Reprinted from

The Physics of Fluids

Volume 19 February 1976 Number 2

Conditional stability of shock waves—a criterion for detonation

G. R. Fowles

Department of Physics, Washington State University, Pullman, Washington 99163

pp. 227-238

a publication of the American Institute of Physics

Conditional stability of shock waves—a criterion for detonation

G. R. Fowles

Department of Physics, Washington State University, Pullman, Washington 99163
(Received 7 July 1975)

The stability of plane shock waves is treated by examining the amplitudes of acoustic waves reflected from shock fronts, and by methods of irreversible thermodynamics. Both approaches yield the same conditions for stability, $-1 \le j^2(dV/dP)_H \le 1$, where j^2 is the negative slope of the Rayleigh line, and the derivative is taken along the Hugoniot P-V curve. The thermodynamic method indicates that instabilities are associated either with local maxima in the entropy, or shock velocity; or with local minima in the reduced internal energy, or particle velocity, along the Hugoniot curve. It is proposed that the latter case corresponds to detonation with the detonation state given by the particle velocity minimum.

I. INTRODUCTION

Earlier studies of the stability of shock waves have established the existence of two limits outside which a shock splits spontaneously into two waves traveling in the same or in opposite directions. Bethe first derived sufficient conditions for plane shocks to be stable against such breakup.[1] Later studies by D'yakov,[2] and by Erpenbeck,[3] based on analysis of the stability with respect to two-dimensional perturbations also established two bounds; these were shown by Gardner to be equivalent to Bethe's criteria for plane shocks.[4,5]

In this paper we consider a region within the above limits in which a shock is evidently potentially unstable for other reasons. We show that in this region small amplitude acoustic waves incident on the shock front from the compressed region behind the front undergo amplification upon reflection at the front. This can lead to an oscillatory type of instability proposed earlier,[6] although it is not clear from this treatment that instability necessarily occurs when the amplification criterion is satisfied.

We have also approached the stability problem from the point of view of irreversible thermodynamics and show, based on a plausible hypothesis, that in the region under consideration a shock is thermodynamically unstable; whether or not instability actually occurs depends on the magnitude of perturbations. The acoustic wave approach and the thermodynamic approach thus exhibit a nice correspondence.

Technical interest in the shock stability problem derives from applications in which it is desired to relate wave propagation behavior to properties of the transmitting medium. In solids, for example, polymorphic phase changes and yielding at the elastic limit may lead to splitting of a single shock into two shocks traveling in the same direction. In reactive media, self-sustaining waves or detonation waves, may form under conditions that are not well understood.

The problem is also of exceptional theoretical interest because of the existence of several apparently distinct methods of approach, as has been pointed out by Woods.[7] The theory of irreversible thermodynamics is well known to be underdeveloped, and it may be hoped that new insight into the theory will result from application of various methods to a relatively simple problem such as that of plane shock waves.

The thermodynamic method employed here invokes no new principles but requires the recognition that the approach to equilibrium of two systems initially out of equilibrium is characterized by nonnegative entropy production in each system. This can be expressed, at least for adiabatic, viscous flow, by an upper as well as a lower bound to the entropy production rate. Still another statement is that the reduced internal energy (defined later) is minimized *and* the entropy is maximized in equilibrium. These latter statements are not, in general, equivalent; one does not imply the other.

The thermodynamic method predicts a new criterion for detonation that is quite different from the Chapman–Jouguet Theory. We postulate this criterion in Sec. V.

In Sec. II we display the jump conditions and several definitions and transformations that are useful. Section III is a summary of the conclusions of the Bethe–D'yakov theory. The interaction of acoustic waves with the shock front is considered in Sec. IV and the thermodynamic approach is presented in Sec. V.

II. JUMP CONDITIONS

The well-known Rankine–Hugoniot jump conditions applicable to plane shocks with steady profile or to discontinuous jumps can be written,[8]

$$u - u_0 = \rho_0(U - u_0)(V_0 - V) , \tag{1}$$

$$\sigma - P_0 = \rho_0(U - u_0)(u - u_0) , \tag{2}$$

$$E - E_0 = \tfrac{1}{2}(\sigma + P_0)(V_0 - V) . \tag{3}$$

These equations express conservation of mass, momentum, and energy, respectively. Mass velocity is denoted by u, shock velocity by U, specific volume by $V = \rho^{-1}$, normal stress in the direction of propagation by σ (measured positive in compression), and specific internal energy by E. Subscripts 0 refer to the undisturbed state ahead of the shock, assumed to be a thermodynamic equilibrium state. The mechanical conditions, Eqs. (1) and (2) require no assumption about thermodynamic equilibrium and apply throughout the shock transition region; hence, the use of σ to denote stress rather than P which is used to denote the pressure of thermodynamic equilibrium states. Equation (3) is valid whenever no other sources of energy besides mechanical energy are assumed.

Since a shock is an adiabatic process, Eq. (3) applies to equilibrium end states; it only applies to the shock transition region, however, when heat conduction and radiation in that region can be neglected. Equation (3) is termed the Hugoniot relation and, for given (P_0, V_0, E_0), defines a surface,

$$\sigma = \sigma(V, E; P_0, V_0, E_0) \quad (V \neq V_0) ,$$

that represents the locus of states achievable by a shock transition in *any* medium.

For the description of shocks in a specific medium, Eqs. (1)–(3) are supplemented by the equilibrium equation of state of the medium in the form

$$P = P(V, E; E_0) . \tag{4}$$

The simultaneous solution of Eqs. (3) and (4), with $\sigma = P$, yields a curve $P(V)$ termed the "Hugoniot equation of state," or sometimes the "*R-H* curve."

We define several useful quantities

$$j \equiv \rho_0(U - u_0) , \tag{5}$$

whence, from Eqs. (1) and (2),

$$j^2 \equiv (\sigma - P_0)/(V_0 - V) . \tag{6}$$

Also,

$$M \equiv |(U - u)/c| \tag{7}$$

and

$$c^2 \equiv \left(\frac{\partial P}{\partial \rho}\right)_s = -V^2\left(\frac{\partial P}{\partial V}\right)_s . \tag{8}$$

The quantity j is the mass flux through the shock front and is positive when the shock velocity exceeds the initial mass velocity u_0. Its square j^2 is also equal to the negative slope of the Rayleigh line joining the end states. The quantity M is the local Mach number of the shock with respect to the medium, and c is the local sound speed in spatial coordinates. The subscript s denotes the isentropic derivative.

Several combinations of these relations yield useful transformations. Thus, combining Eqs. (1), (2), and (6),

$$(u - u_0)^2 = (\sigma - P_0)(V_0 - V) = j^2(V_0 - V)^2 . \tag{9}$$

This can be differentiated to give

$$2(u - u_0)du = -(\sigma - P_0)dV + (V_0 - V)d\sigma ,$$

or, using Eq. (9),

$$j\left(\frac{du}{dP}\right)_H = \pm\frac{1}{2}\left[1 - j^2\left(\frac{dV}{dP}\right)_H\right] , \tag{10}$$

where the subscript H denotes differentiation along the Hugoniot curve.

For definiteness we consider only compressive shocks traveling in the positive direction, so that,

$$j > 0 ; \quad V < V_0 ; \quad \text{and} \quad u > u_0 .$$

As a result of this assumption we retain only the positive sign in Eq. (10).

An alternate expression for Eq. (7) can be derived, using Eqs. (5), (8), and (9),

$$M^2 = \left|\frac{U - u}{c}\right|^2 = \frac{[V_0 j - (V_0 - V)j]^2}{-V^2(\partial P/\partial V)_s}$$

$$= -j^2\left(\frac{\partial V}{\partial P}\right)_s . \tag{11}$$

For small amplitude acoustic waves we make use of the characteristic equations and associated compatibility conditions[8]

$$C\pm : \; dx/dt = u \pm c \tag{12a}$$

and

$$\Gamma\mp , \text{ or } S\pm : \; dP/du = \pm \rho c . \tag{12b}$$

The upper sign of Eq. (12b) holds *across* forward-facing waves, specified by the positive sign of Eq. (12a). Thus, Γ^+ is valid *on* the characteristic path C^+, and Γ^- holds on C^-. For acoustic waves the flow is assumed to be isentropic, and we therefore adopt the obvious notation for these waves

$$\left(\frac{du}{dP}\right)_s = \pm (V/c) .$$

Combining this with Eqs. (6) and (11) gives,

$$\left(\frac{du}{dP}\right)_s = \pm\left(-\frac{\partial V}{\partial P}\right)_s^{1/2}$$

$$= \pm (M/j) . \tag{13}$$

Still another useful relation can be obtained by writing the slope of the Hugoniot curve as a directional derivative,

$$\left(\frac{dP}{dV}\right)_H = \left(\frac{\partial P}{\partial V}\right)_E + \left(\frac{\partial P}{\partial E}\right)_V \left(\frac{dE}{dV}\right)_H ,$$

and employing Eq. (3), which differentiated is, with $\sigma = P$,

$$\left(\frac{dE}{dV}\right)_H = -\tfrac{1}{2}(P + P_0) + \tfrac{1}{2}(V_0 - V)\left(\frac{dP}{dV}\right)_H .$$

Thus,

$$\left(\frac{\partial P}{\partial V}\right)_E = \left(\frac{dP}{dV}\right)_H + \frac{1}{2}\left(\frac{\partial P}{\partial E}\right)_V \left[P + P_0 - (V_0 - V)\left(\frac{dP}{dV}\right)_H\right] .$$

However, on the equilibrium surface,

$$\left(\frac{\partial P}{\partial V}\right)_E = \left(\frac{\partial P}{\partial V}\right)_s - \left(\frac{\partial P}{\partial E}\right)_V \left(\frac{\partial E}{\partial V}\right)_s = \left(\frac{\partial P}{\partial V}\right)_s + P\left(\frac{\partial P}{\partial E}\right)_V .$$

The Grüneisen parameter is

$$\Gamma = V(\partial P/\partial E)_V .$$

Hence, equating the two expressions for $(\partial P/\partial V)_E$,

$$\left(\frac{dV}{dP}\right)_H = \frac{1 - (\Gamma/2V)(V_0 - V)}{(\partial P/\partial V)_s + (\Gamma/2V)(P - P_0)} . \tag{14}$$

This can be simplified by the substitution

$$a = (\Gamma/2V)(V_0 - V) , \tag{15}$$

together with Eq. (11). We get

$$j^2(dV/dP)_H = M^2(a - 1)/(1 - M^2 a) . \tag{16}$$

A graph of this equation is shown in Fig. 1.

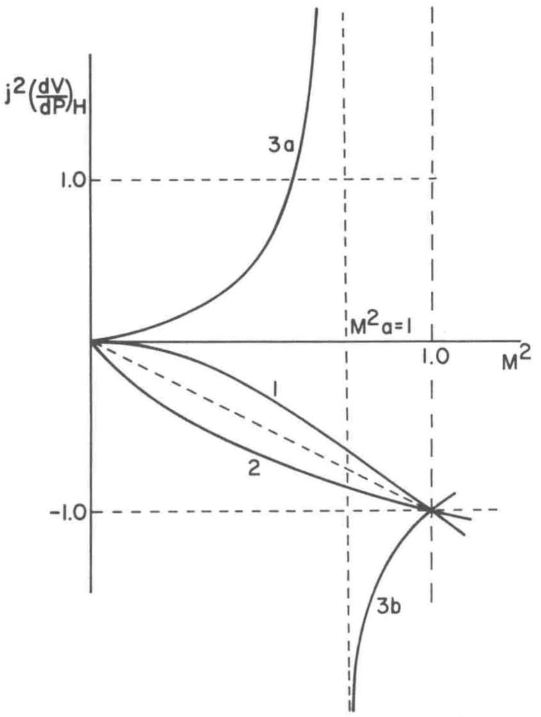

FIG. 1. Plot of $j^2(dV/dP)_H$ as function of M^2 for various values of a. Branch 1: $0<a<1$; Branch 2: $a<0$; Branch 3: $1<a$; Branch $3b$: $M^2a>1$.

III. STABILITY WITH RESPECT TO TWO-DIMENSIONAL PERTURBATIONS

In this section we summarize the results of studies by D'yakov and by Erpenbeck of the structural stability of shocks with respect to two-dimensional perturbations.[2,3,5] These results are of special interest in the present context because the limits derived also correspond to the absolute instability limits for breakup of a plane shock into two waves, derived by Bethe.[1] This correspondence was first pointed out by Gardner.[4]

The results of these studies show that shock waves are unstable outside the limits given by

$$-1 \leqslant j^2(dV/dP)_H \leqslant 1+2M . \tag{17}$$

When either of these inequalities is exceeded, small sinusoidal perturbations of the front grow in amplitude with time.

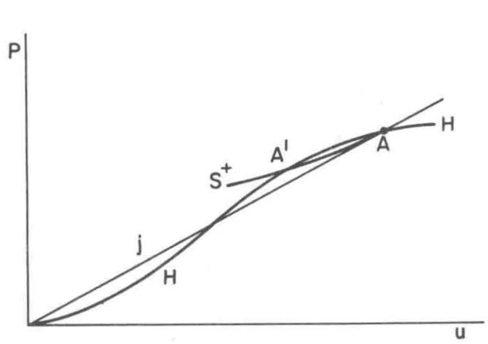

FIG. 2. Unstable Hugoniot curve, $j^2(dV/dP)_H<-1$. Hugoniot, H, and characteristic curve, S^+, lie above Rayleigh line, j, at A. Subsonic condition, $M<1$, violated at A.

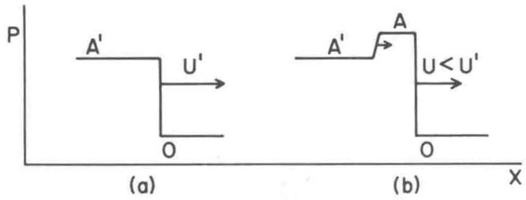

FIG. 3. Alternative wave solutions consistent with Hugoniot of Fig. 2.

It is remarkable that the limits of Ineq. (17) are also those for which a shock can split into two waves. That is, outside either limit a prescribed pressure, particle-velocity boundary condition can be satisfied by either a single shock or by a two-wave configuration. First, consider a case in which the lower limit is violated. Then, it is clear from Fig. 1 that, provided $M^2a<1$, the only solutions consistent with the jump conditions correspond to $M^2>1$. However, this implies that the shock travels faster than the speed of sound in the compressed medium behind the shock, and it has been shown that the Second Law would then be violated in the shock transition.[9] It will be shown later that the branch $M^2a>1$ is also unstable.

Another point of view that can be taken is illustrated in Fig. 2, which shows a Hugoniot curve in the P-u plane for which the lower limit of Ineq. (17) is violated at point A. The isentropic curve through point A intersects the Hugoniot curve again at point A'. We note that both the Hugoniot curve and the isentropic curve must lie on the same side of the Rayleigh line and are simultaneously tangent to that line at the lower stability limit of Ineq. (17). This is shown by Eq. (10), which can be inverted to give

$$j^2\left(\frac{dV}{dP}\right)_H = 1 - 2j\left(\frac{du}{dP}\right)_H ,$$

so that

$$-1 < j^2\left(\frac{dV}{dP}\right)_H$$

implies

$$j\left(\frac{du}{dP}\right)_H < 1 .$$

Moreover, as noted previously, when $M^2a<1$, this same restriction implies $M<1$, and from Eq. (13),

$$j\left(\frac{du}{dP}\right)_s < 1 .$$

This result has also been discussed by Landau and Lifshitz (Ref. 10, p. 326).

The configuration shown in Fig. 2 admits two solutions for prescribed boundary conditions corresponding to state A'. These are (a) a single shock to A', and (b) a shock to state A followed by a slower rarefaction wave to A', as illustrated in Fig. 3. In order for (b) to be a stable configuration (and a single shock to A to be unstable) the speed of the rarefaction wave must be less than the speed of the shock, i.e., the shock must be supersonic with respect to the medium behind, or $M>1$.

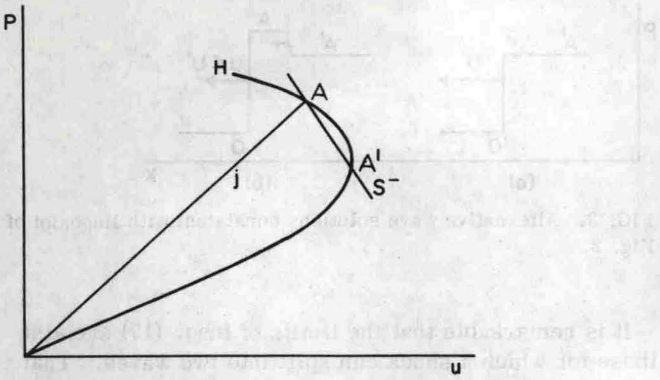

FIG. 4. Unstable Hugoniot curve, $j^2(dV/dP)_H > 1+2M$. Characteristic curve, S^-, intersects Hugoniot, H, twice, at A and A′.

An analogous argument applies when the upper limit of Ineq. (17) is violated. In this case, using Eq. (10),

$$j^2\left(\frac{dV}{dP}\right)_H = 1-2j\left(\frac{du}{dP}\right)_H > 1+2M\ ,$$

or, since $j>0$,

$$\left(\frac{du}{dP}\right)_H < -\frac{M}{j}\ .$$

Employing Eq. (13) this implies, for the negative solution of Eq. (13),

$$\left(\frac{dP}{du}\right)_s < \left(\frac{dP}{du}\right)_H < 0\ .$$

A configuration satisfying this inequality is shown in Fig. 4; the isentrope through state A crosses the Hugoniot curve again at state A′. A prescribed P-u state at the boundary corresponding to state A′ can then be satisfied by two different wave configurations: (a) a single shock to state A′, or (b) a shock to state A and a rarefaction to state A′ traveling in the opposite direction to the shock. These solutions are illustrated in Fig. 5.

It is thus clear that the limits of Ineq. (17) correspond to the limits outside which a shock can spontaneously split into two waves. These limits are illustrated in the P-V plane in Fig. 6.

It has been noted previously that the region for which

$$j(du/dP)_H < 0$$

is peculiar in that it admits multi-valued solutions to an impact problem.[5] Figure 7 shows an impedance-match solution in the P-u plane for a projectile with normal

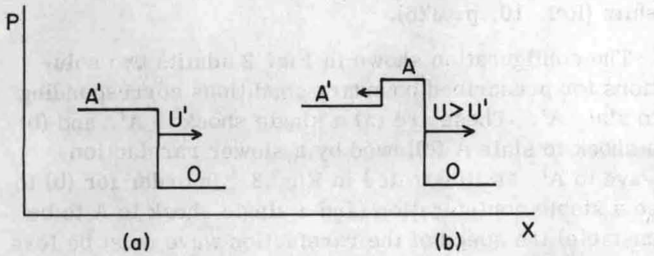

FIG. 5. Alternative wave solutions consistent with Hugoniot of Fig. 4.

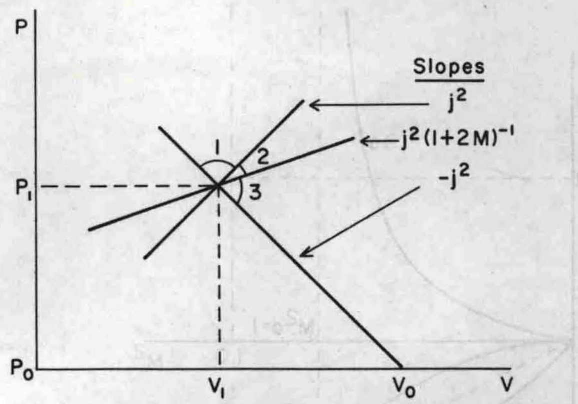

FIG. 6. Stable and unstable regions of P-V plane. Hugoniot curves with slopes in region 3 are unstable according to Eq. (17). In region 2, $j(du/dP)_H < 0$.

Hugoniot curve impacting a target whose Hugoniot curve does not violate Ineq. (17), but which contains a region in which $j(du/dP)_H < 0$. The two solutions for the common P-u state at the interface are indicated by A and B. This indeterminancy of the solution to an impact problem suggests that the criteria of Ineq. (17) are insufficient to guarantee stability. This possibility is examined further in the following sections.

IV. REFLECTION OF ACOUSTIC WAVES AT SHOCK FRONTS

Since a shock travels with subsonic velocity with respect to the compressed medium behind the shock, small amplitude, or acoustic waves in the compressed medium will overtake and reflect from the front. Figure 8(a) shows a diagram of such a reflection in the time-distance plane, and Fig. 8(b) is the corresponding diagram in the pressure-particle velocity plane. The Hugoniot curve is labeled H and the characteristic curves, Eq. (12b), by S+ and S− in the P-u plane. State

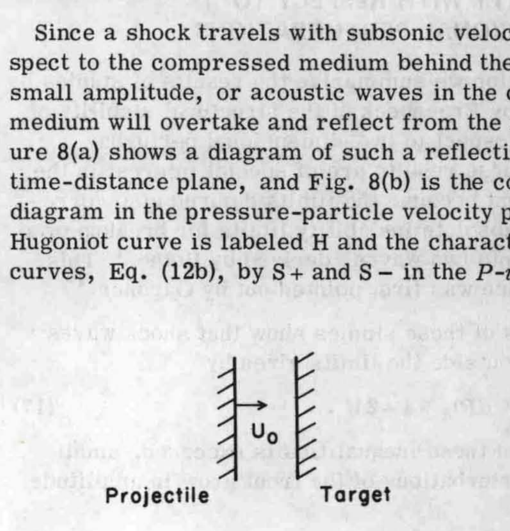

FIG. 7. Impedance match solution for impact of a projectile with a target whose Hugoniot contains a region for which $(dP/du)_H < 0$. States A and B satisfy interface conditions.

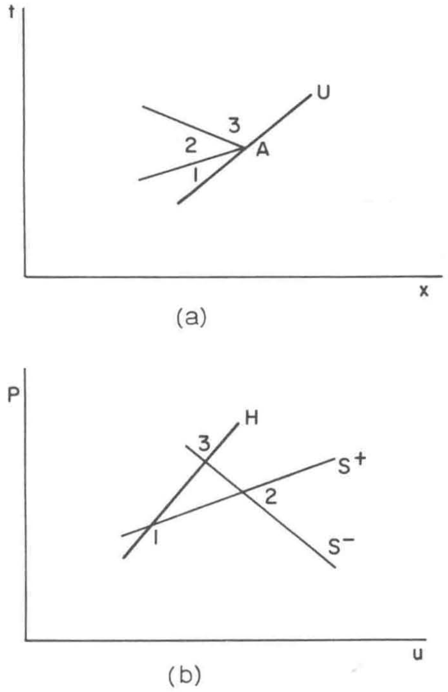

FIG. 8. Reflection of an acoustic wave at a shock front. (a) Time-distance plane. Reflection from shock front at A. (b) Corresponding pressure-particle velocity plane. Numbered states correspond to those at part (a). H is Hugoniot curve, S^+ and S^- are characteristic curves.

1 is the initial shocked state; the state behind the incident acoustic wave, assumed to be a compressional wave, is state 2; and the state behind the reflected acoustic wave is state 3.

The amplitudes of the acoustic waves are assumed to be small; consequently, we retain only first-order terms, and,

$$P_3 - P_1 = (dP/du)_H (u_3 - u_1) + \cdots ,$$

$$P_2 - P_1 = (j/M)(u_2 - u_1) + \cdots ,$$

$$P_3 - P_2 = (-j/M)(u_3 - u_2) + \cdots ,$$

where Eq. (13) has been employed. Eliminating the velocities among these equations yields,

$$u_3 - u_1 - (u_3 - u_2) - (u_2 - u_1)$$
$$= \left(\frac{du}{dP}\right)_H (P_3 - P_1) + \frac{M}{j}(P_3 - P_2) - \frac{M}{j}(P_2 - P_1) = 0 .$$

Or, in obvious notation,

$$\frac{P_{32}}{P_{21}} = \frac{M - j(du/dP)_H}{M + j(du/dP)_H} , \tag{18}$$

is the ratio of amplitudes of the reflected and incident acoustic waves.

As noted the subsonic condition requires

$$0 < M < 1 ; \; j(du/dP)_H < 1 ,$$

and this condition clearly must be satisfied in order that a reflection occur at all. Let us first, therefore, consider a portion of the range within the limits of Ineq. (17), namely,

$$-1 \leq j^2 (dV/dP)_H \leq 1 , \tag{19}$$

or, from Eq. (10),

$$0 \leq j(du/dP)_H \leq 1 . \tag{20}$$

From Eqs. (18) and (20) we deduce,

$$0 \leq j\left(\frac{du}{dP}\right)_H = \frac{M(1 - P_{32}/P_{21})}{1 + P_{32}/P_{21}} \leq 1 .$$

This gives

$$-1 \leq \frac{M-1}{M+1} \leq \frac{P_{32}}{P_{21}} \leq 1 , \tag{21}$$

as the only solution. Within the restrictions specified by Ineq. (19) or (20), therefore, the absolute magnitude of the amplitude of the reflected acoustic wave is not greater than that of the incident wave.

The remainder of the region limited by Ineq. (17) is,

$$1 < j^2 (dV/dP)_H < 1 + 2M . \tag{22}$$

Using Eq. (10) this can be written

$$-M < j(du/dP)_H < 0 ,$$

whence, we deduce from Eq. (18),

$$1 < P_{32}/P_{21} .$$

We conclude that amplification of acoustic wave amplitudes occurs in the region specified by Ineq. (22). This is just the region for which multi-valued solutions to the impact problem are admitted by Ineq. (17), and this suggests that shocks in this region are at least conditionally unstable.

It has been shown earlier that an oscillatory type of instability can occur under these circumstances.[6] Thus, for example, consider the special case illustrated in Figs. 9 and 10. A shock to state 1 is perturbed by applying a pressure increment at the boundary, $x = 0$, at time t_1, and the pressure at the boundary is then held at its new value P_2, indefinitely. This perturbation is transmitted into the shocked region along a C^+ characteristic and undergoes successive reflections

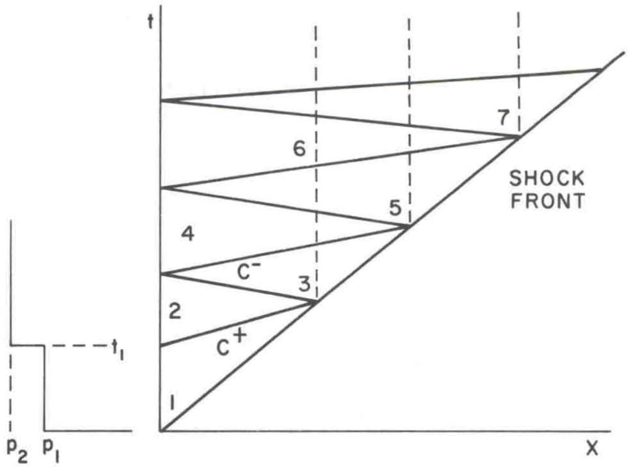

FIG. 9. Time-distance plane showing shock wave and acoustic interactions. Boundary $x = 0$ is perturbed at time t_1 by imposing constant pressure increment, $P_2 - P_1$. Forward and backward facing acoustic waves are labeled C^+ and C^-. Motion of boundary, $x = 0$, and variations in shock velocity neglected.

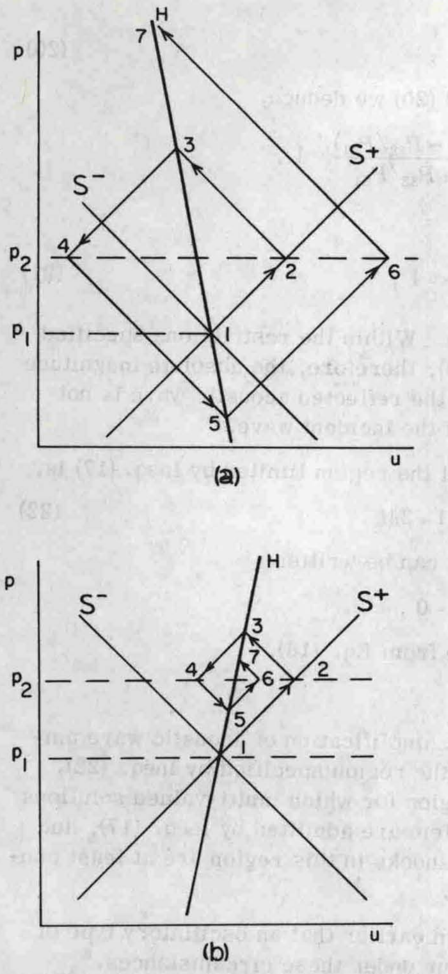

FIG. 10. (a) Pressure, particle velocity plane corresponding to Fig. 9. Numbered states represent P-u states of Fig. 9. Hugoniot, H, has negative slope. Characteristics (isentropes) are labeled S^+ and S^-. (b) Same as Fig. 10(a) except Hugoniot has positive slope.

at the shock front and at the boundary, producing the states labeled 3, 4---. Figure 10 is the associated pressure, particle velocity plane with the numbered states corresponding to those of Fig. 9. The Hugoniot of the material is labeled H and the Γ characteristics, or isentropes, by S^+ and S^-.

The Hugoniot in Fig. 10(a) is assumed to have nega-

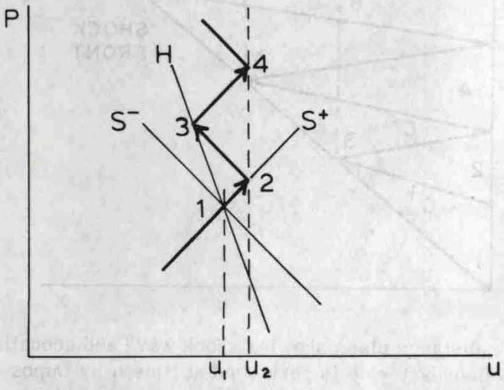

FIG. 11. Similar interaction as shown in Figs. 9 and 10 except perturbation at boundary is in particle velocity, $u_2 - u_1$ = const.

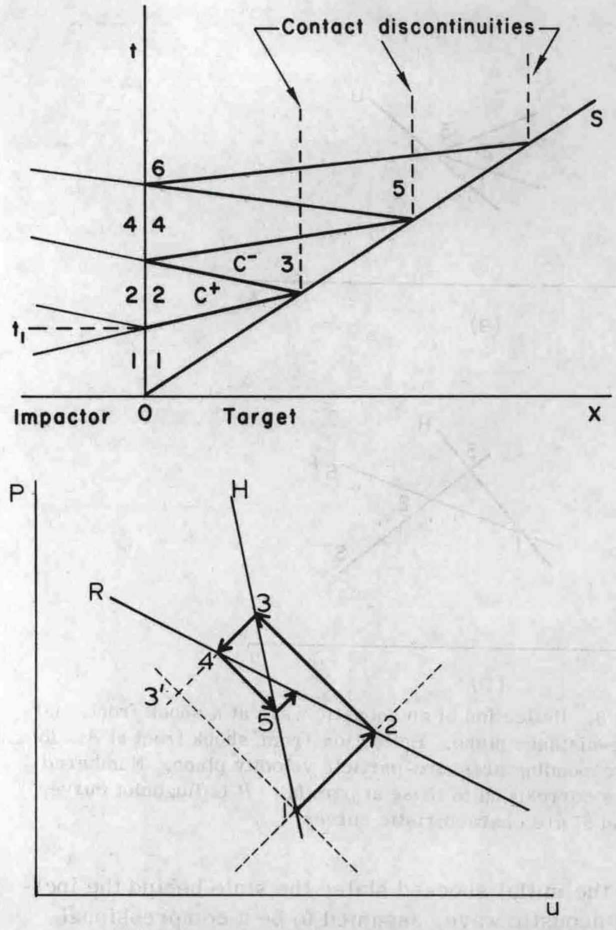

FIG. 12. (a) Similar diagram to that of Fig. 9 except boundary condition is determined by properties of impactor material to left of boundary. (b) Pressure, particle velocity plane corresponding to Fig. 12(a).

tive slope and, as a result, the successive reflections form a kind of divergent spiral about the original state, 1. Conversely, it can easily be seen that when the Hugoniot has a positive slope, the spiral is convergent and the state asymptotically approaches a new Hugoniot state at P_2 as in Fig. 10(b).

Another special case is one in which the perturbation is assumed to be an increment in particle velocity, $u_2 - u_1$, as shown in Fig. 11. When the slope of the Hugoniot is negative, the successive acoustic reflections again grow in amplitude with time as illustrated.

The diagrams of Figs. 9–11 have been simplified in an important respect. Each time an acoustic interaction occurs at the shock front a contact discontinuity is produced, as indicated by the dashed lines in Fig. 9. These present contrasts in acoustic impedance to the acoustic waves with the result that additional internal reflections occur, complicating the process. We know no simple method for treating these internal reflections analytically, but note that they have the ultimate effect of increasing the entropy of the shocked region.

Both of the cases illustrated in Figs. 10 and 11 have a common feature: no acoustic energy is transmitted across the boundary at $x = 0$. If we consider a more general case in which the shock is produced by impact with a normal material, we may have the situation depicted by Fig. 12. The pertinent isentrope of the impactor ($x<0$) is labeled R and we see that, neglecting contact discontinuities, the instability does not develop in spite of the negative slope of the Hugoniot. In this case the slope of R is such that it intersects the isentrope $3-3'$ at an intermediate point; the acoustic wave is sufficiently weakened by transmission of energy across the boundary, $x=0$, that there is a net diminution of the acoustic pulse with time.

Because of the internal reflections at contact discontinuities, it is not obvious that any of these cases is either stable or unstable. We note, however, that these discontinuities appear with increasing frequency in the vicinity of the shock front as the interaction progresses. This "turbulence" may tend to isolate the region immediately behind the front and reduce the influence of the rear boundary conditions. In that event all of the cases considered would be expected to be unstable. In any case, it seems clear that Ineq. (19) must be satisfied in order for a shock to be unconditionally stable.

V. THERMODYNAMIC STABILITY

To treat the shock stability problem by means of thermodynamics it is helpful to first consider a simpler problem in which two subsystems, each in internal equilibrium but not in mutual equilibrium, are allowed to interact. The initial thermodynamic states are the same as for the shock problem, but particle velocities, as well as heat conduction, are assumed negligible. There are then no mass or momentum fluxes to stabilize the configuration and we inquire into the conditions obtaining as the system approaches mutual equilibrium. Figure 13 illustrates this situation.

There are two ways to think about the static problem. In Fig. 14 we show a conceptual Rube–Goldberg device that permits the system to come to equilibrium while maintaining each subsystem in internal equilibrium. The insulated piston is attached to a paddle wheel entropy-generator of zero-heat capacity that delivers heat to either subsystem in varying amounts. The heat flow is controlled by a valve that can be switched arbitrarily but, to maintain thermal isolation of the two subsystems, must be considered to be always fully switched in one position or the other. Energy and volume of the entire system are constant and each subsystem contains unit mass.

As independent variables we choose the specific volume V and a reduced internal energy E', defined by

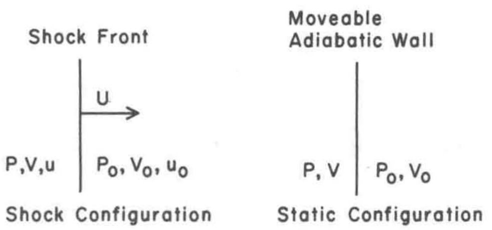

FIG. 13. Shock and static configurations with same thermodynamic states.

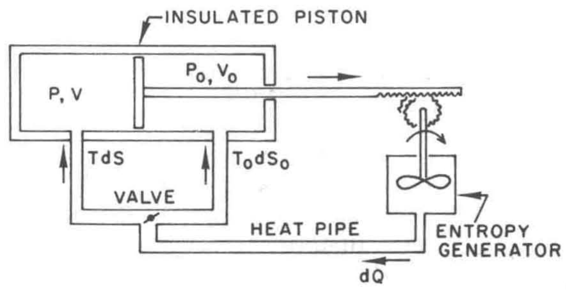

FIG. 14. Equilibration machine. Static configuration of Fig. 13 approaches equilibrium while each subsystem remains in internal equilibrium.

$$dE' = dE + P_0 dV . \tag{23}$$

The differential of this quantity is therefore given by the change in internal energy less the work done on one subsystem by the other subsystem. We refer to it as the reduced internal energy. In mutual equilibrium, $P=P_0$, $dE=-P_0 dV$, and $dE'=0$.

When the system is permitted to relax toward equilibrium, we have

$$dV + dV_0 = 0, \quad dE + dE_0 = 0 ,$$

and

$$dE' = dE + P_0 dV , \quad dE'_0 = dE_0 + P dV_0 .$$

Invoking the requirement that each subsystem be in internal equilibrium implies

$$dE = TdS - PdV$$

and

$$dE_0 = T_0 dS_0 - P_0 dV_0 .$$

Hence,

$$dE' = TdS - (P - P_0) dV$$

and

$$dE'_0 = T_0 dS_0 - (P - P_0) dV .$$

Finally, energy conservation requires

$$dE + dE_0 = 0 ,$$

or

$$TdS + T_0 dS_0 - (P - P_0) dV = 0 ,$$

so that

$$dE' = -T_0 dS_0 ,$$

and

$$dE'_0 = -TdS . \tag{24}$$

Moreover,

$$TdS = (P - P_0) dV - T_0 dS_0 ,$$

and

$$T_0 dS_0 = (P - P_0) dV - TdS . \tag{25}$$

We now note that both conditions $TdS \geq 0$ and $T_0 dS_0 \geq 0$, must apply. Consequently, the approach to equilibrium is characterized by, from Eq. (24),

$$dS \geq 0 \quad \text{and} \quad dE' \leq 0. \tag{26}$$

Equivalently, we can write, from Eq. (25),

$$0 \leq TdS \leq (P - P_0)dV \, . \tag{27}$$

Both inequalities in Eqs. (26) or (27) must hold if entropy is to increase in each subsystem. The usual thermodynamic stability criterion for systems in equilibrium states that the availability, defined by

$$A = E - T_0 S + P_0 V \, ,$$

where T_0 and P_0 are the temperature and pressure of the surroundings, considered to be reservoirs, is minimum in equilibrium.[11] In the present context this implies

$$dA = dE + P_0 dV - T_0 dS$$
$$= dE' - T_0 dS = -T_0(dS_0 + dS) \leq 0 \, .$$

This statement, however, is insufficient in that it does not specify that, in general, entropy must be produced in the surroundings as well as in the subsystem under consideration. For nonconducting systems we therefore take Ineq. (26) or (27), as the more complete statement of the Second Law.

Another way to derive this result that is somewhat simpler is to allow the viscous entropy production to occur internally within each subsystem. We denote by Σ the mechanical stress acting at the interface between the two subsystems and assume that each medium is sufficiently viscous so that stress equilibrium is maintained and the kinetic energy is negligible as the systems approach thermodynamic equilibrium. The equilibrium pressure P is no longer the mechanical stress and is defined only by the equilibrium equation of state, i.e., $P = P(V, E)$.

We now have

$$dE = -\Sigma dV \, ,$$

and

$$dE_0 = -\Sigma dV_0 = \Sigma dV \, ,$$

to be combined with the equilibrium relations

$$dE = TdS - PdV \, , \quad dE_0 = T_0 dS_0 - P_0 dV_0 \, .$$

This gives

$$TdS = -(\Sigma - P)dV \, , \quad T_0 dS_0 = (\Sigma - P_0)dV \, .$$

We now require that entropy be produced in each subsystem, so that

$$-(\Sigma - P)dV \geq 0 \, , \quad (\Sigma - P_0)dV \geq 0 \, .$$

Hence, if $dV > 0$, we must have

$$P_0 \leq \Sigma \leq P \, .$$

This relation implies that during the approach to equilibrium

$$0 \leq TdS \leq (P - P_0)dV \, ,$$

and

$$dE' = -(\Sigma - P_0)dV \leq 0$$

as before.

We now apply this result, Ineqs. (26) or (27), to the shock stability problem. Differentiating the expression for the Hugoniot surface, Eq. (3), gives

$$dE = \tfrac{1}{2}(V_0 - V)d\sigma - \tfrac{1}{2}(\sigma + P_0)dV \, ,$$

or

$$dE' = dE + P_0 dV = \tfrac{1}{2}[(V_0 - V)d\sigma - (\sigma - P_0)dV]$$
$$= \tfrac{1}{2}(V_0 - V)(d\sigma - j^2 dV) \, . \tag{28}$$

From Eq. (8) we note that this is also equal to the differential of the kinetic energy density, $\frac{1}{2}(u - u_0)^2$. We can also express this equation in terms of V and S as independent variables by means of the transformation

$$dE' = TdS - (P - P_0)dV \, .$$

In invoking this equation we do not imply that the Hugoniot surface is a thermodynamic equilibrium surface. Equation (28) then becomes,

$$TdS = \tfrac{1}{2}(V_0 - V)\left[d\sigma - \left(j^2 - \frac{2(P - P_0)}{V_0 - V}\right)dV\right] \, . \tag{29}$$

The Hugoniot P-V curve is defined by the intersection of the Hugoniot surface with the equilibrium surface. Hence, along this curve, $\sigma \equiv P$ and Eqs. (28) and (29) reduce to

$$dE' = \tfrac{1}{2}(V_0 - V)[(dP/dV)_H - j^2]dV \, , \tag{30}$$

and

$$TdS = \tfrac{1}{2}(V_0 - V)[(dP/dV)_H + j^2]dV \, . \tag{31}$$

We now posit the following:

POSTULATE: A shock transition from an initial state to a given final state is thermodynamically unstable if there exists a neighboring final state on the Hugoniot curve for which the entropy is larger and the reduced internal energy smaller than for the given state.

According to this postulate, shocks are thermodynamically unstable when thermodynamically permissible adiabatic fluctuations, i.e., satisfying Ineq. (27), about a shocked state can occur that result in a new state also compatible with the jump conditions. By "thermodynamically unstable" we mean that the system is unstable given fluctuations of sufficient magnitude, in accord with the usual thermodynamic point of view.

From Ineq. (26) or (27) we can derive necessary conditions for stability. Since $P > P_0$, we consider only $dV > 0$ and Eqs. (30) and (31) are incompatible with Ineq. (26) when

$$\left(\frac{dE'}{dV}\right)_H \geq 0, \Rightarrow \left(\frac{dP}{dV}\right)_H \geq j^2 \, , \tag{32a}$$

or

$$T\left(\frac{dS}{dV}\right)_H \leq 0, \Rightarrow \left(\frac{dP}{dV}\right)_H \leq -j^2 \, . \tag{32b}$$

These can be combined in the statement

$$-1 \leq j^2(dV/dP)_H \leq 1 \, ,$$

which is exactly the result obtained for stability with respect to acoustic amplification, Ineq. (19).

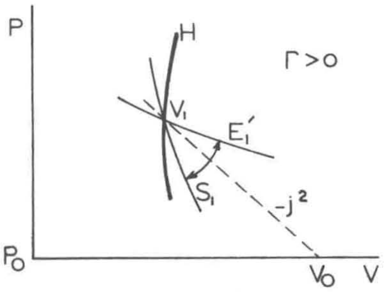

FIG. 15. Paths in P-V plane for $\Gamma > 0$. Adiabatic expansion from V_1 takes place on path between S_1 and E_1'. Hugoniot curve H, excluded from this region.

We can illustrate this restriction by means of a P-V diagram as shown in Fig. 15, for the case $\Gamma > 0$. On the equilibrium surface we have

$$\left(\frac{\partial P}{\partial V}\right)_{E'} = \left(\frac{\partial P}{\partial V}\right)_s + \left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_{E'}$$

$$= \left(\frac{\partial P}{\partial V}\right)_s + \frac{\Gamma}{V}(P - P_0) .$$

Hence, for $\Gamma > 0$ and $P > P_0$ the curve of constant E' lies above the isentrope S as shown, and adiabatic fluctuations consistent with Ineq. (27) lie between these curves. When $\Gamma < 0$, the relative positions are reversed. For stable shocks the Hugoniot curve is excluded from the region bounded by these curves.

We can also consider the stability problem from the point of view of the restoring forces invoked during a virtual displacement. Returning to Eqs. (28) and (29) and retaining only first order terms in an expansion about a Hugoniot state, specified by $P = P_1$, $V = V_1$, gives

$$\sigma = P_1 + \left[\left(\frac{2}{V_0 - V_1}\right)\frac{dE'}{dV} + j^2\right] dV + \cdots , \qquad (33a)$$

$$= P_1 + \left[\left(\frac{2}{V_0 - V_1}\right) T_1 \frac{dS}{dV} - j^2\right] dV + \cdots . \qquad (33b)$$

The paths along which the derivatives are taken is so far arbitrary. [In Eqs. (30) and (31) we also specified $d\sigma/dV = dP/dV$.]

Expressions analogous to Eq. (33) can be written for the equilibrium surface; thus,

$$P = P_1 + \left[\left(\frac{\partial P}{\partial E'}\right)_V \frac{dE'}{dV} + \left(\frac{\partial P}{\partial V}\right)_{E'}\right] dV + \cdots$$

$$= P_1 + \left[\frac{\Gamma_1}{V_1}\frac{dE'}{dV} + \left(\frac{\partial P}{\partial V}\right)_{E'}\right] dV + \cdots \qquad (34a)$$

$$= P_1 + \left[\frac{\Gamma_1 T_1}{V_1}\left(\frac{dS}{dV}\right) + \left(\frac{\partial P}{\partial V}\right)_s\right] dV + \cdots . \qquad (34b)$$

The difference between Eq. (33) and Eq. (34) is

$$\sigma - P = \left[\left(\frac{2}{V_0 - V_1}\right)(1 - a_1)\frac{dE'}{dV} + j^2 - \left(\frac{\partial P}{\partial V}\right)_{E'}\right] dV, \qquad (35a)$$

or

$$\sigma - P = \left[\left(\frac{2}{V_0 - V_1}\right)(1 - a_1) T_1 \frac{dS}{dV} - j^2 - \left(\frac{\partial P}{\partial V}\right)_s\right] dV, \qquad (35b)$$

where the definition of "a," Eq. (15), has been used.

We now consider fluctuations in volume δV consistent with the thermodynamic restriction, Ineq. (26) and require for stability that the restoring force be opposed to the displacement, i.e.,

$$(\sigma - P)\delta V \geq 0 , \qquad (36)$$

for stability. Along the two bounding curves, $dE' = 0$ and $dS = 0$, this implies

$$[j^2 - (\partial P/\partial V)_{E'}](\delta V)^2 \geq 0 ,$$

and

$$[-j^2 - (\partial P/\partial V)_s](\delta V)^2 \geq 0 .$$

Thus,

$$(\partial P/\partial V)_{E'} \leq j^2 , \qquad (37a)$$

and

$$(\partial P/\partial V)_s \leq -j^2 . \qquad (37b)$$

These restrictions are shown in Fig. 16.

For intermediate paths between these bounds, Ineq. (36) stipulates, from Eq. (35),

$$\left(\frac{2}{V_0 - V_1}\right)(1 - a_1) T_1 \frac{dS}{dV} - j^2 - \left(\frac{\partial P}{\partial V}\right)_s$$

$$= \left(\frac{2}{V_0 - V_1}\right)(1 - a_1)\frac{dE'}{dV} + j^2 - \left(\frac{\partial P}{\partial V}\right)_{E'} \geq 0 . \qquad (38)$$

The former of these is clearly satisfied, provided Ineqs. (37) are valid, for $a < 1$ and $dS/dV \geq 0$; the latter when $a > 1$ and $dE'/dV \leq 0$. Thus, stability with respect to all admissible fluctuations consistent with Ineq. (26) is guaranteed by Ineqs. (37).

The restrictions on the slope of the Hugoniot P-V curve implied by Ineqs. (37) can be derived from Eq. (13). We note that Ineq. (37b) is just the subsonic condition,

$$M^2 = -j^2 (dV/dP)_s \leq 1 ,$$

and this restriction implies, for $M^2 a < 1$,

$$-1 \leq j^2 (dV/dP)_H ,$$

as shown in Fig. 1.

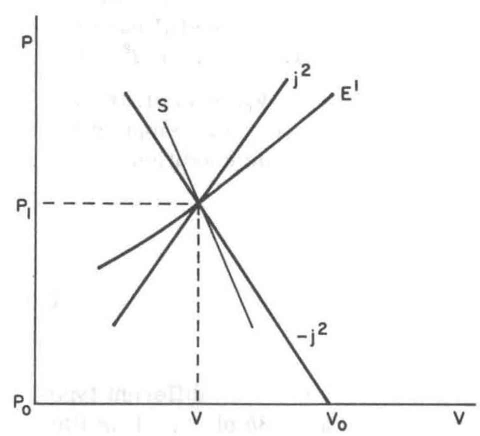

FIG. 16. Relative positions of Rayleigh line, $-j^2$, reflected Rayleigh line, j^2, isentrope, S, and isoenergetic line, E', for stable shocks.

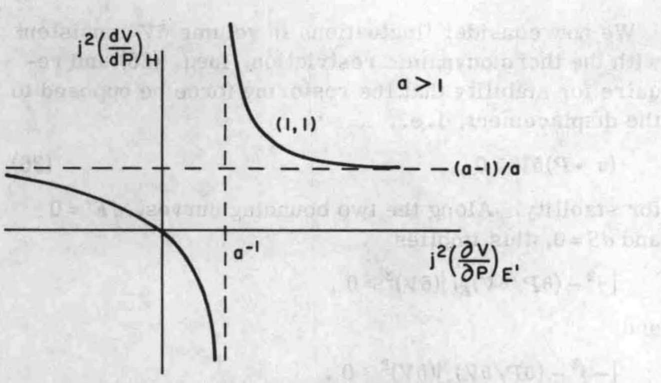

FIG. 17. Plot of $j^2\ (dV/dP)_H$ as function of $j^2\ (\partial V/\partial P)_{E'}$ when $a>1$. Stable case corresponds to $j^2\ (\partial V/\partial P)_{E'}>1$, and $j^2 \times (dV/dP)_H<1$.

With the substitutions

$$\left(\frac{\partial P}{\partial V}\right)_{E'}=\left(\frac{\partial P}{\partial V}\right)_s+\frac{\Gamma(P-P_0)}{V}$$

$$=\left(\frac{\partial P}{\partial V}\right)_s+2aj^2 \qquad (\sigma=P),$$

Eq. (16) can be written

$$j^2\left(\frac{dV}{dP}\right)_H=\frac{j^2(\partial V/\partial P)_{E'}(a-1)}{aj^2(\partial V/\partial P)_{E'}-1}\ . \tag{39}$$

A plot of this function for the case $a>1$ which, excluding the region $M^2a>1$, is the only remaining case of interest, is shown as Fig. 17. From this figure it is clear that the restriction, Ineq. (37a), also implies the inequality

$$j^2(dV/dP)_H\leqslant 1\ .$$

We therefore conclude that the stability condition, Ineq. (36), when combined with the thermodynamic restriction, Ineq. (27), implies the criterion for shock stability

$$-1\leqslant j^2(dV/dP)_H\leqslant 1$$

in agreement with earlier arguments.

To complete the theory we must include the other well-known condition for stability, namely, that the shock travel with supersonic velocity with respect to the undisturbed medium ahead of the shock. This has been shown elsewhere.[9] Moreover, we still have to consider the branch 3*b* of Fig. 1, for which $M^2a>1$.

From Eq. (14), with $P=P_0$, $V=V_0$, it is clear that the Hugoniot and isentrope have the same slope at the initial state. Hence, the supersonic condition

$$M_0^2=-j^2(\partial V/\partial P)_s>1$$

also implies

$$j^2(dV/dP)_H<-1 \tag{40}$$

in the initial state.

Now consider Hugoniot curves of two different types that are assumed to lie on branch 3*b* of Fig. 1 as illustrated in Fig. 18. A Hugoniot curve of type I, that approaches the shocked state 1 from below the Rayleigh line can be ruled out on the basis that one or the other of the limits of Ineq. (19) would be exceeded before the slope of the Hugoniot could take on values pertaining to the region in question, i.e., $j^2(dV/dP)_H<-1$. Alternatively, a Hugoniot of type II necessarily crosses the Rayleigh line at a lower pressure as at point 2. This state, however, is a thermodynamic equilibrium state and could therefore be considered an initial state for the shock transition from 2 to 1. However, according to Ineq. (40), the supersonic condition would be violated. We conclude, therefore, that the branch 3*b* of Fig. 1, for which $M^2a>1$, is unattainable.

TABLE I. Limits of various derivatives for stable shocks.

$-1\leq j^2\ (dV/dP)_H\leq 1$
$(\partial P/\partial V)_S\leq -j^2$
$(\partial P/\partial V)_{E'}\leq j^2$
$0\leq T\ (dS/dP)_H\leq (V_0-V)$
$0\leq (dE'/dP)_H\leq (V_0-V)$
$0\leq (dU/dP)_H\leq U/(P-P_0)$
$0\leq (du/dP)_H\leq u/(P-P_0)$
$(dS/dE')_H\geq 0$

The symmetry of Ineq. (19) is reflected in other equivalent relations derived by substituting from the jump conditions, Eqs. (1)–(3). These are shown in Table I. We note that one consequence is that the shock velocity is a monotonic function of the particle velocity.

Let us now consider further the consequences of violation of each of the limits of Ineq. (19). Figure 19 shows a case in which the lower limit is violated between points A and C. From Eq. (31) it is seen that the entropy along the Hugoniot curve is a maximum at A and a minimum at B with respect to neighboring Hugoniot states. If we plot entropy as a function of pressure along the Hugoniot, we get a curve like that in Fig. 20.

From our criteria we deduce that shock waves whose final states fall within A–C are unstable. If the final pressure falls within this range, a two-wave configuration is produced in which the first wave carries the material to state A, and a subsequent shock with initial state A carries the material to higher pressure, less than C; if the final pressure exceeds C, a single shock is again stable. Instabilities of this type and the two-shock configuration have been widely observed.[12] It is important to notice that under these conditions the pres-

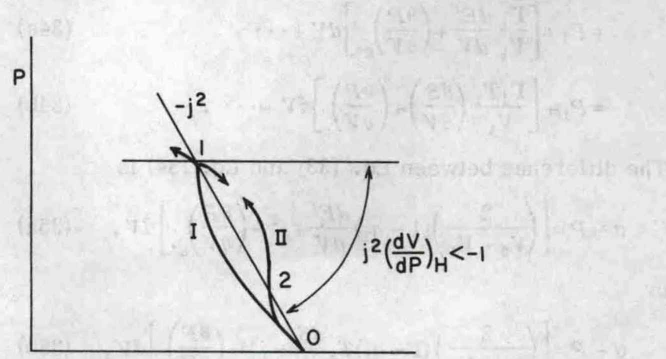

FIG. 18. Unstable Hugoniot curves for which $j^2\ (dV/dP)_H<-1$ at point 1.

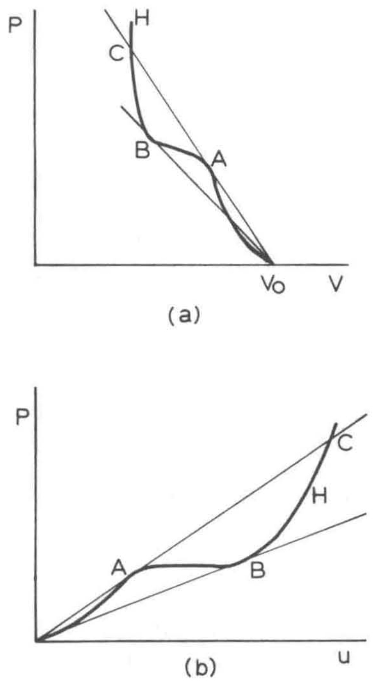

FIG. 19. Hugoniot curve with region of instability between A and C: (a) P-V plane, (b) P-u plane. Point A is entropy maximum along H; B is entropy minimum.

sure of the first wave is stationary at state A with respect to higher shock pressures, (less than C).

Now, consider a situation where the upper limit of Ineq. (19) is exceeded, as illustrated in Fig. 21. In this case a plot of E' as function of P has the appearance shown in Fig. 22. The region between A and B is thermodynamically unstable according to Ineq. (19). Consequently, a shock to state B tends to be stabilized in pressure with respect to lower shock pressures. This is just the situation required for detonation, and we put forward the hypothesis that detonation is indeed the result of a minimum in E' along the Hugoniot curve.

We note that this criterion for detonation is quite different from the Chapman–Jouguet Theory. In that theory detonation corresponds to a local minimum in the entropy along the equilibrium Hugoniot curve. Moreover, it requires the assumption of two effective equations of state, applicable in different regions of the shock transition, a frozen equation of state for the initial shock transition and a relaxed equation of state for the equilibrium state finally achieved (Ref. 10, p. 480).

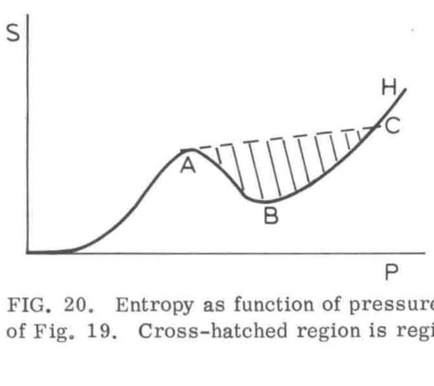

FIG. 20. Entropy as function of pressure along Hugoniot curve of Fig. 19. Cross-hatched region is region of instability.

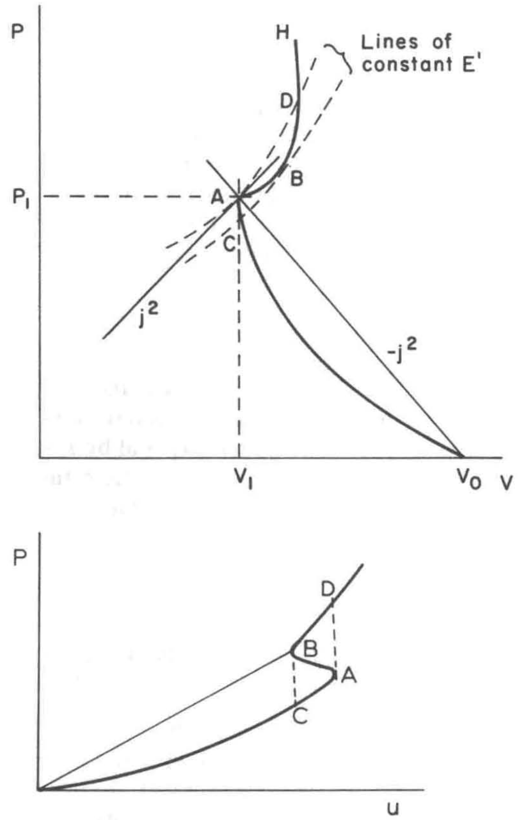

FIG. 21. Hugoniot curve with unstable region $1 < j^2\ (dV/dP)_H$, between A and B: (a) P-V plane, (b) P-u plane. Point A is relative maximum in E' along H; B is relative minimum.

In summary then, stable shocks are characterized by monotonically increasing entropy and reduced internal energy along the Hugoniot curve, and unstable shocks are associated with either a local maximum in the derivative $(dS/dP)_H$, or with a local minimum in the derivative $(dE'/dP)_H$. In the former case, a two-shock configuration results in which the pressure of the first wave is stationary at the entropy maximum. The latter case corresponds to detonation with the pressure stationary at the minimum in E'.

The unstable regions are shown as the cross-hatched areas of Figs. 20 and 22. The upper bound of the unstable region of Fig. 20 is determined by the equivalence of the shock velocity there with that at the entropy maximum. The region CA of Fig. 22 is metastable; shock waves in this range require adequate pertur-

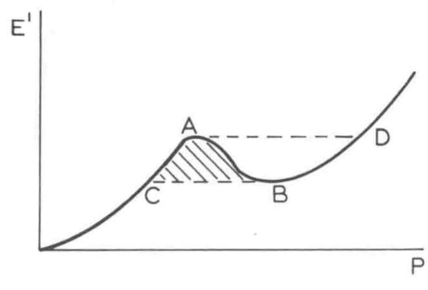

FIG. 22. Plot of E' as function of P along Hugoniot curve of Fig. 21. Cross-hatched region is thermodynamically unstable. Point B is detonation state.

bation to overcome the energy barrier. Just as a liquid can be cooled below the stable transition temperature, the existence of a minimum in E' does not guarantee that a detonation will form; however, state B is the thermodynamically more stable state. It may be for this reason that detonations are observed to propagate more readily in materials that are initially somewhat porous and why turbulence is commonly observed behind detonations. There is an obvious analogy to the onset of turbulence in viscous, steady, subsonic flow.

VI. CONCLUSIONS

We have treated the problem of stability of plane shock waves by considering the reflection of small amplitude acoustic waves from the shock front, and by irreversible thermodynamics. Both approaches yield the same criteria for stability, which can be stated as a restriction on the relative slopes of the Hugoniot curve and the Rayleigh line

$$-1 \leq j^2(dV/dP)_H \leq 1 .$$

Violation of the lower limit leads to a two-shock structure; violation of the upper limit to detonation.

The thermodynamic treatment requires the recognition that, at least in an adiabatic mechanical process, the entropy production is bounded above as well as below. This can be stated alternatively by the relations, applicable to real processes,

$$0 \leq TdS \leq (P - P_0)\,dV , \quad (T > 0)$$

or by the equivalent relations,

$$0 \leq dS ; \quad dE' \leq 0 ,$$

where $dE' = dE + P_0 dV$, is the reduced internal energy.

For shock waves E' is also equal to the kinetic energy density of the shocked state in a coordinate system in which the initial state is stationary; conversely it is the kinetic energy density of the initial state in a coordinate system in which the shocked state is stationary.

Shocks are thermodynamically unstable whenever there is a local maximum in the entropy or a local minimum in the reduced internal energy along the Hugoniot curve. These correspond to a local maximum in the shock velocity and to a local minimum in the particle velocity, respectively. In the former case a two-shock structure develops in which the pressure of the first shock corresponds to the entropy maximum. The latter case gives rise to turbulence that tends to stabilize the shock pressure at the minimum in the reduced internal energy. We posit that detonations are instabilities of this type.

Because E' is also the kinetic energy density, there is another sense in which the stability criteria can be understood. Thus, in a coordinate system fixed in the shocked material the shock front tends to produce maximum entropy with minimum expenditure of the kinetic energy of the incoming material. Instability occurs when there are neighboring Hugoniot states that permit greater production at less cost. It is tempting to speculate that similar thermodynamic conditions may also be valid for biological systems.

We note that the results are in satisfying agreement with a generalized form of the Le Chatelier principle. Thus, for stable shocks both the shock velocity and the particle velocity increase monotonically with pressure.

ACKNOWLEDGMENTS

Numerous people contributed to this work. I wish to thank especially Dr. G. W. Swan for stimulating my interest in this problem, and Drs. Wm. Band and S. Lowell for much encouragement. M. Cowperthwaite and J. Shaner pointed out to me the case described in Fig. 12.

Much of the work was completed while I was a Fulbright-Hayes Research Scholar at the University of Auckland under the auspices of the New Zealand-United States Educational Foundation. This research was supported by the Earth Sciences Section National Science Foundation, NSF Grant DES72-01517 A02.

[1]H. A. Bethe, Office of Scientific Research and Development, Report 445 (1942).
[2]S. P. D'Yakov, Zh. Eksp. Teor. Fiz. **27**, 288 (1956).
[3]J. J. Erpenbeck, Phys. Fluids **5**, 1181 (1962).
[4]C. Gardner, Phys. Fluids **6**, 1366 (1963).
[5]G. W. Swan and G. R. Fowles, Phys. Fluids **18**, 28 (1975).
[6]G. R. Fowles and G. W. Swan, Phys. Rev. Lett. **30**, 1023 (1973).
[7]L. C. Woods, J. Plasma Phys. **6**, 615 (1971).
[8]R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Wiley, New York, 1948), Chap. 2.
[9]G. R. Fowles, Phys. Fluids **18**, 776 (1975).
[10]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959).
[11]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1969), p. 99.
[12]G. E. Duvall, *Les Ondes de Detonation* (Editions du Centre National de la Recherche Scientifique, Paris, 1962), p. 337. Also, M. Cowperthwaite, J. Franklin Inst. **285**, 275 (1968).

Conditional stability of shock waves—a criterion for detonation

G. R. Fowles

Department of Physics, Washington State University, Pullman, Washington 99163

(Received 7 July 1975)

The stability of plane shock waves is treated by examining the amplitudes of acoustic waves reflected from shock fronts, and by methods of irreversible thermodynamics. Both approaches yield the same conditions for stability, $-1 \leq j^2(dV/dP)_H \leq 1$, where j^2 is the negative slope of the Rayleigh line, and the derivative is taken along the Hugoniot P-V curve. The thermodynamic method indicates that instabilities are associated either with local maxima in the entropy, or shock velocity; or with local minima in the reduced internal energy, or particle velocity, along the Hugoniot curve. It is proposed that the latter case corresponds to detonation with the detonation state given by the particle velocity minimum.

I. INTRODUCTION

Earlier studies of the stability of shock waves have established the existence of two limits outside which a shock splits spontaneously into two waves traveling in the same or in opposite directions. Bethe first derived sufficient conditions for plane shocks to be stable against such breakup.[1] Later studies by D'yakov,[2] and by Erpenbeck,[3] based on analysis of the stability with respect to two-dimensional perturbations also established two bounds; these were shown by Gardner to be equivalent to Bethe's criteria for plane shocks.[4,5]

In this paper we consider a region within the above limits in which a shock is evidently potentially unstable for other reasons. We show that in this region small amplitude acoustic waves incident on the shock front from the compressed region behind the front undergo amplification upon reflection at the front. This can lead to an oscillatory type of instability proposed earlier,[6] although it is not clear from this treatment that instability necessarily occurs when the amplification criterion is satisfied.

We have also approached the stability problem from the point of view of irreversible thermodynamics and show, based on a plausible hypothesis, that in the region under consideration a shock is thermodynamically unstable; whether or not instability actually occurs depends on the magnitude of perturbations. The acoustic wave approach and the thermodynamic approach thus exhibit a nice correspondence.

Technical interest in the shock stability problem derives from applications in which it is desired to relate wave propagation behavior to properties of the transmitting medium. In solids, for example, polymorphic phase changes and yielding at the elastic limit may lead to splitting of a single shock into two shocks traveling in the same direction. In reactive media, self-sustaining waves or detonation waves, may form under conditions that are not well understood.

The problem is also of exceptional theoretical interest because of the existence of several apparently distinct methods of approach, as has been pointed out by Woods.[7] The theory of irreversible thermodynamics is well known to be underdeveloped, and it may be hoped that new insight into the theory will result from application of various methods to a relatively simple problem such as that of plane shock waves.

The thermodynamic method employed here invokes no new principles but requires the recognition that the approach to equilibrium of two systems initially out of equilibrium is characterized by nonnegative entropy production in each system. This can be expressed, at least for adiabatic, viscous flow, by an upper as well as a lower bound to the entropy production rate. Still another statement is that the reduced internal energy (defined later) is minimized *and* the entropy is maximized in equilibrium. These latter statements are not, in general, equivalent; one does not imply the other.

The thermodynamic method predicts a new criterion for detonation that is quite different from the Chapman–Jouguet Theory. We postulate this criterion in Sec. V.

In Sec. II we display the jump conditions and several definitions and transformations that are useful. Section III is a summary of the conclusions of the Bethe–D'yakov theory. The interaction of acoustic waves with the shock front is considered in Sec. IV and the thermodynamic approach is presented in Sec. V.

II. JUMP CONDITIONS

The well-known Rankine–Hugoniot jump conditions applicable to plane shocks with steady profile or to discontinuous jumps can be written,[8]

$$u - u_0 = \rho_0(U - u_0)(V_0 - V) \ , \tag{1}$$

$$\sigma - P_0 = \rho_0(U - u_0)(u - u_0) \ , \tag{2}$$

$$E - E_0 = \tfrac{1}{2}(\sigma + P_0)(V_0 - V) \ . \tag{3}$$

These equations express conservation of mass, momentum, and energy, respectively. Mass velocity is denoted by u, shock velocity by U, specific volume by $V = \rho^{-1}$, normal stress in the direction of propagation by σ (measured positive in compression), and specific internal energy by E. Subscripts 0 refer to the undisturbed state ahead of the shock, assumed to be a thermodynamic equilibrium state. The mechanical conditions, Eqs. (1) and (2) require no assumption about thermodynamic equilibrium and apply throughout the shock transition region; hence, the use of σ to denote stress rather than P which is used to denote the pressure of thermodynamic equilibrium states. Equation (3) is valid whenever no other sources of energy besides mechanical energy are assumed.

Since a shock is an adiabatic process, Eq. (3) applies to equilibrium end states; it only applies to the shock transition region, however, when heat conduction and radiation in that region can be neglected. Equation (3) is termed the Hugoniot relation and, for given (P_0, V_0, E_0), defines a surface,

$$\sigma = \sigma(V, E; P_0, V_0, E_0) \quad (V \neq V_0) ,$$

that represents the locus of states achievable by a shock transition in *any* medium.

For the description of shocks in a specific medium, Eqs. (1)–(3) are supplemented by the equilibrium equation of state of the medium in the form

$$P = P(V, E; E_0) . \tag{4}$$

The simultaneous solution of Eqs. (3) and (4), with $\sigma = P$, yields a curve $P(V)$ termed the "Hugoniot equation of state," or sometimes the "R-H curve."

We define several useful quantities

$$j \equiv \rho_0(U - u_0) , \tag{5}$$

whence, from Eqs. (1) and (2),

$$j^2 \equiv (\sigma - P_0)/(V_0 - V) . \tag{6}$$

Also,

$$M \equiv |(U - u)/c| \tag{7}$$

and

$$c^2 \equiv \left(\frac{\partial P}{\partial \rho}\right)_s = -V^2\left(\frac{\partial P}{\partial V}\right)_s . \tag{8}$$

The quantity j is the mass flux through the shock front and is positive when the shock velocity exceeds the initial mass velocity u_0. Its square j^2 is also equal to the negative slope of the Rayleigh line joining the end states. The quantity M is the local Mach number of the shock with respect to the medium, and c is the local sound speed in spatial coordinates. The subscript s denotes the isentropic derivative.

Several combinations of these relations yield useful transformations. Thus, combining Eqs. (1), (2), and (6),

$$(u - u_0)^2 = (\sigma - P_0)(V_0 - V) = j^2(V_0 - V)^2 . \tag{9}$$

This can be differentiated to give

$$2(u - u_0)du = -(\sigma - P_0)dV + (V_0 - V)d\sigma ,$$

or, using Eq. (9),

$$j\left(\frac{du}{dP}\right)_H = \pm\frac{1}{2}\left[1 - j^2\left(\frac{dV}{dP}\right)_H\right], \tag{10}$$

where the subscript H denotes differentiation along the Hugoniot curve.

For definiteness we consider only compressive shocks traveling in the positive direction, so that,

$$j > 0 ; \quad V < V_0 ; \quad \text{and} \quad u > u_0 .$$

As a result of this assumption we retain only the positive sign in Eq. (10).

An alternate expression for Eq. (7) can be derived, using Eqs. (5), (8), and (9),

$$M^2 = \left|\frac{U - u}{c}\right|^2 = \frac{[V_0 j - (V_0 - V)j]^2}{-V^2(\partial P/\partial V)_s}$$

$$= -j^2\left(\frac{\partial V}{\partial P}\right)_s . \tag{11}$$

For small amplitude acoustic waves we make use of the characteristic equations and associated compatibility conditions[8]

$$C\pm : \ dx/dt = u \pm c \tag{12a}$$

and

$$\Gamma\mp , \text{ or } S\pm : \ dP/du = \pm \rho c . \tag{12b}$$

The upper sign of Eq. (12b) holds *across* forward-facing waves, specified by the positive sign of Eq. (12a). Thus, Γ^+ is valid *on* the characteristic path C^+, and Γ^- holds on C^-. For acoustic waves the flow is assumed to be isentropic, and we therefore adopt the obvious notation for these waves

$$\left(\frac{du}{dP}\right)_s = \pm (V/c) .$$

Combining this with Eqs. (6) and (11) gives,

$$\left(\frac{du}{dP}\right)_s = \pm\left(-\frac{\partial V}{\partial P}\right)_s^{1/2}$$

$$= \pm (M/j) . \tag{13}$$

Still another useful relation can be obtained by writing the slope of the Hugoniot curve as a directional derivative,

$$\left(\frac{dP}{dV}\right)_H = \left(\frac{\partial P}{\partial V}\right)_E + \left(\frac{\partial P}{\partial E}\right)_V\left(\frac{dE}{dV}\right)_H ,$$

and employing Eq. (3), which differentiated is, with $\sigma = P$,

$$\left(\frac{dE}{dV}\right)_H = -\tfrac{1}{2}(P + P_0) + \tfrac{1}{2}(V_0 - V)\left(\frac{dP}{dV}\right)_H .$$

Thus,

$$\left(\frac{\partial P}{\partial V}\right)_E = \left(\frac{dP}{dV}\right)_H + \frac{1}{2}\left(\frac{\partial P}{\partial E}\right)_V\left[P + P_0 - (V_0 - V)\left(\frac{dP}{dV}\right)_H\right] .$$

However, on the equilibrium surface,

$$\left(\frac{\partial P}{\partial V}\right)_E = \left(\frac{\partial P}{\partial V}\right)_s - \left(\frac{\partial P}{\partial E}\right)_V\left(\frac{\partial E}{\partial V}\right)_s = \left(\frac{\partial P}{\partial V}\right)_s + P\left(\frac{\partial P}{\partial E}\right)_V .$$

The Grüneisen parameter is

$$\Gamma = V(\partial P/\partial E)_V$$

Hence, equating the two expressions for $(\partial P/\partial V)_E$,

$$\left(\frac{dV}{dP}\right)_H = \frac{1 - (\Gamma/2V)(V_0 - V)}{(\partial P/\partial V)_s + (\Gamma/2V)(P - P_0)} . \tag{14}$$

This can be simplified by the substitution

$$a = (\Gamma/2V)(V_0 - V) , \tag{15}$$

together with Eq. (11). We get

$$j^2(dV/dP)_H = M^2(a - 1)/(1 - M^2 a) . \tag{16}$$

A graph of this equation is shown in Fig. 1.

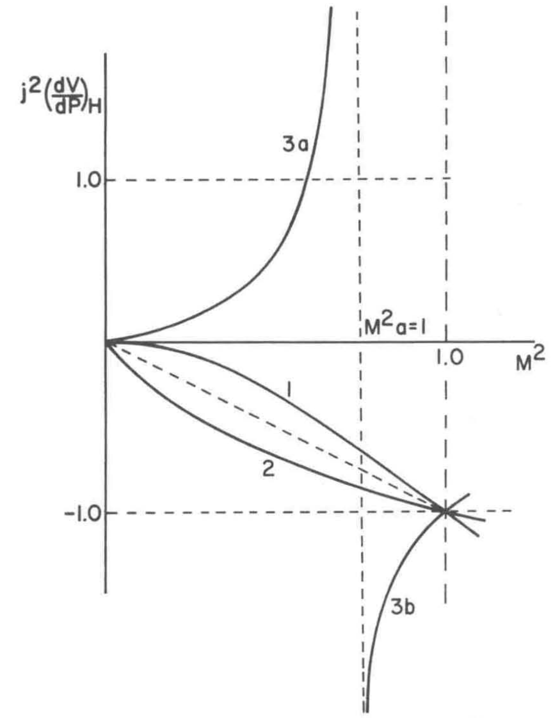

FIG. 1. Plot of $j^2(dV/dP)_H$ as function of M^2 for various values of a. Branch 1: $0<a<1$; Branch 2: $a<0$; Branch 3: $1<a$; Branch 3b: $M^2a>1$.

III. STABILITY WITH RESPECT TO TWO-DIMENSIONAL PERTURBATIONS

In this section we summarize the results of studies by D'yakov and by Erpenbeck of the structural stability of shocks with respect to two-dimensional perturbations.[2,3,5] These results are of special interest in the present context because the limits derived also correspond to the absolute instability limits for breakup of a plane shock into two waves, derived by Bethe.[1] This correspondence was first pointed out by Gardner.[4]

The results of these studies show that shock waves are unstable outside the limits given by

$$-1 \leqslant j^2(dV/dP)_H \leqslant 1+2M . \qquad (17)$$

When either of these inequalities is exceeded, small sinusoidal perturbations of the front grow in amplitude with time.

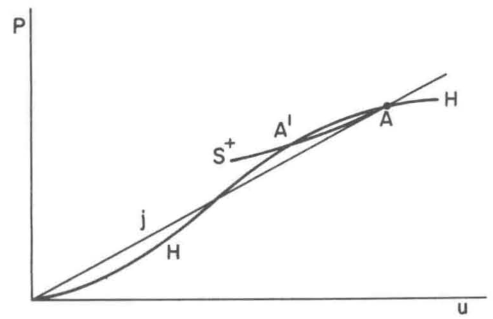

FIG. 2. Unstable Hugoniot curve, $j^2(dV/dP)_H<-1$. Hugoniot, H, and characteristic curve, S^+, lie above Rayleigh line, j, at A. Subsonic condition, $M<1$, violated at A.

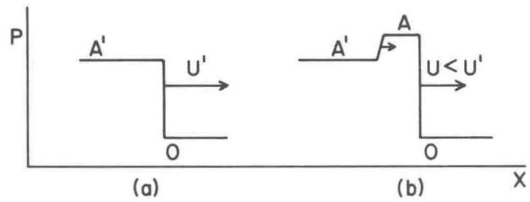

FIG. 3. Alternative wave solutions consistent with Hugoniot of Fig. 2.

It is remarkable that the limits of Ineq. (17) are also those for which a shock can split into two waves. That is, outside either limit a prescribed pressure, particle-velocity boundary condition can be satisfied by either a single shock or by a two-wave configuration. First, consider a case in which the lower limit is violated. Then, it is clear from Fig. 1 that, provided $M^2a<1$, the only solutions consistent with the jump conditions correspond to $M^2>1$. However, this implies that the shock travels faster than the speed of sound in the compressed medium behind the shock, and it has been shown that the Second Law would then be violated in the shock transition.[9] It will be shown later that the branch $M^2a>1$ is also unstable.

Another point of view that can be taken is illustrated in Fig. 2, which shows a Hugoniot curve in the P-u plane for which the lower limit of Ineq. (17) is violated at point A. The isentropic curve through point A intersects the Hugoniot curve again at point A′. We note that both the Hugoniot curve and the isentropic curve must lie on the same side of the Rayleigh line and are simultaneously tangent to that line at the lower stability limit of Ineq. (17). This is shown by Eq. (10), which can be inverted to give

$$j^2\left(\frac{dV}{dP}\right)_H = 1 - 2j\left(\frac{du}{dP}\right)_H ,$$

so that

$$-1 < j^2\left(\frac{dV}{dP}\right)_H$$

implies

$$j\left(\frac{du}{dP}\right)_H < 1 .$$

Moreover, as noted previously, when $M^2a<1$, this same restriction implies $M<1$, and from Eq. (13),

$$j\left(\frac{du}{dP}\right)_s < 1 .$$

This result has also been discussed by Landau and Lifshitz (Ref. 10, p. 326).

The configuration shown in Fig. 2 admits two solutions for prescribed boundary conditions corresponding to state A′. These are (a) a single shock to A′, and (b) a shock to state A followed by a slower rarefaction wave to A′, as illustrated in Fig. 3. In order for (b) to be a stable configuration (and a single shock to A to be unstable) the speed of the rarefaction wave must be less than the speed of the shock, i.e., the shock must be supersonic with respect to the medium behind, or $M>1$.

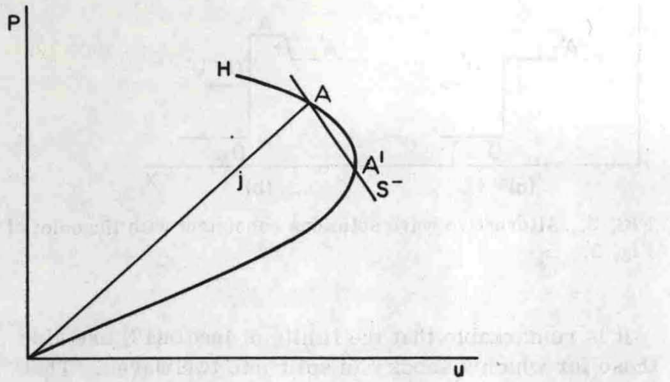

FIG. 4. Unstable Hugoniot curve, $j^2(dV/dP)_H > 1 + 2M$. Characteristic curve, S^-, intersects Hugoniot, H, twice, at A and A′.

An analogous argument applies when the upper limit of Ineq. (17) is violated. In this case, using Eq. (10),

$$j^2\left(\frac{dV}{dP}\right)_H = 1 - 2j\left(\frac{du}{dP}\right)_H > 1 + 2M \;,$$

or, since $j > 0$,

$$\left(\frac{du}{dP}\right)_H < -\frac{M}{j} \;.$$

Employing Eq. (13) this implies, for the negative solution of Eq. (13),

$$\left(\frac{dP}{du}\right)_s < \left(\frac{dP}{du}\right)_H < 0 \;.$$

A configuration satisfying this inequality is shown in Fig. 4; the isentrope through state A crosses the Hugoniot curve again at state A′. A prescribed P-u state at the boundary corresponding to state A′ can then be satisfied by two different wave configurations: (a) a single shock to state A′, or (b) a shock to state A and a rarefaction to state A′ traveling in the opposite direction to the shock. These solutions are illustrated in Fig. 5.

It is thus clear that the limits of Ineq. (17) correspond to the limits outside which a shock can spontaneously split into two waves. These limits are illustrated in the P-V plane in Fig. 6.

It has been noted previously that the region for which

$j(du/dP)_H < 0$

is peculiar in that it admits multi-valued solutions to an impact problem.[5] Figure 7 shows an impedance-match solution in the P-u plane for a projectile with normal

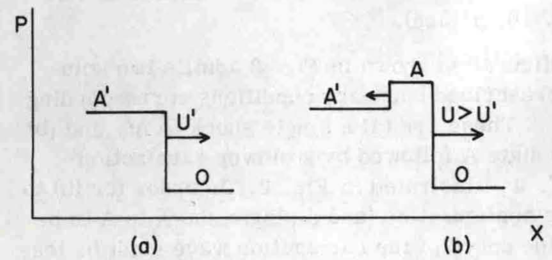

FIG. 5. Alternative wave solutions consistent with Hugoniot of Fig. 4.

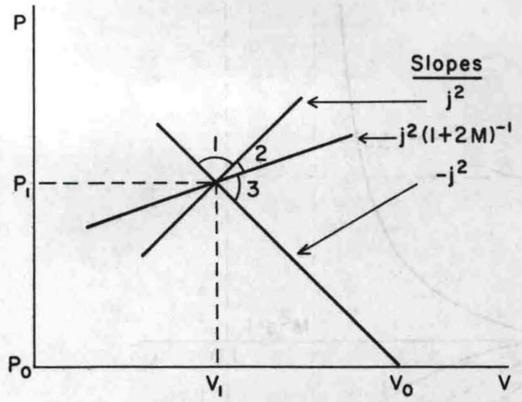

FIG. 6. Stable and unstable regions of P-V plane. Hugoniot curves with slopes in region 3 are unstable according to Eq. (17). In region 2, $j(du/dP)_H < 0$.

Hugoniot curve impacting a target whose Hugoniot curve does not violate Ineq. (17), but which contains a region in which $j(du/dP)_H < 0$. The two solutions for the common P-u state at the interface are indicated by A and B. This indeterminancy of the solution to an impact problem suggests that the criteria of Ineq. (17) are insufficient to guarantee stability. This possibility is examined further in the following sections.

IV. REFLECTION OF ACOUSTIC WAVES AT SHOCK FRONTS

Since a shock travels with subsonic velocity with respect to the compressed medium behind the shock, small amplitude, or acoustic waves in the compressed medium will overtake and reflect from the front. Figure 8(a) shows a diagram of such a reflection in the time-distance plane, and Fig. 8(b) is the corresponding diagram in the pressure-particle velocity plane. The Hugoniot curve is labeled H and the characteristic curves, Eq. (12b), by S+ and S− in the P-u plane. State

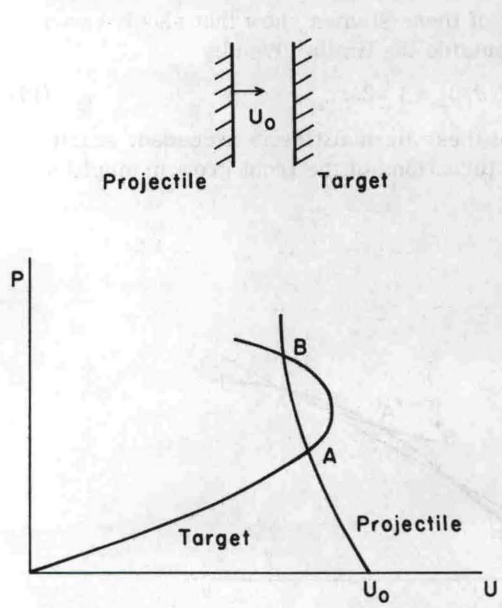

FIG. 7. Impedance match solution for impact of a projectile with a target whose Hugoniot contains a region for which $(dP/du)_H < 0$. States A and B satisfy interface conditions.

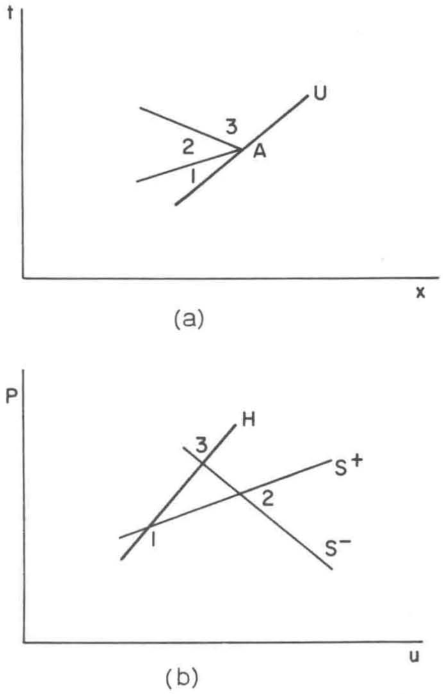

FIG. 8. Reflection of an acoustic wave at a shock front. (a) Time-distance plane. Reflection from shock front at A. (b) Corresponding pressure-particle velocity plane. Numbered states correspond to those at part (a). H is Hugoniot curve, S^+ and S^- are characteristic curves.

1 is the initial shocked state; the state behind the incident acoustic wave, assumed to be a compressional wave, is state 2; and the state behind the reflected acoustic wave is state 3.

The amplitudes of the acoustic waves are assumed to be small; consequently, we retain only first-order terms, and,

$$P_3 - P_1 = (dP/du)_H (u_3 - u_1) + \cdots \ ,$$

$$P_2 - P_1 = (j/M)(u_2 - u_1) + \cdots \ ,$$

$$P_3 - P_2 = (-j/M)(u_3 - u_2) + \cdots \ ,$$

where Eq. (13) has been employed. Eliminating the velocities among these equations yields,

$$u_3 - u_1 - (u_3 - u_2) - (u_2 - u_1)$$

$$= \left(\frac{du}{dP}\right)_H (P_3 - P_1) + \frac{M}{j}(P_3 - P_2) - \frac{M}{j}(P_2 - P_1) = 0 \ .$$

Or, in obvious notation,

$$\frac{P_{32}}{P_{21}} = \frac{M - j(du/dP)_H}{M + j(du/dP)_H} \ , \qquad (18)$$

is the ratio of amplitudes of the reflected and incident acoustic waves.

As noted the subsonic condition requires

$$0 < M < 1 \ ; \ j(du/dP)_H < 1 \ ,$$

and this condition clearly must be satisfied in order that a reflection occur at all. Let us first, therefore, consider a portion of the range within the limits of Ineq. (17), namely,

$$-1 \leq j^2 (dV/dP)_H \leq 1 \ , \qquad (19)$$

or, from Eq. (10),

$$0 \leq j(du/dP)_H \leq 1 \ . \qquad (20)$$

From Eqs. (18) and (20) we deduce,

$$0 \leq j\left(\frac{du}{dP}\right)_H = \frac{M(1 - P_{32}/P_{21})}{1 + P_{32}/P_{21}} \leq 1 \ .$$

This gives

$$-1 \leq \frac{M-1}{M+1} \leq \frac{P_{32}}{P_{21}} \leq 1 \ , \qquad (21)$$

as the only solution. Within the restrictions specified by Ineq. (19) or (20), therefore, the absolute magnitude of the amplitude of the reflected acoustic wave is not greater than that of the incident wave.

The remainder of the region limited by Ineq. (17) is,

$$1 < j^2 (dV/dP)_H < 1 + 2M \ . \qquad (22)$$

Using Eq. (10) this can be written

$$-M < j(du/dP)_H < 0 \ ,$$

whence, we deduce from Eq. (18),

$$1 < P_{32}/P_{21} \ .$$

We conclude that amplification of acoustic wave amplitudes occurs in the region specified by Ineq. (22). This is just the region for which multi-valued solutions to the impact problem are admitted by Ineq. (17), and this suggests that shocks in this region are at least conditionally unstable.

It has been shown earlier that an oscillatory type of instability can occur under these circumstances.[6] Thus, for example, consider the special case illustrated in Figs. 9 and 10. A shock to state 1 is perturbed by applying a pressure increment at the boundary, $x = 0$, at time t_1, and the pressure at the boundary is then held at its new value P_2, indefinitely. This perturbation is transmitted into the shocked region along a C^+ characteristic and undergoes successive reflections

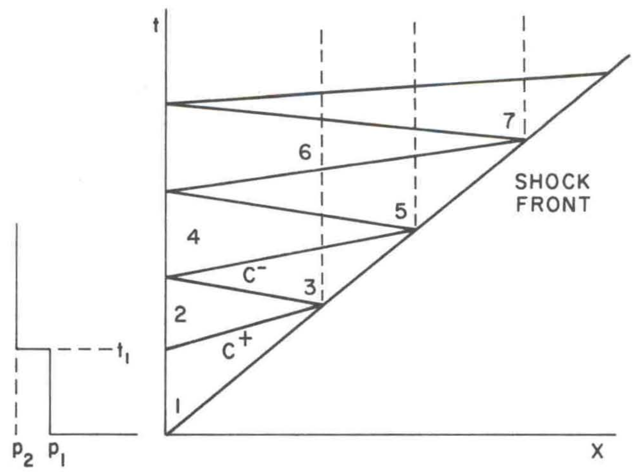

FIG. 9. Time-distance plane showing shock wave and acoustic interactions. Boundary $x = 0$ is perturbed at time t_1 by imposing constant pressure increment, $P_2 - P_1$. Forward and backward facing acoustic waves are labeled C^+ and C^-. Motion of boundary, $x = 0$, and variations in shock velocity neglected.

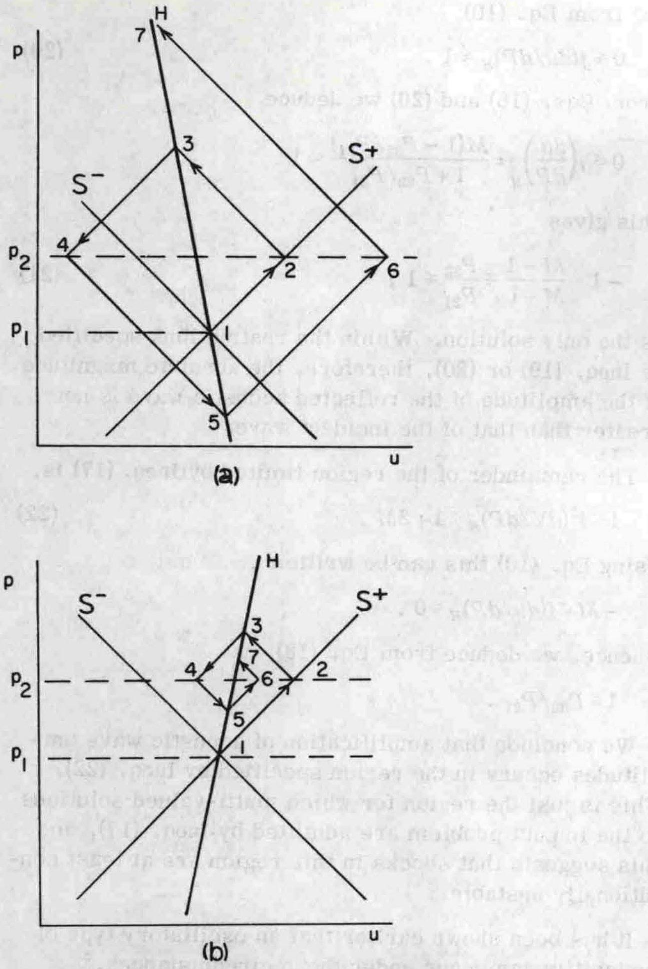

FIG. 10. (a) Pressure, particle velocity plane corresponding to Fig. 9. Numbered states represent P-u states of Fig. 9. Hugoniot, H, has negative slope. Characteristics (isentropes) are labeled S^+ and S^-. (b) Same as Fig. 10(a) except Hugoniot has positive slope.

at the shock front and at the boundary, producing the states labeled 3, 4---. Figure 10 is the associated pressure, particle velocity plane with the numbered states corresponding to those of Fig. 9. The Hugoniot of the material is labeled H and the Γ characteristics, or isentropes, by S^+ and S^-.

The Hugoniot in Fig. 10(a) is assumed to have negative slope and, as a result, the successive reflections form a kind of divergent spiral about the original state, 1. Conversely, it can easily be seen that when the Hugoniot has a positive slope, the spiral is convergent and the state asymptotically approaches a new Hugoniot state at P_2 as in Fig. 10(b).

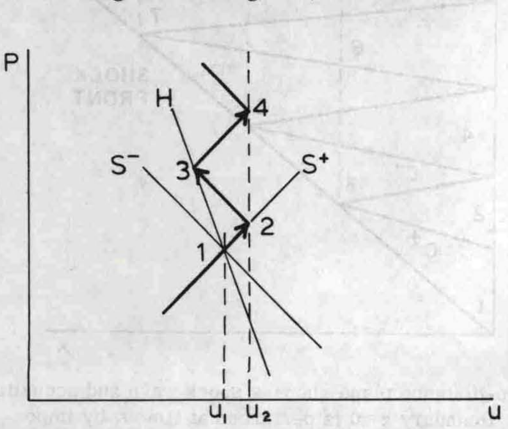

FIG. 11. Similar interaction as shown in Figs. 9 and 10 except perturbation at boundary is in particle velocity, $u_2 - u_1$ = const.

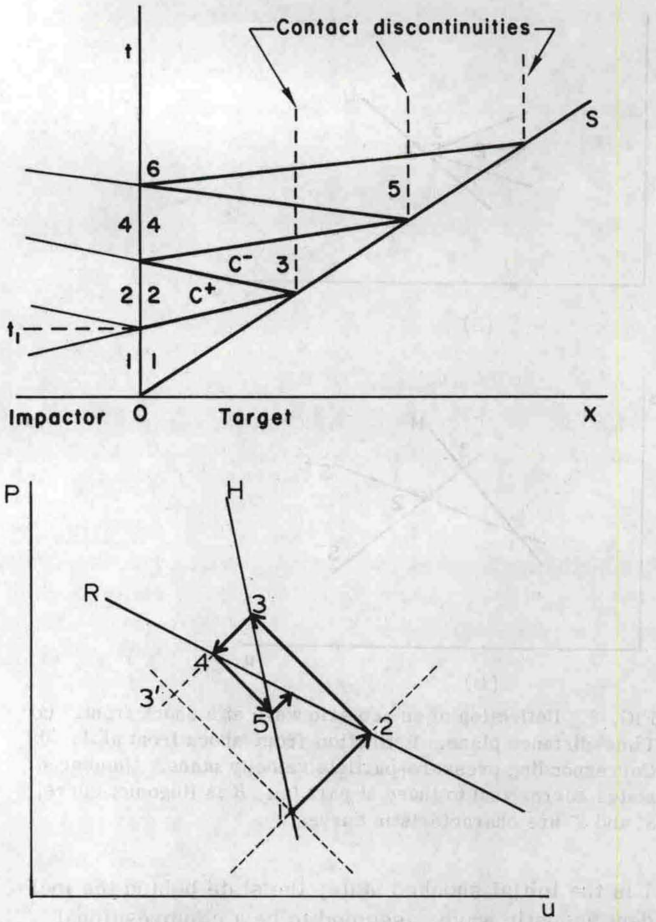

FIG. 12. (a) Similar diagram to that of Fig. 9 except boundary condition is determined by properties of impactor material to left of boundary. (b) Pressure, particle velocity plane corresponding to Fig. 12(a).

Another special case is one in which the perturbation is assumed to be an increment in particle velocity, $u_2 - u_1$, as shown in Fig. 11. When the slope of the Hugoniot is negative, the successive acoustic reflections again grow in amplitude with time as illustrated.

The diagrams of Figs. 9–11 have been simplified in an important respect. Each time an acoustic interaction occurs at the shock front a contact discontinuity is produced, as indicated by the dashed lines in Fig. 9. These present contrasts in acoustic impedance to the acoustic waves with the result that additional internal reflections occur, complicating the process. We know no simple method for treating these internal reflections analytically, but note that they have the ultimate effect of increasing the entropy of the shocked region.

Both of the cases illustrated in Figs. 10 and 11 have a common feature: no acoustic energy is transmitted across the boundary at $x = 0$. If we consider a more general case in which the shock is produced by impact with a normal material, we may have the situation depicted by Fig. 12. The pertinent isentrope of the impactor ($x<0$) is labeled R and we see that, neglecting contact discontinuities, the instability does not develop in spite of the negative slope of the Hugoniot. In this case the slope of R is such that it intersects the isentrope $3-3'$ at an intermediate point; the acoustic wave is sufficiently weakened by transmission of energy across the boundary, $x=0$, that there is a net diminution of the acoustic pulse with time.

Because of the internal reflections at contact discontinuities, it is not obvious that any of these cases is either stable or unstable. We note, however, that these discontinuities appear with increasing frequency in the vicinity of the shock front as the interaction progresses. This "turbulence" may tend to isolate the region immediately behind the front and reduce the influence of the rear boundary conditions. In that event all of the cases considered would be expected to be unstable. In any case, it seems clear that Ineq. (19) must be satisfied in order for a shock to be unconditionally stable.

V. THERMODYNAMIC STABILITY

To treat the shock stability problem by means of thermodynamics it is helpful to first consider a simpler problem in which two subsystems, each in internal equilibrium but not in mutual equilibrium, are allowed to interact. The initial thermodynamic states are the same as for the shock problem, but particle velocities, as well as heat conduction, are assumed negligible. There are then no mass or momentum fluxes to stabilize the configuration and we inquire into the conditions obtaining as the system approaches mutual equilibrium. Figure 13 illustrates this situation.

There are two ways to think about the static problem. In Fig. 14 we show a conceptual Rube–Goldberg device that permits the system to come to equilibrium while maintaining each subsystem in internal equilibrium. The insulated piston is attached to a paddle wheel entropy-generator of zero-heat capacity that delivers heat to either subsystem in varying amounts. The heat flow is controlled by a valve that can be switched arbitrarily but, to maintain thermal isolation of the two subsystems, must be considered to be always fully switched in one position or the other. Energy and volume of the entire system are constant and each subsystem contains unit mass.

As independent variables we choose the specific volume V and a reduced internal energy E', defined by

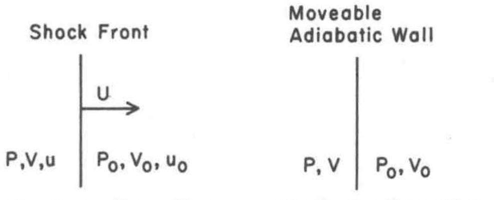

FIG. 13. Shock and static configurations with same thermodynamic states.

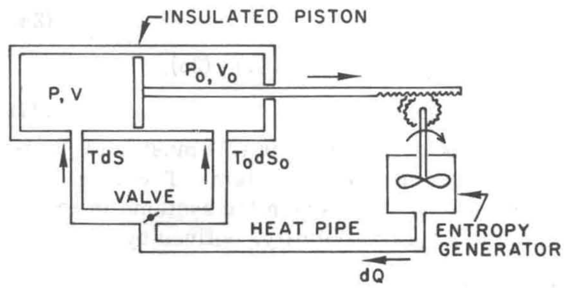

FIG. 14. Equilibration machine. Static configuration of Fig. 13 approaches equilibrium while each subsystem remains in internal equilibrium.

$$dE' = dE + P_0 dV \; . \tag{23}$$

The differential of this quantity is therefore given by the change in internal energy less the work done on one subsystem by the other subsystem. We refer to it as the reduced internal energy. In mutual equilibrium, $P=P_0$, $dE=-P_0dV$, and $dE'=0$.

When the system is permitted to relax toward equilibrium, we have

$$dV + dV_0 = 0, \quad dE + dE_0 = 0 \; ,$$

and

$$dE' = dE + P_0 dV \; , \quad dE_0' = dE_0 + P dV_0 \; .$$

Invoking the requirement that each subsystem be in internal equilibrium implies

$$dE = TdS - PdV$$

and

$$dE_0 = T_0 dS_0 - P_0 dV_0 \; .$$

Hence,

$$dE' = TdS - (P - P_0) dV$$

and

$$dE_0' = T_0 dS_0 - (P - P_0) dV \; .$$

Finally, energy conservation requires

$$dE + dE_0 = 0 \; ,$$

or

$$TdS + T_0 dS_0 - (P - P_0) dV = 0 \; ,$$

so that

$$dE' = - T_0 dS_0 \; ,$$

and

$$dE_0' = - TdS \; . \tag{24}$$

Moreover,

$$TdS = (P - P_0) dV - T_0 dS_0 \; ,$$

and

$$T_0 dS_0 = (P - P_0) dV - TdS \; . \tag{25}$$

We now note that both conditions $TdS \geq 0$ and $T_0 dS_0 \geq 0$, must apply. Consequently, the approach to equilibrium is characterized by, from Eq. (24),

$$dS \geq 0 \text{ and } dE' \leq 0. \qquad (26)$$

Equivalently, we can write, from Eq. (25),

$$0 \leq TdS \leq (P - P_0)dV . \qquad (27)$$

Both inequalities in Eqs. (26) or (27) must hold if entropy is to increase in each subsystem. The usual thermodynamic stability criterion for systems in equilibrium states that the availability, defined by

$$A = E - T_0 S + P_0 V ,$$

where T_0 and P_0 are the temperature and pressure of the surroundings, considered to be reservoirs, is minimum in equilibrium.[11] In the present context this implies

$$dA = dE + P_0 dV - T_0 dS$$
$$= dE' - T_0 dS = -T_0(dS_0 + dS) \leq 0 .$$

This statement, however, is insufficient in that it does not specify that, in general, entropy must be produced in the surroundings as well as in the subsystem under consideration. For nonconducting systems we therefore take Ineq. (26) or (27), as the more complete statement of the Second Law.

Another way to derive this result that is somewhat simpler is to allow the viscous entropy production to occur internally within each subsystem. We denote by Σ the mechanical stress acting at the interface between the two subsystems and assume that each medium is sufficiently viscous so that stress equilibrium is maintained and the kinetic energy is negligible as the systems approach thermodynamic equilibrium. The equilibrium pressure P is no longer the mechanical stress and is defined only by the equilibrium equation of state, i.e., $P = P(V, E)$.

We now have

$$dE = -\Sigma dV ,$$

and

$$dE_0 = -\Sigma dV_0 = \Sigma dV ,$$

to be combined with the equilibrium relations

$$dE = TdS - PdV , \quad dE_0 = T_0 dS_0 - P_0 dV_0 .$$

This gives

$$TdS = -(\Sigma - P)dV , \quad T_0 dS_0 = (\Sigma - P_0)dV .$$

We now require that entropy be produced in each subsystem, so that

$$-(\Sigma - P)dV \geq 0 , \quad (\Sigma - P_0)dV \geq 0 .$$

Hence, if $dV > 0$, we must have

$$P_0 \leq \Sigma \leq P .$$

This relation implies that during the approach to equilibrium

$$0 \leq TdS \leq (P - P_0)dV ,$$

and

$$dE' = -(\Sigma - P_0)dV \leq 0$$

as before.

We now apply this result, Ineqs. (26) or (27), to the shock stability problem. Differentiating the expression for the Hugoniot surface, Eq. (3), gives

$$dE = \tfrac{1}{2}(V_0 - V)d\sigma - \tfrac{1}{2}(\sigma + P_0)dV ,$$

or

$$dE' = dE + P_0 dV = \tfrac{1}{2}[(V_0 - V)d\sigma - (\sigma - P_0)dV]$$
$$= \tfrac{1}{2}(V_0 - V)(d\sigma - j^2 dV) . \qquad (28)$$

From Eq. (8) we note that this is also equal to the differential of the kinetic energy density, $\frac{1}{2}(u - u_0)^2$. We can also express this equation in terms of V and S as independent variables by means of the transformation

$$dE' = TdS - (P - P_0)dV .$$

In invoking this equation we do not imply that the Hugoniot surface is a thermodynamic equilibrium surface. Equation (28) then becomes,

$$TdS = \tfrac{1}{2}(V_0 - V)\left[d\sigma - \left(j^2 - \frac{2(P - P_0)}{V_0 - V}\right)dV\right] . \qquad (29)$$

The Hugoniot P-V curve is defined by the intersection of the Hugoniot surface with the equilibrium surface. Hence, along this curve, $\sigma \equiv P$ and Eqs. (28) and (29) reduce to

$$dE' = \tfrac{1}{2}(V_0 - V)[(dP/dV)_H - j^2]dV , \qquad (30)$$

and

$$TdS = \tfrac{1}{2}(V_0 - V)[(dP/dV)_H + j^2]dV . \qquad (31)$$

We now posit the following:

POSTULATE: A shock transition from an initial state to a given final state is thermodynamically unstable if there exists a neighboring final state on the Hugoniot curve for which the entropy is larger and the reduced internal energy smaller than for the given state.

According to this postulate, shocks are thermodynamically unstable when thermodynamically permissible adiabatic fluctuations, i.e., satisfying Ineq. (27), about a shocked state can occur that result in a new state also compatible with the jump conditions. By "thermodynamically unstable" we mean that the system is unstable given fluctuations of sufficient magnitude, in accord with the usual thermodynamic point of view.

From Ineq. (26) or (27) we can derive necessary conditions for stability. Since $P > P_0$, we consider only $dV > 0$ and Eqs. (30) and (31) are incompatible with Ineq. (26) when

$$\left(\frac{dE'}{dV}\right)_H \geq 0, \Rightarrow \left(\frac{dP}{dV}\right)_H \geq j^2 , \qquad (32a)$$

or

$$T\left(\frac{dS}{dV}\right)_H \leq 0, \Rightarrow \left(\frac{dP}{dV}\right)_H \leq -j^2 . \qquad (32b)$$

These can be combined in the statement

$$-1 \leq j^2(dV/dP)_H \leq 1 ,$$

which is exactly the result obtained for stability with respect to acoustic amplification, Ineq. (19).

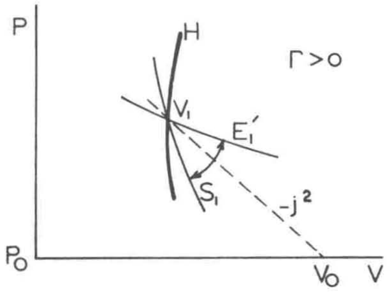

FIG. 15. Paths in P-V plane for $\Gamma>0$. Adiabatic expansion from V_1 takes place on path between S_1 and E_1'. Hugoniot curve H, excluded from this region.

We can illustrate this restriction by means of a P-V diagram as shown in Fig. 15, for the case $\Gamma>0$. On the equilibrium surface we have

$$\left(\frac{\partial P}{\partial V}\right)_{E'}=\left(\frac{\partial P}{\partial V}\right)_s+\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial S}{\partial V}\right)_{E'}$$

$$=\left(\frac{\partial P}{\partial V}\right)_s+\frac{\Gamma}{V}(P-P_0)\ .$$

Hence, for $\Gamma>0$ and $P>P_0$ the curve of constant E' lies above the isentrope S as shown, and adiabatic fluctuations consistent with Ineq. (27) lie between these curves. When $\Gamma<0$, the relative positions are reversed. For stable shocks the Hugoniot curve is excluded from the region bounded by these curves.

We can also consider the stability problem from the point of view of the restoring forces invoked during a virtual displacement. Returning to Eqs. (28) and (29) and retaining only first order terms in an expansion about a Hugoniot state, specified by $P=P_1$, $V=V_1$, gives

$$\sigma=P_1+\left[\left(\frac{2}{V_0-V_1}\right)\frac{dE'}{dV}+j^2\right]dV+\cdots\ , \tag{33a}$$

$$=P_1+\left[\left(\frac{2}{V_0-V_1}\right)T_1\frac{dS}{dV}-j^2\right]dV+\cdots\ . \tag{33b}$$

The paths along which the derivatives are taken is so far arbitrary. [In Eqs. (30) and (31) we also specified $d\sigma/dV=dP/dV$.]

Expressions analogous to Eq. (33) can be written for the equilibrium surface; thus,

$$P=P_1+\left[\left(\frac{\partial P}{\partial E'}\right)_V\frac{dE'}{dV}+\left(\frac{\partial P}{\partial V}\right)_{E'}\right]dV+\cdots$$

$$=P_1+\left[\frac{\Gamma_1}{V_1}\frac{dE'}{dV}+\left(\frac{\partial P}{\partial V}\right)_{E'}\right]dV+\cdots \tag{34a}$$

$$=P_1+\left[\frac{\Gamma_1 T_1}{V_1}\left(\frac{dS}{dV}\right)+\left(\frac{\partial P}{\partial V}\right)_s\right]dV+\cdots\ . \tag{34b}$$

The difference between Eq. (33) and Eq. (34) is

$$\sigma-P=\left[\left(\frac{2}{V_0-V_1}\right)(1-a_1)\frac{dE'}{dV}+j^2-\left(\frac{\partial P}{\partial V}\right)_{E'}\right]dV, \tag{35a}$$

or

$$\sigma-P=\left[\left(\frac{2}{V_0-V_1}\right)(1-a_1)T_1\frac{dS}{dV}-j^2-\left(\frac{\partial P}{\partial V}\right)_s\right]dV, \tag{35b}$$

where the definition of "a," Eq. (15), has been used.

We now consider fluctuations in volume δV consistent with the thermodynamic restriction, Ineq. (26) and require for stability that the restoring force be opposed to the displacement, i.e.,

$$(\sigma-P)\delta V\geq 0\ , \tag{36}$$

for stability. Along the two bounding curves, $dE'=0$ and $dS=0$, this implies

$$[j^2-(\partial P/\partial V)_{E'}](\delta V)^2\geq 0\ ,$$

and

$$[-j^2-(\partial P/\partial V)_s](\delta V)^2\geq 0\ .$$

Thus,

$$(\partial P/\partial V)_{E'}\leq j^2\ , \tag{37a}$$

and

$$(\partial P/\partial V)_s\leq -j^2\ . \tag{37b}$$

These restrictions are shown in Fig. 16.

For intermediate paths between these bounds, Ineq. (36) stipulates, from Eq. (35),

$$\left(\frac{2}{V_0-V_1}\right)(1-a_1)T_1\frac{dS}{dV}-j^2-\left(\frac{\partial P}{\partial V}\right)_s$$

$$=\left(\frac{2}{V_0-V_1}\right)(1-a_1)\frac{dE'}{dV}+j^2-\left(\frac{\partial P}{\partial V}\right)_{E'}\geq 0\ . \tag{38}$$

The former of these is clearly satisfied, provided Ineqs. (37) are valid, for $a<1$ and $dS/dV\geq 0$; the latter when $a>1$ and $dE'/dV\leq 0$. Thus, stability with respect to all admissible fluctuations consistent with Ineq. (26) is guaranteed by Ineqs. (37).

The restrictions on the slope of the Hugoniot P-V curve implied by Ineqs. (37) can be derived from Eq. (13). We note that Ineq. (37b) is just the subsonic condition,

$$M^2=-j^2(dV/dP)_s\leq 1\ ,$$

and this restriction implies, for $M^2a<1$,

$$-1\leq j^2(dV/dP)_H\ ,$$

as shown in Fig. 1.

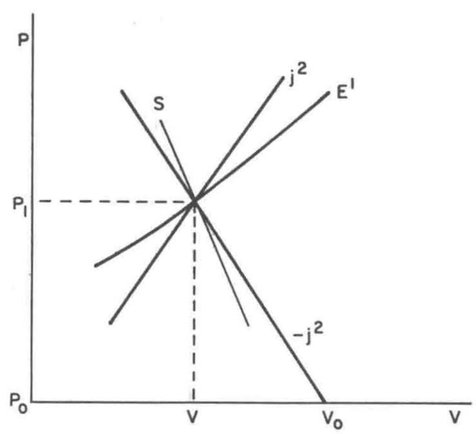

FIG. 16. Relative positions of Rayleigh line, $-j^2$, reflected Rayleigh line, j^2, isentrope, S, and isoenergetic line, E', for stable shocks.

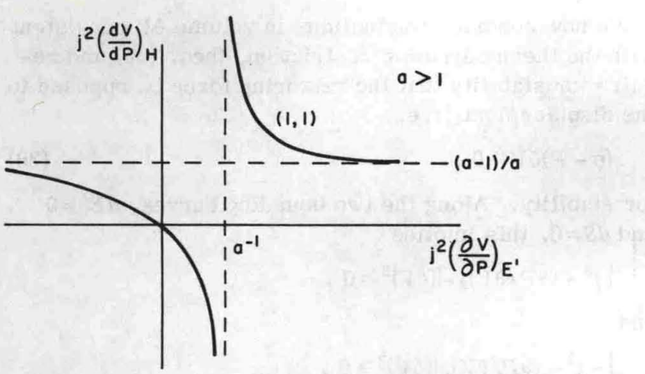

FIG. 17. Plot of j^2 $(dV/dP)_H$ as function of j^2 $(\partial V/\partial P)_{E'}$ when $a>1$. Stable case corresponds to j^2 $(\partial V/\partial P)_{E'}>1$, and $j^2 \times (dV/dP)_H<1$.

With the substitutions

$$\left(\frac{\partial P}{\partial V}\right)_{E'}=\left(\frac{\partial P}{\partial V}\right)_s+\frac{\Gamma(P-P_0)}{V}$$

$$=\left(\frac{\partial P}{\partial V}\right)_s+2aj^2 \qquad (\sigma=P),$$

Eq. (16) can be written

$$j^2\left(\frac{dV}{dP}\right)_H=\frac{j^2(\partial V/\partial P)_{E'}(a-1)}{aj^2(\partial V/\partial P)_{E'}-1}. \tag{39}$$

A plot of this function for the case $a>1$ which, excluding the region $M^2a>1$, is the only remaining case of interest, is shown as Fig. 17. From this figure it is clear that the restriction, Ineq. (37a), also implies the inequality

$$j^2(dV/dP)_H\leqslant 1 .$$

We therefore conclude that the stability condition, Ineq. (36), when combined with the thermodynamic restriction, Ineq. (27), implies the criterion for shock stability

$$-1\leqslant j^2(dV/dP)_H\leqslant 1$$

in agreement with earlier arguments.

To complete the theory we must include the other well-known condition for stability, namely, that the shock travel with supersonic velocity with respect to the undisturbed medium ahead of the shock. This has been shown elsewhere.[9] Moreover, we still have to consider the branch 3*b* of Fig. 1, for which $M^2a>1$.

From Eq. (14), with $P=P_0$, $V=V_0$, it is clear that the Hugoniot and isentrope have the same slope at the initial state. Hence, the supersonic condition

$$M_0^2=-j^2(\partial V/\partial P)_s>1$$

also implies

$$j^2(dV/dP)_H<-1 \tag{40}$$

in the initial state.

Now consider Hugoniot curves of two different types that are assumed to lie on branch 3*b* of Fig. 1 as illustrated in Fig. 18. A Hugoniot curve of type I, that approaches the shocked state 1 from below the Rayleigh line can be ruled out on the basis that one or the other

TABLE I. Limits of various derivatives for stable shocks.

$-1\le j^2(dV/dP)_H\le 1$
$(\partial P/\partial V)_S\le -j^2$
$(\partial P/\partial V)_{E'}\le j^2$
$0\le T(dS/dP)_H\le (V_0-V)$
$0\le (dE'/dP)_H\le (V_0-V)$
$0\le (dU/dP)_H\le U/(P-P_0)$
$0\le (du/dP)_H\le u/(P-P_0)$
$(dS/dE')_H\ge 0$

of the limits of Ineq. (19) would be exceeded before the slope of the Hugoniot could take on values pertaining to the region in question, i.e., $j^2(dV/dP)_H<-1$. Alternatively, a Hugoniot of type II necessarily crosses the Rayleigh line at a lower pressure as at point 2. This state, however, is a thermodynamic equilibrium state and could therefore be considered an initial state for the shock transition from 2 to 1. However, according to Ineq. (40), the supersonic condition would be violated. We conclude, therefore, that the branch 3*b* of Fig. 1, for which $M^2a>1$, is unattainable.

The symmetry of Ineq. (19) is reflected in other equivalent relations derived by substituting from the jump conditions, Eqs. (1)–(3). These are shown in Table I. We note that one consequence is that the shock velocity is a monotonic function of the particle velocity.

Let us now consider further the consequences of violation of each of the limits of Ineq. (19). Figure 19 shows a case in which the lower limit is violated between points A and C. From Eq. (31) it is seen that the entropy along the Hugoniot curve is a maximum at A and a minimum at B with respect to neighboring Hugoniot states. If we plot entropy as a function of pressure along the Hugoniot, we get a curve like that in Fig. 20.

From our criteria we deduce that shock waves whose final states fall within A–C are unstable. If the final pressure falls within this range, a two-wave configuration is produced in which the first wave carries the material to state A, and a subsequent shock with initial state A carries the material to higher pressure, less than C; if the final pressure exceeds C, a single shock is again stable. Instabilities of this type and the two-shock configuration have been widely observed.[12] It is important to notice that under these conditions the pres-

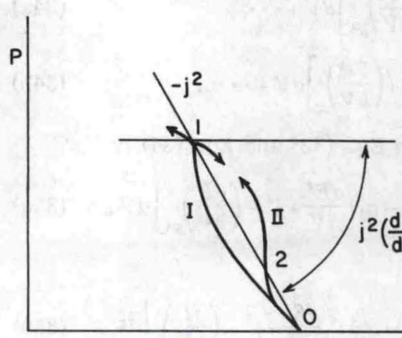

FIG. 18. Unstable Hugoniot curves for which j^2 $(dV/dP)_H<-1$ at point 1.

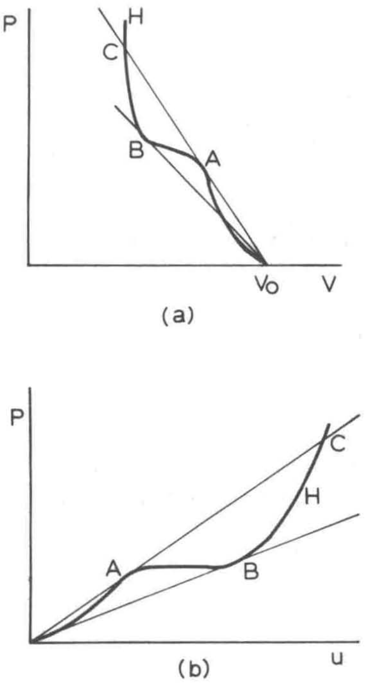

FIG. 19. Hugoniot curve with region of instability between A and C: (a) P-V plane, (b) P-u plane. Point A is entropy maximum along H; B is entropy minimum.

sure of the first wave is stationary at state A with respect to higher shock pressures, (less than C).

Now, consider a situation where the upper limit of Ineq. (19) is exceeded, as illustrated in Fig. 21. In this case a plot of E' as function of P has the appearance shown in Fig. 22. The region between A and B is thermodynamically unstable according to Ineq. (19). Consequently, a shock to state B tends to be stabilized in pressure with respect to lower shock pressures. This is just the situation required for detonation, and we put forward the hypothesis that detonation is indeed the result of a minimum in E' along the Hugoniot curve.

We note that this criterion for detonation is quite different from the Chapman–Jouguet Theory. In that theory detonation corresponds to a local minimum in the entropy along the equilibrium Hugoniot curve. Moreover, it requires the assumption of two effective equations of state, applicable in different regions of the shock transition, a frozen equation of state for the initial shock transition and a relaxed equation of state for the equilibrium state finally achieved (Ref. 10, p. 480).

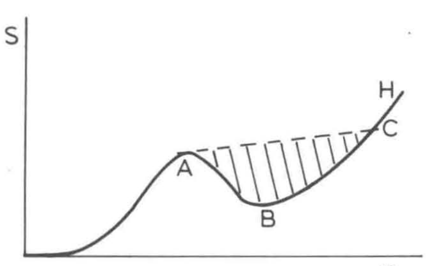

FIG. 20. Entropy as function of pressure along Hugoniot curve of Fig. 19. Cross-hatched region is region of instability.

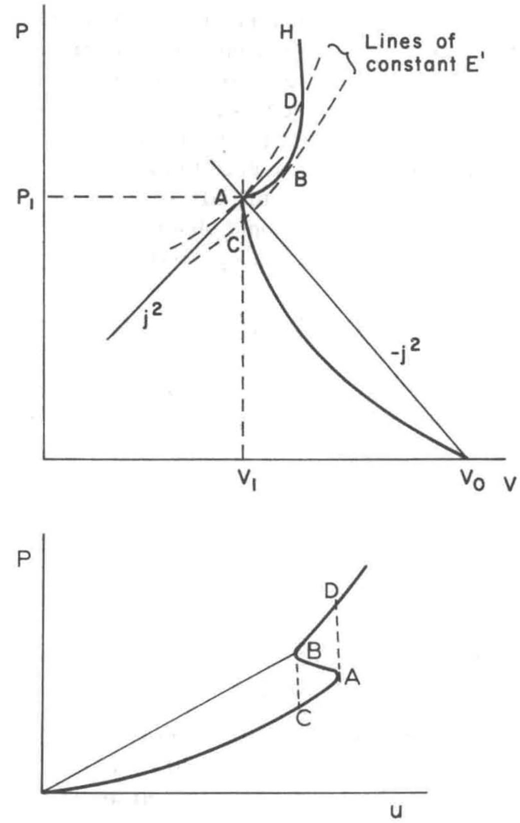

FIG. 21. Hugoniot curve with unstable region $1 < j^2\,(dV/dP)_H$, between A and B: (a) P-V plane, (b) P-u plane. Point A is relative maximum in E' along H; B is relative minimum.

In summary then, stable shocks are characterized by monotonically increasing entropy and reduced internal energy along the Hugoniot curve, and unstable shocks are associated with either a local maximum in the derivative $(dS/dP)_H$, or with a local minimum in the derivative $(dE'/dP)_H$. In the former case, a two-shock configuration results in which the pressure of the first wave is stationary at the entropy maximum. The latter case corresponds to detonation with the pressure stationary at the minimum in E'.

The unstable regions are shown as the cross-hatched areas of Figs. 20 and 22. The upper bound of the unstable region of Fig. 20 is determined by the equivalence of the shock velocity there with that at the entropy maximum. The region CA of Fig. 22 is metastable; shock waves in this range require adequate pertur-

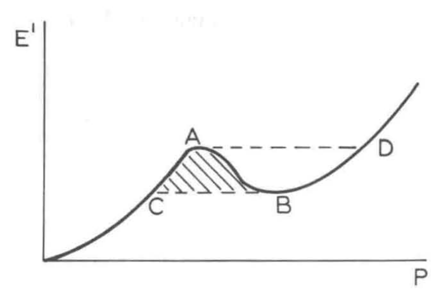

FIG. 22. Plot of E' as function of P along Hugoniot curve of Fig. 21. Cross-hatched region is thermodynamically unstable. Point B is detonation state.

bation to overcome the energy barrier. Just as a liquid can be cooled below the stable transition temperature, the existence of a minimum in E' does not guarantee that a detonation will form; however, state B is the thermodynamically more stable state. It may be for this reason that detonations are observed to propagate more readily in materials that are initially somewhat porous and why turbulence is commonly observed behind detonations. There is an obvious analogy to the onset of turbulence in viscous, steady, subsonic flow.

VI. CONCLUSIONS

We have treated the problem of stability of plane shock waves by considering the reflection of small amplitude acoustic waves from the shock front, and by irreversible thermodynamics. Both approaches yield the same criteria for stability, which can be stated as a restriction on the relative slopes of the Hugoniot curve and the Rayleigh line

$$-1 \leq j^2(dV/dP)_H \leq 1 .$$

Violation of the lower limit leads to a two-shock structure; violation of the upper limit to detonation.

The thermodynamic treatment requires the recognition that, at least in an adiabatic mechanical process, the entropy production is bounded above as well as below. This can be stated alternatively by the relations, applicable to real processes,

$$0 \leq TdS \leq (P - P_0)\, dV, \quad (T > 0)$$

or by the equivalent relations,

$$0 \leq dS; \quad dE' \leq 0 ,$$

where $dE' = dE + P_0 dV$, is the reduced internal energy.

For shock waves E' is also equal to the kinetic energy density of the shocked state in a coordinate system in which the initial state is stationary; conversely it is the kinetic energy density of the initial state in a coordinate system in which the shocked state is stationary.

Shocks are thermodynamically unstable whenever there is a local maximum in the entropy or a local minimum in the reduced internal energy along the Hugoniot curve. These correspond to a local maximum in the shock velocity and to a local minimum in the particle velocity, respectively. In the former case a two-shock structure develops in which the pressure of the first shock corresponds to the entropy maximum. The latter case gives rise to turbulence that tends to stabilize the shock pressure at the minimum in the reduced internal energy. We posit that detonations are instabilities of this type.

Because E' is also the kinetic energy density, there is another sense in which the stability criteria can be understood. Thus, in a coordinate system fixed in the shocked material the shock front tends to produce maximum entropy with minimum expenditure of the kinetic energy of the incoming material. Instability occurs when there are neighboring Hugoniot states that permit greater production at less cost. It is tempting to speculate that similar thermodynamic conditions may also be valid for biological systems.

We note that the results are in satisfying agreement with a generalized form of the Le Chatelier principle. Thus, for stable shocks both the shock velocity and the particle velocity increase monotonically with pressure.

ACKNOWLEDGMENTS

Numerous people contributed to this work. I wish to thank especially Dr. G. W. Swan for stimulating my interest in this problem, and Drs. Wm. Band and S. Lowell for much encouragement. M. Cowperthwaite and J. Shaner pointed out to me the case described in Fig. 12.

Much of the work was completed while I was a Fulbright-Hayes Research Scholar at the University of Auckland under the auspices of the New Zealand-United States Educational Foundation. This research was supported by the Earth Sciences Section National Science Foundation, NSF Grant DES72-01517 A02.

[1]H. A. Bethe, Office of Scientific Research and Development, Report 445 (1942).
[2]S. P. D'Yakov, Zh. Eksp. Teor. Fiz. **27**, 288 (1956).
[3]J. J. Erpenbeck, Phys. Fluids **5**, 1181 (1962).
[4]C. Gardner, Phys. Fluids **6**, 1366 (1963).
[5]G. W. Swan and G. R. Fowles, Phys. Fluids **18**, 28 (1975).
[6]G. R. Fowles and G. W. Swan, Phys. Rev. Lett. **30**, 1023 (1973).
[7]L. C. Woods, J. Plasma Phys. **6**, 615 (1971).
[8]R. Courant and K. O. Friedrichs, *Supersonic Flow and Shock Waves* (Wiley, New York, 1948), Chap. 2.
[9]G. R. Fowles, Phys. Fluids **18**, 776 (1975).
[10]L. D. Landau and E. M. Lifshitz, *Fluid Mechanics* (Addison-Wesley, Reading, Mass., 1959).
[11]L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley, Reading, Mass., 1969), p. 99.
[12]G. E. Duvall, *Les Ondes de Detonation* (Editions du Centre National de la Recherche Scientifique, Paris, 1962), p. 337. Also, M. Cowperthwaite, J. Franklin Inst. **285**, 275 (1968).