the thermodynamical relation

$$\left(\frac{\partial H}{\partial \rho}\right)_p \left(\frac{\partial \rho}{\partial p}\right)_S = \frac{1}{\rho} - \left(\frac{\partial H}{\partial p}\right)_\rho,$$

it is seen that c corresponds to the usual value for the sound speed when q is kept fixed. This is to be expected since the reaction will be frozen at sufficiently high frequencies. On the other hand, $\bar{c}$ can be obtained by supposing that equilibrium is maintained throughout, i.e. $q = \bar{q}$. Writing $H\{p, \rho, \bar{q}(p, \rho)\} = \bar{H}(p, q)$, we have

$$\bar{H}_\rho = H_\rho + H_q \bar{q}_\rho, \qquad \bar{H}_p = H_p + H_q \bar{q}_p,$$

which proves this contention.

Substituting (9) in (8), we obtain

$$\frac{\omega^2}{k^2} = c^2 - \frac{c^2 - \bar{c}^2}{1 + i\omega\tau}, \tag{10}$$

where

$$\tau = \frac{1}{\alpha}\frac{\bar{c}^2}{c^2}\frac{H_\rho}{H_\rho + H_q \bar{q}_\rho}.$$

At intermediate frequencies the phase velocity is complex, which means that there is absorption of sound.

We note here for further reference that owing to the absorption the variable parts of pressure and density are not in phase. The continuity equation (1), after linearization, reduces to

$$i\omega\rho_1 - \rho_0 ikv_1 = 0,$$

and the Eulerian equation (2) to

$$i\omega v_1 - \frac{1}{\rho_0} ikp_1 = 0.$$

Therefore $p_1/\rho_1 = \omega^2/k^2$, which is complex.

In the usual theory of sound dispersion due to lagging heat capacities

$$H = C_p T + C'\theta,$$

where C_p is the non-lagging specific heat and θ the temperature of the lagging degrees of freedom. If we now take $\theta = q$, $H = (C_p/R)(p/\rho) + C'q$, it can be verified that this theory is a special case of the formalism of this section.

4. Characteristics

The set of equations (1), (3), (6) and (7) is quasi-linear, which means that it is linear in the derivatives of the dependent variables v, p, ρ and q but not in these variables themselves. A characteristic equation of this type involves only one specific combination of derivatives. We consider in this section only one-dimensional unsteady flow. A characteristic equation then can be interpreted as a law of propagation. Speed and decrement of this characteristic propagation depend only on the variables, not on their derivatives.

In our problem, (6) and (7) are already characteristic equations as they stand. The speeds involved are equal to v, and the equations therefore determine relations between rates of change of some quantities along the path of a fluid element.

Using (7) and (9), we write (6) in the form

$$c^2\frac{D\rho}{Dt} - \frac{Dp}{Dt} = \alpha\frac{c^2 H_q}{H_\rho}(q-\bar{q}). \tag{11}$$

The remaining two characteristic equations are linear combinations of the continuity and Eulerian equations. When (11) is used to write the former equation in terms of derivatives of p, it is easily seen that the required combinations are

$$D_{\pm c}p \pm \rho c(D_{\pm c}v) = -\alpha c^2(H_q/H_\rho)(q-\bar{q}), \tag{12}$$

where

$$D_{\pm c} = \frac{D}{Dt} \pm c\frac{\partial}{\partial x}.$$

This equation corresponds to characteristic speeds $v \pm c$. According to the results of § 3, this implies that the characteristics correspond to propagation of a disturbance of infinite frequency.

In the general theory of characteristics, which was not needed here since the required linear combination could be found by inspection, the characteristic speeds are found from a determinant equation. It is easily verified that this determinant has exactly the same structure as that required in the dispersion theory, apart from the terms in α, which do not occur in the characteristic determinant. The algebraic reason for our result is therefore obvious. The physical interpretation, however, has caused some difficulties.

5. MOTION NEAR EQUILIBRIUM STATE

The trouble with the interpretation of the characteristic speed lies in the motion near equilibrium. In this case, the change in condition of a fluid element is slow compared with α, and $q-\bar{q}$ therefore remains very small. It is to be noted that this does not mean small Mach number or Mach number change. The restriction is on the acceleration, not on the velocity.

When $q-\bar{q}$ is exactly zero, the energy equation takes the form

$$\bar{H}_p \frac{Dp}{Dt} + \bar{H}_\rho \frac{D\rho}{Dt} = \frac{Dp}{Dt},$$

or

$$\bar{c}^2 \frac{D\rho}{Dt} - \frac{Dp}{Dt} = 0.$$

Using this equation in the continuity equation, we obtain the linear combinations

$$D_{\pm\bar{c}}\, p \pm \rho\bar{c} D_{\pm\bar{c}}\, v = 0, \tag{13}$$

which are again characteristic equations, but now with $v \pm \bar{c}$ as characteristic speeds.

This result is not unexpected as the gas in equilibrium can be considered as a non-reacting gas with appropriate equation of state, since its condition depends only on the two variables p and ρ. The question, however, is what happens when the reaction rate, although large, is finite. One could conjecture that the characteristic speeds would in some way change continuously from $v \pm c$ to $v \pm \bar{c}$, but this appears not to be true. As long as there is a finite reaction rate, the theory of § 4 applies and $v \pm c$ is the characteristic speed, although it would be expected that the motion tends to a solution of (13) with characteristic speeds $v \pm \bar{c}$.

Before investigating this behaviour, we first point out that for motion near equilibrium $q-\bar{q}$, but not $\alpha(q-\bar{q})$, is a small quantity since this motion is realized only when α is large enough. We have in fact, from (7),

$$-\alpha(q-\bar{q}) = \frac{Dq}{Dt} \div \frac{D\bar{q}}{Dt} = \bar{q}_p \frac{Dp}{Dt} + \bar{q}_\rho \frac{D\rho}{Dt}.$$

Therefore, there is at any rate no direct contradiction between (12) and (13), since the right-hand side of (12) does not tend to zero with increasing reaction rate.

We shall now derive equations equivalent to (12) but with their left-hand sides identical with (13). We start from the energy equation (6) and substitute

$$\frac{Dq}{Dt} = \frac{D\bar{q}}{Dt} + \frac{D}{Dt}(q-\bar{q}) = \bar{q}_p \frac{Dp}{Dt} + \bar{q}_\rho \frac{D\rho}{Dt} + \frac{D}{Dt}(q-\bar{q}).$$

In this way we obtain

$$\frac{D\rho}{Dt} - \frac{1}{\bar{c}^2}\frac{D}{Dt} = -\frac{1}{\bar{H}_\rho}\frac{D}{Dt}(q-\bar{q}). \tag{14}$$

When (14) is substituted into the continuity equation, we can form the linear combinations

$$D_{\pm\bar{c}}p \pm \rho\bar{c}D_{\pm\bar{c}}v = \frac{\bar{c}^2}{\bar{H}_\rho}\frac{D}{Dt}(q-\bar{q}). \tag{15}$$

These equations tend directly to (13) when the reaction rate α goes to infinity, because the right-hand side depends on $(q-\bar{q})$ but does not, as in (12), contain a factor α.

In a numerical calculation procedure use of (15), instead of (12), could be advantageous when the reaction rate is sufficiently high. Nevertheless it must be kept in mind that the set (15) is not a set of characteristic equations in the usual sense. The reason is that the coefficient at the right-hand side does not depend on the variables only but contains derivatives. A consequence of this fact is that (15) does not have all the properties of characteristic equations. For example, discontinuities in derivatives do not propagate with the velocity $\pm\bar{c}$ but with $\pm c$ relative to the gas, no matter what the reaction rate is as long as it is finite. Only when $q = \bar{q}$ exactly, do the derivatives drop out from the coefficients in (15) which then goes over into (13) and so assumes all the properties of a characteristic set of equations.

The remark on the propagation of discontinuities of derivatives furnishes another clue to the situation. Let us consider a small disturbance, confined in a bounded region at some moment and having discontinuities in some derivative at the boundary of this region. When we linearize the equations and take Fourier transforms the spectra will extend to infinity. It is therefore not unexpected that the boundary of the disturbance will propagate with the high frequency sound speed c.

6. AN ALTERNATIVE FORM OF THE EQUATIONS

A very simple variant on the equations (12) and (15) has been proposed by Resler (1957). It is easy to show, starting from the one-dimensional continuity and Euler equations, that

$$D_{\pm a}p \pm \rho a D_{\pm a}v = 0, \tag{16}$$

where

$$a^2 = \frac{Dp}{Dt}\bigg/\frac{D\rho}{Dt}. \tag{17}$$

These equations look like characteristic equations. However, it is not possible to express a in terms of v and the variables of state without using derivatives. One could eliminate, for example, $D\rho/Dt$ by means of (11) or (14) but then Dp/Dt will still persist. The equations (16) do not therefore have the properties of characteristic equations. They might, however, on occasion be useful for numerical work, just like (15).

It could easily be assumed that a would lie between c and $\bar{c}$, but this would be fallacious; it is not even true that a always exists. This would require that Dp/Dt and $D\rho/Dt$ were of the same sign everywhere, and we saw in § 3 that in the simple example of a plane travelling sound wave there is a phase difference between the variable parts of p and ρ owing to the reaction rate. This entails a phase difference between $\partial p/\partial t$ and $\partial \rho/\partial t$, which therefore change sign at different moments.

In view of the engaging simplicity of (16) this result is somewhat annoying. It has, however, a sound physical basis. The equations (12) essentially describe propagation of waves with velocity c and a certain attenuation owing to dissipation of mechanical energy which is given by the right-hand side. Equation (17), in connection with (16), means that one looks for the speed of propagation a of a point which has a constant wave amplitude as the propagation equations have no right-hand sides in this case. This is possible only as long as the chosen value of the amplitude is less than that at the summit of the wave.

7. DISSIPATION

In terms of the usual thermodynamic variables, we can write

$$dH = T\,dS + dp/\rho + Q\,dq \tag{18}$$

and consider H as a function of S, p and q. $Q = (\partial H/\partial q)_{p,S}$ is a quantity of the nature of a chemical potential. (Q is different from $H_q = (\partial H/\partial q)_{p,\rho}$ as defined in § 2.)

As the enthalpy H tends to a minimum for constant values of p and S we can calculate $\bar{q}$ from the equation $Q(\bar{q}, p, S) = 0$. Therefore, when q is close to $\bar{q}$, Q will be approximately equal to $\beta(q-\bar{q})$, where $\beta = \partial^2 H/\partial q^2$ is a positive quantity since H must be a minimum for $q = \bar{q}$.

When, for given values of p and S, only one equilibrium value of q is of interest, Q does not change sign at other values of q. Hence, $Q(q-\bar{q})$ is always positive or zero. We now combine (5) and (18), obtaining

$$T\frac{DS}{Dt} + Q\frac{Dq}{Dt} = 0.$$

This equation corresponds to $DS/Dt = 0$ in ordinary gasdynamics, and it could be used instead of the energy equation. Substituting the rate equation (7) we find the dissipation equation

$$T\frac{DS}{Dt} = \alpha Q(q-\bar{q}). \tag{19}$$

It is seen, therefore, that the dissipation is always non-negative.

When α is large, (19) is approximately

$$T\frac{DS}{Dt} = \alpha\beta(q-\bar{q})^2,$$

which is then of order α^{-1}. This yields the expected result that the dissipation vanishes in the limit of fast reaction.

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REFERENCES

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